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## SUMMARY

On irradiation di-*p-t*-butylphenyl carbonate has been shown to rearrange via a novel photo-catalysed double Fries reaction to yield 5,5'-di-*t*-butyl-2,2'-dihydroxybenzophenone. The unsubstituted phenyl carbonate gave rise to 2,2'-dihydroxy and 2,4'-dihydroxybenzophenone. An indication that the mechanism of the reaction involved the formation and eventual rearrangement of the corresponding salicylate was obtained by isolation of 5-*t*-butylsalicylic acid and by the irradiation of phenyl salicylate.

The photolysis of aryl formate esters has indicated that the primary decomposition process may well be intramolecular extrusion of carbon monoxide although there is some evidence that other dissociation processes are in operation. The irradiation of  $\beta$ -naphthyl, phenyl, *p-t*-butylphenyl, 2,6-xylyl and *p*-chlorophenyl formates in cyclohexene gave rise to the corresponding aryl cyclohexyl ether. This photocatalysed addition to an olefin is not restricted to cyclohexene and irradiation of *p-t*-butylphenyl formate in pent-2-ene and 2-methylpent-1-ene gave rise to the respective ethers. Attempts were made to elucidate the mechanism by irradiation of 2-allyl-4-*t*-butylphenyl formate and 2-(3',3'-dimethylallyl)phenol. Both irradiations gave rise to good yields of the normal addition products.

Another route to the generation of aryloxy radicals

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was investigated involving the synthesis and decomposition of peroxy compounds containing phenoxy ether groups. The synthesis and decomposition of Bis-( $\beta$ -phenoxypropionyl)peroxide has been carried out showing the generation of phenoxyethyl radicals. O,O-t-Butyl-O-phenylmonopercarbonate has been synthesised and analysis of the mixture obtained from its decomposition in cyclohexene has shown the presence of phenyl cyclohexyl ether.

Methyl and ethyl 5-phenoxy-penta-2,4-dienoate were synthesised, the former by condensation of phenol with methyl but-1-en-3-yne-1-carboxylate, the latter by reaction of carbethoxymethylene-triphenyl phosphorane and  $\beta$ -phenoxyacrolein. Attempts to synthesise this system by reaction of  $\beta$ -phenoxyacrolein with several compounds having an active methylene group were unsuccessful. Diels-Alder reactions were carried out on the ethyl ester to give, 1-ethyl 2,5-dimethylbenzene-1,2,5-tricarboxylate with dimethylacetylenedicarboxylate, ethyl 1-naphthoate with benzyne and 3-carbethoxy-6-phenoxy-1,2,3,6-tetrahydrophthalic anhydride and the corresponding acid with maleic anhydride.

Ethyl 2-methyl-5-phenoxy-penta-2,4-dienoate, synthesised by reaction of  $\beta$ -phenoxyacrolein and 1-carbethoxyethylidene-triphenyl phosphorane did not react with the above dienophiles.

T H E S I S

submitted to

THE UNIVERSITY OF GLASGOW

in fulfilment of the  
requirements for the

DEGREE OF DOCTOR OF PHILOSOPHY

by

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AUGUST, 1964

### ACKNOWLEDGEMENTS

The author wishes to express his indebtedness for advice and encouragement to Professor P. L. Pauson under whose guidance this investigation was carried out, to Drs. A. C. Syme and P. Bladen and their respective staffs for micro-analysis, and infrared and nuclear magnetic resonance spectra, to Mrs. L. Rees and Miss J. Buchanan for technical assistance and also to the Carnegie Trust for a research scholarship.

PHOTOLYSIS OF PHENOL DERIVATIVES.

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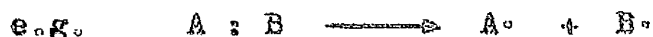
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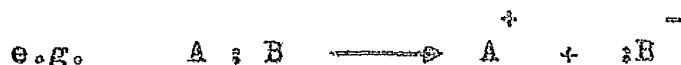
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I N T R O D U C T I O N

There are two ways in which a covalent molecule may be ruptured during the course of a chemical reaction. Either the bond is broken symmetrically to yield neutral entities or radicals, each possessing an unpaired electron,



or the bond is broken heterolytically to yield an ion pair of opposite charge.



Subsequently the liberated ions or free radicals, being very reactive species, react readily with other activated fragments or with neutral molecules to yield, eventually, stable molecular reaction products.

Radicals can be produced by various routes but in the preparation of aryloxy radicals oxidative methods have been by far the most extensively employed. Oxidation of organic molecules involves the rupture of an electron pair bond, like all other reactions of covalently bonded molecules. This, as shown above, can either be heterolysis or homolysis. Nearly all heterolytic oxidation processes are recognisable addition or eliminations involving polar electrophilic reagents while homolytic oxidations, since they sever electron pairs, necessarily involve the transient production of free radicals which can often be detected. Homolytic oxidation can be effected either by

hydrogen atom removal



or merely by removal of an electron



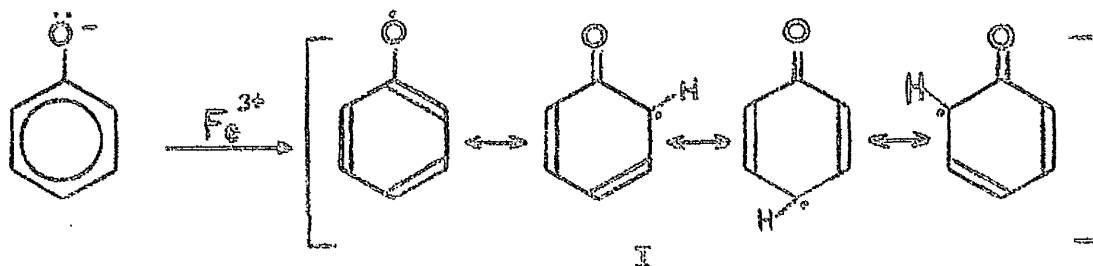
and can be divided into two groups according to the above reaction schemes. Active free atoms such as chlorine, active free radicals, such as  $\cdot\text{OH}$ ,  $\cdot\text{C}_6\text{H}_5$  or  $\cdot\text{CH}_3$ , together with molecules from which they may be generated, e.g. benzoyl peroxide, fall into the first group, while higher valence ions such as  $\text{Fe}^{3+}$ ,  $\text{Mn}^{3+}$  and  $\text{Ce}^{4+}$  are oxidants of the second group. While in many oxidations it is possible to determine what route the reaction may be taking it is sometimes difficult to decide whether the bond fissions, which take place in some concerted electron removal processes, are heterolytic or homolytic processes.

### PHENOLIC OXIDATION

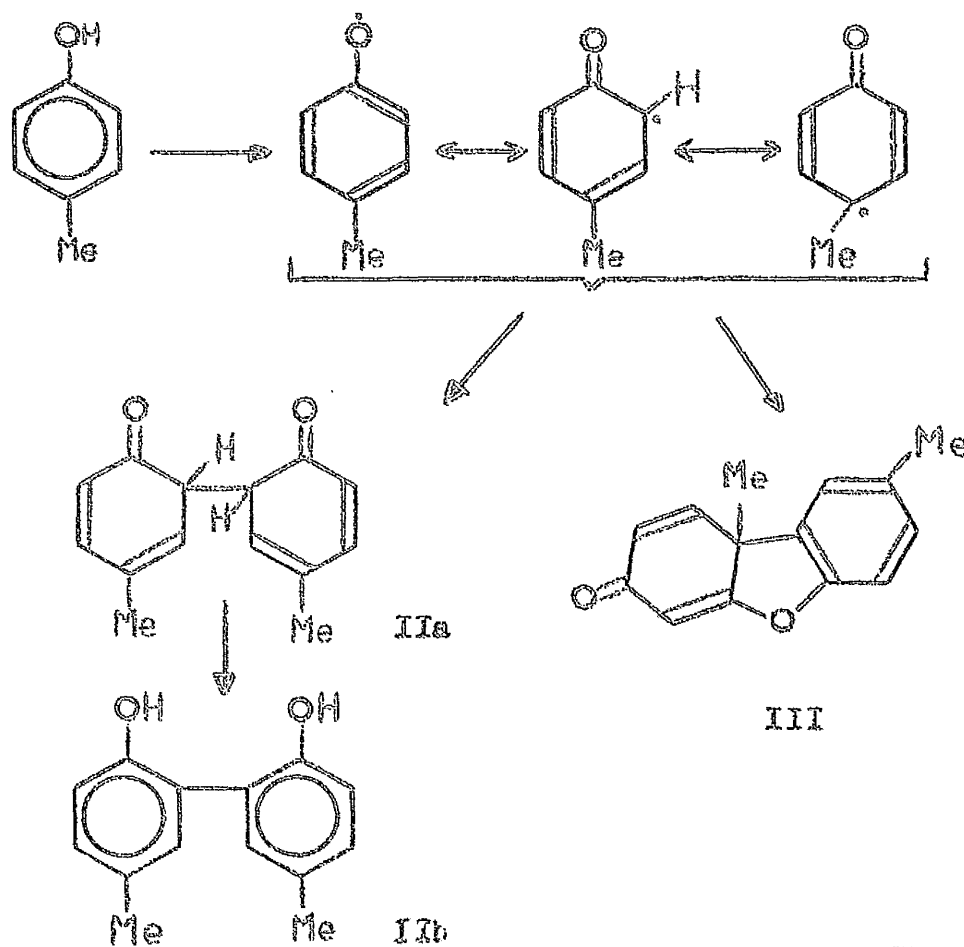
#### (a) Reactions of Simple Phenols

In recent years phenolic oxidation and the reagents used to effect it has been extensively reviewed.<sup>1 2 3 4</sup> Pummerer<sup>5</sup> commenced an investigation of the oxidation of phenols by alkaline ferricyanide forty years ago. Oxidation of the phenolate anion, in this case by an electron abstraction reaction, gives rise to

a mesomeric free radical (I).

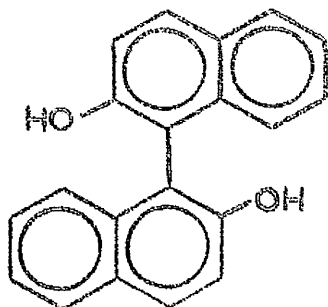


Such a free radical is very reactive and can react to give many dimeric products in which the aromatic rings have been united by carbon-carbon coupling in the ortho or para position (IIb, III). Coupling through oxygen is also found. Generally the intermediate quinonoid form (IIa) cannot be isolated, in the simpler molecules, but rearranges to give the phenolic compound. A typical example of this is:-

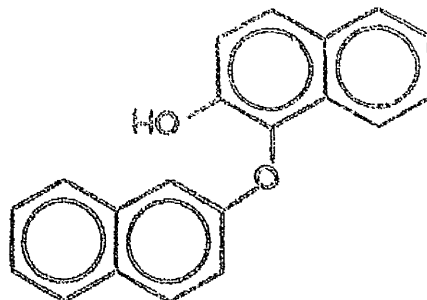


Of particular interest is the formation of Pummerer's ketone (III) the structure of which was fully elucidated by Barton, Defflorin and Edwards.<sup>6</sup> A similar range of products was obtained by other oxidative processes such as electrolysis<sup>7,8</sup> and Fenton's reagent.<sup>9</sup>

Naphthols also give similar products.  $\alpha$ -Naphthol reacts to give all three possible ortho and para carbon-carbon bonded products.<sup>10</sup> In acidic or neutral solutions with ferric chloride  $\beta$ -naphthol gives a good yield of 1,1'-binaphthol (IV), but with alkaline ferricyanide only a small amount of the hydroxynaphthyl ether (IVa) could be isolated.<sup>11,12</sup>



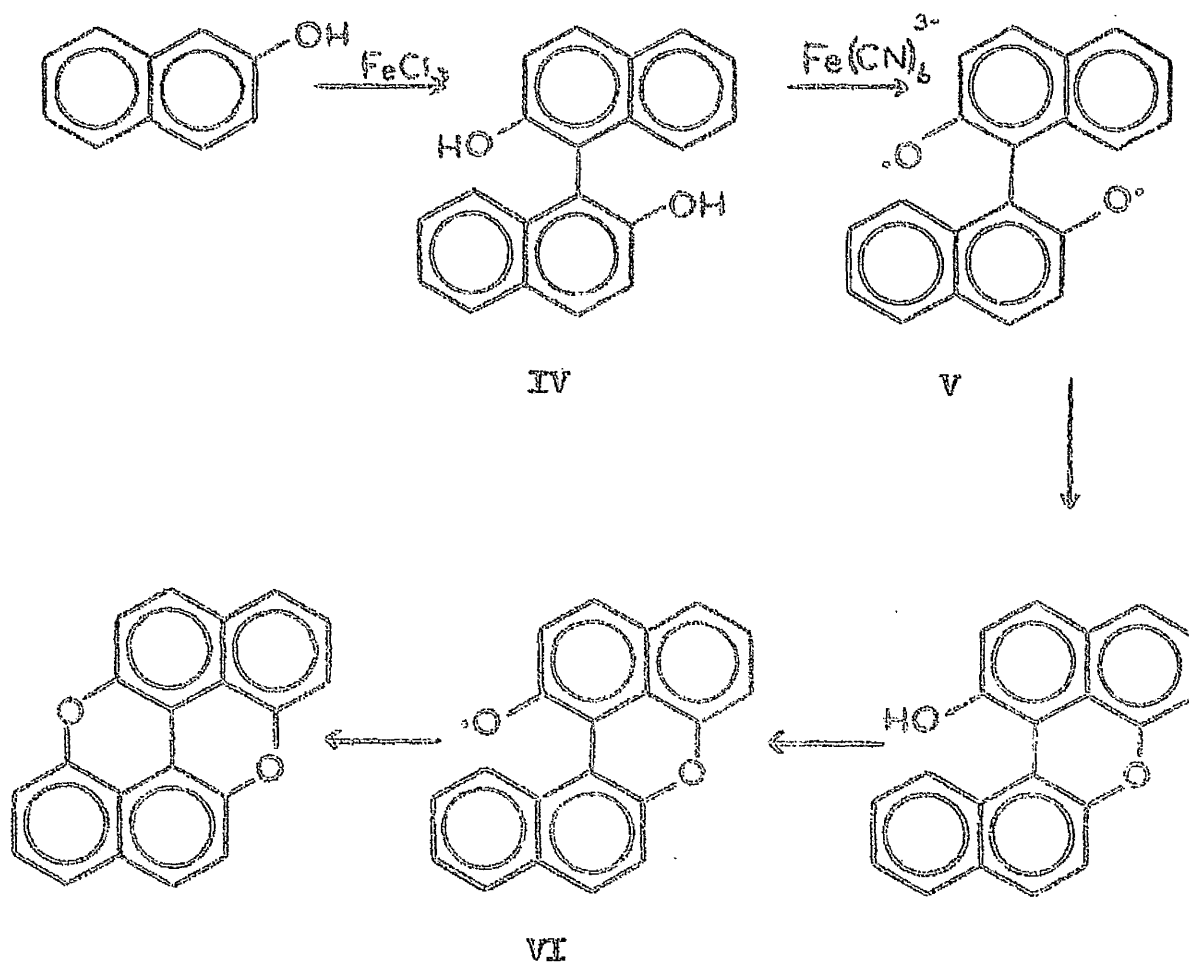
IV



IVa

$\beta$ -Naphthol can be oxidised, beyond the dinaphthol (IV), by ferricyanide according to the following scheme. The existence of the diradical (V) and of radical (VI) has been proposed from analysis of the signals obtained from electron

spin resonance measurements.<sup>13</sup>

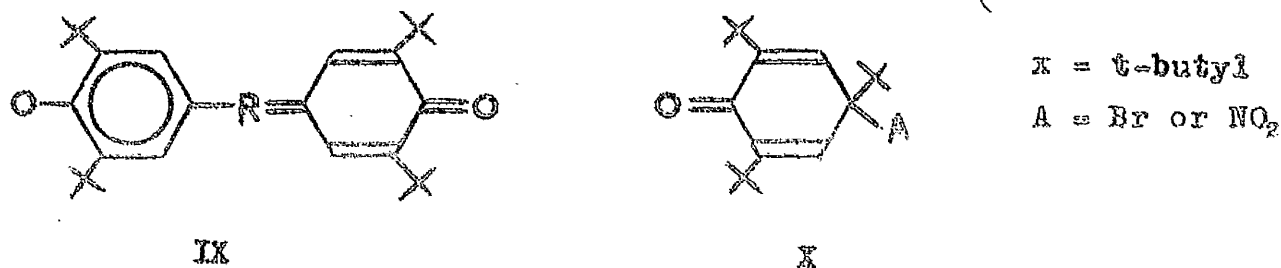


(b) Stable Phenoxy Free Radicals

In the last ten years a significant advance has been made in parallel observations by Cook<sup>14,15</sup> and Muller and Ley<sup>16,17,18</sup> that 2,4,6-tri-*t*-butylphenol (VII, R = *t*-butyl) was readily oxidised to yield a blue solution of 2,4,6-tri-*t*-butylphenoxy (VIII, R = Bu<sup>t</sup>) which is stable in the absence of air or oxygen.

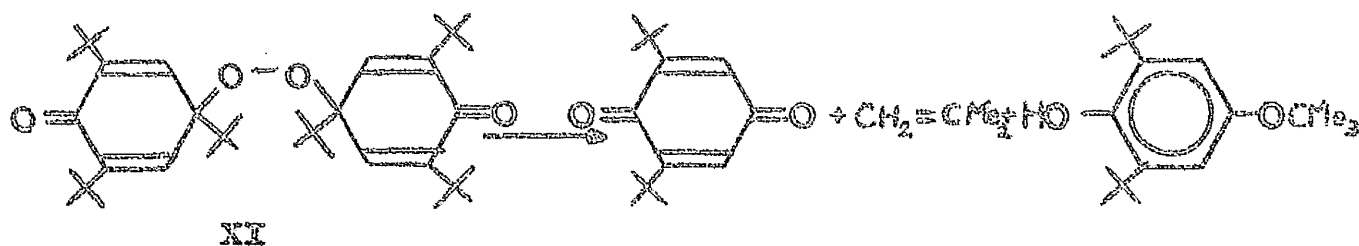


The stability of this radical has allowed a detailed study of the spatial distribution of the unpaired electron about the molecule.<sup>19</sup> Various polysubstituted radicals of this sort have been prepared<sup>20,21,22</sup> the most stable being galvinoxyl (IX, R = CH). A stable nitrogen analogue (IX, R = N) has also been prepared.<sup>23</sup>



These free aryloxy radicals (VIII, R = Bu<sup>t</sup>) react immediately with halogens and nitrogen dioxide to give quinonoid adducts of structure (X) and with oxygen to give peroxides (XI) which decompose thermally as shown.<sup>24,25,26</sup>

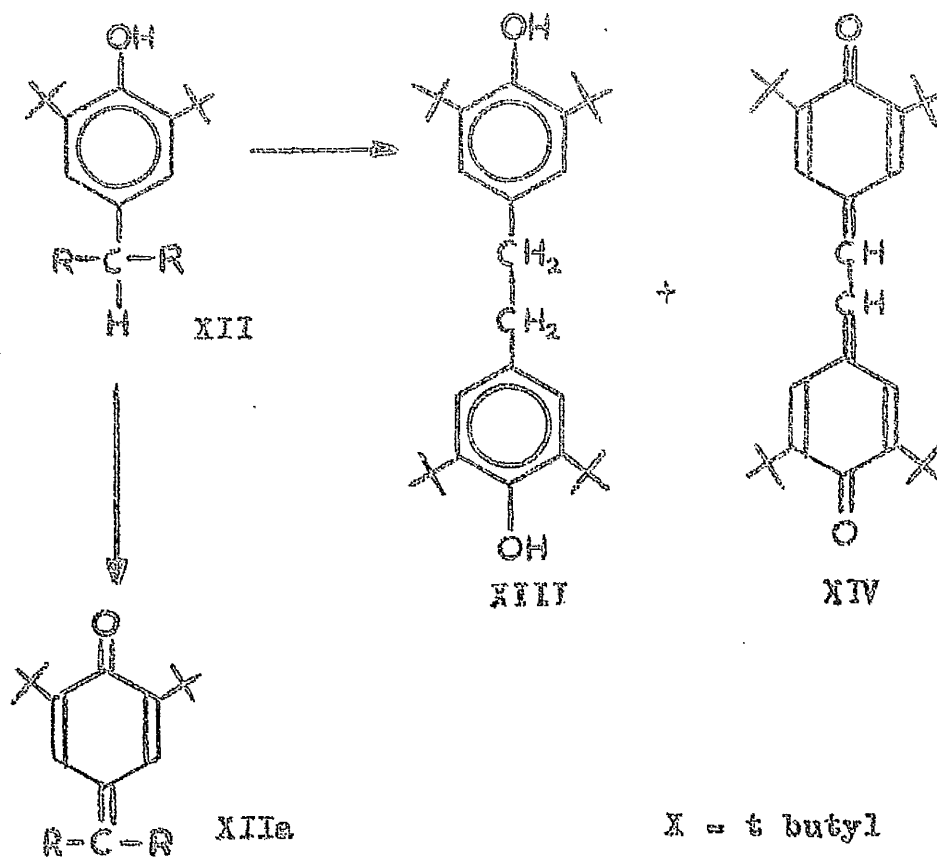




The reactivity of the radicals towards oxygen decreases with increasing phenyl substitution, 2,4,6-triphenylphenoxy (VIII, R = Ph) being quite stable.<sup>27</sup> The radicals have almost all been detected and examined by magnetic susceptibility and electron spin resonance measurements. Analysis of the hyperfine splitting of the E.S.R. spectrum indicated that the probability of the free electron occurring at the para-carbon was much greater than at the ortho position and that the electron could distribute itself over alkyl groups and hetero-atoms in the ortho and para position.<sup>28-33</sup>

The radicals are all characteristically coloured and show an absorption band in the infrared near  $1560 \text{ cm.}^{-1}$  thus differing quite markedly from the colourless quinol dimers which have a doublet at  $1660, 1640 \text{ cm.}^{-1}$

When the ortho and para positions of the phenols were substituted with a methyl group, as in 2,6-di-*t*-butyl-4-methylphenol (XII, R = H), the phenoxy radical rearranges to give two products (XIII, XIV)<sup>38, 41, 42</sup> linked through the para methyl group.



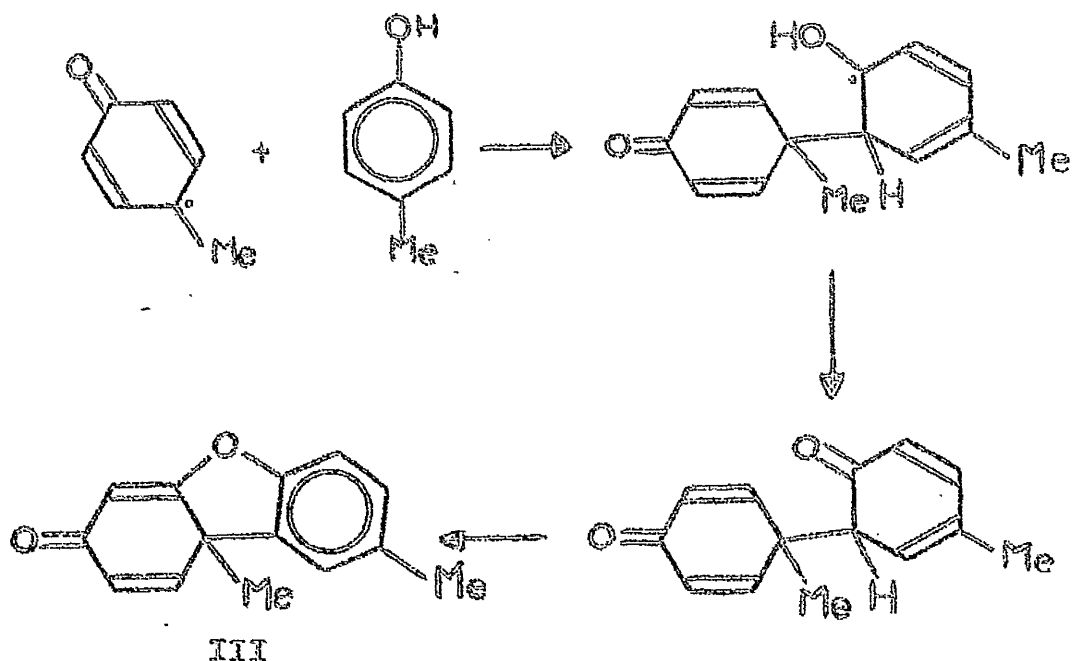
The substituted 4-methyl derivatives (XII, R = Ph, Me) and their reactions to give the corresponding quinone methides (XIIIa, R = Ph, Me) have been studied.<sup>39,40</sup>

The proposal to account for the formation of these two dimers (XIII, XIV) was that the phenoxy radical, almost immediately after it was produced, rearranged to the benzylradical. Similarly 2,4,6-tri-methylphenol<sup>43,44</sup> and 2,6-di-*t*-butylphenol<sup>45</sup> afforded para-para linked dimers on oxidation.

The requirements for a stable monocyclic phenoxy radical are therefore that the ortho and para positions must be substituted to prevent nuclear dimerisation and the substituent groups must not have  $\alpha$ -hydrogen atoms since this, as exemplified above, can give rise to benzyl radicals.

(c) Phenoxy Radical Coupling Mechanisms.

The coupling mechanisms of phenols and their biosynthetic implications have been extensively reviewed by Barton and Cohen<sup>46</sup> and Erdtman and Wachtmeister.<sup>47</sup> In the reaction of phenoxy radicals it is essential to distinguish between the substitution of a phenoxy radical into a molecule of phenol followed by further oxidation and the radical pairing reaction. In both cases certain restrictions have to be enforced on the mode of coupling and in fact both mechanisms predict ortho-para coupling but have different implications in biosynthesis, the coupling mechanism being more restrictive than the substitution reaction. Barton et al.<sup>48</sup> favour the coupling mechanism since the oxidation of p-cresol in the presence of excess veratrole gave no veratrole incorporated in the phenolic products. Thus the weight of evidence appears to be in favour of radical coupling and almost all products from phenolic oxidation can be accounted for by this mechanism. However it is also pointed out that cases exist where products could be accounted for by a substitution mechanism as in the following scheme for the formation of Pummerer's ketone (III).



Barton et al. point out that while the radical coupling mechanism is favoured the oxidation-substitution-oxidation mechanism does not alter any biogenetic arguments which have been made and only by long and exhaustive radio-tracer studies will the mechanism be finally verified.

#### PHOTOCHEMICAL FRIES REACTION

It is an elementary prerequisite for photochemical action that the irradiating light must be absorbed. Thus Einstein's Law of photochemical equivalence states that one molecule reacts per quantum absorbed. The energy absorbed by the molecule, 48 K.cal per mole at 6000 Å. and 96 K.cal. per mole at 3000 Å., may be dissipated in many ways, by fluorescence, collision or bond rupture. Thus rupture of a bond is not always a consequence of light absorption and a variety of

chemical transformations can result. Often these photochemical rearrangements and transformations give rise to structures which are difficult to obtain by other means. These rearrangements have been extensively reviewed by Schonberg,<sup>49</sup> Barton,<sup>50</sup> Schenok<sup>51</sup> and Mayo.<sup>52</sup>

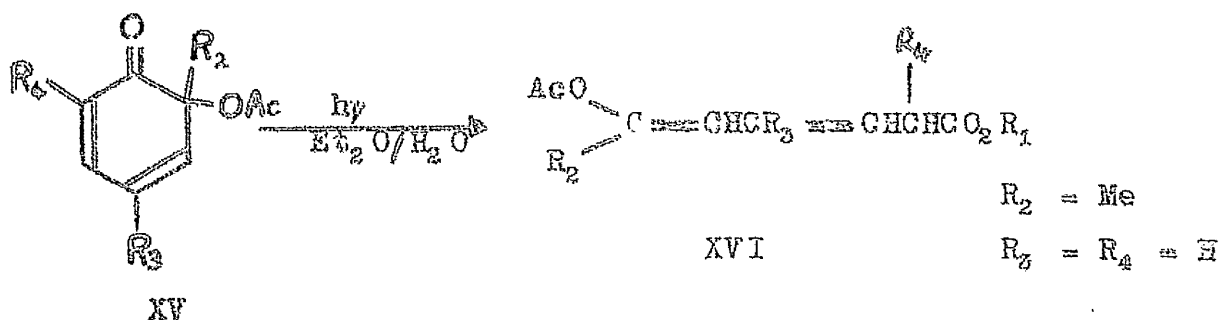
The detailed mechanism<sup>53</sup> of many of these photochemical reactions is only partly understood. Typically they involve unsaturated molecules often with carbonyl groups or one or more carbon-carbon double bond. Initial light absorption by molecules of this type is believed to involve excitation of an electron in a  $\pi$  orbital or in an unshared pair to an excited singlet state.<sup>54</sup> This excited state very quickly loses its energy by fluorescence, thermal degradation or chemical reaction or it may pass to a longer lived triplet state which may in turn emit light, react or dissipate its energy thermally. Since the triplet state is a diradical, any reaction, in which it is involved, can be considered as a radical process even though cleavage of the molecule into radical fragments does not take place.

(a) Applications of the Photo-Fries Reaction.

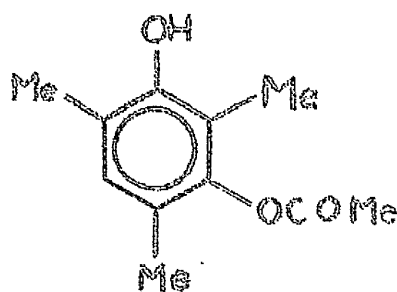
Recently the photo-catalysed Fries rearrangement has been recognised and investigated. The corresponding classical acid catalysed rearrangement is well established.<sup>55</sup> It was found by various workers that where the acid catalysed rearrangement almost always favoured the para isomer, if both

the ortho and para positions were vacant, the photochemical reaction favoured the ortho. Another obvious advantage of the photo-reaction is that in no reported case has a para-alkyl substituent been displaced.

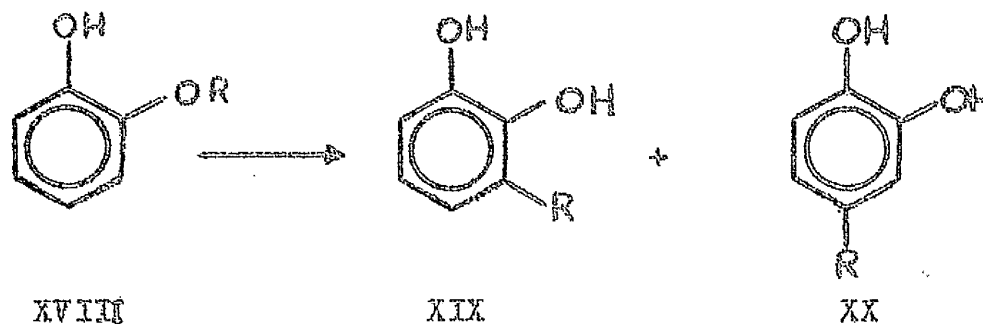
This photo-reaction was first carried out as an analogy to a rearrangement studied by Barton and Quinkert.<sup>56,57</sup>



The irradiation of (XV) in a saturated solution of water in ether effected ring opening to yield the unsaturated acid (XVI,  $R_1 = \text{H}$ ) and with aniline as the nucleophile, the anilide (XVI,  $R_1 = \text{NH-C}_6\text{H}_5$ ). In the absence of strong nucleophiles irradiation of (XV) ( $R_2 = R_3 = R_4 = \text{Me}$ ) brought about slow aromatisation to the phenol (XVII).

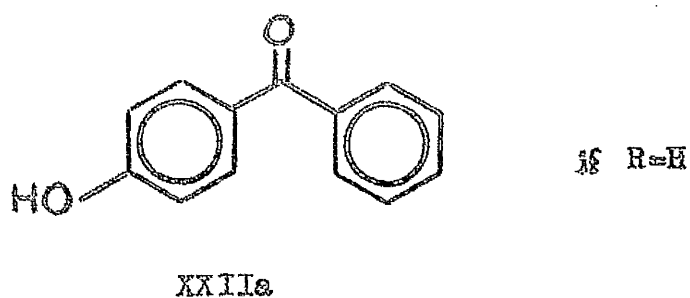
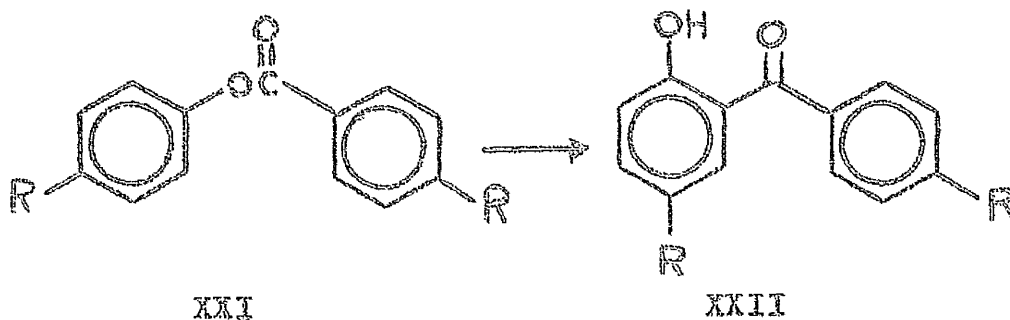


Anderson and Reese<sup>58</sup>, recognising the possible scope of this latter rearrangement in the aromatic series, irradiated the simplest aromatic analogue (XVIII, R = MeCO).

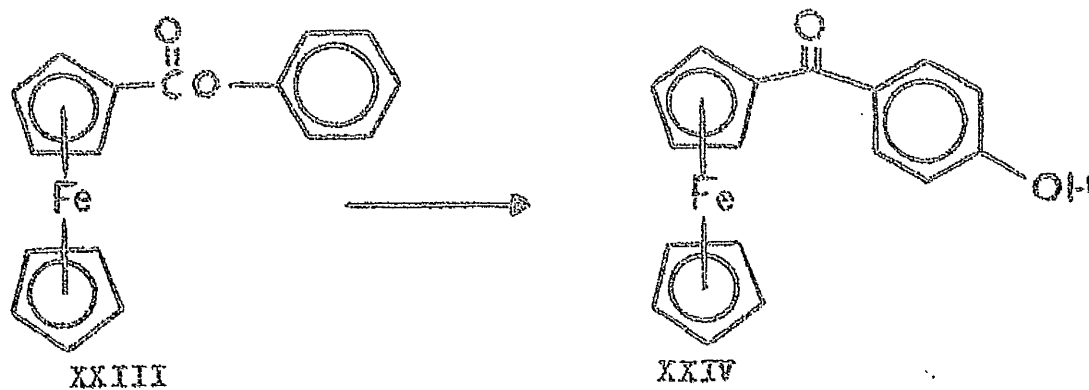


This caused the molecule to rearrange yielding the two possible isomers 2,3-dihydroxyacetophenone (XIX, R = MeCO), 3,4-dihydroxyacetophenone (XX, R = MeCO) and deacylated material, pyrocatechol (XVII, R = H).

More recently Kobse<sup>59</sup> irradiated a series of substituted aryl esters in ethanol and benzene to obtain the expected substituted 2-hydroxybenzophenones. A typical example of this is the irradiation of (XXI) (R = Bu<sup>t</sup>) to give the substituted benzophenone (XXII, R = Bu<sup>t</sup>).

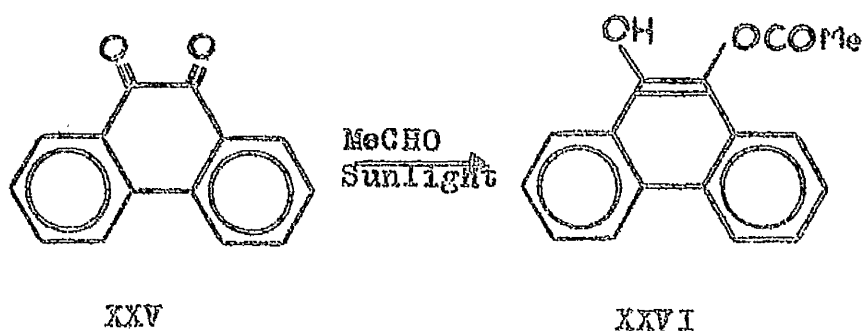


Anderson and Reese<sup>60</sup> and Finnegan et al.<sup>64</sup> have irradiated phenyl benzoate (XXI, R = H) which gave the two possible isomers (XXII, XXIIa, R = H). Phenyl ferrocene carboxylate<sup>64</sup> (XXIII) gave only the para isomer, parahydroxybenzoyl ferrocene (XXIV), which indicated a possible role, in the reaction mechanism, for the iron atom.

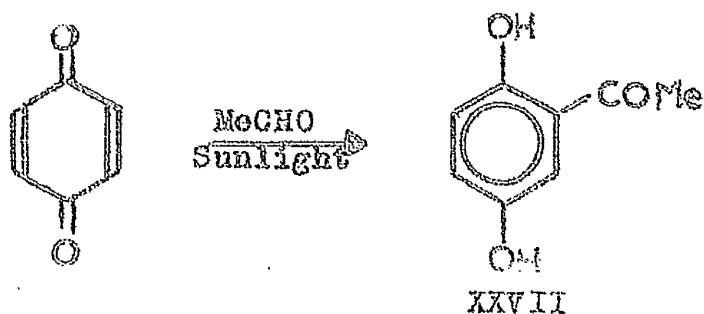




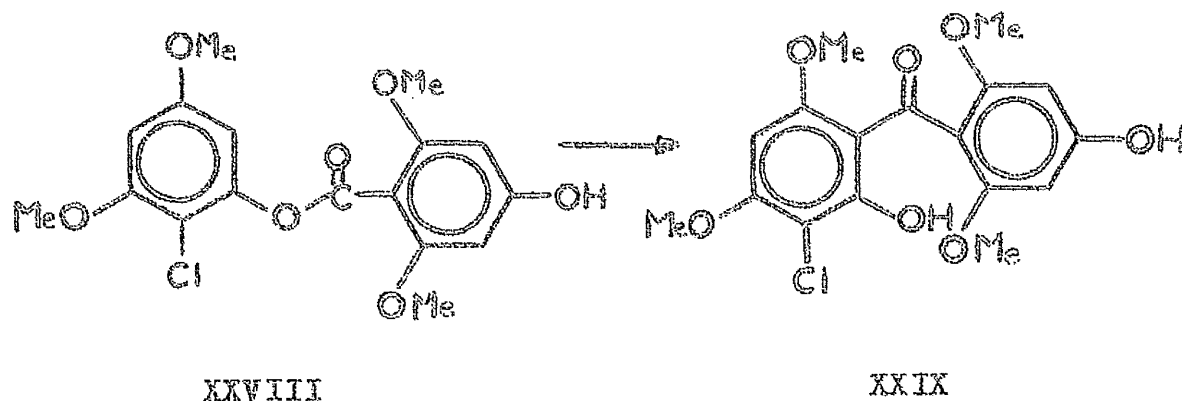
A proposal<sup>60</sup> was made that the photochemical Fries reaction was predictable from observations made by Klinger<sup>61</sup> who allowed a solution of phenanthraquinone (XXV) and acetaldehyde to stand in sunlight, the product isolated being the substituted phenanthrene (XXVI), whereas hydroquinone, under the same



conditions,<sup>62</sup> gave 2,4-dihydroxyacetophenone (XXVII).



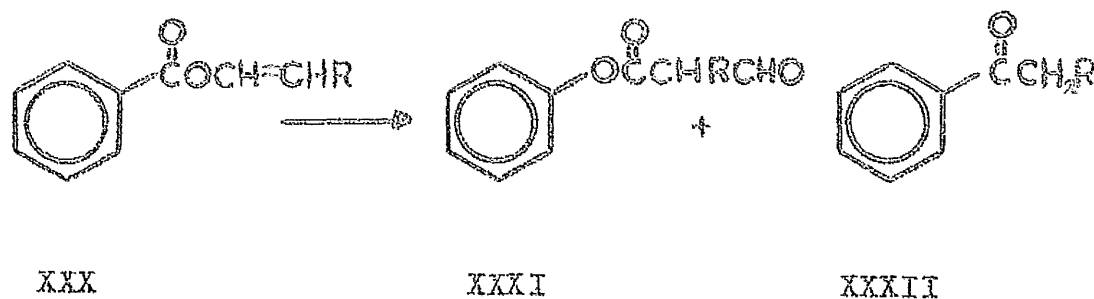
Various extensions have since appeared in the literature. Kno et al.<sup>63</sup> used the rearrangement as a step (XXVIII, XXIX) in the total synthesis of griseofulvin.



On structural considerations the reaction need not be restricted to phenyl esters since any system which can be represented by  $X - ABC$  where  $X$  is a chromophore capable of excitation and  $ABC$  is a triad capable of resonance stabilisation

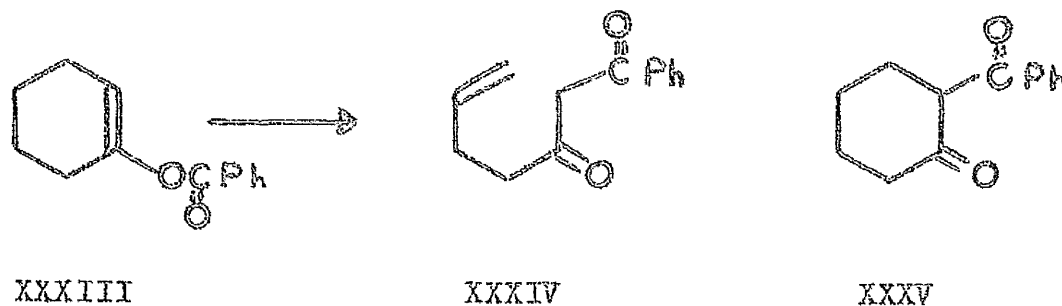
i.e.  $\overset{\cdot}{A} - B = C \longleftrightarrow A = B - \overset{\cdot}{C}$   
 could in theory be expected to rearrange. Thus Finnegan and Hagen<sup>64</sup> and Gorodetsky and Mazue<sup>65</sup> irradiated vinyl benzoates.

In the case of vinyl benzoate (XXX,  $R = H$ ) the products benzoyl-acetaldehyde (XXXI,  $R = H$ ) and acetophenone (XXXII,  $R = H$ ) were the same as those obtained during pyrolysis studies.<sup>66</sup>

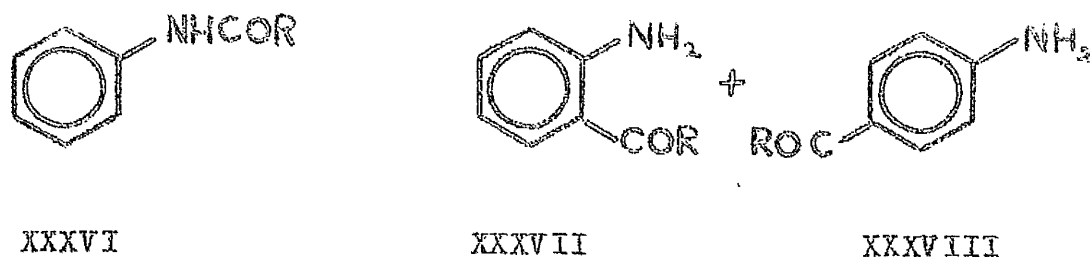


In the case of (XXXIII),<sup>65</sup> however, differences were found from

the pyrolysis in that photolysis was accompanied by ring opening to yield the unsaturated diketone (XXXIV) whereas only (XXXV) was obtained on pyrolysis.<sup>69</sup>



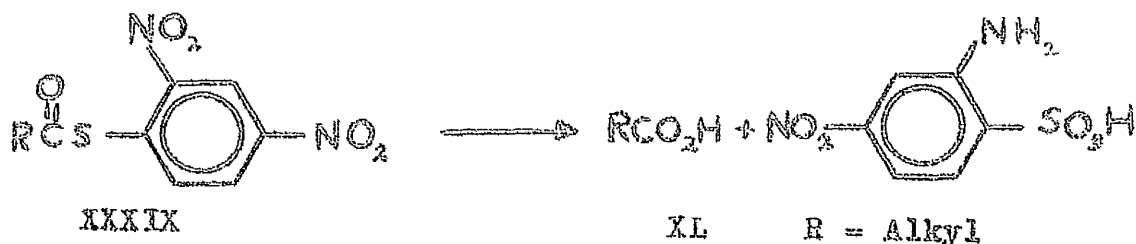
Photolysis of N-acyl anilines (XXXVI) to the corresponding 2- and 3-aminophenyl ketones (XXXVII, XXXVIII) and deacylated amine has been reported<sup>68</sup> thus showing that the rearrangement can be applied to compounds having hetero-atoms other than oxygen. N-Acyl anilines have been rearranged by acid catalysis<sup>69,70</sup> but gave only poor yields of the para isomers.



where R = methyl, n-propyl or n-butyl

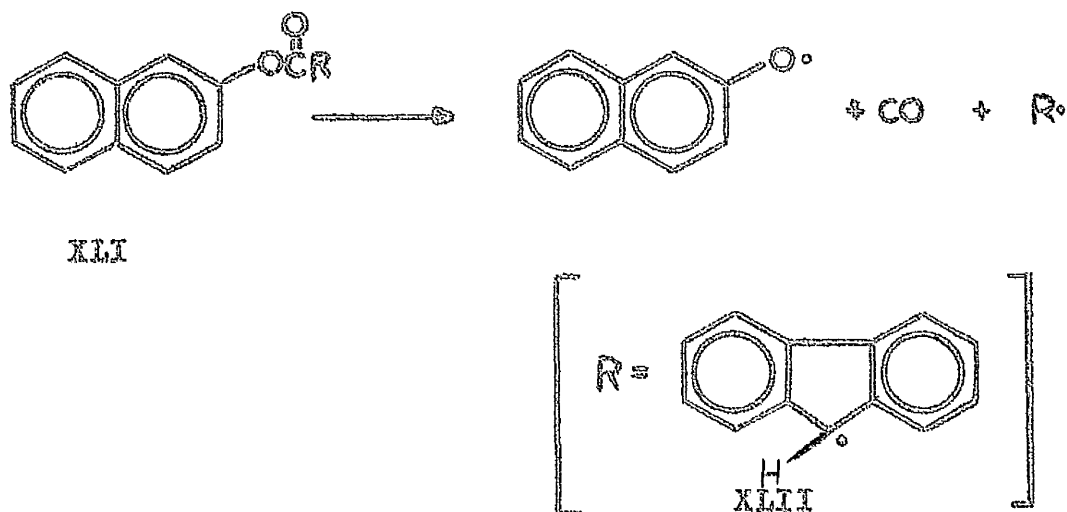
b. Photo-removable Protecting Groups.

Such a reaction has obvious uses in synthetic organic chemistry, not only for the synthesis of molecules, which are difficult to prepare by the more conventional routes, but also for readily removable protecting groups. Barton *et al.*<sup>71</sup> reported that 2,4-dinitrophenylthio esters of carboxylic acids (XXXIX) can be cleaved photochemically to give good yields of the corresponding acid (XL).



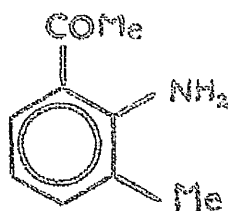
The fact that the 2-nitro group was reduced during the reaction indicated that it must participate in the reaction, no doubt similarly to the ortho-nitro group in the ortho-nitrobenzaldehyde rearrangement.<sup>72</sup>

$\beta$ -Naphthyl esters have been studied to find a suitable photo-active protecting group.<sup>71</sup> It has been found that esters which give rise to a stable radical regenerate the naphthalene in good yield. The best results have been obtained using fluorene-9-carboxylic esters (XLI) which give rise to the stable fluorenyl radical (XLII).

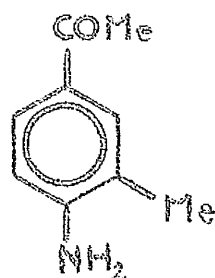


### (c) Proposed Mechanisms

Various attempts have been made to elucidate the mechanism of the photo-Fries reaction. All the investigators agree that it is free radical but there are certain major differences. Anderson and Reese<sup>60</sup> propose that the mechanism is predominantly intramolecular basing this on the fact that irradiation of a solution of phenol and pyrocatechol monoacetate gave only a trace of 4-hydroxyacetophenone. However, Elad,<sup>68</sup> who investigated the closely analogous N-acylanilines, proposed that the rearrangement, in this case could be intermolecular. Irradiation of a mixture of acetanilide (XXXVI, R = Me) and o-toluidine gave rise to a mixture of the ortho- and para-aminoacetophenones (XXXVII, XXXVIII; R = Me) and also 2-amino-3-methyl- and 3-methyl-4-aminoacetophenones (XLIII, XLIV) which can only arise from attack of the acetyl radical on o-toluidine.

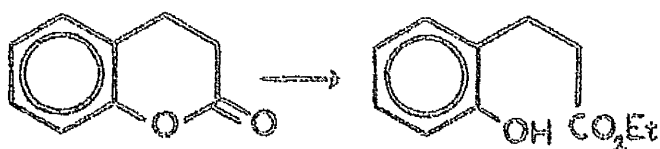


XLIII



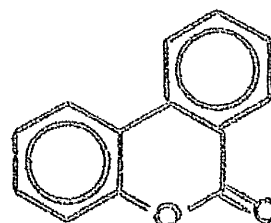
XLIV

The resistance of the meta position to substitution has been shown,<sup>60,64</sup> independently, by the irradiation of dihydrocoumarin (XLV) and benzcoumarin (XLVI). Both these reactions gave none of the hydroxy-indanone nor hydroxy-fluorenone which would have resulted from meta attack. In the case of (XLV) only the corresponding ester (XLVII), which resulted from solvolysis of the coumarin ring, was isolated.



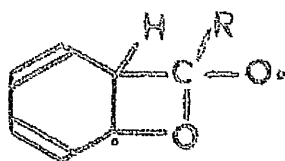
XLV

XLVII

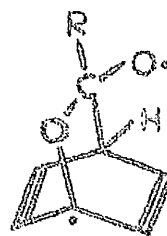


XLVI

Anderson and Reese<sup>60</sup> propose that the reaction goes via an intermediate diradical system (XLVIII, XLIX) which can collapse to give dienones capable of enolising to the corresponding aromatic compounds.



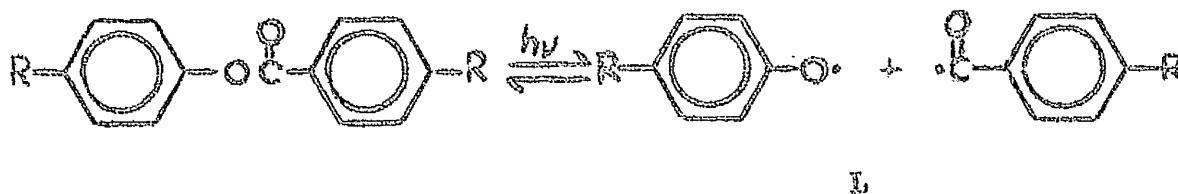
XLVIII



XLIX

The fact that phenol was obtained in all reactions of this sort was explained by a separate intermolecular reaction similar to the solvolysis encountered with (XIV).

On the other hand Kobsa<sup>59</sup> proposed that the reaction took place by absorption of a quantum of light bringing about rupture of the ester linkage to give a radical pair (L) contained within a solvent cage. Such a system could yield all the products identified from the reaction mixture.



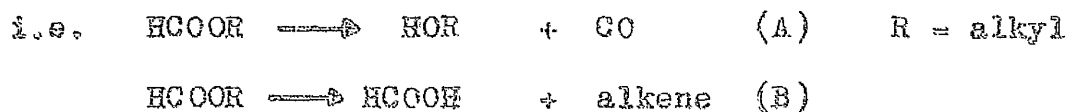
By the irradiation of the ester in benzene solution the possibility of phenol arising from solvolysis, proposed above, is eliminated. Since phenol is isolated regardless of solvent it would appear that the latter mechanism is favoured.

#### PHOTOLYSIS OF FORMATES

Although alkyl formates have been known for many years little has been done to study their unsensitized decomposition

by ultraviolet irradiation.

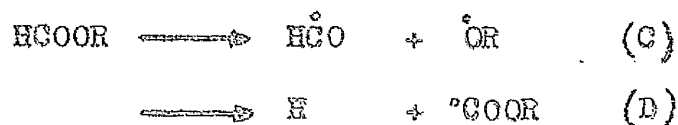
The alkyl formates have absorption below 2400 Å. and in ethanol show strong absorption at 2150 Å. Ausloos<sup>75, 74</sup> irradiated a series of alkyl formates to investigate the primary decomposition processes both in the gas and liquid phase and investigated the effect of dilution with a solvent.<sup>74</sup> The most important primary processes were found to be intramolecular rearrangements (A and B).



(A) was found to be independent of both temperature and intensity over a wide range and (B) was dependent on the alkyl group (R) having a β-hydrogen.

The rate of decomposition was slowed by a factor of twenty when a filter, cutting off light below 2250 Å., was inserted. It was suggested that, since evolution of carbon monoxide occurred at lower wavelengths than the elimination reaction (B), the rearrangements took place from different electronic levels.

To a lesser extent dissociation processes (C) and (D) were also necessary to account for the quantities of other volatile products, i.e. hydrogen, methane, ethane, obtained. In general



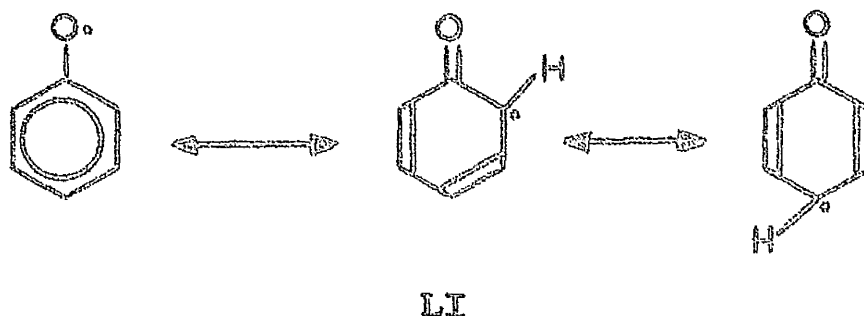


it was found that processes (A) and (C) occurred mostly at low wavelengths.

Dilution with solvents, e.g. n-heptane, ethyl alcohol and ethyl ether, tended to diminish the primary process (B), but process (A), the evolution of carbon monoxide, was unaffected.

#### PHOTOLYSIS OF PHENOLS,

The resonance stabilisation which is, to a large extent, responsible for the existence, at room temperature, of triphenylmethyl and similar radicals of the type first described by Gomberg<sup>76</sup> results in a reduction of the bond dissociation energy in many aromatic molecules,<sup>76</sup> although it may not be sufficient to give a detectable equilibrium concentration of free radicals. Photolytic bond fission will take place at the weakest bond in the molecule and it might be expected that a common photochemical dissociation process in an aromatic molecule will be that which results in the formation of two radicals possessing together a greater resonance energy than that of the parent molecule.<sup>77</sup> Thus in the aromatic series the simplest cases are the benzyli, anilino and phenoxy free radicals. These radicals are capable of existing in both benzenoid and quinonoid forms, typified by the canonical forms of the aryloxy radical, (LI), which give rise to considerable resonance stabilisation.

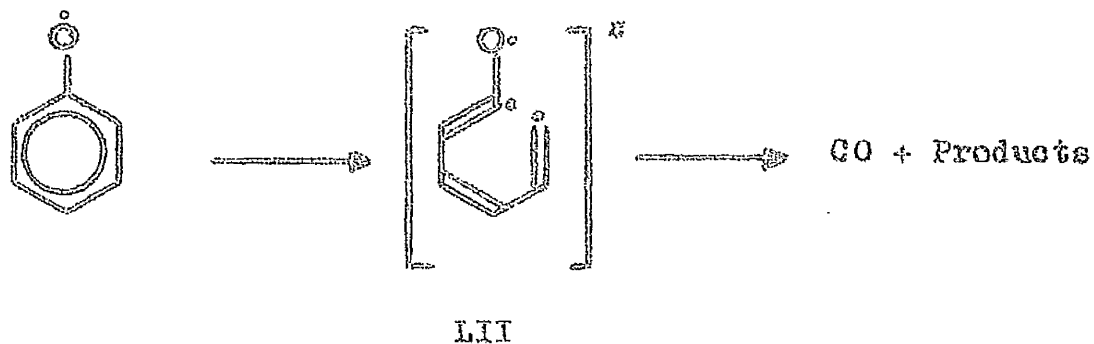


In recent years the spectra, both in the ultraviolet and infrared regions, of the aryloxy radical has been studied. Initial study carried out by Porter and Wright<sup>76</sup> was in the gas phase and due to the short life-time of the radicals generated,  $<10^{-4}$  sec., little could be ascertained from the spectra obtained. On the basis that, at low temperatures and in a rigid medium, the radicals would have less chance of reacting either with the solvent or other radicals due to immobility, research was carried out in solvent glasses<sup>79,80</sup> and solid nitrogen.<sup>77</sup>

Trapped phenoxyl radicals, produced by irradiating phenol, anisole or phenetole with ultraviolet in the range 3450-2250 Å. were shown to have an ultraviolet spectrum with bands at 2400 and 2950 Å.,<sup>77</sup> and at 3950 and 3800 Å.<sup>80</sup> Photolysis of the trapped radicals, with a high pressure mercury arc tube, brought about decomposition and a distinct change in both the ultraviolet and infrared spectra.<sup>77</sup>

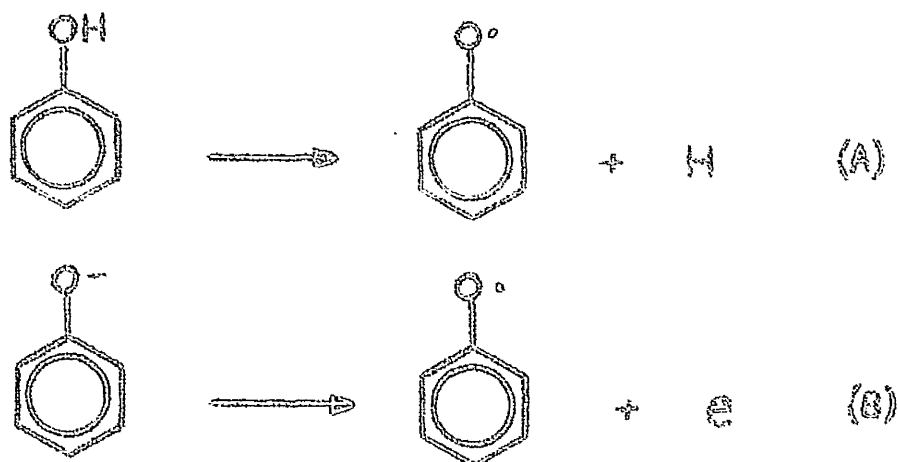
From the data obtained the 2950 Å. band was assigned to the excitation of a  $\pi$  electron<sup>80</sup> from a bonding to an anti-bonding orbital producing rupture of the adjacent carbon-carbon bond to

yield an activated 6-oxo-1,3,5-hexatrienyl-1 radical (LII).



The fate of this particular radical is either deactivation to give the trapped radical or decomposition to yield carbon monoxide and other unspecified decomposition products.

In all the cases studied by Land *et al.*<sup>80</sup> the primary product on photolysis of a phenol or phenolate anion was the formation of a phenoxy radical process (A) being the ejection of a hydrogen atom and (B) the ejection of an electron.



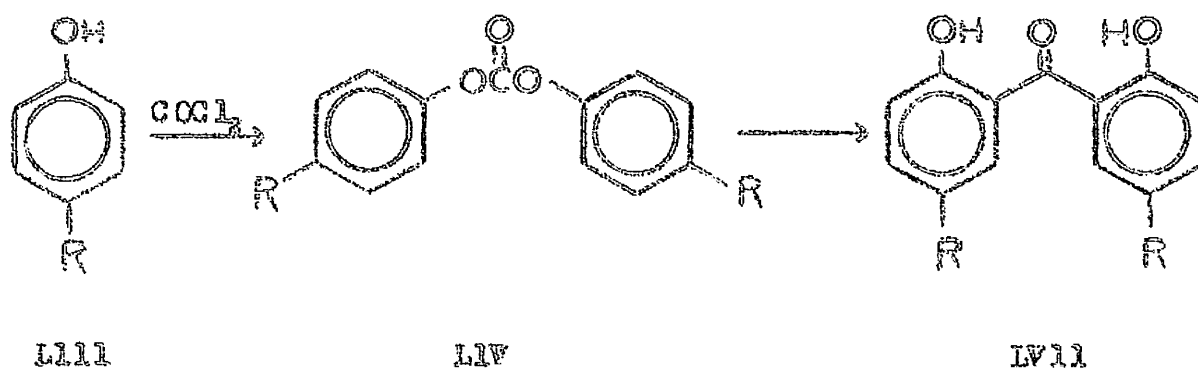
DISCUSSION

This work was carried out in an attempt to find a non-oxidative route to the production of aryloxy free radicals. Photochemical studies were carried out on a series of esters and attempts to trap the free radicals formed were made. Another route via the decomposition of peroxides was investigated. The synthesis of the 5-phenoxy-penta-2,4-dienic acid system is described together with some attempts to synthesise a cyclohexadiene system via Diels-Alder addition reactions.

Irradiation of Aryl Carbonates, Phenyl Salicylate and Phenyl Benzoate.

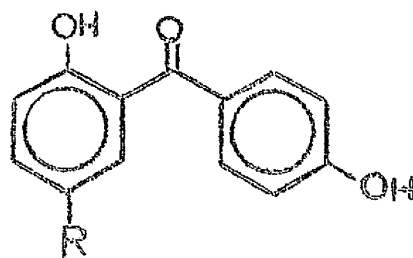
The photo-chemical Fries rearrangement has been known for a few years but as yet no rigorous proof of the mechanism has been produced. Two mechanisms have been proposed 1. by Anderson and Reese<sup>68</sup> which involves a cyclic diradical intermediate (XLVIII, XLIX) capable of collapsing to give the rearrangement products and 2. by Kobsa<sup>69</sup>, who studied a series of substituted phenyl benzoates, involving the formation of a radical pair (L), after absorption of a quantum of light had caused rupture of the acyl carbon-oxygen bond. Since phenoxy radicals might be produced in this manner it was hoped that the following study might well lead to a convenient source of aryloxy radicals. To be of practical application the ester decomposition would have to give a good yield of phenol. Since the ester rearrangements carried out by the above workers gave only a small yield of the corresponding phenol the irradiation of a series of previously uninvestigated esters was carried out with a view to obtaining phenol without the inconvenience of rearrangement products.

Di-*p-t*-butylphenyl carbonate <sup>81</sup> (LIV, R=Bu<sup>t</sup>) was readily prepared by the reaction of the corresponding phenol (LIII, R=Bu<sup>t</sup>) with phosgene in the presence of a base. Irradiation of the ester in ethanol gave a mixture of products readily separable by chromatography on silica gel. These were, in order of ease of elution, unchanged starting material (LIV, R=Bu<sup>t</sup>), 5,5'-di-*t*-butyl-2,2'-di-hydroxybenzophenone (LVII, R=Bu<sup>t</sup>), *p-t*-butylphenol (LIII, R=Bu<sup>t</sup>) and a gum, apparently polymeric, which gave on slow crystallisation a trace of 5,5'-di-*t*-butyl-2,2'-dihydroxybiphenyl <sup>82</sup> (LX, R=Bu<sup>t</sup>). Examination of the recovered impure starting material gave, after hydrolysis, 5-*t*-butylsalicylic acid, <sup>83</sup> thus accounting for the carbonyl frequency at 5.95 $\mu$  (LVIIa, R=Bu<sup>t</sup>).



The rearrangement of aryl carbonates to yield dihydroxybenzophenones was further exemplified by irradiation of phenyl

carbonate (LIV, R=H) in ethanol to give 2,2'-dihydroxy(LVII, R=H) and 2,4'-dihydroxy-(LIX, R=H) benzophenones. It was obvious from the effect of the t-butyl group on the stability of the ester since the t-butyl substituted carbonate rearranged in 24 hr. whereas the

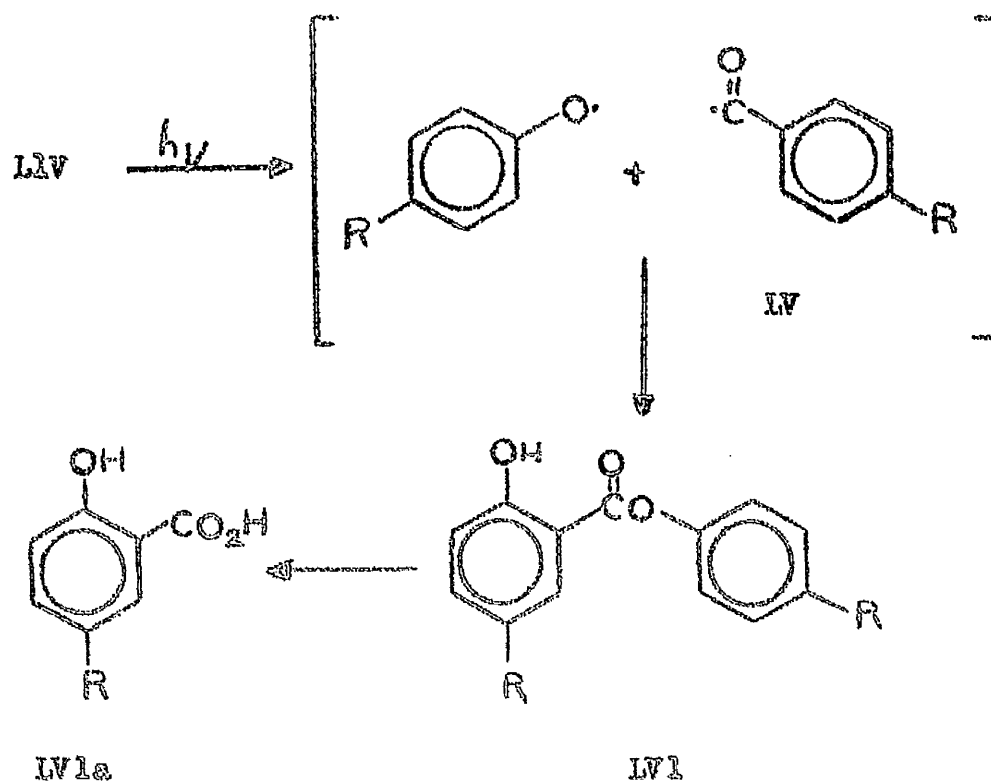


LIX

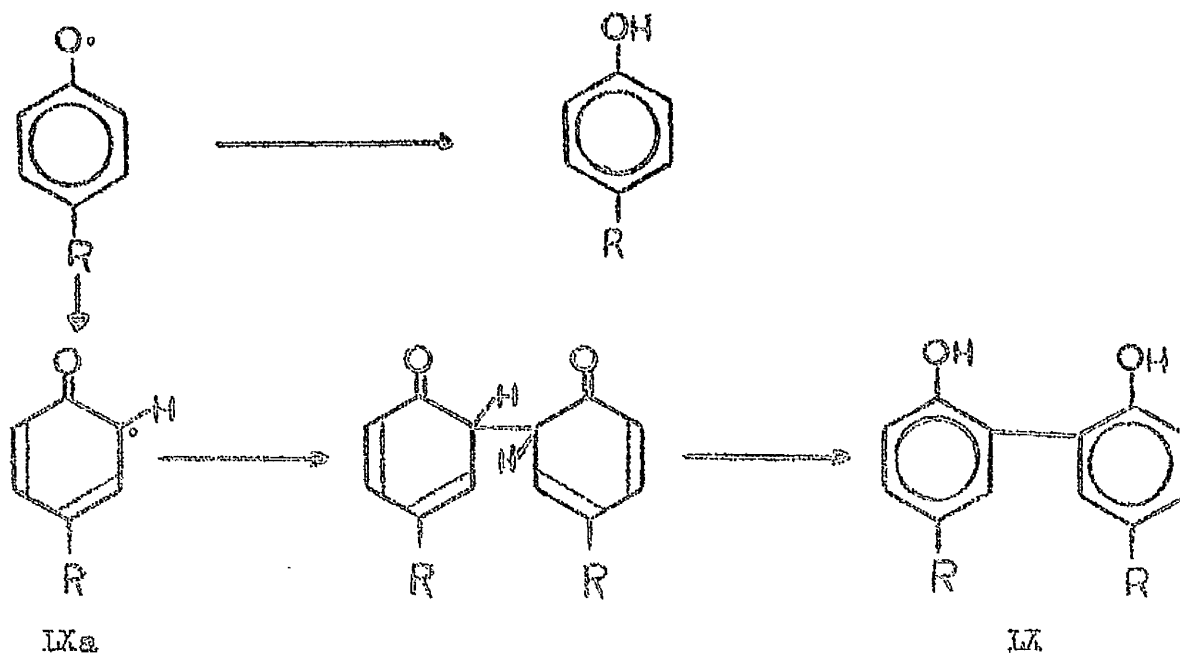
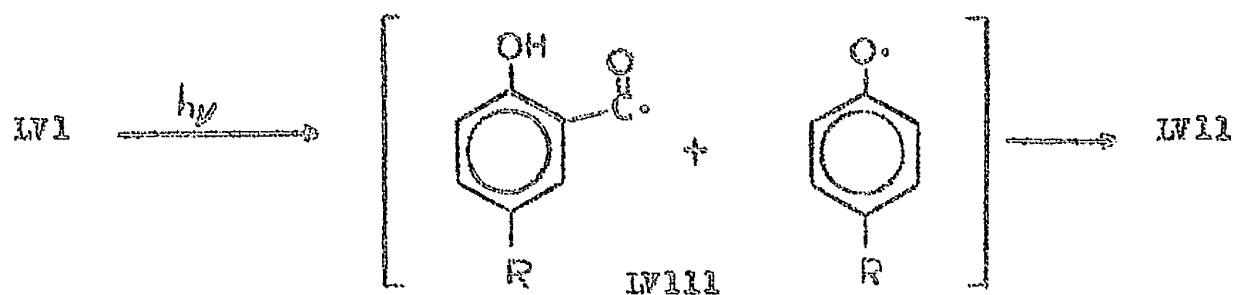
unsubstituted ester took 150 hr. to only partially rearrange. It is possible that the presence of the t-butyl group reduces the energy required to bring about a transition to the first excited state of the molecule.

On the assumption that the photo-Fries rearrangement proceeds via a radical mechanism the reaction scheme would be absorption of a quantum of light giving the radical pair (LV, R=H or Bu<sup>†</sup>) resulting in the formation of the intermediate salicylate (LVI, R=Bu<sup>†</sup>). The intermediate salicylate step was confirmed by the isolation, after hydrolysis, of the free acid (LVla).

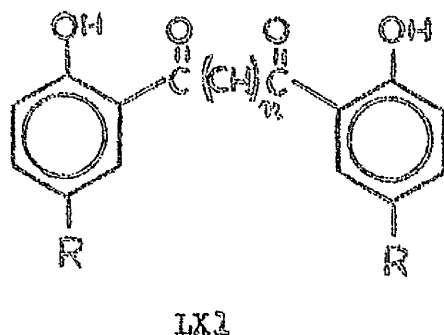




The salicylate can then absorb light giving the intermediate (LVlll,  $R = \text{Du}^t$ ) to yield the benzophenone (LVll). The phenol can be accounted for at two places in this scheme i.e. where aryloxyradicals (LV, LVlll) are generated. Similarly the biphenol (IX) is accounted for at the same stage by dimerisation of the mesomeric radical (LXa) to give the carbon-carbon bonded biphenol on enolisation. It would seem to be a reasonable assumption that a radical mechanism is in operation since an intramolecular cyclic mechanism could not account for the production of phenol or the carbon-carbon bonded dimer.

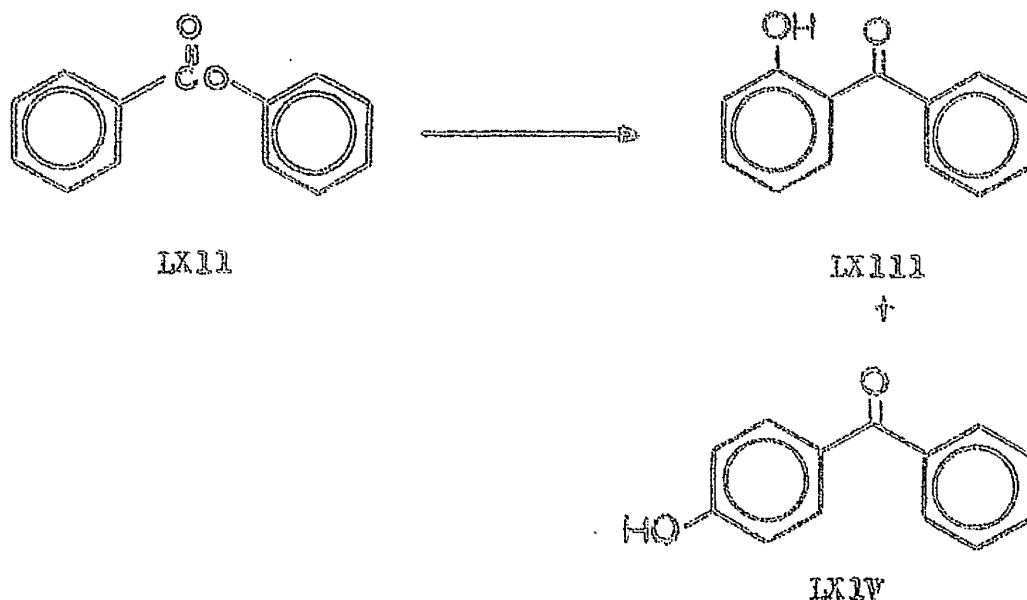


The literature failed to reveal an example of an acid catalysed Fries rearrangement of an aryl carbonate. However the double Fries rearrangement is reported in the literature involving the rearrangement of aryl esters of various aliphatic di-carboxylic acids<sup>84-89</sup> to give hydroxydiketones of the type (LXI) ( $n=2$  or more),



The postulated instability of phenyl salicylate (LXI, R=H) to ultra-violet light was verified by its irradiation to yield the two expected isomers 2,2'-dihydroxy-(LXII, R=H) and 2,4'-dihydroxybenzophenone (LXIII, R=H) as well as a little phenol (LXIV, R=H).

Phenyl benzoate (LXI) was similarly photolysed in ethanol giving 2-hydroxy-(LXII) and 4-hydroxybenzophenone (LXIII).



After the author had completed this work similar results were reported by two groups of workers.<sup>60,64</sup> The results obtained differ only slightly from the published results the difference being attributable to the use by the author of a more concentrated solution of reactant.

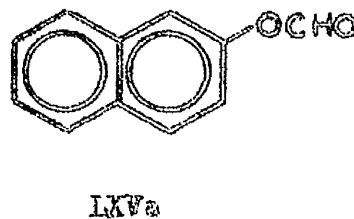
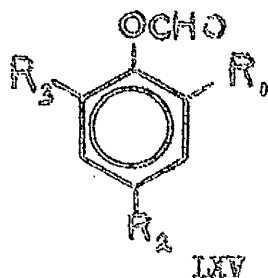
From this initial series of irradiations it was apparent that rearrangement, was by far the major reaction and as a source of phenol did not justify further examination. Furthermore it would appear that the mechanism is probably via free radicals which are capable of withstanding the initial collisions with molecules i.e. a cage reaction, to recombine to give the rearrangement products. It is also of note that it was impossible to account for all of the initial phenoxy material in the recovered phenol and rearrangement products, contrary to the observations of Kobza. The seemingly polymeric material could be explained either by secondary photolysis of the reaction products derived from the phenyl-acyl radical or more probably by polymerisation of the aryloxy radical (LXa) to give units of poly-phenol. This was given additional weight by isolation of a trace of the biphenol (LX, R=Bu<sup>t</sup>) from the irradiation of di-p-t-butylphenyl carbonate and from the fact that the infra-red spectra of the gums, obtained from the tail-end of the chromatographic separation, only indicated the presence of hydroxyl functional groups.

Since these esters had not proved useful in the quantity of phenol produced it was felt that an examination of simpler

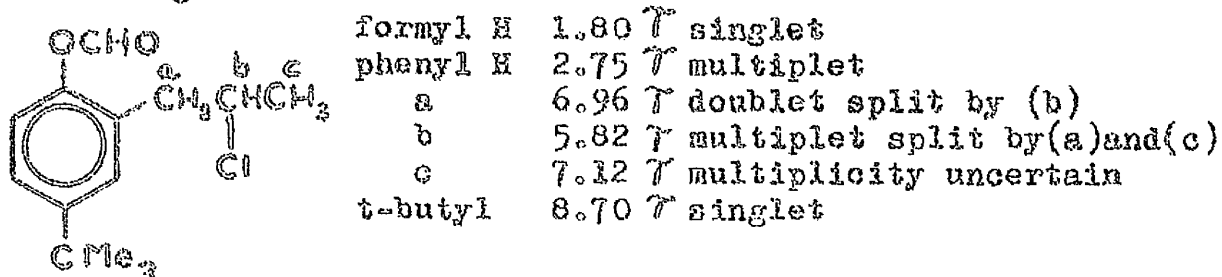
esters, namely formates, might prove fruitful.

### Synthesis of Esters.

A literature search revealed that few aryl formates had been previously prepared. Phenyl formate had been prepared by several groups of workers by reaction of phenol and formic acid<sup>90,91</sup> or sodium formate<sup>92</sup> with phosphorus oxychloride and more recently by reaction of formyl fluoride<sup>93</sup> and phenol. *m*-Tolyl formate is also reported having been synthesised by reaction of silico formic acid on *m*-cresol.<sup>94</sup> It was decided, due to ease of application, to use the synthesis described by Adickes et al.<sup>91</sup> for the preparation of most of the aryl formates used. Slightly better yields were obtained from this synthesis by decreasing the temperature of the reaction by 10°. Distillation of the reaction mixture did not give a pure product but it was found that chromatography on silica gel gave ready separation of the ester from unreacted phenol. By this method the following new formates were prepared, *p*-*t*-butylphenyl (LXV,  $R_1 = R_3 = H$ ;  $R_2 = Bu^t$ ), *p*-chlorophenyl (LXV,  $R_1 = R_3 = H$ ;  $R_2 = Cl$ ), 2,6-xyllyl (LXV,  $R_2 = H$ ;  $R_1 = R_3 = Me$ ) and 2-naphthyl formate (LXVa).

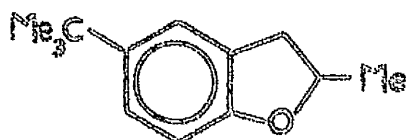


For a later experiment it was necessary to synthesise 2-allyl-4-t-butyl-phenyl formate (LXV,  $R_3 = H$ ;  $R_2 = Bu^t$ ;  $R_1 = allyl$ ). An attempt by the above method yielded a formate ester but the n.m.r. spectrum and micro-analysis showed that hydrochlorination of the allyl side-chain had taken place. Analysis of the n.m.r. spectrum showed that 'normal' addition had probably taken place to give predominantly the 2'-chloro-propyl side-chain. It was, however, difficult to determine the multiplicity of the splitting of the terminal methyl group (c) due to the strong t-butyl resonance signal occurring in the same region. The spectrum of 4-t-butyl-2-(2'-chloro-propyl)-phenyl formate (A) had the following peaks and assignments.



(A)

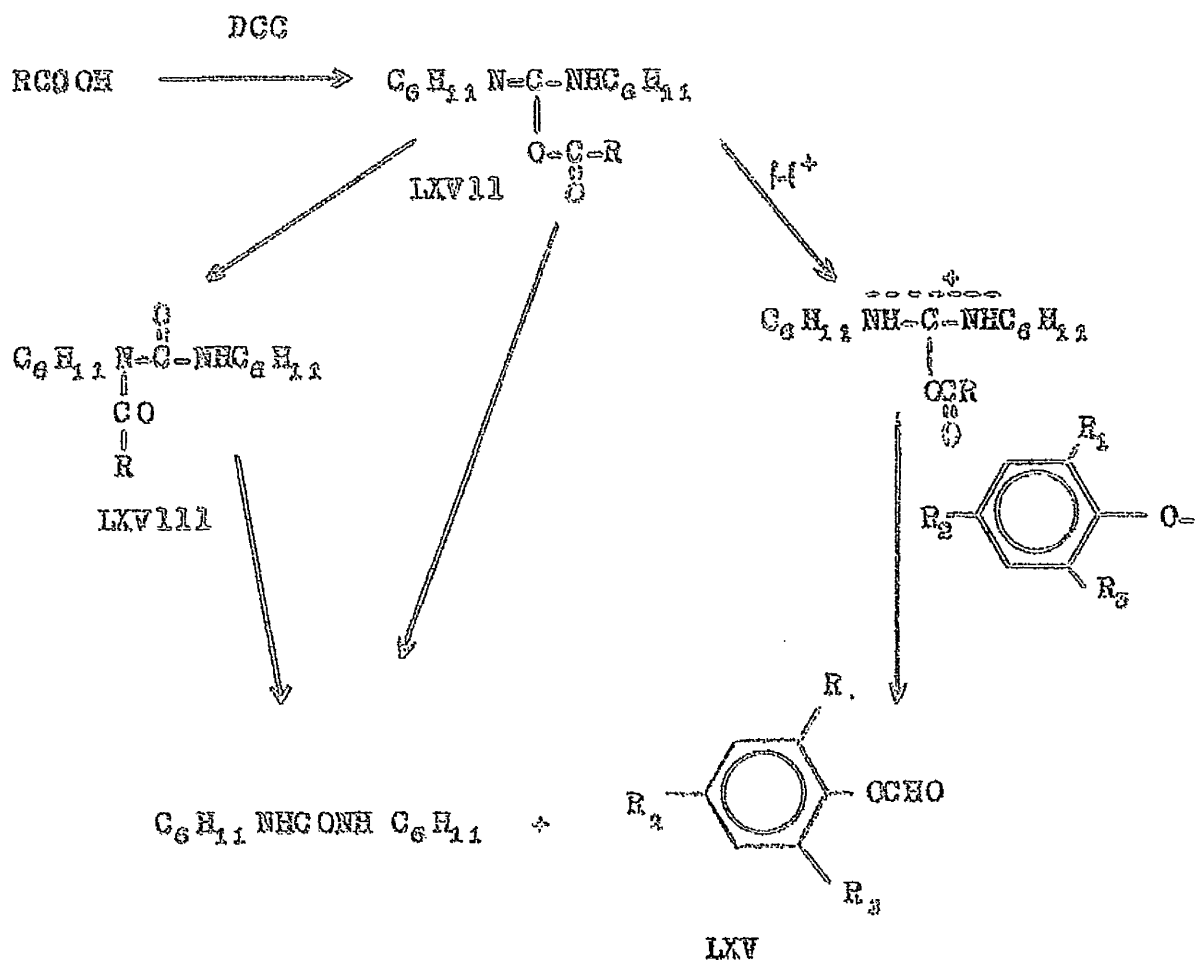
Formates<sup>96</sup> have been synthesised in good yield by heating the corresponding alcohol with formic acid however an attempted synthesis with 2-allyl-4-t-butyl phenol<sup>96</sup> and formic acid gave only the cyclisation product 5-t-butyl-2,3-dihydro-2-methylbenzofuran<sup>96</sup> (LXVI) reported originally by Sen and Rastoji who used more vigorous acid catalysed conditions.



LXVI

A less rigorous method of esterification was therefore sought. Dicyclohexyl-carbodiimide (DCC) has been used for the synthesis of peptides<sup>97, 98</sup> and esters of aromatic acids<sup>99</sup> and more recently for the esterification of phenols.<sup>100, 101</sup> By application of this method 2-allyl-4-t-butylphenyl (LXV,  $R_2 = H$ ,  $R_3 = Bu^t$ ,  $R_1 = allyl$ ) and p-tolylformate (LXV,  $R_1 = R_3 = H$ ,  $R_2 = Me$ ) were prepared. For the mechanism of this esterification the following scheme (R = H) analogous to that proposed by Khorana<sup>98</sup> for the formation of peptide linkages may be suggested.

This involves the initial addition of the acid to the DCC, since weakly acidic phenols do not react in this manner at room temperature. The low yields from the reaction could be accounted for by the intramolecular rearrangement (LXVII-LXVIII) to yield the acyl urea (LXVIII) which was not isolated. The evolution of gas noticed during the esterification could be attributed either to the loss of carbon monoxide from (LXVIII, R=H) to give dicyclohexylurea or by a direct loss of carbon monoxide from intermediate (LXVII) to yield, on ketonisation, the urea.





### Irradiation of Aryl Formate Esters.

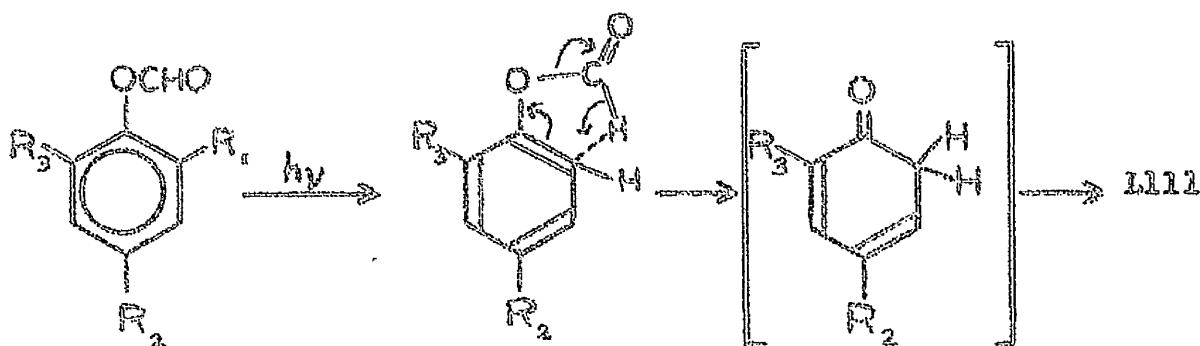
Previous work on the non-sensitised irradiation of alkyl formates has been carried out by Ausloos<sup>73, 74</sup> who studied the possible mechanisms of decomposition in the gas and liquid phase and the effect of solvent dilution. The results obtained indicated that evolution of carbon monoxide tended to be an intra-molecular elimination reaction. However, to account for other products obtained, it was essential to postulate other dissociation processes giving rise to radicals. It was thought that on this basis there was sufficient justification to investigate the aryl formate decomposition as a possible radical source.

p-t-Butylphenyl formate (LXV,  $R_1 = R_2 = H$ ,  $R_3 = Bu^t$ ) on irradiation in ethanol gave a good yield (80%) of p-t-butylphenol (LIII,  $R = Bu^t$ ) accompanied by a gum from which was isolated a trace of the carbon-carbon bonded biphenol (LX,  $R = Bu^t$ ). Tests on the ethanol solvent showed the presence of acetaldehyde. The gas evolved during the reaction (1.5 mole per mole of ester) was shown, by its infra-red spectrum, to be predominantly carbon monoxide. From these observations it is difficult to propose by what mechanism the phenol is produced. The results indicate that at least part of the reaction scheme is free radical since it is possible to isolate 5,5'-di-t-butyl-

2,2'-dihydroxy-biphenyl and acetaldehyde from the reaction mixture, acetaldehyde being explained by radical abstraction of hydrogen from a molecule of ethanol and subsequent loss of hydrogen to yield the aldehyde, a mechanism proposed by Merz and Waters.<sup>102</sup>



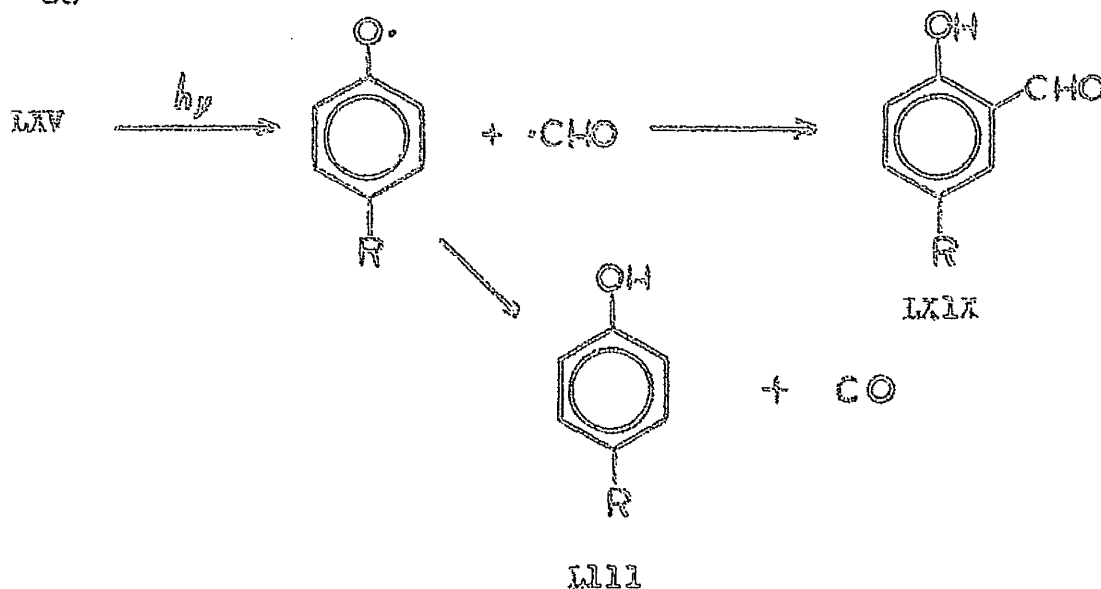
While part of the reaction would seem to account for the production of radicals an intramolecular rearrangement can be proposed to account for the production of phenol as follows:-



LXV

Irradiation of the formate in benzene, however, gave a reduced yield of the phenol as well as the expected rearrangement product 5-t-butyl salicylaldehyde (LXIX,  $R=\text{Bu}^t$ ). The slowness of the decomposition rate in benzene could be

attributable to the opacity of benzene to the ultra-violet light below  $270\text{m}\mu$ . This tends to indicate that the formate is decomposed primarily by the high energy light between 200 and  $270\text{m}\mu$ . In benzene solution it appears that the formyl radical ( $\cdot\text{CHO}$ ), generated by ester cleavage, is more stable than in ethanol giving rise to a small amount (6%) of the rearrangement product (LXIX,  $\text{R}=\text{Bu}^t$ ). Thus it would appear that in benzene, as well as the intramolecular rearrangement suggested above, there is a slightly better yield of the products generated by formation of radicals by the following suggested scheme:-

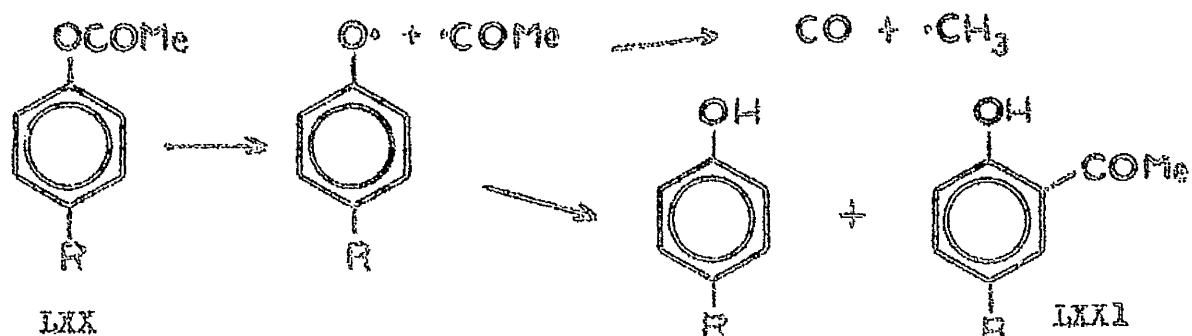


It is thus difficult to make a definite mechanistic proposal based on the author's observations. It appears

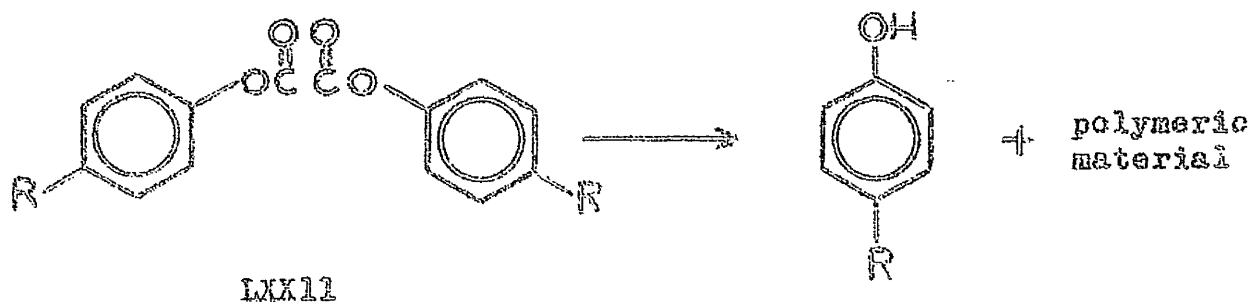
that two schemes are competing 1. the major reaction being an intramolecular elimination of carbon monoxide and 2. ester cleavage giving rise to radicals. The fate of the formyl radical is however obscure. It would appear that reaction with the solvent probably takes place, giving rise to formaldehyde, before any collision with the phenoxy radical, to give the o-rearrangement product, can occur. Secondary photolysis of the formaldehyde could take place to yield carbon monoxide and hydrogen.

Due to the difficulty of detecting hydrogen in a mixture containing hydrogen and carbon monoxide it was decided to irradiate *p*-*t*-butyl-phenyl acetate (LXX, R= $\text{Bu}^t$ ). It was hoped that photolysis would give rise to the acetoxy radical ( $\text{CH}_3\overset{\circ}{\text{C}}\text{O}$ ) capable of decomposing to give, ultimately, carbon monoxide and methane, readily detectable by infra-red spectroscopy. Thus irradiation of *p*-*t*-butylphenyl acetate in ethanol gave, on chromatography, 5-*t*-butyl-2-hydroxyacetophenone (LXXI, R= $\text{Bu}^t$ ), originally obtained by an acid catalysed Fries reaction<sup>102</sup>, and *p*-*t*-butylphenol as the identifiable products. An infra-red spectrum of the gas evolved indicated the presence of carbon monoxide and a hydrocarbon gas thought to be methane.

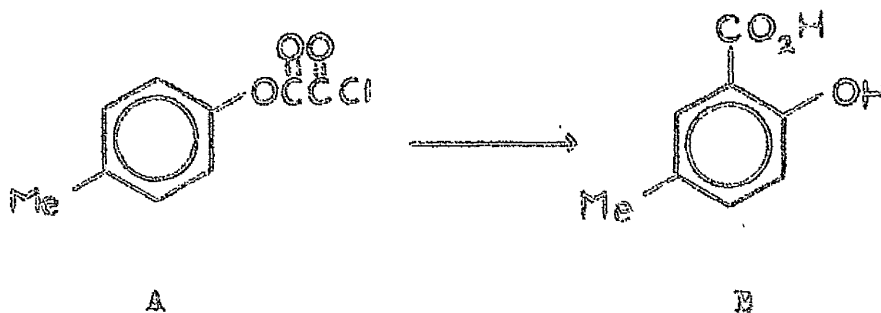
The probable mechanism is as follows:-



In order to complete this series of esters the irradiation of phenyl formate (LXIII,  $R_1 = R_2 = R_3 = \text{H}$ ) was carried out in ethanol. Diphenyl (LXII,  $R = \text{H}$ ) and di-*p-t*-butylphenyl oxalate (LXIII,  $R = \text{Bu}^t$ ) were synthesised analogously to the formates<sup>92</sup> and irradiated in ethanol. In all cases only the phenol was isolated. Large quantities (50%) of apparently polymeric material were also obtained from which no identifiable products could be isolated. It was of interest, however, that the oxalates yielded the phenol since intramolecular extrusion of carbon monoxide, as in the case of the formates, is impossible. This fact helps to strengthen the case for a free radical mechanism.



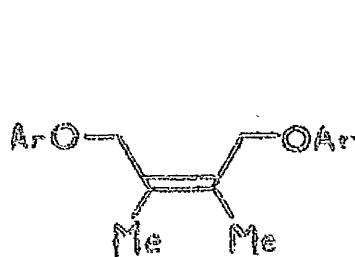
No rearrangement products were obtained during the photolysis of the oxalates. This is predictable since the acid catalysed Fries reaction with oxalates and malonates does not yield rearrangement products.<sup>88</sup> Little direct study of the acid catalysed reaction has been carried out although work on the attempted formation of the coumarandiones<sup>104</sup> showed that rearrangement of p-tolyl-oxalyl chloride (A) in presence of aluminium chloride gave a trace of 2-hydroxy-5-methylbenzoic acid (B).



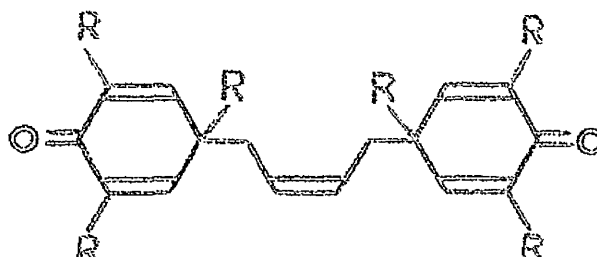
#### Irradiation of Formates in Olefins.

The reactions of free radicals in solution is a subject which has been extensively reviewed both as a general topic<sup>105, 106,</sup>  
<sup>107</sup> and from the stereochemical<sup>108</sup> viewpoint. Alkoxy radicals, generated by decomposition of hydroperoxides in aqueous systems have been trapped and studied by Kharasch et al.<sup>109, 110</sup> employing conjugated dienes as the trapping medium. However there are few references to the trapping of phenoxy radicals by

this technique. Pummerer et al.<sup>111</sup> prepared an adduct (LXXIII) from 2,3-dimethyl-but-1,3-diene and methyltetra-chlorophenoxy. A series of adducts



LXXIII



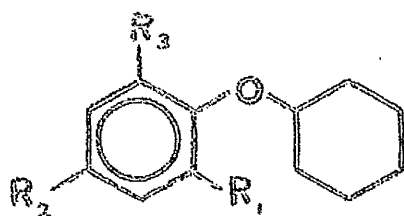
LXXIV

have also been prepared from 2,4,6-tri-*t*-butylphenoxy<sup>112</sup> and various conjugated dienes giving rise to the 2:1 radical: diene ratio obtained by Pummerer but different in the respect of forming quinonoid structures (LXXIV) and not the ethers as in (LXXIII). The closely analogous thiophenoxy radicals and their additions to olefinic systems have also been examined.<sup>115-119</sup>

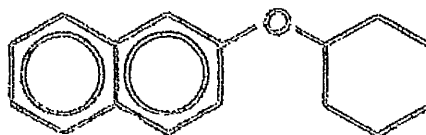
Due to the scale of the reaction that was being employed in this case the author felt that it was more advantageous to use an olefin which was readily obtainable and readily retained in the reaction mixture, at ambient temperatures, for the time involved to decompose the ester. With these restrictions in mind cyclohexene was chosen as

a suitable material.

A series of aryl formates namely, *p*-*t*-butylphenyl (LXV,  $R_1 = R_3 = H$ ;  $R_2 = Bu^t$ ), phenyl (LXV,  $R_1 = R_2 = R_3 = H$ ), 2,6-xyllyl (LXV,  $R_1 = R_3 = Me$ ;  $R_2 = H$ ) and  $\beta$ -naphthyl formate (LXVa) were irradiated in redistilled cyclohexene. Chromatography of the residues from these reactions yielded, in order of ease of elution, a hydrocarbon oil, described later in the text (page 55), the aryl cyclohexyl ether (LXXV, LXVa), unchanged ester plus, in two cases (LXV,  $R_1 = R_3 = H$ ;  $R_2 = Bu^t$  and  $R_1 = R_2 = R_3 = H$ ), rearrangement products (LXIX,  $R = Bu^t$  and  $R = H$  respectively) and the corresponding phenol in all cases. The amount of cyclohexyl ether isolated in each case was less than 10% of the theoretical yield.



LXXV



LXXVa



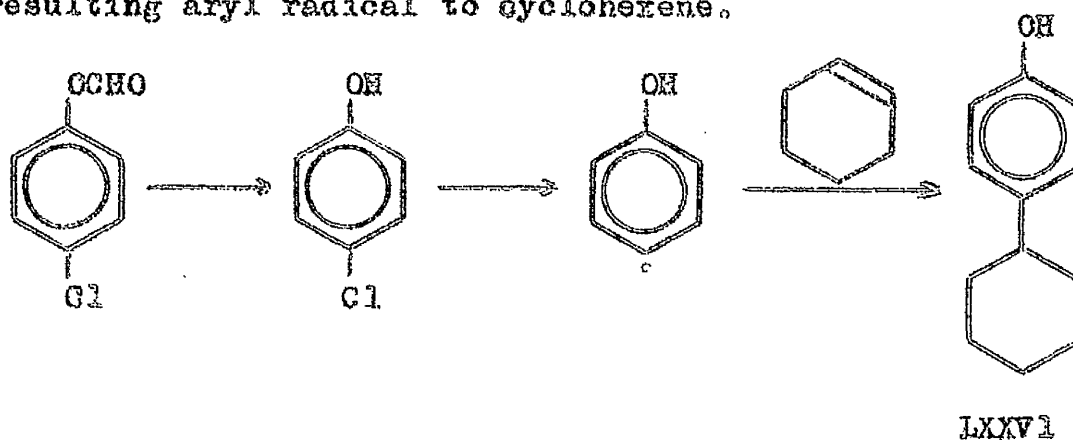
Irradiation of Formate Esters in Cyclohexene.

Formate Ester.	Product.
p-t-butylphenyl- LXV, $R_1 = R_3 = H$ ; $R_2 = Bu^t$	p-t-butylphenyl cyclohexyl ether LXXV, $R_1 = R_3 = H$ $R_2 = Bu^t$ (8% yield)
phenyl- LXV, $R_1 = R_2 = R_3 = H$	phenyl cyclohexyl ether LXXV, $R_1 = R_2 = R_3 = H$ (1% yield)
2,6-xylol- LXV, $R_1 = R_3 = Me$ ; $R_2 = H$	2,6-dimethylphenyl cyclohexyl ether LXXV, $R_1 = R_3 = Me$ ; $R_2 = H$ (6% yield)
$\beta$ -Naphthyl- LXVa	$\beta$ -naphthyl cyclohexyl ether LXXVa (4% yield)

The n.m.r. spectra of the ethers obtained are discussed later in the text (page 56 ) and the data are recorded in Appendix II.

The irradiation of p-chlorophenyl formate (LXV,  $R_1 = R_3 = H$ ;  $R_2 = Cl$ ) in cyclohexene exhibited certain differences. As well as the hydrocarbon fraction and p-cyclohexyl cyclohexyl ether (LXXV,  $R_1 = R_3 = H$ ;  $R_2 = Cl$ ) two phenolic products were isolated. A small amount of a crystalline material, which analysed for and had the same melting point as p-cyclohexylphenol (LXXVI) was obtained. The n.m.r. spectrum, recorded in Appendix II, showed, a quartet at 3.17 $\tau$ , typical of the  $A_2B_2$

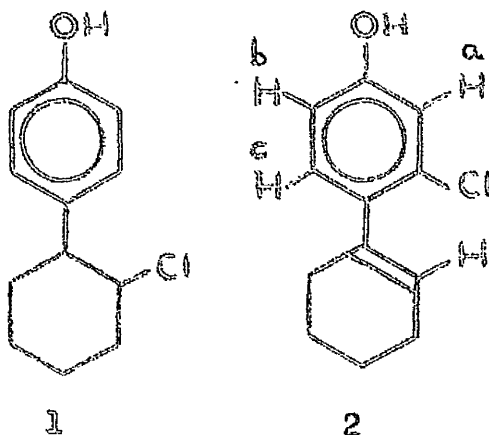
system of a p-disubstituted aromatic ring, a singlet at 5.2  $\tau$  for the phenolic proton and an unresolved multiplet at 8.4  $\tau$  accounting for the cyclohexyl protons. It is possible to account for the formation of LXXVI by photolytic removal of the chlorine atom, in p-chlorophenol, and addition of the resulting aryl radical to cyclohexene.



No report of addition of this sort to cyclohexene could be found in the literature, however, the closely analogous photolysis of substituted iodo-benzenes<sup>119-121</sup> in benzene give rise, by this proposed mechanism, to substituted bi-phenyls. It is conceivable that although the C-Cl bond is stronger at 80K.cals per mole than the C-I bond (52.6K.cal. per mole) that the polychromatic source employed is capable of severing such a bond.

The other phenolic product, designated Product A, was

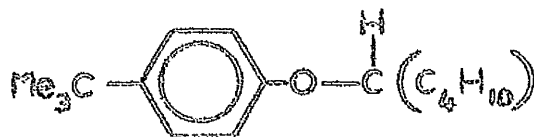
harder to characterise and justify. From the infra-red spectrum it was not possible to determine whether the aromatic nucleus was 1,4-di- or tri-substituted. The presence of a phenolic hydroxyl group and an alkyl substituent was indicated. Elementary analysis of the benzoate from product A was in agreement with a molecular formula of  $C_{12}H_{15}ClO$  for A. Reaction of Product A with zinc and ethanol gave unchanged material whereas reaction with alcoholic potassium hydroxide yielded a gum. On this basis the halogen was thought to be bonded to the aromatic ring. Two structures are therefore proposed for Product A, 1. being rejected on the chemical evidence that the halogen is attached to the benzene nucleus, 2. on the basis of the n.m.r. spectrum, could be a possible structure, although a mechanism for its production is obscure. The cyclohexenyl group is preferred to the cyclohexyl group because of the sharpening of the alkyl resonance at  $8.33\tau$ . The phenolic proton occurs at  $5.2\tau$ . The group of peaks



<u>N.M.R. Spectrum</u>	
<u><math>\tau</math> values</u>	<u>Integral</u>
2.6-3.4	4.3
5.20	1
8.33	8.8

between 2.6 and 3.4  $\tau$  are more difficult to assign. It is feasible that the peaks at 3.0 and 3.14  $\tau$  could be attributed to protons (a) and (b) and protons (c) and (d) be assigned to the peaks at 2.64 and 2.75  $\tau$ . Such a structure is backed up by the integral which shows a ratio of 4.3:1:8.8 which is in reasonable agreement with II requiring 4:1:8.

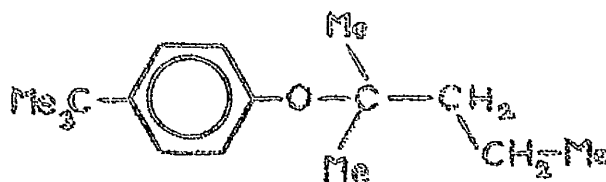
To demonstrate the versatility of this photochemical addition reaction the irradiation of p-t-butylphenyl formate in pent-2-ene was carried out giving the corresponding ether (LXXVII). It was, however, not possible to decide from the n.m.r. spectrum (Appendix II) whether the ether was the 2- or the 3-isomer or, whether it was a mixture of both.



LXXVII

To obtain some indication of the mechanism of addition it was necessary to use an olefin which would give rise to either a primary or tertiary ether since it would then be possible to investigate the preponderance of one of the isomers by analysis of the n.m.r. spectrum with reference to the

hydrogen attached to the ether carbon. Irradiation of the formate in 2-methyl-pent-1-ene was carried out giving a sample of an ether shown to be wholly *p*-*t*-butylphenyl 2-(2-methylpentyl) ether (LXXVIII).



LXXVIII

The n.m.r. spectrum of this ether did not show the presence of the primary ether. From these observations it appeared that the addition was taking the normal or ionic route since attachment of the phenoxy grouping was taking place at the potential positive centre.

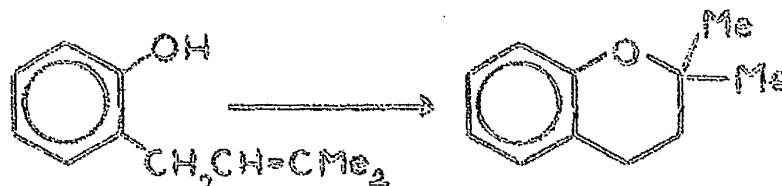
Since the yields of ethereal product from the above reactions were poor irradiations of formates embodying their own olefinic systems were contemplated. The irradiation of 2-allyl-4-*t*-butylphenyl formate (LXV,  $R_3 = H$ ;  $R_2 = Bu^t$ ;  $R_1 = Allyl$ ) in benzene was therefore carried out giving 5-*t*-butyl-2,3-dihydro-2-methylbenzofuran (LXVI) the predicted normal cyclisation product. The isomerisation of the allyl side-chain was

considered probable but examination of recovered 2-allyl-4-t-butylphenol did not exhibit any change.

At this stage in the study it was shown that p-t-butylphenol, on irradiation in cyclohexene, gave a small yield of the cyclohexyl ether as the only identifiable material. A reaction between p-t-butylphenol and cyclohexene at reflux temperature did not yield any cyclohexyl ether thus eliminating the possibility of self-catalysed addition.

Prior to further studies with allyl phenols it was found that the formate ester grouping was not essential for photocatalysed cyclisation since the irradiation of 2-allyl-4-t-butylphenol gave rise to a good yield of the benzofuran.

To eliminate the possibility of the suggested isomerisation (see page 49) the irradiation of 2-(3,3'-dimethylallyl)phenol (LXXIX) prepared by the method of Hurd and Hoffman,<sup>122</sup> was carried out in benzene. The ethereal product isolated was shown to be the six membered cyclic ether 2,2-dimethylchroman<sup>123</sup> (LXXX).



LXXIX

LXXX

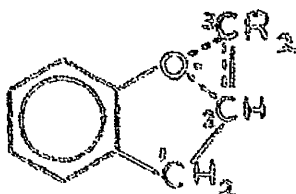
The isolation of this ether added weight to the possibility of an ionic mechanism. It is worthwhile noting that Hurd and Hoffman<sup>122</sup> carried out attempts to bring about the 'abnormal' addition of hydrogen bromide to the allyl side-chain but in no case were they able to effect cyclisation to the dihydrofuran.

It is difficult to draw any definite conclusions for the mechanism of this observed addition of phenols to olefins. It is probable, however, that the predominant step in the photolysis of formates is the extrusion of carbon monoxide to give the phenol although there may well also be a little ester cleavage. Thus the formate group appears to be acting as a photo-sensitive protecting group since it is possible to isolate unreacted phenol and formate from irradiation in cyclohexene while a parallel experiment using the phenol alone in cyclohexene gave no recoverable phenol.

The generation of radicals by photolysis of the phenol thus seems to be important in the addition to olefins. The results published by a number of authors showed conclusively that the photolysis of a phenol<sup>77-80</sup> in the 2500-3000Å. region gave rise to a detectable concentration of phenoxy radicals.

On this assumption two radical mechanisms can be proposed to account for the observed products.

1. The generated radical interacts with the  $\pi$  electrons of the double bond giving rise to a bridged or resonating radical (LXXXI, R=H or Me).



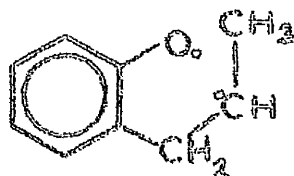
LXXXI

Such an intermediate has an analogy in the attack of a bromine atom at a double or triple bond.<sup>124</sup> Recent studies by Abell and Piette<sup>125</sup> have shown that a cyclic intermediate is possible and that the attaching bromine atom is held in the electron cloud evenly placed, in symmetrical compounds, between the two carbon atoms of the double bond. However, in the closely analogous field of thiyl radicals this cyclic intermediate is not favoured and a classical open-chain radical<sup>126, 130</sup> is used to explain the stereochemistry of the addition encountered. With the above cyclic intermediate the free electron on the oxygen would have to form a bond at the more positive centre

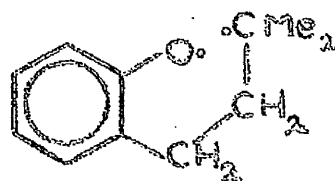


at carbon 2(R=H) or carbon 3(R=Me) to account for the formation of the benz-furan (R=H) and the chroman (R=Me) formed after hydrogen abstraction. This would imply that radical addition to an olefin which commonly gives rise to the anti-Markownikoff product, was giving the normal addition product. This would mean that polar effects, originally<sup>131</sup> thought to have no directive effect during such attack, were determining the direction of free radical addition. Recently a suggestion<sup>132</sup> has been made that polar effects can contribute in certain cases where there is little difference in the stability of the intermediate radicals.

2. Another more probable mechanism depends on the formation of the more stable radical resulting from hydrogen atom attack on the olefin. This gives rise to normal addition products and is initially a Markownikoff addition leading to the more stable radicals, secondary in the case of LXXXI and tertiary in the case of LXXXII.

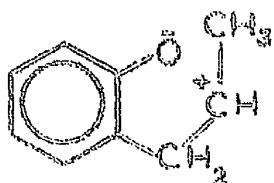


LXXXI

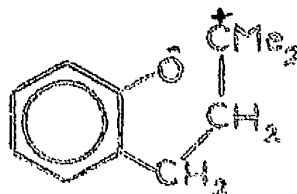


LXXXII

Cyclisation would then take place to give the observed products. It is however possible to explain the results by an ionic mechanism. This would involve heterolytic cleavage of the phenol oxygen-hydrogen bond. The resulting addition of the proton to the allyl side-chain would give rise to the more stable carbonium ion (LXXXlla, LXXXllla) which would then cyclise to the observed products.



LXXXlla



LXXXllla

On the basis of the experiments described here, it has not been possible to ascribe a definite mechanism to the addition. However, while it is known that ultra-violet irradiation can bring about heterolysis, a free radical mechanism is preferred. The evidence obtained by other workers shows that the first proposal of a cyclic intermediate is not feasible and therefore the second proposal, involving addition of hydrogen as the first step, is preferred.

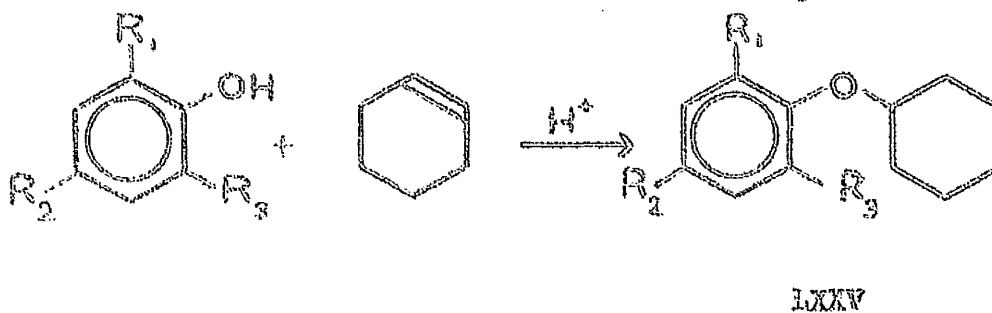
#### Hydrocarbon Fraction.

From all the irradiations carried out in cyclohexene a

hydrocarbon fraction was obtained at the fore-front of the chromatographic separation. This was purified by distillation and subjected to vapour phase chromatography. The material was shown to consist of three major components one of them having the same retention time as an authentic specimen of 2, 2'-dicyclohexenyl.<sup>125</sup> Attempts to identify the other two components were unsuccessful. Chemical proof of the existence of dicyclohexenyl in the mixture was obtained by isolation of dicyclohexenyl tetrabromide after bromination of the mixture in chloroform. It was at first thought that the presence of dicyclohexenyl was indicative of the generation of free radicals during the irradiation by abstraction of an allylic hydrogen followed by dimerisation of two cyclohexenyl radicals to give dicyclohexenyl. However, irradiation of redistilled cyclohexene gave rise to the same hydrocarbon material with the same components. Vapour phase chromatography of redistilled cyclohexene showed only one component. Thus it would seem that photolysis must be generating radicals presumably by cleavage of allyl carbon-hydrogen bond. The fate of such a cyclohexenyl radical could give rise to a mixture of hydrocarbons one of which would be the dimer dicyclohexenyl.

### Aryl Cyclohexyl Ethers.

Samples of the aryl cyclohexyl ethers encountered during the irradiation experiments were synthesised independently for identification purposes. The synthesis<sup>154, 155</sup> employed was the reaction of the corresponding phenol with cyclohexene and a catalytic amount of concentrated sulphuric acid.



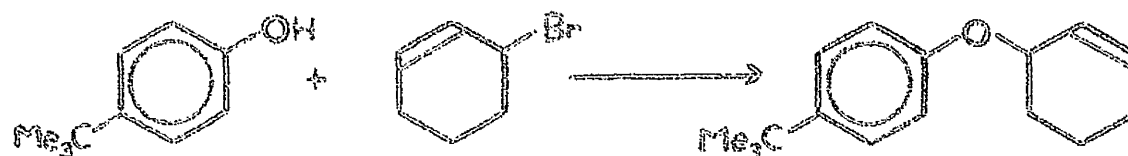
Chromatography was used to separate the resulting ether from the phenol and any C-alkylated material which might have been formed during the reaction. By this method pure samples of p-t-butylphenyl (LXXV,  $R_1=R_3=H$ ;  $R_2=Bu^t$ ), 2,6-di-methylphenyl (LXXV,  $R_1=R_3=Me$ ;  $R_2=H$ ) and p-chlorophenyl (LXXV,  $R_1=R_3=H$ ;  $R_2=Cl$ ) cyclohexyl ethers were prepared. The n.m.r. spectra of these ethers are contained in Appendix II. Generally they exhibit typical aromatic proton resonance at 2.5-3.5  $\tau$ , ether proton at 5.8  $\tau$  and the cyclohexyl protons, complicated by the substituent alkyl groups, as an unresolved multiplet at 8.4  $\tau$ .

It was found, however, that a sample of  $\beta$ -naphthylcyclo-

hexyl ether (LXXVa) synthesised by this route differed in its melting point (66-68°) from that reported in the literature (116°) by Wang<sup>136</sup> who prepared a sample by reaction of chlorocyclohexane with the sodium salt of  $\beta$ -naphthol. The sample prepared in this case was shown to be authentic by its n.m.r. spectrum (Appendix II), the integral of which agreed with the proposed structure, and micro-analysis.

p-t-Butylphenyl Cyclohex-2-enyl Ether.

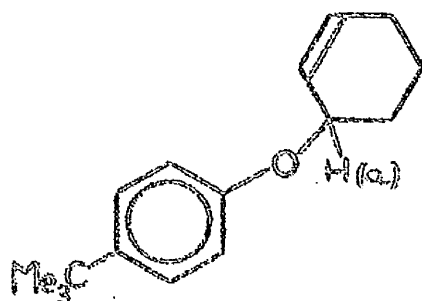
As a possible extension of the photolytic cyclisation of allyl phenols it was proposed to attempt the synthesis of 4-t-butyl-2-cyclohex-2'-enylphenol. The synthetic route chosen was by the synthesis of p-t-butylphenyl cyclohex-2-enyl ether (LXXXIV) by reaction of p-t-butylphenol and 2-bromocyclohexene, prepared by Ziegler bromination of cyclohexene,<sup>137</sup> in the presence of anhydrous potassium carbonate in acetone.<sup>138</sup>



LXXXIV

The ether was obtained in good yield as a colourless liquid. Verification of the structure was obtained from analysis of its

n.m.r. spectrum. The integral obtained was in good agree-



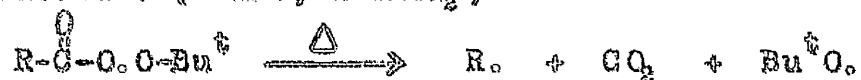
Phenyl protons	Quartet 3.05 T
vinyllic protons	Doublet 4.15 T
proton (a)	Bump 5.3 T
remaining cyclohexenyl protons	Bump 6.2 T
Bu <sup>t</sup>	Singlet 8.7 T

ment with the expected structure. An attempted Claisen rearrangement proved unsuccessful, p-t-butylphenol being recovered as the only phenolic material. Germforth et al.<sup>15a</sup> had previously investigated the pyrolysis of phenyl cyclohexenyl ether obtaining only a poor yield of the ortho rearrangement product. Even on increasing the reaction time from 5 min. to 2 hr. no rearrangement product could be isolated.

#### Preparation and Decomposition of O,O-t-Butyl-O-Phenyl Monopercarbonate.

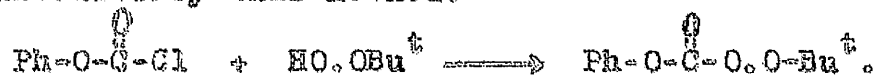
Another possible route to the generation of phenoxy radicals was sought. The decomposition of peroxides appeared to be worthy of investigation and it was decided to synthesise a phenyl monopercarbonate, chosen because attempts to synthesise diphenyl peroxydicarbonate<sup>152</sup> had been unsuccessful.

This approach to the generation of phenoxy radicals appeared to be reasonable since experiments by Bartlett et al.<sup>150,151</sup> had shown that per-esters of the type (LXXXV) would decompose by a concerted mechanism, severing two bonds, to give rise to t-butoxy and R· radicals as well as carbon dioxide, provided that the R group possessed sufficient stability to exist as a free radical on its own. This postulate was exemplified by the generation of benzyl radicals by decomposition of t-butyl-phenylperacetate (LXXXV, R=PhCH<sub>2</sub>)



LXXXV

Thus the synthesis of O, O-t-butyl-O-phenylmonopercarbonate (LXXXVI) was carried out by reaction of phenylchloroformate<sup>152</sup> with purified t-butyl hydroperoxide<sup>151</sup> by an extension of the procedure of Davies and Hunter,<sup>154</sup> who synthesised dialkyl monopercarbonates by this method.

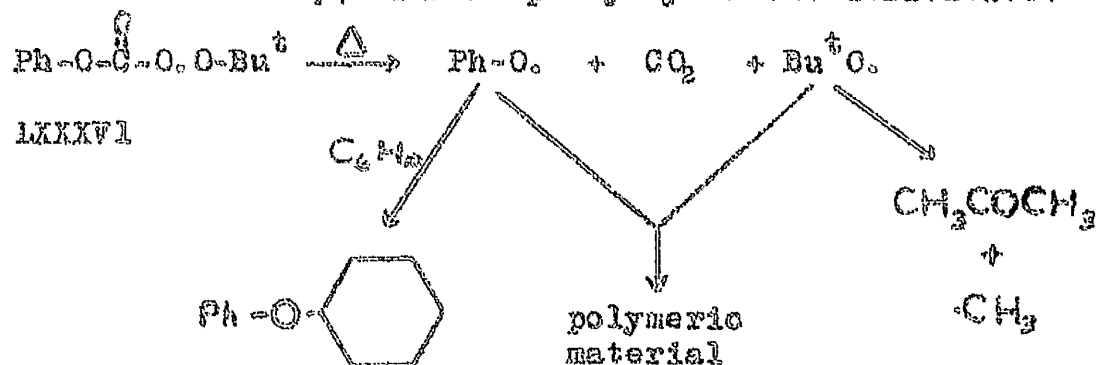


LXXXVI

The ester was obtained as a sweet smelling oil which, being heat sensitive, could not be purified by distillation.

Chromatography was carried out until titrimetric analysis for active oxygen<sup>155</sup> showed that the ester was greater than

97% pure. The infra-red spectrum of the ester always had a small shoulder present on the ester carbonyl peak attributed to the presence of diphenyl carbonate as an impurity. Pyrolysis of the ester was carried out by refluxing in cyclohexene with a view to trapping any phenoxy radicals formed. Separation of the mixture, after decomposition was complete, gave a trace of hydrocarbon oil, having a similar infra-red spectrum to that of dicyclohexenyl, phenyl cyclohexenyl ether and diphenyl carbonate. A large quantity of insoluble amorphous material was also present. This was not identified and could have arisen by radical-radical coupling giving rise to a complex mixture. The presence of acetone was shown by the isolation of its 2,4-dinitro-phenylhydrazosone derivative.



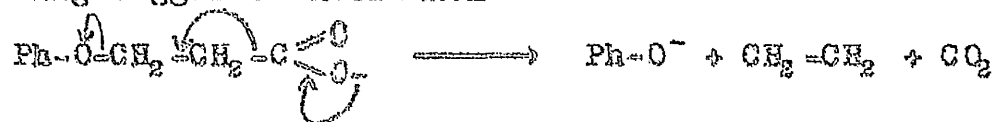
The presence of carbon dioxide and a hydrocarbon gas was shown by the infra-red spectrum of a gas sample. The above homolysis and reaction scheme could well account for all the products isolated.



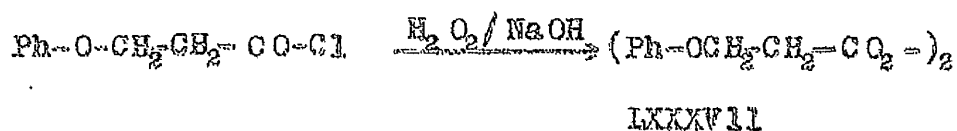
Synthesis and Decomposition of Bis( $\beta$ -phenoxypropionyl)  
peroxide.

The synthesis and decomposition of this peroxide was undertaken to investigate the possibility of such a system giving rise to phenoxy free radicals. The homolysis would, however, have to bring about rupture of two bonds in order to generate the desired radical since rupture of the oxygen-oxygen bond would give only acyl radicals.

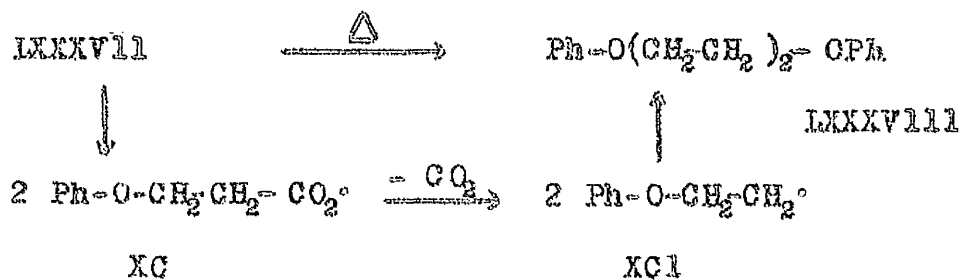
The synthesis of ethyl  $\beta$ -phenoxypropionate was effected by the method of Hall and Stern,<sup>159</sup> an extension of the addition of alcohols to acrylic double bonds<sup>140-142</sup> by condensation of phenol with ethyl acrylate. Hydrolysis of the ester by the method described in the literature, did not give the free acid in good yield. No unchanged ester could be recovered from the hydrolysis mixture and it was thought, since a strong smell of phenol was evident after acidification of the mixture, that elimination of phenoxide ion was taking place by the following suggested mechanism:-



Acidic hydrolysis was therefore used giving reasonable conversion to the free acid and allowing recovery of unchanged ester. Conversion to the acid chloride was carried out by reaction with purified thionyl chloride giving the chloride as a low melting crystalline solid, contrary to the observations of Powell.<sup>145</sup> It was purified by vacuum sublimation. The peroxide, Bis( $\beta$ -phenoxypropionyl) peroxide (LXXXVII) was synthesised by the method of Fieser et al.<sup>144</sup>



The peroxide, obtained as colourless plates, exhibited a doublet carbonyl stretching frequency separated by 25  $\text{cm}^{-1}$  agreeing with the observations of Davison<sup>145</sup> who studied a series of alkyl and aryl peroxides in the infra-red. Decomposition was carried out by heating the crystalline peroxide under reduced pressure to a few degrees above its melting point. Chromatography of the residual gum yielded 1,4-diphenoxybutane (LXXXVIII).

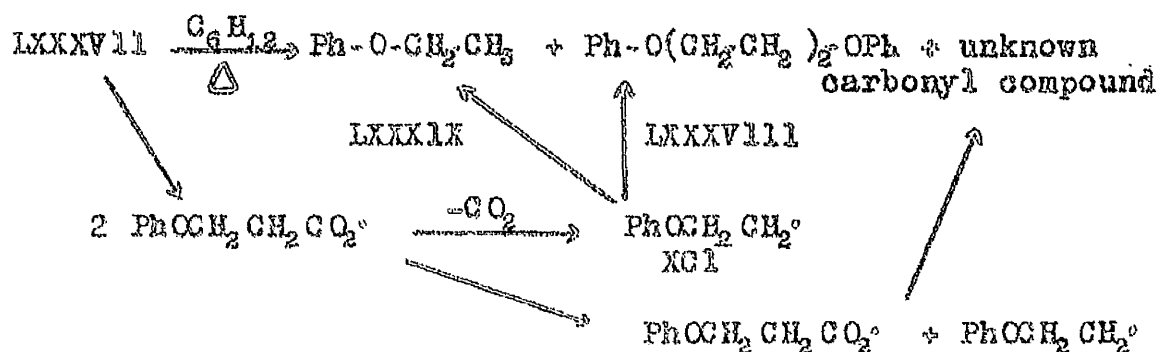


Decomposition was also carried out by refluxing in cyclohexane. Separation of the mixture showed the presence of phenetole (LXXXIX), 1,4-diphenoxybutane, unchanged peroxide and an unidentified carbonyl compound.

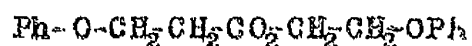
Pyrolysis of an acyl peroxide generally brings about homolysis<sup>148-149</sup> of the weak oxygen-oxygen bond giving rise to two acyl radicals (XC). Such an acyl radical is relatively short lived and if the quantity of abstractable hydrogen is low i.e. in the solid phase or in a non hydrocarbon solvent<sup>149</sup>, the fate is loss of carbon dioxide to give the alkyl radical (XCI) which yields the dimer (LXXXVIII).

In the above decomposition the amount of 1,4-diphenoxybutane does not account for all the residue obtained from the pyrolysis. It is thought that the gums obtained could well be due to various radical-radical or radical-product attacks giving rise to an inseparable mixture.

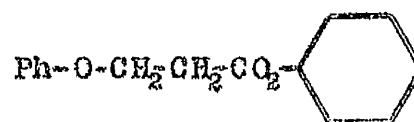
In a hydrocarbon solvent, however, the fate of a radical becomes more complex. Attack of the alkyl radical (XCI) on the solvent would give rise to phenetole (LXXXIX).



Dimerisation of the alkyl radical (XC1) gives rise to 1,4-diphenoxybutane (LXXXVIII). Formation of esters, a known reaction of acyl radicals, can be by alkyl-carboxyl radical union or by carboxyl-cyclohexyl radical union, thus two possible structures are XCII and XCIII to account for the unidentified carbonyl compound.



XCII



XCIII

Micro-analysis failed to facilitate identification although the results indicated that XCII was more probable. Further identification could not be carried out due to lack of material.

The earlier experiment with Bis( $\beta$ -phenoxypropionyl) peroxide had shown that this system, generating initially acyl radicals, did not yield the desired phenoxy radicals. It was thought that, by synthesising peroxides derived from phenyl substituted propionic acids, the chance of rupturing the oxygen-carbon bond might well be enhanced. By the presence of the phenyl groups it was hoped that the formation of the phenyl substituted ethylenic fragment might be favoured on homolysis of the peroxide, thus providing a driving force

for the rupture of the ether linkage. The methods employed for the syntheses of  $\beta$ -phenoxyphenyl substituted propionic acids were unsuccessful. The experimental details are contained in Appendix I. Another possible example considered was the synthesis of cyclohexadiene systems bearing a phenoxy and a carboxyl grouping on the 1 and 4 position respectively. Such a system, if it could be synthesised, would give a peroxide whose decomposition could well yield phenoxy radicals. The driving force for cleavage of the ether bond would be aromatisation of the cyclohexadienyl radical, formed on initial decomposition of the peroxide, to yield benzene. The routes investigated to achieve this aim were via the novel ethyl 5-phenoxy-penta-2,4-dienoate (XCIV, R=Et). The following discussion outlines the attempts to synthesise this molecule and its Diels-Alder addition reactions with various dienophiles.

The synthesis of the desired system was effected by condensation of phenol with methyl but-1-en-3-yne-1-carboxylate<sup>160</sup> (XCV, R=Me), a modification of a method described by Ruhemann<sup>161</sup>. This condensate afforded methyl 5-phenoxy-penta-2,4-dienoate (XCIV, R=Me) as an oil which crystallised slowly to give colourless needles. Hydrolysis to the free acid

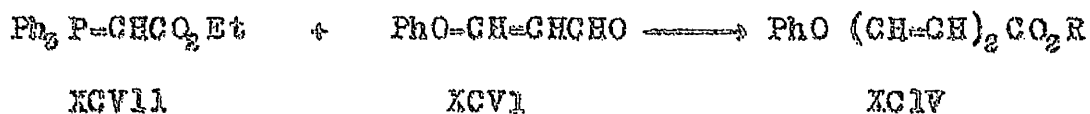


(XCIVa) was effected with dilute alcoholic pot. hydroxide solution. The overall yield of the ester was extremely low and a more profitable synthesis was sought for using condensations with  $\beta$ -phenoxycrolein.

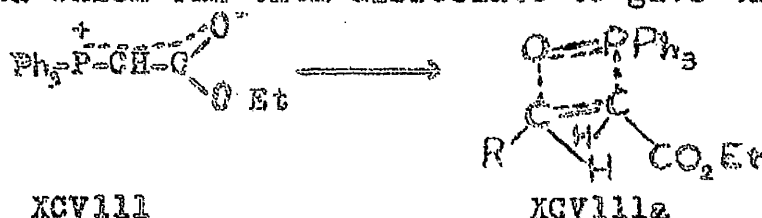
$\beta$ -Phenoxycrolein<sup>156</sup> (XCVI) was readily synthesised by condensation of phenol with propargylaldehyde in the presence of base. Attempts were made to achieve condensation of this aldehyde with the active methylene group of malonic and<sup>157</sup> and ethyl cyanoacetate<sup>158</sup>. In both cases gums were obtained which could not be induced to crystallise. With ethylcyanoacetate a small amount of an amorphous solid was obtained which showed the presence of  $\text{C}\equiv\text{N}$ ,  $\text{C} \cdot \text{O}_2 \text{Et}$  and conjugated double bonds in its infra-red spectrum but owing to the trivial amounts obtained this route was abandoned. Polymerisation, induced by the reaction conditions, is a possible reason for the lack of identifiable products.

An attempted Reformatsky<sup>159</sup> reaction between the aldehyde and ethyl bromoacetate failed to yield any desired material. Phenol was recovered in good yield from the reaction mixture and it was assumed that elimination of phenol from the reactant or the product was being induced by the conditions employed.

5-Phenoxyacrolein and carbethoxymethylene-triphenyl phosphorane<sup>162 163</sup> (XCVII) were allowed to react in ethyl acetate by an extension of a method of Bestmann and Schulz.<sup>164</sup> By this synthesis an excellent yield of ethyl 5-phenoxy-penta-2,4-dienoate (XCIV, R=Et) was obtained.

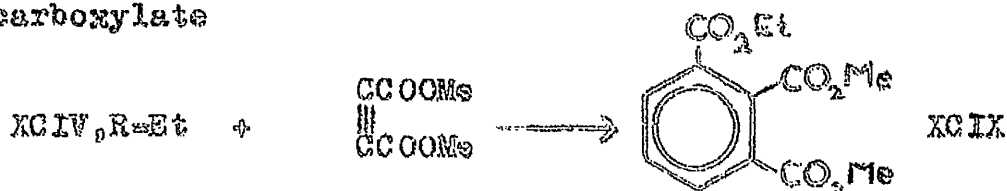


Bergelson and Shemyakin<sup>165</sup> have proposed that reactions with this phosphorane proceed via a mechanism involving nucleophilic attack by the aldehyde carbonyl oxygen on the ylide phosphorous atom, the electron distribution being represented by (XCVIII). The resulting intermediate di-ion then rearranges to give the sterically favoured intermediate XCVIIIa which can then dissociate to give the trans olefin.



In the n.m.r. spectrum (reported in Appendix II) it was difficult to identify the olefinic protons. Consideration of the integral showed that the protons were in the ratio of 7:2:2:3 the latter two groups making up the ethyl ester group, the methylene at 5.85  $\tau$  and the methyl at 8.75  $\tau$ . The other two groups of protons were therefore split into phenyl protons plus the two most highly shielded olefinic protons at 2.3-3.2  $\tau$ , making up seven protons, and the two de-shielded protons occurring at 4.08  $\tau$ .

The ester (XCIV, R=Et) was treated with dimethyl acetylenedicarboxylate

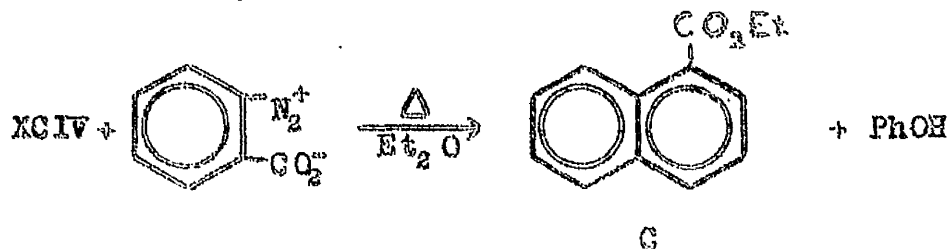


in xylene. Chromatography did not yield the desired product. The infra-red spectrum showed the absence of a phenoxy group and it was proposed that elimination of phenol had taken place giving rise to the aromatic compound 1-ethyl 2,3-dimethyl benzene-1,2,3-tricarboxylate (XCIX). This structure was proved by micro-analysis and study of the n.m.r. spectrum (recorded in Appendix II) of the product and its hydrolysis to hemimellitic acid.

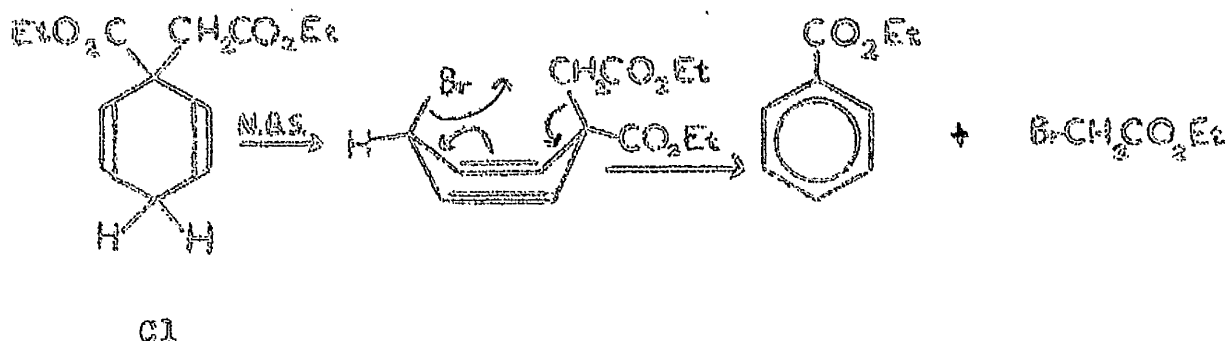
A reaction with benzene diazonium-2-carboxylate<sup>166 167</sup> and the ester (XCIV) gave ethyl 1-naphthoate (C) and phenol as



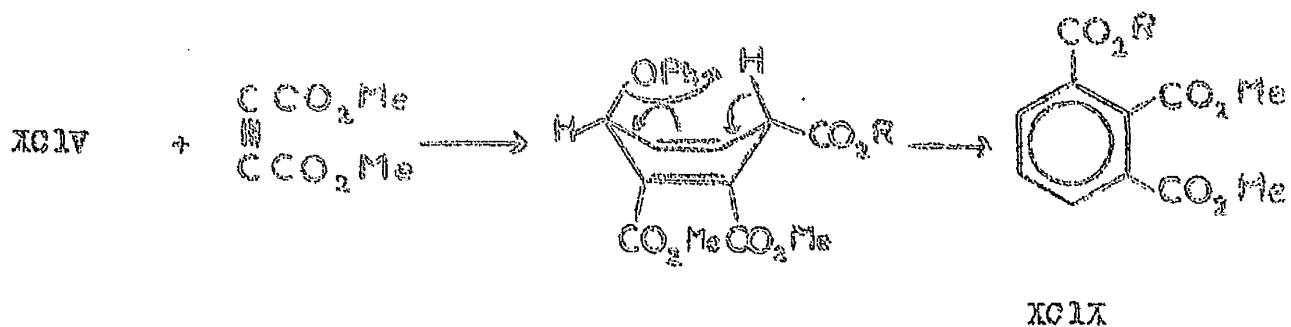
well as unchanged ester.



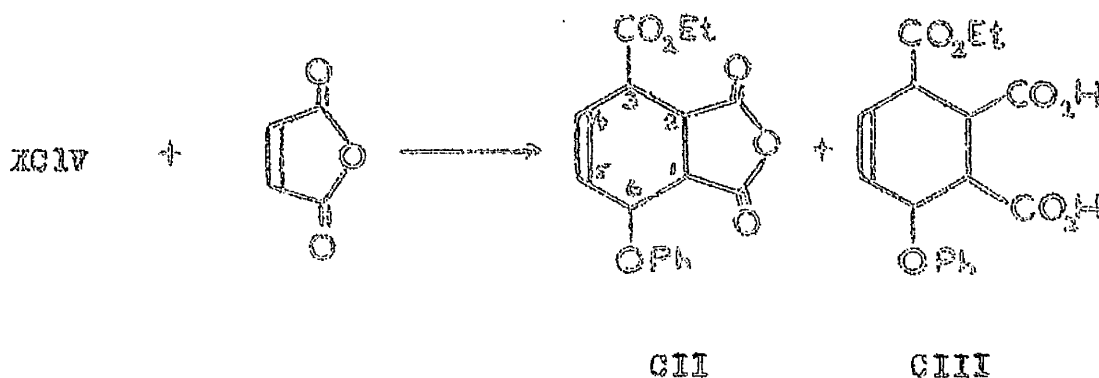
An analogy for the observed elimination of phenol was found in the investigations reported by Plieninger and Ege.<sup>168</sup> In their studies on the prephenic acid system, Ziegler bromination of (Cl) brought about elimination of ethyl bromoacetate to give ethyl benzoate. The proposed mechanism is shown below.



On this basis the elimination encountered by the author can also be explained.



In an effort to obtain Diels-Alder addition without elimination of phenol a reaction was carried out with maleic anhydride in benzene.<sup>169</sup> After hydrolysis of the reaction mixture with boiling water two products 3-carbethoxy-1,2,3,6-tetrahydro-6-phenoxy-phthalic anhydride (CII), as the neutral compound and 3-carbethoxy-1,2,3,6-tetrahydro-6-phenoxy-phthalic acid (CIII), as the acidic compound, were isolated.



Treatment of the ester (XCIV) with toluene gave no reaction. It was thus apparent that the synthesis of the desired cyclohexadiene system could not be accomplished by this approach due to the observed elimination. To prevent this elimination the synthesis of ethyl 2-methyl-5-phenoxy-penta-2,4-dienoate (CIV) was carried out by reaction of 3-phenoxy-acrolein with  $\alpha$ -carbethoxyethylidene-triphenylphosphorane<sup>162, 163</sup> (CV). Hydrolysis of the ester gave the free acid (CVI).



gums which yielded no crystalline material on chromatography. With diphenylacetylene and benzene diazonium-2-carboxylate no reaction took place. The explanation of this poor reactivity could be due to the steric effect of the two substituents on carbon 2. The literature shows that in only a few cases could dienes with a cis substituent in this position be made to undergo addition.<sup>170 - 172</sup> It is an established fact that cis methyl groups deactivate the diene towards addition and enhance the possibility of side reactions to give polymeric products.<sup>173</sup>

EXPERIMENTAL

### General Experimental Procedures

Melting Points:- were determined on a Gallenkamp Melting Point Apparatus and are uncorrected.

Infrared Spectra:- were generally measured as potassium chloride discs (2 mg./200 mg.). In other specified cases spectra were measured as carbon tetrachloride solutions at a concentration of 10 mg./ml. in sodium chloride cells.

Nuclear Magnetic Resonance Spectra. Spectra refer to carbon tetrachloride solutions and were measured on a Perkin Elmer 40 M/C spectrometer.

Reagents. The silica gel used for chromatography was Hopkin and Williams, M.F.C. Grade. Petroleum ether had a boiling point of 60-80°. Cyclohexene, used in irradiations, was B.D.H. reagent grade and was distilled through a Hempel column (9 in.) prior to use.

Irradiation Technique. The irradiations were carried out in an annular apparatus having a capacity of 650 ml. The 500 watt medium pressure mercury arc lamp (Hanovia 509/12) was immersed in the solution in a water-cooled quartz down tube. The material was dissolved in the desired solvent and flushed out overnight with a stream of dried, deoxygenated nitrogen. Irradiation was carried out until almost no ester carbonyl frequencies were detectable in the infrared. The reaction

was followed by removing samples (2 ml.) at regular intervals, boiling off the solvent, dissolving the residue in carbon tetrachloride (1 ml.) and running an infrared spectrum in the region 4.0-7.0  $\mu$ .

Irradiation of Di-p-t-Butylphenyl Carbonate.

Di-p-t-butylphenyl carbonate (8.0 g.; 0.024 mole), m.p. 109-112° (lit.<sup>81</sup> m.p. 108°) was irradiated in absolute ethanol (650 ml.) for 24 hr. After removal of the solvent the resulting yellow oil was chromatographed on silica gel. Elution with petroleum ether-benzene (3:1; 800 ml.) gave a mixture of unchanged starting material and a compound having a carbonyl stretching frequency in the infrared at 5.95  $\mu$  (1.2 g.; 15%). Further elution with petroleum ether-benzene (3:1; 2.4 litres) gave 5,5'-di-t-butyl-2,2'-dihydroxybenzophenone (2.1 g.; 26.3%) as long yellow needles, m.p. 104-106°, from aqueous ethanol. (Found: C, 77.5; H, 8.2.  $C_{12}H_{26}O_2$  requires C, 77.4; H, 8.0%).  $\nu_{max}$ . (CCl<sub>4</sub> soln.) 1626 cm.<sup>-1</sup> (C=O). The 2,4-dinitrophenylhydrazone, m.p. 253-255°, crystallised from ethanol. (Found: C, 63.5; H, 6.6; N, 10.7.  $C_{27}H_{30}N_4O_6$  requires C, 64.0; H, 5.9; N, 11.1%). Benzene eluted p-t-butylphenol (1.8 g.; 22.5%), m.p. 99-100°, undepressed on admixture with an authentic specimen. Benzene-ether (4:1) eluted polymeric material (2.1 g.; 26.3%). Slow crystallisation of this material from petroleum ether gave a colourless crystalline compound identified as 5,5'-di-t-butyl-2,2'-dihydroxybiphenyl, m.p. 210-212° (lit.<sup>82</sup> m.p. 208°), crystallised as small colourless needles from iso-octane. (Found: C, 80.4; H, 8.8.



Calculated for  $C_{10}H_{26}O_2$ : C, 80.5; H, 8.7%.  $\nu_{\max}$ . (KCl disc) 3175  $\text{cm.}^{-1}$  (OH).

Hydrolysis of the first fraction from chromatography (1.2 g.) was carried out by refluxing with alcoholic potassium hydroxide (50 ml.; 50%; 1N) for 2 hr. The material was extracted with ether, after dilution with water and acidification to Congo-red. The ethereal extract was washed with aqueous sodium bicarbonate solution which, after acidification, was extracted with ether. The ethereal extract was washed with water, dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated to dryness to give 5-t-butylsalicylic acid (0.11 g.). Crystallisation of this from aqueous ethanol gave fine colourless needles, m.p. 154-155° (lit.<sup>85</sup> m.p. 151°). (Found: C, 67.5; H, 7.6. Calculated for  $C_{11}H_{14}O_3$ : C, 68.0; H, 7.2%).

Irradiation of Di-p-t-Butylphenyl Carbonate in Benzene and Phenyl Carbonate in Ethanol.

Results described in Table I, page 77.

Irradiation of Phenyl Salicylate.

Phenyl salicylate (10.7 g.; 0.05 mole), m.p. 42-43° (lit. m.p. 43°) was irradiated in absolute ethanol (650 ml.) for 76 hr. After removal of the solvent by distillation the residue was chromatographed on silica gel. Elution with petroleum ether-benzene (3:1; 5 litres) gave phenyl salicylate

TABLE I

Irradiation of di-p-t-butylphenyl carbonate in benzene and of phenyl carbonate in ethanol

$$\text{ArCOOAr} \xrightarrow{0} 2,2'\text{-di(OH)ArCOAr} + 2,4'\text{-di(OH)ArCOAr} + \text{ArOH} + \text{Polymer}$$

Ar	Quantity	Time	Solvent	Conversion	2,2'-di(OH)ArCOAr	2,4'-di(OH)ArCOAr	ArOH	Polymer
p-t-Butyl-phenyl	8.0 g.; 0.024 mole	24 hr.	C <sub>6</sub> H <sub>6</sub>	81.2%	2.9 g.; 36.3%	-	2.0 g. 27.1%	1.2 g. 15.0%
Phenyl	10.0 g.; 0.046 mole	150 hr.	EtOH	42.2%	0.41 g.; 4.1%	1.1 g.; 11.0%	-	2.0 g. 20.0%

a. m.p. 80-81° (lit. m.p. 81°). Irradiation mixture separated by extraction with sodium hydroxide solution to yield the phenolic material which was then chromatographed on silica gel.

b. Mixed with benzene, M.p. 58° (lit. m.p. 59-60°) N.m.r. data are recorded in Appendix II.

c. Mixed with benzene-ether (19:1). M.p. 119-150° (lit. m.p. 151°) (Found: C, 73.7%; H, 5.0. Calculate for C<sub>13</sub>H<sub>10</sub>O<sub>3</sub>: C, 72.9%; H, 4.7%).

(5.15 g., 48.1%). Further elution gave a yellow band yielding 2,2'-dihydroxybenzophenone (2.0 g., 18.7%) as a pale yellow oil, distillation, bath temp. 180°/0.5 mm., gave the benzophenone as pale yellow prisms, m.p. 58-60° (lit. m.p. 59-60°)  $\nu_{\max}$ . (KCl disc.) 1626  $\text{cm.}^{-1}$  (C = O). N.M.R. data are reported in Appendix II. Benzene eluted phenol (0.12 g., 1.0%) isolated as its benzoate (0.25 g.), m.p. 69-70°. Benzene-ether (19:1) eluted 2,4'-dihydroxybenzophenone (2.32 g., 21.7%) as pale yellow plates, m.p. 147-150° (lit. m.p. 151°), mixed melting point undepressed. Benzene-ether (1:1) eluted a brown gum (0.9 g.) which failed to crystallise.

#### Irradiation of Phenyl Benzoate.

Phenyl benzoate (10.0 g.; 0.05 mole), m.p. 69-71° (crystallised from ethanol) (lit. m.p. 70°), was irradiated in absolute ethanol (650 ml.) for 70 hr. After removal of the solvent the residue was dissolved in ether. Extraction with sodium hydroxide solution (3 x 100 ml. 10%) removed the phenolic material. The ethereal extract after washing with water and drying ( $\text{Na}_2\text{SO}_4$ ) gave phenyl benzoate (6.2 g., 62.0%). The sodium hydroxide extract was acidified with dilute hydrochloric acid (10%) and extracted with ether. The organic layer was washed with water, dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated to give phenolic material (3.8 g., 38.0%).

Chromatography of this material on silica gel gave the following results. Benzene eluted 2-hydroxybenzophenone (1.77 g.; 17.7%), m.p. 36-38° (lit. m.p. 39°). (Found: C, 78.9; H, 5.5. Calculated for  $C_{13}H_{10}O_2$ : C, 78.9; H, 5.4%). Benzene-ether (19:1) eluted phenol (0.45 g.; 4.5%) isolated as the benzoate (0.94 g.). Benzene-ether eluted 4-hydroxybenzophenone (1.60 g.; 16.0%), m.p. 135° (lit. m.p. 135°). (Found: C, 78.9; H, 5.4. Calculated for  $C_{13}H_{10}O_2$ : C, 78.9; H, 5.4%).

#### Synthesis of Formates.

The formates used in the irradiation experiments were synthesised by a slight modification of the method of Adickes, Brunnert and Lucker. The phenol (0.5 mole), phosphorusoxychloride (0.75 mole), formic acid (100%; 2.5 mole) and aluminium trichloride (0.045 mole) were heated on a water bath at 60° for 10 hr. After cooling the mixture was extracted into ether (250 ml.) and washed twice with cold water. The ethereal extract was dried ( $Na_2SO_4$ ), filtered and the ether removed by distillation. The residue was distilled under reduced pressure (12-15 mm.). The distillate was chromatographed on silica gel (30 g. per 1 g. formate) petroleum ether-benzene (3:1) eluting the desired formate uncontaminated with unchanged phenol. Further

distillation yielded the formate as a colourless oil.

Phenyl formate:- 24.9% yield; b.p. 74-76°/12 mm.

(lit. <sup>91</sup> b.p. 72.5-73.5°/10 mm.)  $\checkmark$  (liq. film) 1762,   
 1742 cm.<sup>-1</sup> (C=O). max.

p-t-Butylphenyl formate:- 36.0% yield; b.p. 128°/20 mm.,

$n_D^{22}$ : 1.5011. (Found: C, 74.0; H, 8.3. C<sub>11</sub>H<sub>14</sub>O<sub>2</sub> requires C, 74.1;   
 H, 7.9%).  $\checkmark$  max. (CCl<sub>4</sub> soln.) 1786, 1760 cm.<sup>-1</sup> (C = O).

2,6-Xylyl formate:- 58.5% yield; b.p. 91°/12-15 mm.;

$n_D^{20}$ : 1.5065. (Found: C, 72.3; H, 7.0. C<sub>9</sub>H<sub>10</sub>O<sub>2</sub> requires C, 72.0;   
 H, 6.7%).  $\checkmark$  max. (liq. film) 1770, 1740 cm.<sup>-1</sup> (C = O)

p-Chlorophenyl formate:- 29.6% yield; b.p. 87-88°/12 mm.;

$n_D^{24}$ : 1.5298. (Found: C, 54.0; H, 3.2; Cl, 23.1. C<sub>7</sub>H<sub>6</sub>ClO<sub>2</sub> requires   
 C, 53.5; H, 3.2; Cl, 22.7%).  $\checkmark$  max. (liq. film) 1773, 1754 cm.<sup>-1</sup>   
 (C = O).

2-Naphthyl formate:- 21.0% yield; b.p. 148°/12 mm.;

colourless needles, m.p. 23-24° (Found: C, 77.4; H, 4.7.

C<sub>11</sub>H<sub>8</sub>O<sub>2</sub> requires C, 76.8; H, 4.7%).  $\checkmark$  max. (liq. film) 1767,   
 1742 cm.<sup>-1</sup> (C = O)

#### Attempted Synthesis of 2-Allyl-4-t-butylphenyl formate

(a) 2-Allyl-4-t-butylphenol (15.5 g.; 0.08 mole; b.p. 78°/0.3 mm)   
 (lit b.p. <sup>96</sup> 125-126°/0.5 mm.) phosphorus oxychloride (17.6 ml.;   
 30 g.; 0.2 mole), formic acid (22 g.; 18 ml.; 0.5 mole) and   
 aluminium trichloride (0.6 g.) were heated on an oil-bath for

8 hr. at 70°C. The resulting black material was dissolved in ether and washed with cold water (2 x 50 ml.). After the ethereal solution had been dried over anhydrous sodium sulphate and evaporated the residue was chromatographed on silica gel. Petroleum ether-benzene (3:1) eluted 4-t-butyl-2-(2'-chloropropyl)-phenyl formate (5.8 g.; 28%); b.p. 99-101°/0.15 mm.,  $n_D^{24}$ : 1.5111. (Found: C, 66.9; H, 8.0; Cl, 14.0.  $C_{14}H_{19}ClO_2$  requires C, 66.0; H, 7.5; Cl, 14.0%).  $\nu_{max}$ . (liq. film) 1770, 1745  $cm^{-1}$  (C = O). N.M.R. data are reported in Appendix II.

(b) 2-Allyl-4-t-butylphenol (9.5 g.; 0.05 mole) and formic acid (100%; 28 g.; 23 ml.; 0.5 mole) were refluxed for 24 hr. After cooling, the mixture was dissolved in ether (100 ml.) and washed twice with cold water (2 x 50 ml.). The ethereal solution was dried over anhydrous sodium sulphate and distilled to remove ether. The residue was chromatographed on silica gel, petroleum ether-benzene (3:1) eluting 6-t-butyl-2,3-dihydro-2-methylbenzofuran (3.8 g.), b.p. 62-64°/0.2 mm. (lit. <sup>9e</sup> b.p. 106-107°/2 mm.). Benzene-ether (9:1) eluted unchanged 2-allyl-4-t-butylphenol (4.3 g.).  
2-Allyl-4-t-butylphenyl formate.

2-Allyl-4-t-butylphenol (19.0 g.; 0.1 mole), formic acid (100%; 4.6 g.; 0.1 mole) and dicyclohexylcarbodiimide (20.6 g.; 0.1 mole) were allowed to react in dry tetrahydrofuran (500 ml.)

according to the method of Buzas.<sup>100°101</sup> During the addition of the carbodiimide to the reaction mixture the temperature was maintained at 0° and stored in a refrigerator for 24 hr. During this time occasional evolution of gas was noticed. After filtration, to remove dicyclohexylurea, the solvent was removed by distillation and the residue was chromatographed on a long column (4 ft. x 5/8 in.) of silica gel. Petroleum ether-benzene (3:1) eluted 6-t-butyl-2,3-dihydro-2-methylbenzofuran (49 g.) identical with sample obtained from the preceding experiment. Further elution with petroleum ether-benzene (3:1) eluted the desired ester 2-allyl-4-t-butylphenyl formate (7.4 g.; 34.0%) b.p. 111°/12 mm.;  $n_D^{24}$ : 1.5079 (Found: C, 78.0; H, 8.8.  $C_{18}H_{18}O_2$  requires C, 77.0; H, 8.3%).  $\nu$  max. (liq. film) 1770, 1748  $cm^{-1}$  (C = O).

#### p-Tolyl Formate.

p-Tolyl formate was synthesised similarly by the reaction of p-cresol (13.6 g.; 0.1 mole), m.p. 32-34° (lit. m.p. 36°), formic acid (100%, 46 g.; 0.1 mole) and dicyclohexylcarbodiimide (20.6 g.; 0.1 mole) in dry tetrahydrofuran (250 ml.) for 24 hr. in a refrigerator. Chromatography on silica gel yielded the desired ester p-tolyl formate on elution with petroleum ether-benzene (3:1) (4.7 g.; 34.5%) b.p. 74-75°/12 mm.;  $n_D^{24}$ : 1.5070.

(Found: C, 70.6; H, 5.9.  $C_8H_8O_2$  requires C, 70.5; H, 5.9%).  $\nu_{\max}$ . (liq. film) 1786, 1755  $cm^{-1}$  (C = O).

#### Synthesis of Oxalates.

The two oxalates used were prepared, in poor yield, by the method of Adickes, Brunnet and Lucker which involved the reaction of oxalic acid (0.5 mole), phenol (1.5 mole), phosphorus-oxychloride (0.8 mole) and stannic chloride (as catalyst) on an oil-bath at 70° for 16-20 hr. This yielded the desired products.

Di-phenyl oxalate:- 15%; m.p. 142° as prisms from ethanol (lit.<sup>91</sup> m.p. 134°).  $\nu_{\max}$ . ( $CCl_4$  soln.) 1788, 1764  $cm^{-1}$  (C = O).

Di-p-t-butylphenyl oxalate:- 135%; m.p. 152.5-154.5° as prisms from petroleum ether. (Found: C, 74.1; H, 7.4.  $C_{22}H_{26}O_4$  requires C, 74.5; H, 7.4%).  $\nu_{\max}$ . ( $CCl_4$  soln.) 1789, 1767  $cm^{-1}$  (C = O).

#### Irradiation of Aryl Formates and Oxalates.

Generally the ester was irradiated in absolute ethanol (650 ml.) or benzene (650 ml.; sodium dried) for a sufficient time to effect complete decomposition. The solvent was removed by distillation and the residue chromatographed on silica gel. Petroleum ether-benzene (3:1) eluted unchanged starting material followed, in one case by, the rearrangement product 5-t-butylsalicylaldehyde. In the case of p-t-butylphenyl acetate the



arrangement product was eluted with petroleum ether-benzene (1:1). The corresponding phenol was eluted with petroleum ether-benzene (1:5) or benzene. Benzene-ether (1:1) eluted, extremely slowly, polymeric material as a brown gum.

The gas evolved from the irradiation of p-t-butylphenyl formate in ethanol was trapped over water and had an uncorrected volume of 1.75 litres (equivalent to 1.5 mole per mole of formate). The infrared spectrum of a sample showed the presence of carbon monoxide  $\nu_{\max.}(\text{gas})$  2198, 2137  $\text{cm.}^{-1}$

The gas evolved from the irradiation of p-t-butylphenyl acetate amounted to 234 ml. (equivalent to 21% of the theoretical) and showed the presence of carbon monoxide,  $\nu_{\max.}(\text{gas})$  2198, 2137  $\text{cm.}^{-1}$  and of a hydrocarbon gas, probably methane,  $\nu_{\max.}(\text{gas})$  3012, 2959, 2899  $\text{cm.}^{-1}$

Distillation of the ethanol, recovered from the irradiation of p-t-butylphenyl formate and acetate, into Brady's Reagent gave samples of acetaldehyde 2,4-dinitrophenylhydrazone (0.4 and 0.24 g. respectively), m.p. 160-162° (lit. m.p. 163.5-164.5°).

TABLE 2

Decelling the irradiations of p-t-butyl-phenyl formate and acetate  
 AROCO → O Ar(OH)CO + ArOH + polymer

Ar	Quantity	Solvent	Time of Conversion	% Ar(OH)CO	ArOH	Polymer
p-Bu <sup>t</sup> -phenyl R = H	8.9 g. 0.05 mole	Ethanol	12 hr. 98.6%	-	6.02 g.; 80.4%	1.05 g. 11.8%
p-Bu <sup>t</sup> -phenyl R = H	8.9 g. 0.05 mole	Benzene	39 hr. 75.2%	0.6 g.; 6.8%	4.16 g.; 55.4%	0.76 g.; 8.6%
p-Bu <sup>t</sup> -phenyl R = Me	4.8 g.; 0.025 mole	Methanol	31 hr. 100%	1.41 g.; 34.0%	1.3 g.; 34.6%	1.11 g.; 23.1%

- a. Yielded 5,5'-di-t-butyl-2,2'-dihydroxy-biphenyl (50 mg.), m.p. 210-212° (m.w.p. under-pressed) on slow crystallisation from petroleum ether.
- b. Lit. b.p. 251-252°. Found: C, 74.7%; H, 8.4. Calculated for C<sub>18</sub>H<sub>14</sub>O<sub>2</sub>: C, 74.1%; H, 7.9%.  
 V<sub>max</sub>. (11g. film) 1662 cm<sup>-1</sup> (C=O). 2,4-dinitrophenylhydrazone m.p. 267-270° (decomp.)  
 (Found: N, 15.4. C<sub>17</sub>H<sub>13</sub>N<sub>2</sub>O<sub>7</sub> requires N, 15.6%).
- c. B.p. 214-216°/760 mm (lit. 203 b.p. 165°/5 mm.)
- d. B.p. 72-73°/0.15 mm. (lit. 103 b.p. 130°/12 mm.), V<sub>max</sub>. (11g. film) 1646 cm<sup>-1</sup> (C = O).  
 2,4-Dinitrophenylhydrazone, m.p. 173-174° (lit. 103 m.p. 170°).

TABLE 3

Detailing the irradiations of phenyl formate, diphenyl- and di-p-t-butylphenyloxalates. Percentage conversion is based on recovered starting material.

Ester	Quantity	Solvent	Time Conversion	Phenol	Polymeric Material
Phenyl formate	6.1 g., 0.05 mole	Ethanol 650 ml.	20 hr. 100%	2.13 g. <sup>a</sup> 49.0%	3.0 g. 50%
Phenyl oxalate	3.63 g., 0.015 mole	Ethanol 700 ml.	32 hr. 91.7%	0.78 g. <sup>b</sup> 23.5%	1.8 g. 54%
Di-p-t-butyl-phenyl oxalate	4.0 g., 0.012 mole	Ethanol 700 ml.	24 hr. 81.5%	1.37 g. <sup>c</sup> 40.4%	1.5 g. 37.5%

a, b, phenol isolated as the benzoate (4.85 g. and 1.63 g. respectively), m.p. 69-70° (m.m.p. undepressed).

c, m.p. 99-100° (lit. m.p. 99°).

Irradiation of Formate Esters in Olefins.

Generally the formate ester (0.05 mole) was dissolved in redistilled olefin (cyclohexene, pent-1-ene and 2-methyl-pent-2-ene), flushed out overnight with a stream of nitrogen and photolysed for 24 hr., or until most of the ester had been decomposed. The solvent was removed by distillation and the residue was chromatographed on silica gel. Petroleum ether eluted hydrocarbon material. Petroleum ether-benzene (3:1) rapidly eluted any aryl cyclohexyl ether followed slowly by the rearrangement product and/or unchanged starting material. Benzene eluted the corresponding phenol and unidentified material, apparently polymeric, was eluted with benzene-ether (1:1).

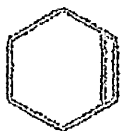
In the case of a mixture of salicylaldehyde and unchanged formate ester being obtained in fraction 3, separation could only be effected by the following procedure. The mixture was hydrolysed in aqueous sodium hydroxide solution (20%) by warming for 0.5 hr. on a steam bath. The mixture was cooled, acidified with dilute hydrochloric acid and extracted with ether. The organic layer was washed with water, dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated to give a mixture of salicylaldehyde and phenol. Chromatography of this on silica gel gave the pure salicylaldehyde on elution with petroleum ether-benzene (3:1).

Table 4: details the products and amounts isolated from the irradiation of phenyl, p-t-butylphenyl, 2,6-xilyl and 2-naphthyl formates in cyclohexene.

Table 5: details the products isolated from the irradiation of p-t-butylphenyl formate in pent-2-ene and 2-methylpent-1-ene.

Table 6: details the products isolated from the irradiation of allylphenols and esters in benzene or cyclohexene. Separation of the mixtures was carried out by the above technique. Generally petroleum ether-benzene (3:1) eluted the cyclisation product and petroleum ether-benzene (1:1) or benzene eluted unchanged phenol or ester.

TABLE I



\*  $\text{ArOCHO} \rightarrow \text{Dicyclohexenyl} + \text{ArOC}_6\text{H}_5 + \text{o-Ar(OH)CHO} + \text{ArOH} + \text{polymeric material}$

Ar	Quantity of ArOCHO	Time Conversion	H/C Material	$\text{ArOC}_6\text{H}_5$	$\text{o-Ar(OH)CHO}$	$\text{ArOH}$	Polymer
Phenyl	10.0 g.; 0.082 mole	24 hr. 91%	1.3 g. b.p. 98-99°/ 12 mm.	0.19 g. 1.3%	0.4 g.; 4%	1.91 g. 24.3%	2.4 g.; 24%
p-t-Butyl-phenyl	8.9 g.; 0.05 mole	24 hr. 100%	5.5 g. b.p. 36-37°/ 0.15 mm.	1.14 g. 8.3% <sup>b</sup>	0.5 g.; 5.6%	2.4 g. 32.0%	2.4 g.; 27%
2,6-Xylyl	7.5 g.; 0.05 mole	24 hr. 88.3%	5.94 g. b.p. 99°/ 12 mm.	0.62 g. 6.2%	-	0.3 g.; 7.3%	3.1 g.; 41.4%
$\beta$ -Naphthyl	8.6 g. 0.05 mole	90 hr. 67.4%	0.9 g.; b.p. 31°/ 0.1 mm.	0.42 g. 3.7% <sup>d</sup>	-	2.7 g.; 34.4%	1.46 g.; 17%

\* Isolated as phenylbenzoate (3.95 g.), m.p. 69-70° (mixed m.p. undepressed). The identity of the other phenols isolated verified by undepressed mixed melting points with authentic specimens.

Aldehydes isolated were identified by their infrared spectra and formation of the corresponding 2,4-dinitrophenylhydrazones.

The hydrocarbon oil isolated in all the above cases was purified by distillation and examined by V.P.C. analysis.

Notes for Table 1.

- |    |                               |   |                      |
|----|-------------------------------|---|----------------------|
| a. | Phenylcyclohexyl ether:-      | ) |                      |
|    | bath temp. 105-110°/0.25 mm.  | ) |                      |
| b. | p-t-Butyl-phenylcyclohexyl    | ) | The identities of    |
|    | ether:- b.p. 81°/0.05 mm.     | ) | the ethers were      |
|    |                               | ) | confirmed by         |
| c. | 2,6-Dimethyl-phenylcyclohexyl | ) | comparison with      |
|    | ether:- bath temp. 98-100°/   | ) | authentic specimens. |
|    | 0.04 mm.                      | ) |                      |
| d. | β-Naphthylcyclohexyl ether:-  | ) |                      |
|    | m.p. 65-67°                   | ) |                      |

TABLE 5.

Ar	Quantity of AroCHO	Time	Olefin	H/C fraction	ArO-alkyl
p-t-butyl-phenyl	8.9 g. 0.05 mole	24 hr.	pent-2-ene b.p. 36-37° (lit. b.p. 36.5°)	4.16 g.	<sup>a</sup> 1.58 g.; 14.4%
	6.58 g.; 0.037 mole	48 hr.	2-methyl-pent-1-ene, b.p. 62-63° (lit. b.p. 62°)	1.07 g.	<sup>b</sup> 0.8 g.; 9.3%

a. 2- and 3-pentyl p-t-butylphenyl ether: b.p. 94°/0.035 mm

(Found: C, 81.2; H, 12.1.  $C_{15}H_{24}O$  requires C, 81.6; H, 10.9%).

$\nu$  max. (liq. film) 1242  $cm^{-1}$ , 1182  $cm^{-1}$  (ArO and RO respectively).

b. p-t-butylphenyl 2-(2-methylpentyl) ether: bath temp. 115-120°/

0.5 mm.,  $n_D^{24}$ : 1.4887. (Found: C, 82.5; H, 11.1.  $C_{16}H_{26}O$

requires C, 82.0; H, 11.1%)  $\nu$  max. (liq. film) 1232, 1169  $cm^{-1}$

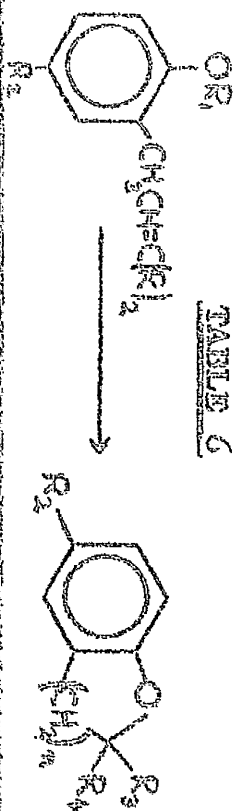
(8.0-9.0  $\mu$  region).

Nuclear magnetic resonance spectral data are recorded

in Appendix II.



TABLE 6



Compound	Quantity	Solvent	Time	Product	Quantity
R <sub>1</sub> = ClO <sub>2</sub> R = H R <sub>2</sub> = Bu <sup>t</sup>	3.27 g.; 0.015 mole	Benzene	24 hr.	R <sub>3</sub> = H, R <sub>4</sub> = Me R <sub>2</sub> = Bu <sup>t</sup> , n=1	1.18 g. <sup>b</sup> ; 41.4%
R <sub>1</sub> = H, R = H R <sub>2</sub> = Bu <sup>t</sup>	6.75 g.; 0.036 mole	Benzene	24 hr.	R <sub>3</sub> = H, R <sub>4</sub> = Me R <sub>2</sub> = Bu <sup>t</sup> , n=1	2.63 g. <sup>c</sup> ; 39.0%
R <sub>1</sub> = R <sub>2</sub> = H R = Me	8.1 g. <sup>a</sup> ; 0.036 mole	Benzene	24 hr.	R <sub>3</sub> = R <sub>4</sub> = Me R <sub>2</sub> = H, n=2	1.0 g. <sup>d</sup> ; 12.3%
R <sub>1</sub> = R <sub>2</sub> = H R = Me	3.44 g. 0.021 mole	Cyclo- hexene	24 hr.	R <sub>3</sub> = R <sub>4</sub> = Me R <sub>2</sub> = H, n=2	1.55 g. <sup>e</sup> ; 45.0%

a. b.p. 125-127°/15 mm. (lit.<sup>122</sup> b.p. 120-122°/12 mm.)

b. b.p. 64-66°/0.2 mm.

c. b.p. 112-113°/12 mm. (lit. b.p. 106-107°/2 mm.)<sup>123</sup> ) max. (liq. film) 1041 cm.<sup>-1</sup>  
(five numbered ether)

d, e. bath temp. 70-75°/0.2 mm (lit.<sup>123</sup> b.p. 98-98.5°/11.5 mm.)<sup>123</sup> ) max. (liq. film)  
1222, 1157, 1124 cm.<sup>-1</sup> (region 8.0-9.0 μ).

Irradiation of p-Chlorophenyl Formate in Cyclohexene

p-Chlorophenyl formate (7.85 g.; 0.05 mole) was irradiated in redistilled cyclohexene (650 ml.) for 24 hr. After removal of the solvent the residue (11.6 g.) was chromatographed on silica gel. Petroleum ether rapidly eluted a hydrocarbon fraction (1.44 g.). Petroleum ether-benzene (3:1) eluted p-chlorophenylcyclohexyl ether (0.64 g.; 6.1%) distilled to give a colourless oil, bath temp. 150-155°/0.07 mm. Further elution with petroleum ether-benzene (3:1) gave unchanged p-chlorophenyl formate (1.8 g.; 22.9%). Benzene eluted an oil (2.44 g.) which slowly crystallised to yield p-cyclohexylphenol (0.2 g.); recrystallised from benzene-petroleum ether, as fine colourless needles, m.p. 128.5-130.5° (lit.<sup>17a</sup> m.p. 130°). (Found: C, 81.6; H, 9.5. Calculated C, 81.8; H, 9.1%)  $\nu_{\max}$ . (KCl disc) 3333  $\text{cm}^{-1}$  (OH), the N.M.R. spectrum is reported in the appendix II; and p-chlorophenol (2.2 g.; 34.3%) m.p. 42-43°, undepressed on admixture with an authentic specimen. Ether-benzene (9:1) gave a colourless crystalline product (2.33 g.) [Product A], recrystallised from petroleum ether-benzene as fine colourless needles, m.p. 144-145°. (Found: C, 69.7; H, 8.0%)  $\nu_{\max}$ . (KCl disc) 3195  $\text{cm}^{-1}$  (OH). The N.M.R. spectrum is reported in Appendix II. This compound formed a benzoate, as colourless needles from ethanol, m.p. 175-177° (Found: C, 72.4;

H, 6.1; Cl, 11.0%).  $\nu_{\text{max}}$ . (KCl disc) 1739  $\text{cm.}^{-1}$  (C = O).

Ether-benzene (1:1) gave a brown gum (1.2 g.) which did not crystallise.

Reaction of Product A with Zinc and Ethanol.

Product A (0.21 g.; c. 1 mmole) and zinc (1.6 g.; 0.028 g. atom) were refluxed in ethanol (25 ml.) for 11 hr. The reaction mixture was filtered hot and the precipitate was washed with boiling ethanol. The ethanol was removed by distillation and the product crystallised from benzene-petroleum ether as colourless needles, m.p. 140-143°, undepressed on admixture with starting material.

Reaction of Product A with Alcoholic Potassium Hydroxide.

Product A (0.21 g.; c. 1 mmole) was refluxed for 11 hr. with a solution of potassium hydroxide in ethanol (15 ml.; 0.6 g./ml.). After cooling the mixture was poured into water, acidified with dilute hydrochloric acid and ether added. The organic layer was separated, washed with water, dried ( $\text{Na}_2\text{SO}_4$ ) and the ether removed to give an orange gum (0.15 g.) which could not be made to crystallise.

Irradiation of p-t-Butylphenyl Formate in Benzene-cyclohexene Mixture.

p-t-Butylphenyl formate (8.9 g.; 0.05 mole) in benzene (325 ml.; sod. dried) and cyclohexene (325 ml.; redistilled b.p. 83°) was irradiated for 24 hr. The reaction mixture was

worked up similarly to the previous experiments. The column was eluted with petroleum ether to remove any hydrocarbon material. Petroleum ether-benzene (3:1) eluted the desired p-t-butylphenylcyclohexyl ether (0.43 g.; 3.7%), bath temp. 130°/0.03 mm., identified by comparison with an authentic specimen.

#### Aryl Cyclohexyl Ethers

The aryl cyclohexyl ethers obtained from the irradiation experiments were identified by their infrared and N.M.R. spectra, which are reported in Appendix II, and by comparison of these and their refractive indices and boiling points, in one case the melting point, with authentic samples synthesised independently by the following method.

Phenol (0.01 mole), cyclohexene (0.05 mole) and concentrated sulphuric acid (4 drops) were heated on a steam bath for 6 hr. The material was dissolved in ether (25 ml.) and unchanged phenol was extracted by washing with sodium hydroxide solution (10%; 3 x 20 ml.). The ethereal solution was washed further with water, dried over anhydrous sodium sulphate, filtered and the ether removed by distillation. The residue was chromatographed on silica gel, petroleum ether-benzene (3:1) eluting the aryl ether. Further purification was obtained by distillation at reduced pressure.

p-t-Butylphenylcyclohexyl Ether: - 21.8% yield; b.p. 90-91°/  
0.1 mm.;  $n_D^{20}$ : 1.5152. (Found: C, 82.0; H, 10.9.  $C_{16}H_{24}O$  requires  
C, 82.7; H, 10.4%).  $\nu_{\max}$ . (liq. film) 1242, 1182  $cm^{-1}$  (Ar-O,  
R-O respectively).

p-Chlorophenylcyclohexyl Ether: - 61.5% yield; b.p. 87-88°/  
0.1 mm.;  $n_D^{20}$  1.5361. (Found: C, 69.2; H, 7.5; Cl, 16.0.  $C_{12}H_{15}ClO$   
requires C, 68.4; H, 7.1; Cl, 16.9%).  $\nu_{\max}$ . (liq. film) 1241,  
1170  $cm^{-1}$  (Ar-O, R-O respectively).

2,6-Dimethylphenylcyclohexyl Ether: - 53.9% yield;  
bath temp. 110°/0.1 mm.;  $n_D^{20}$  1.5169 (Found: C, 82.2; H, 9.5.  
 $C_{14}H_{20}O$  requires C, 82.4; H, 9.8%).  
 $\nu_{\max}$ . (liq. film) 1202, 1185  $cm^{-1}$  (Ar-O, R-O respectively).

2-Naphthylcyclohexyl Ether: - 38.4% yield; b.p. 115°/0.2 mm.  
recrystallised as fine colourless needles from petroleum ether,  
m.p. 66-68° (Found: C, 83.2; H, 8.2.  $C_{16}H_{18}O$  requires C, 83.2;  
H, 8.9%)  $\nu_{\max}$ . (KCl disc) 1214, 1178  $cm^{-1}$  (Ar-O, R-O respectively).

Irradiation of p-t-Butylphenol in Cyclohexene.

p-t-Butylphenol (7.5 g.; 0.05 mole), m.p. 99-100°,  
(lit. m.p. 100°) was irradiated in cyclohexene (650 ml.), b.p.  
83-84°, for 24 hr.. After removal of the solvent the residue  
(14.0 g.), a red oil, was chromatographed on silica gel.  
Petroleum ether rapidly eluted a hydrocarbon fraction (7.2 g.)  
which when distilled yielded a colourless oil (1.9 g.) b.p.

38°/0.1 mm. The remainder of the material did not distil nor could it be made to crystallise. Petroleum ether-benzene (3:1) eluted p-t-butylphenylcyclohexyl ether (0.51 g. 4.4%) b.p. 88-90°/0.1 mm. identical to previous samples obtained. No unchanged p-t-butylphenol was obtained on further elution of the column with benzene and mixtures of benzene-ether.

#### Reaction of p-t-Butylphenol in Cyclohexene

p-t-Butylphenol (3.75 g.; 0.025 mole), m.p. 100-102° (recrystallised from ethanol) was refluxed for 80 hr. in redistilled cyclohexene (325 ml.) b.p. 83°. Chromatography of the residue, after removal of the solvent, yielded p-t-butylphenol (3.7 g.) on elution with benzene.

#### Irradiation of Cyclohexene.

Cyclohexene (650 ml.; redistilled, b.p. 83°) was irradiated for 24 hr. Removal of the excess cyclohexene by distillation yielded a residue (3.66 g.) as a pale yellow oil. Distillation yielded a colourless oil (1.54 g.); b.p. 90°/2 mm. This material had an identical infrared spectrum to that of the oils obtained from previous irradiation in cyclohexene. The residue (2.1 g.) could not be made to crystallise and was in the form of a gum.

Column Packing: 20% Silicone E301 elastomer on silicone-ised  
Ceslite 80-120 mesh.

Material	No. of Peaks	Retention Time (mins)	Column Data (length 6ft.)
1 H/C fraction 1	3	4.4, 5.0, 5.2	Temp. 212° inlet press. 57.1 cm. outlet press. 29.5 cm. N <sub>2</sub> flow rate 1.0 litre / hr. detector current 95m amp.
2 H/C fraction 2	3	4.4, 5.0, 5.1	
dicyclohexenyl	1	2.76	Temp. 219° inlet press. 61.6 cm. outlet press. 19.5 cm. N <sub>2</sub> flow rate 1.4 litre / hr. detector current 100 m amp.
H/C fraction 1	2	2.28, 2.72	
H/C fraction 2	2	2.36, 2.76	
dicyclohexenyl	1	3.8	Temp. 197° inlet press. 63.1 cm. outlet press. 22.4 cm. N <sub>2</sub> flow rate 2.4 litre / hr. detector current 90 m amp.
H/C fraction 1	2	3.0, 3.75	
H/C fraction 3	2	3.0, 3.75	

Fraction 1: H/C fraction from irradiation of p-t-butylphenyl formate in cyclohexene.

Fraction 2: H/C fraction from irradiation of p-t-butylphenol in cyclohexene.

Fraction 3: H/C fraction from irradiation of cyclohexene.

### Bromination of Hydrocarbon Fractions.

The hydrocarbon fraction (0.2 g.) from the irradiation of p-t-butylphenyl formate in cyclohexene was dissolved in chloroform (10 ml.) and a solution of bromine in chloroform was added until a faint permanent colour was obtained. Removal of the solvent left a viscous oil which crystallised slowly from chloroform to yield dicyclohexenyl tetrabromide (70 mg.), m.p. 160-161° undepressed on admixture with an authentic specimen, m.p. 162-163° (lit.<sup>175</sup> m.p. 159°<sup>176</sup>, 189-190°).

Similarly the hydrocarbon fraction from the irradiation of p-t-butylphenol in cyclohexene yielded dicyclohexenyl tetrabromide, m.p. 160-162° (mixed m.p. undepressed).

### p-t-Butylphenylcyclohex-2-enyl Ether.

3-Bromocyclohexene (20 g.; 0.12 mole), b.p. 56-57°/12 mm. (lit.<sup>137</sup> b.p. 74°/28 mm); p-t-butylphenol (17.7 g.; 0.12 mole) and finally ground anhydrous potassium carbonate (18 g.) were stirred at reflux temperature in acetone (40 ml.; anhydrous) for 4 hr. The reaction mixture was filtered hot and allowed to cool. The acetone was removed by distillation and the residue was dissolved in ether and washed with dilute sodium hydroxide solution (x 3). After washing with water, drying ( $\text{Na}_2\text{SO}_4$ ) the ether was removed to yield the desired product.



Distillation gave p-t-butylphenylcyclohex-2-enyl ether (12.6 g. 68.0%) as a colourless oil, b.p. 96°/0.04 mm. (Found: C, 83.7, H, 9.5. C<sub>16</sub>H<sub>22</sub>O requires C, 83.5; H, 9.6%),  $n_D^{25}$ : 1.5309,  $\mu_{\max}$ . (liq. film) 1238, 1182 cm<sup>-1</sup> (Ar-C, R-O). N.M.R. data are recorded in Appendix II.

Attempted Claisen Rearrangement of p-t-butylphenylcyclohex-2-enyl Ether.

p-t-Butylphenylcyclohex-2-enyl ether (6.6 g.) was heated under nitrogen for 2 hr. at 210°. The residue was allowed to cool and dissolved in ether. The ethereal solution was extracted with dilute sodium hydroxide solution (x 3). The sodium hydroxide solution was acidified and extracted with ether. The organic layer was washed with water, dried (Na<sub>2</sub>SO<sub>4</sub>) and the ether removed by distillation to yield p-t-butylphenol (1.33 g.; 30.9%). No other phenolic product was obtained.

Hydrolysis of Ethyl  $\beta$ -phenoxy propionate.

Ethyl  $\beta$ -phenoxy propionate<sup>159</sup> (30 g.) was hydrolysed by refluxing in aqueous sulphuric acid (300 ml.; 3N) for 18 hr. The mixture was cooled and ether was added. The organic layer was separated, washed with sodium hydroxide solution (3 x 100 ml.), water and dried ( $\text{Na}_2\text{SO}_4$ ). The ether was removed by distillation to yield ethyl  $\beta$ -phenoxy propionate (8.0 g.). The sodium hydroxide layer was acidified with dilute hydrochloric acid to yield, on filtration,  $\beta$ -phenoxy propionic acid (16.8 g.; 65.5%) crystallised from aqueous ethanol as colourless plates, m.p. 94-96° (lit.<sup>159</sup> m.p. 97-98°).

(Found: C, 64.9; H, 6.0. Calculated for  $\text{C}_9\text{H}_{10}\text{O}_3$ : C, 65.0; H, 6.1%)

$\nu_{\text{max}}$  (KCl disc) 1695  $\text{cm}^{-1}$  (C = O).

Synthesis of Bis( $\beta$ -phenoxy propionyl) peroxide.

$\beta$ -Phenoxypropionic acid (5.0 g.; 0.03 mole) and purified thionyl chloride (5.6 g.; 0.03 mole) were allowed to stand for 60 hr. Excess thionyl chloride was removed under vacuum to yield a crystalline solid, m.p. 24-26° (sublimed to yield colourless needles, m.p. 28°) which was taken to be the acid chloride  $\nu_{\text{max}}$  (liq. film) 1800  $\text{cm}^{-1}$  (C=O).  $\beta$ -Phenoxypropionyl chloride (7.6 g.; 0.04 mole) was converted to the desired bis-( $\beta$ -phenoxy propionyl) peroxide (2.5 g.; 36.0%), obtained as colourless plates from aqueous ethanol, m.p. 93-94° (Found: C, 65.5; H, 5.8.  $\text{C}_{18}\text{H}_{18}\text{O}_6$  requires C, 65.4;

H, 5.5%).  $\nu_{\text{max}}$ . (KCl disc) 1810, 1785  $\text{cm.}^{-1}$  (C=O), by reaction with hydrogen peroxide (3.65 ml., 0.03 mole, 28%) and sodium hydroxide (6.0 ml., 0.06 mole, 10N) in anhydrous ether at  $-10^{\circ}\text{C}$  according to the method of Fieser et al.<sup>144</sup>

Decomposition of Bis-( $\beta$ -phenoxypropionyl)peroxide.

(a) Bis-( $\beta$ -phenoxypropionyl)peroxide (0.4 g.) was heated in a flask, under reduced pressure (12 mm.), at  $95^{\circ}$ . Violent decomposition took place yielding a brown gum. Chromatography of the residue on alumina, with benzene as eluent gave 1,4-diphenoxybutane (0.12 g.), m.p.  $96-97^{\circ}$  (lit.<sup>177</sup> m.p.  $99-100^{\circ}$ )

$\nu_{\text{max}}$ . (KCl disc) 1250, 1170  $\text{cm.}^{-1}$  (ArO, RO respectively) undepressed on admixture with an authentic specimen.

(b) In Cyclohexane.

Bis-( $\beta$ -phenoxypropionyl) peroxide (0.5 g.) was refluxed in redistilled cyclohexane (10 ml.) for 3 hr. The solvent was removed by distillation. The residue (0.3 g.) was chromatographed on silica gel. Petroleum ether-benzene (1:1) eluted 1,4-diphenoxybutane (56 mg.). Benzene eluted unchanged peroxide (0.12 g.) and benzene-ether (4:1) eluted an unidentified material (102 mg.) purified by sublimation under reduced pressure, m.p.  $82-84^{\circ}$  (colourless prisms). (Found: C, 68.4; H, 6.6%)  $\nu_{\text{max}}$ . (KCl disc) 1740  $\text{cm.}^{-1}$  (C = O). The presence of phenetole in the distillate was shown by V.P.C. analysis.

A sample of the distillate exhibited two peaks one corresponding cyclohexane and the other to phenetole.

O,O-t-Butyl-O-phenylmonopercarbonate

Phenylchloroformate (4.7 g.; 0.03 mole) b.p. 68°/12 mm.

(lit.<sup>152</sup> b.p. 74-75°/13 mm.) and purified t-butylhydroperoxide (2.7 g.; 0.03 mole), b.p. 36-38°/20 mm. (lit.<sup>153</sup> b.p. 36°/16 mm.) were allowed to react at 0° with pyridine (4.7 g.; 0.06 mole) according to the method of Davies and Hunter.<sup>154</sup> The product could not be distilled and was purified by chromatography on silica gel. Benzene eluted the pure O,O-t-butyl-O-phenylmonopercarbonate (5.9 g.; 93%) as a colourless oil. Analysis for active oxygen<sup>155</sup> showed 98% purity  $n_D^{20}$  1.4863. (Found: C, 63.0; H, 6.6.  $C_{11}H_{14}O_4$  requires C, 62.9, H, 6.7%).  $\nu_{max.}$  (liq. film) 1812  $cm^{-1}$  (C=O)

Decomposition of O,O-t-Butyl-O-phenylmonopercarbonate.

In Cyclohexene.

O,O-t-Butyl-O-phenylmonopercarbonate (1.0 g.) was dissolved in cyclohexene (10 ml.) and the solution refluxed for 20 hr. under nitrogen. Gas evolution during the reaction was 120 ml. The infrared spectrum of the gas showed the presence of carbon dioxide,  $\nu_{max.}$  (gas) 2355  $cm^{-1}$  and a hydrocarbon gas  $\nu_{max.}$  (gas) 2985  $cm^{-1}$ . Chromatography of the residue, on removal of the cyclohexene, on silica gel gave, on

elution with petroleum ether, a hydrocarbon material (13 mg.) which had an infrared spectrum similar to that of an authentic sample of dicyclohexenyl. Petroleum ether-benzene (3:1) gave phenylcyclohexyl ether (57 mg.). Petroleum ether-benzene (1:1) eluted diphenyl carbonate (30 mg.), m.p. 79-80°, undepressed on admixture with an authentic specimen. No further material could be eluted from the column. The ether insoluble material (0.7 g.) was not chromatographed.

3-Phenoxyacrolein

Propargyl aldehyde (25 g.; 0.46 mole) b.p. 54° (lit.<sup>178</sup> b.p. 53-55°) was passed as its vapour, into a mixture of phenol (47 g.; 0.5 mole), water (120 ml.) and pyridine (1.2 g.) kept below 40°C by immersion in an ice-bath. When the addition was complete the mixture was extracted with ether (250 ml.). The organic layer was washed with sodium hydroxide solution (10%), dilute hydrochloric acid, water and dried (Na<sub>2</sub>SO<sub>4</sub>). Removal of the ether by distillation yielded a red oil which was further purified by distillation to give 3-phenoxyacrolein (46.8 g.; 69%), b.p. 96-98°/1.2 mm. (lit.<sup>156</sup> b.p. 130-136°/11mm.)  $\nu_{\text{max}}$  (liq. film) 1684 cm.<sup>-1</sup> (C = O), as a colourless oil.

Attempted Reaction between 3-Phenoxyacrolein and Ethylcyanoacetate

3-Phenoxyacrolein (5.0 g.; 0.034 mole) and ethylcyanoacetate (3.8 g.; 0.034 mole) were dissolved in ethyl alcohol (16 ml.) and potassium fluoride (2.0 g.; 0.009 mole) as catalyst, was added. The reaction was distinctly exothermic and the reaction mixture became red after 10 min. The mixture was allowed to stand for 1 hr. Dilution with ethyl alcohol and filtration, to remove the potassium fluoride, yielded a black gum, on removal of the solvent. Slow crystallisation

from ethyl alcohol-benzene yielded a pale orange material (0.1 g.) m.p. 195-200°. Further attempts to purify this material proved to be unsuccessful due to its insolubility in all but ethanol and water. The infrared spectrum showed the following strong bands (KCl disc) 2260 (C≡N), 1692 (C=O), 1648 (C=C), 1550 cm.<sup>-1</sup> 1231, 1194, 1162, 1089 cm.<sup>-1</sup> (region 8.0-10.0 μ); 976, 761 cm.<sup>-1</sup>

Attempted Reaction between 3-Phenoxyacrolein with Malonic Acid

3-Phenoxyacrolein (5.0 g.; 0.034 mole), malonic acid (3.53 g.; 0.03 mole) and pyridine (4.3 g.; 0.054 mole) were heated on a steam-bath for 3 hr. The mixture was neutralised by addition of sulphuric acid (1.5 ml., conc.) in water (3 ml.). Extraction of this mixture with ether (3 x 100 ml.), drying with anhydrous sodium sulphate and evaporation to dryness gave a red gum which failed to crystallise.

Attempted Reaction between 3-Phenoxyacrolein and Ethyl bromoacetate.

Zinc (1.77 g.; 0.027 g.-atom) was covered with ether (10 ml.) in a 100 ml. flask. To this was added half of a solution of 3-phenoxyacrolein (4.0 g.; 0.027 mole) and ethyl bromoacetate (4.51 g.; 0.027 mole) in ether (25 ml.). The reaction was initiated by the addition of a crystal of iodine. The remainder of the solution was added dropwise at such a rate as to maintain boiling. When the addition was complete

the mixture was refluxed for 0.5 hr. on a steam-bath.

Hydrolysis was effected by addition of a dilute acetic acid solution (100 ml.; 10% aqueous). Ether (100 ml.) was added and the organic layer was separated, washed with saturated sodium bicarbonate solution, water and dried ( $\text{Na}_2\text{SO}_4$ ).

Removal of the ether by distillation yielded a red oil (4.0 g.).

Fractional distillation of this gave phenol (2.1 g.; b.p.

36-38/0.5 mm.) and a fraction boiling over a large range

(116°-130°/1.2 mm.). Further distillation of this failed

to Methyl 5-Phenoxy-penta-2,4-dienoate.

Me Methylbut-1-en-3-yne-1-carboxylate (4.5 g.; 0.041 mole), b.p. 52-54°/30 mm. (lit.<sup>160</sup> b.p. 59°/34 mm.) prepared mole), b.p. 52-54°/30 mm. (lit.<sup>160</sup> b.p. 59°/34 mm.) prepared by the method of Heilbron et al. was added to a mixture of sodium (0.94 g.; 0.041 g.-atom) dissolved in phenol (15 g.; 0.16 mole) and xylene (15 ml.). The whole was heated at 140-150° for 14 hr. After cooling the mixture was dissolved in ether, excess phenol was removed by extraction with sodium hydroxide solution (3 x 50 ml.; 10%) and after washing with water, drying over anhydrous sodium sulphate, the ether and xylene were removed by distillation under reduced pressure to give a colourless oil. Distillation of this oil gave methyl 5-phenoxy-penta-2,4-dienoate (1.8 g., 34.5%), b.p. 92-96°/0.05 mm.;  $n_D^{16}$ : 1.577 as a colourless oil which crystallised on



standing to give colourless needles, m.p. 66-68° (Found: C, 70.7; H, 6.6.  $C_{12}H_{12}O_3$  requires C, 70.6; H, 5.9%)  $\nu$  max. (liq. film) 1711  $cm^{-1}$  (C=O). Methyl 5-phenoxy-penta-2,4-dienoate (0.6 g.) and alcoholic potassium hydroxide (25 ml.; 1N; 50%) were refluxed for 1 hr. Dilution with water and acidification with dilute hydrochloric acid (10%), to a Congo-red end-point, gave the free acid 5-phenoxy-penta-2,4-dienoic acid (0.2 g.) as colourless needles crystallised from aqueous ethanol, m.p. 136-138° (Found: C, 69.4; H, 6.0.  $C_{11}H_{10}O_3$  requires C, 69.5; H, 5.3%)  $\nu$  max. (KCl disc) 1684  $cm^{-1}$  (C=O).

Ethyl 5-Phenoxy-penta-2,4-dienoate.

Carbethoxymethyl-triphenyl-phosphonium bromide (50 g.; 0.12 mole), m.p. 156°(d) (lit. <sup>162° 165°</sup> m.p. 158°) was dissolved in water (1 litre) and the mixture was neutralised to a phenolphthalein end-point by addition of sodium hydroxide solution (20% aqueous). Filtration yielded the desired carbethoxymethylene-triphenyl-phosphorane (30 g.; 74.0%), m.p. 113-115° (lit. <sup>162° 165°</sup> m.p. 116-117°)

Carbethoxymethylene-triphenyl-phosphorane (25 g.; 0.072 mole) was dissolved in ethyl acetate (800 ml.) and 3-phenoxyacrolein (10.7 g.; 0.072 mole), b.p. 134°/15 mm. was added with stirring. The mixture was allowed to stand for 85 hr. After removal of the solvent by distillation

the residue was extracted several times with petroleum ether which on evaporation yielded a red oil. Chromatography, on silica gel, yielded ethyl 5-phenoxy-penta-2,4-dienoate (13.7 g.; 87%), on elution with benzene-petroleum ether (1:1), m.p. 60-65° as colourless needles from pentane. (Found: C, 71.4; H, 6.6.  $C_{15}H_{14}O_3$  requires C, 71.6; H, 6.4%)  $\nu$  max. (KCl disc) 1702  $cm^{-1}$  (C=O).

Hydrolysis of this ester (0.5 g.) by refluxing with alcoholic potassium hydroxide (25 ml.; 1N; 50%) gave, on dilution with water and acidification to a Congo-red end point, 5-phenoxy-penta-2,4-dienoic acid, m.p. 136-138° (m.m.p. undepressed with acid obtained from methyl ester).

Reaction of Ethyl 5-Phenoxy-penta-2,4-dienoate with dimethylacetylenedicarboxylate.

Ethyl 5-phenoxy-penta-2,4-dienoate (2.18 g.; 0.01 mole) and dimethylacetylenedicarboxylate (1.42 g.; 0.01 mole) were refluxed for 18 hr. in xylene (30 ml.; sodium dried). After removal of the solvent by distillation under reduced pressure the residue was chromatographed on silica gel. Elution with benzene-petroleum ether (1:1) gave a mixture of starting materials (1.54 g.; 43%). Benzene-petroleum ether (3:1) gave phenol (0.1 g.) and ether-benzene (1:19) gave 1-ethyl 2,3-dimethylbenzene-1,2,3-tricarboxylate (1.14 g.; 43%), m.p. 63-65°

obtained as colourless prisms from petroleum ether. (Found: C, 59.1; H, 5.6.  $C_{15}H_{14}O_6$  requires C, 58.6; H, 5.3%).  $\nu_{\text{max}}$ . (KCl disc)  $1739 \text{ cm.}^{-1}$  (C=O).

The ester (0.1 g.) and alcoholic potassium hydroxide (25 ml.; 1 N) were refluxed for 2 hr. After cooling and dilution with water the mixture was extracted with ether. The ethereal extract yielded, after washing with water and drying ( $\text{Na}_2\text{SO}_4$ ) hemimellitic acid (30 mg.); m.p.  $222-223^\circ$  (m.m.p. undepressed on admixture with an authentic specimen (lit. m.p.  $223-224^\circ$ )).

Reaction of Ethyl 5-Phenoxy-penta-2,4-dienoate with Maleic Anhydride.

Ethyl 5-phenoxy-penta-2,4-dienoate, (1.5 g.; 6.9 mmole) and maleic anhydride (0.73 g.; 7.5 mmole, freshly sublimed) were refluxed in dry benzene (15 ml.) for 24 hr. After removal of the solvent the mixture was refluxed in water (25 ml.) for 1 hr. to effect hydrolysis. The aqueous mixture was extracted with ether. Separation of the product into neutral and acidic compounds was effected by extracting the ethereal extract with aqueous sodium bicarbonate solution. The ethereal extract, after washing with water, drying ( $\text{Na}_2\text{SO}_4$ ) and removal of the ether by distillation yielded 3-carbethoxy-6-phenoxy-1,2,3,6-tetrahydrophthalic anhydride (0.54 g.),

m.p. 118-121° as colourless needles crystallised from benzene-petroleum ether. (Found: C, 64.6; H, 5.5.  $C_{17}H_{16}O_6$  requires C, 64.5; H, 5.1%)  $\nu_{\max}$ . (KCl disc) 1869, 1789, 1730  $cm^{-1}$  (C=O). Acidification of the sodium bicarbonate extract, to Congo-red, followed by extraction with ether gave, after washing with water, drying ( $Na_2SO_4$ ) and removing the ether by distillation 3-carbethoxy-6-phenoxy-1,2,3,6-tetrahydrophthalic acid (1.0 g.), m.p. 184-185° as colourless prisms from aqueous ethanol. (Found: C, 61.0; H, 5.4.  $C_{17}H_{16}O_7$  requires C, 61.4; H, 5.9%).  $\nu_{\max}$ . (KCl disc), 1736, 1712  $cm^{-1}$  (C = O).

Reaction of Ethyl 5-Phenoxy-penta-2,4-dienoate with Benzene Diazonium-2-carboxylate.

(a) Benzene diazonium-2-carboxylate (0.7 g.; 4.7mmole), m.p. 54°(d), prepared by the method of Stiles, Miller and Burckhardt,<sup>187</sup> was stirred with ethyl 5-phenoxy-penta-2,4-dienoate (5.0 g.; 0.023 mole) in refluxing ether (50 ml.; sodium dried) for 60 hr. After removal of insoluble material by filtration and evaporation of the ethereal solution to dryness, the residue was chromatographed on silica gel. Elution with benzene-petroleum ether (1:1) gave ethyl 1-naphthoate (0.36 g.; 40.5%) after 1.2 litres and unchanged starting material (3.4 g.; 68.0%) after five litres.

(b) The reaction was repeated on the same scale. The mixture was stirred for 60 hr. in ether at room temperature. The

product was treated in the same way as above and chromatography on silica gel gave ethyl 1-naphthoate (50 mg.; 5.6%) on elution with benzene-petroleum ether (1:1). Further elution gave unchanged starting material (4.0 g.; 80.0%).

Attempted Reaction of Ethyl 5-Phenoxy-penta-2,4-dienoate and Tolane.

Ethyl 5-phenoxy-penta-2,4-dienoate (1.09 g.; 0.01 mole), tolane (0.89 g.; 0.01 mole), m.p. 61-62° (lit. m.p. 62.5°), were refluxed in xylene (15 ml.; sodium dried) for 18 hr. After removal of the solvent the mixture was chromatographed on silica gel. Petroleum ether eluted tolane (0.85 g.; 95%) and petroleum ether-benzene (1:1) eluted unchanged starting material (0.99 g.; 91%). Further elution failed to yield any desired material.

Ethyl 2-Methyl-5-phenoxy-penta-2,4-dienoate.

Triphenylphosphine (26.2 g.; 0.1 mole) and ethyl 2-bromopropionate (18.1 g.; 0.1 mole) were refluxed in benzene (120 ml.; sodium dried) for 6 hr. After allowing to cool the precipitate was removed by filtration and washed with petroleum ether. The 1-carbethoxyethyl-triphenylphosphonium bromide was dissolved in water (500 ml.) and neutralised to a phenolphthalein end-point by addition of aqueous sodium hydroxide solution (20%). The precipitate was removed by filtration to give the desired 1-carbethoxy-ethylidene-

triphenylphosphorane (17 g.) m.p. 162-165° on crystallisation from ethyl acetate-petroleum ether (lit.<sup>185</sup> m.p. 157°).

3-Phenoxyacrolein (5.3 g.; 0.036 mole) and 1-carbethoxy-ethylidene-triphenylphosphorane (13 g.; 0.036 mole) were allowed to stand in ethyl acetate (600 ml.) for 24 hr. The solvent was removed by distillation and the residue was extracted with ether. The ether extract, after evaporation to dryness, was chromatographed on silica gel. Benzene eluted ethyl 2-methyl-5-phenoxy-penta-2,4-dienoate (5.5 g.; 66.0%) as a pale yellow oil. Distillation gave the ester as a colourless oil, b.p. 120-121°/0.1 mm. (Found: C, 72.4; H, 6.9.  $C_{14}H_{16}O_3$  requires C, 72.4; H, 7.3%).  $\nu_{max}$ . (liq. film.) 1718  $cm^{-1}$  (C=O). Hydrolysis of the ester (0.5 g.) was effected by refluxing with alcoholic potassium hydroxide (25 ml.; 1N) for 1 hr. Dilution with water and acidification, to Congo-red, gave 2-methyl-5-phenoxy-penta-2,4-dienoic acid, m.p. 138-140°, as colourless needles from aqueous ethanol. (Found: C, 70.0; H, 5.4.  $C_{12}H_{12}O_3$  requires C, 70.5; H, 5.9%).  $\nu_{max}$ . (KCl disc) 1667  $cm^{-1}$  (C=O).

Attempted Reaction of Ethyl 2-Methyl-5-phenoxy-penta-2,4-dienoate with Toluene.

Ethyl 2-methyl-5-phenoxy-penta-2,4-dienoate (2.32 g.; 0.01 mole) toluene (1.78 g.; 0.01 mole) and hydroquinone (0.2 g.) were heated to 165° in a sealed tube for 30 hr. The residue

was chromatographed on silica gel, petroleum ether eluted toluene (1.63 g., 91.5%) and benzene eluted ethyl 2-methyl-5-phenoxy-penta-2,4-dienoate (2.22g., 95.5%). No desired material was obtained on further elution.

Attempted Reaction of Ethyl 2-Methyl-5-phenoxy-penta-2,4-dienoate with Maleic Anhydride.

Ethyl 2-methyl-5-phenoxy-penta-2,4-dienoate (2.32 g.; 0.01 mole), maleic anhydride (0.98 g.; 0.01 mole, freshly sublimed) and hydroquinone (0.2 g.) were heated in a sealed tube for 30 hr. at 165°. The mixture was hydrolysed by refluxing in water (50 ml.) for 1 hr. The material was extracted into ether. Washing with sodium bicarbonate solution (3 x 50 ml.), water and drying ( $\text{Na}_2\text{SO}_4$ ) gave, on removal of the ether by distillation, unchanged starting material (1.48 g.; 63.5%). After acidification of the sodium bicarbonate extract, extraction with ether yielded a red gum (1.22 g.) which failed to sublime or crystallise.

Attempted Reaction of Ethyl 2-Methyl-5-phenoxy-penta-2,4-dienoate with Dimethyl Acetylenedicarboxylate.

Ethyl 2-methyl-5-phenoxy-penta-2,4-dienoate (1.16 g.; 0.05 mole) and dimethyl acetylene-dicarboxylate (0.71 g.; 0.05 mole) were refluxed in xylene (20 ml.; sodium dried) for 24 hr. The xylene was removed by distillation and the residue, a red gum, was chromatographed on silica gel. Petroleum

ether-benzene (1:1) eluted dimethyl acetylene-dicarboxylate (0.36 g.; 51.0%), benzene eluted unchanged ethyl 2-methyl-5-phenoxy-penta-2,4-dienoate (0.62 g.; 53.5%) and benzene-ether (9:1) eluted a red gum (0.31 g.) which did not crystallise.

Reaction of Ethyl 2-Methyl-5-phenoxy-penta-2,4-dienoate and Benzene Diazonium-2-carboxylate.

Benzene diazonium-2-carboxylate (2.7 g.; 0.018 mole) and ethyl 2-methyl-5-phenoxy-penta-2,4-dienoate (5.0 g.; 0.022 mole) were refluxed in ether (50 ml.), with mechanical stirring, for 60 hr. The insoluble material was removed by filtration and discarded. The ether was removed by distillation and the residue chromatographed on silica gel. Petroleum ether-benzene (1:1) eluted a slightly coloured oil (0.16 g.) distillation bath temp. 90-95° / 0.06 mm. gave a colourless oil. The infrared and N.M.R. spectra failed to show anything conclusive. Further elution with petroleum ether-benzene (1:1) gave unchanged starting material (3.2 g.; 64.0%).



A P P E N D I X I

Attempted syntheses of some phenyl substituted  
2-phenoxypropionic acids

Attempted Synthesis of 2-Phenoxy-1,2-diphenylpropionic Acid.

2-Hydroxy-1,2-diphenylpropionic acid (2.0 g.; 8.3 mmole) m.p. 180-181° (lit.<sup>179</sup> m.p. 175°);  $\nu_{\text{max}}$ . (KCl disc) 3350  $\text{cm.}^{-1}$  (OH); 1697  $\text{cm.}^{-1}$  (C=O), was converted to 2-bromo-1,2-diphenylpropionic acid by reaction with a saturated solution of hydrogen bromide in glacial acetic acid (50 ml.) for 4 days at ambient temperatures. The mixture was poured into water and filtered. Crystallisation of the precipitate from benzene yielded the 2-bromo acid (2.1 g.; 83.3%) as colourless needles, m.p. 195-197° (lit.<sup>180</sup> m.p. 185°) (Found: C, 59.1; H, 4.7; Br, 25.8. Calculated for  $\text{C}_{16}\text{H}_{15}\text{BrO}_2$ . C, 59.0; H, 4.3; Br, 26.2%).

(a) 2-Bromo-1,2-diphenylpropionic acid (0.5 g.; 1.6 mmole) and sodium phenoxide (0.2 g.; 1.6 mmole) were refluxed in benzene (20 ml.) for 8 hr. The mixture was allowed to cool and water was added. The organic layer was separated and dried ( $\text{CaCl}_2$ ). Evaporation to dryness gave unchanged starting material (0.16 g.; 32.0%), m.p. 178-180° undepressed on admixture with an authentic specimen. The aqueous layer was acidified with dil. hydrochloric acid and filtered. The precipitate was crystallised from petroleum ether giving  $\alpha$ -phenylcinnamic acid (0.24 g.; 65.3%), m.p. 173-175° (mixed melting point undepressed (lit.<sup>181</sup> m.p. 172°)).

(b) 2-Bromo-1,2-diphenylpropionic acid (4.5 g.; 0.015 mole), phenol (1.9 g., 0.02 mole) and pyridine (5.0 g.; 0.06 mole) were refluxed in benzene (10 ml.) for 8 hr. After cooling the mixture was diluted with benzene and washed with water, dilute hydrochloric acid, water and dried ( $\text{CaCl}_2$ ). The benzene was removed by distillation and the residue was crystallised from petroleum ether to yield  $\alpha$ -phenylcinnamic acid (1.5 g.; 45.3%), m.p. 173-176° (m.m.p. undepressed). Crystallisation of the petroleum ether soluble fraction gave trans-stilbene (1.0 g.; 43.5%), m.p. 123-124.5° (lit. m.p. 125°) (m.m.p. undepressed).

Attempted Synthesis of 2-Phenoxy-1,2,2-triphenylpropionic Acid.

(a) 2-Hydroxy-1,2,2-triphenylpropionic acid (2.0 g.; 6.3 mmole) m.p. 206-208° (lit. <sup>182, 183</sup> m.p. 206-208°)  $\nu_{\text{max}}$  (KCl disc) 3505  $\text{cm.}^{-1}$  (OH), 1681  $\text{cm.}^{-1}$  (C=O) and phenol (0.59, 6.3 mmole) were refluxed in toluene (50 ml.), similarly to the method of Spivey,<sup>184</sup> for 14 hr. After removal of the solvent the residue was chromatographed on silica gel. Benzene eluted benzophenone (0.94 g.; 47.0%), m.p. 75-76° (m.m.p. undepressed and benzene-ether (4:1) gave phenyl acetic acid (0.73 g.; 36.5%).

(b) 2-Hydroxy-1,2,2-triphenylpropionic acid (0.5 g.; 1.6 mmole) was reacted with hydrogen bromide in glacial acetic acid

(10 ml., 57%) at ambient temperatures for 3 days. The deep red mixture was poured into water and filtered. Unchanged starting material was dissolved in benzene and the residue crystallised from ether to yield 2,3-diphenylindone (0.2 g., 45%), m.p. 153.5-155.5° (lit.<sup>186</sup> m.p. 153°), identified by comparison of the infrared spectrum with that of an authentic specimen.  $\nu_{\text{max}}$  (KCl disc) 1706  $\text{cm.}^{-1}$  (C=O).

Attempted Synthesis of 2-Phenoxy-1,1-diphenylpropionic Acid.

(a) 2-Bromo-1,1-diphenylpropionic acid (5.0 g.; 0.016 mole) m.p. 203-205° (lit. m.p. 195-197°), (Found: C, 60.0; H, 4.3. Calculated for  $\text{C}_{15}\text{H}_{15}\text{BrO}_2$ . C, 59.0; H, 4.3%), prepared by the method of Wegmann and Dahn,<sup>186</sup> phenol (1.6 g.; 0.017 mole) and pyridine (5.0 g.) were refluxed in benzene (20 ml.) for 5 hr. The mixture was dissolved in ether and the organic layer was washed with water, dil. hydrochloric acid, dil. sodium hydroxide solution, water and dried ( $\text{Na}_2\text{SO}_4$ ). The solvent was removed by distillation to yield 1,1-diphenylethylene (2.73 g.; 92.5%) (Found: C, 93.4; H, 7.2. Calculated for  $\text{C}_{14}\text{H}_{12}$ . C, 93.3; H, 6.7%).  $\nu_{\text{max}}$  (liq. film) 894  $\text{cm.}^{-1}$  (C-H).

(b) Methyl 2-Bromo-1,1-diphenylpropionate.

2-Bromo-1,1-diphenylpropionic acid (5.0 g.; 0.016 mole) was reacted with diazomethane<sup>187</sup> in ether and allowed to stand overnight. Removal of the solvent gave the desired methyl 2-bromo-1,1-diphenylpropionate (5.2 g.; 100%)

crystallised as prisms from aqueous ethanol, m.p. 44-46°.

(Found: C, 60.3; H, 4.7.  $C_{16}H_{15}BrO_2$  requires C, 60.1; H, 4.7%).

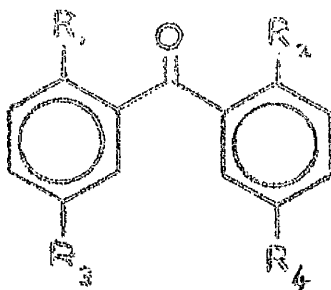
$\nu$  max. (KCl disc) 1712  $cm^{-1}$  (C=O).

Methyl 2-bromo-1,1-diphenylpropionate (1.0 g.; 3 mmole) was reacted with phenol (0.41 g.; 4.4 mmole) and sodium (0.1 g., 0.0044 g., atom.) in ethanol (10 ml., absolute) at reflux temperature for 20 hr. The mixture was cooled, poured into water and extracted with ether. The ethereal extract was washed with sodium hydroxide solution, water and dried ( $Na_2SO_4$ ). Removal of the ether by distillation gave unchanged starting material (0.9 g.; 90%).

A P P E N D I X . . . II

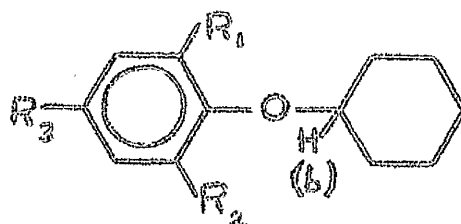
Details of Nuclear Magnetic Resonance Spectra

Substituted Hydroxy-Benzophenones



Substituent	$\tau$ values	Integral	Assignment
$R_1 = R_2 = \text{OH}; R_3 = R_4 = \text{H}$	-0.46 (s) 2.2-3.5	1 9.2	-OH aryl protons
$R_1 = R_2 = \text{OH}; R_3 = R_4 = \text{Bu}^t$	-0.45 (s) 2.41 (m); 2.90 (s) 3.02 (s); 3.13 (s) 8.68 (s)	1 3 11	-OH aryl protons $\text{Bu}^t$
$R_1 = \text{OH}; R_2 = R_3 = R_4 = \text{H}$	-1.88 (s) 2.2-3.5	1 4.2	-OH aryl protons
$R_1 = \text{OH}; R_3 = \text{Bu}^t;$ $R_2 = R_4 = \text{H}$	-1.70 (s) 2.42 (m); 2.98 (s) 3.21 (s) 8.78	1 8.9 10	-OH aryl protons $\text{Bu}^t$

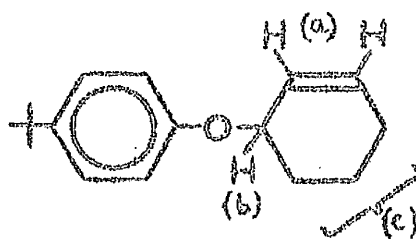
(s) = singlet; (m) = multiplet

Substituted Phenyl Cyclohexyl Ethers

Substituent	$\tau$ values	Integral	Assignment
$R_1 = R_2 = R_3 = H$	2.5-3.5 5.8 8.4	5 0.75 9.6	Ph- Proton b cyclohexyl ring
$R_1 = R_2 = H; R_3 = Bu^t$	3.11 (q) 5.85 8.45 8.75 (s)	4 1 20	aromatic protons Proton b cyclohexyl ring $Bu^t$
$R_1 = R_2 = Me; R_3 = H$	3.15 (s) 5.85 7.80 (s) 8.4	3 0.75 7.7 10.2	aromatic protons Proton b Me- cyclohexyl ring
$R_1 = R_2 = H; R_3 = Cl$	3.08 (q) 5.85 8.45	4.1 1 11.2	aromatic protons Proton b cyclohexyl ring

(s) = singlet; (q) = quartet

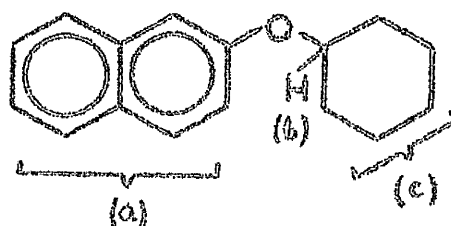


Miscellaneous Aromatic Ethers

Integral:-

4:1.8:0.8:6.6:11.3

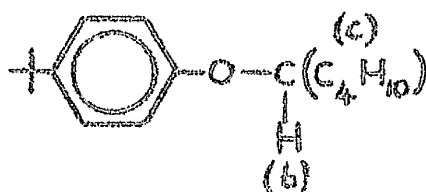
$\tau$  values:- Ph: 3.05 (q); (a) 4.15 (s); (b) 5.35; (c) 8.17 (m)  
 Bu<sup>t</sup> 8.7 (s)



Integral:-

7.2:1:12.3

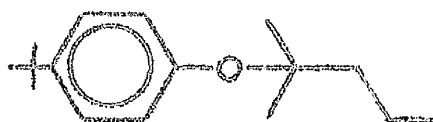
$\tau$  values:- (a) 2.45 (m); 2.92 (m); (b) 5.65; (c) 8.45 (m)



Integral:-

4.2:1 [Ph: (b)]

$\tau$  values:- Ph 3.1 (q); (b) 5.85; Bu<sup>t</sup> 8.75 (s); (c) 8.2-9.4

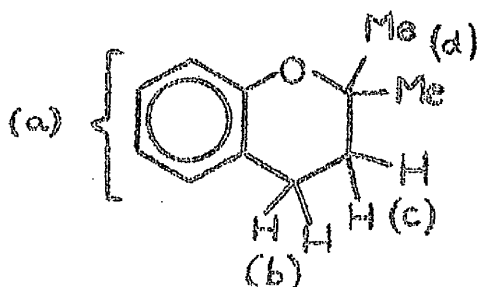


Integral:-

4:23.2

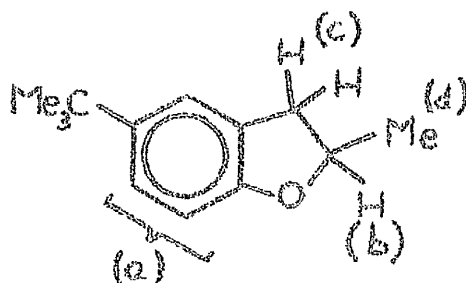
$\tau$  values:- Ph 3.03 (q); Bu<sup>t</sup> 8.75 (s); alkyl residue 8.2-9.3

(s) = singlet; (q) = quartet; (m) = multiplet.

Cyclic Ethers

Integral:-  
4.3:2:2:6.3

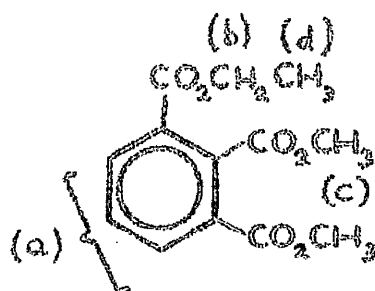
$\tau$  values:- (a) 2.9-3.5; (b) 7.3 (t); (c) 8.30 (t);  
(d) 8.73 (s)



Integral:-  
3:0.8:1.8:13.7

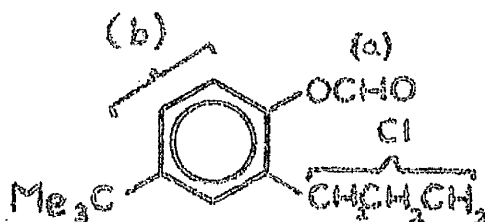
$\tau$  values:- (a) 2.9(m); 3.05(s); 3.38(s); 3.60(s);  
(b) 5.28(m); (c) 7.05(m); (d) 8.52(s);  
Bu<sup>t</sup> 8.6(s)

(s) = singlet; (t) = triplet (m) = multiplet

Miscellaneous Esters

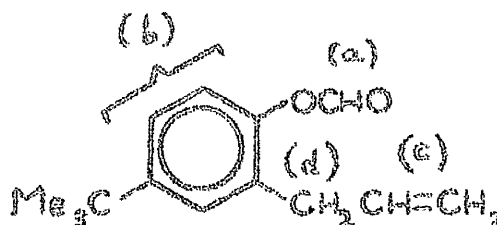
Integral:-  
3.06:2:5:2.8

$T$  values:- (a) 1.78(m); 1.96(s); 2.55(m); (b) 5.68(q);  
(c) 6.13(s); (d) 8.63(t).



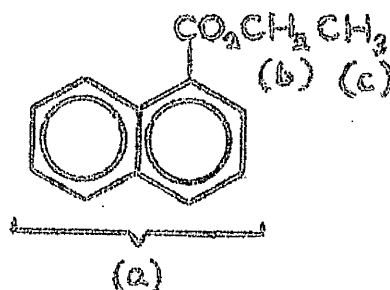
Integral:-  
0.94:3.25:9  
Unassigned peaks:  
1.1:1.1:1.2

$T$  values:- (a) 1.80(s); (b) 2.75(m); 2.94(s); Bu<sup>t</sup>: 8.70(s)  
other unassigned peaks at 5.82(m); 6.96(s); 7.12(s)



Integral:-  
1:4:3.2:1.8

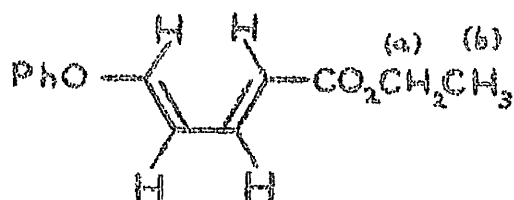
$T$  values:- (a) 1.90(s); (b) 2.88(m); 3.03(s); (c) 3.6-5.6  
(m)  
(d) 6.75(d); Bu<sup>t</sup>: 8.7(s)



Integral:-  
7.4:2:3.4

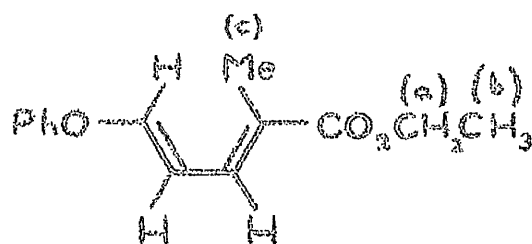
$T$  values:- (a) 1.05(m); 1.75-2.9(m); (b) 5.6(q); (c) 8.6(t)

(s) = singlet; (d) = doublet; (t) = triplet;  
(q) = quartet; (m) = multiplet.



Integral:- 7.3:1.9:1.9:3

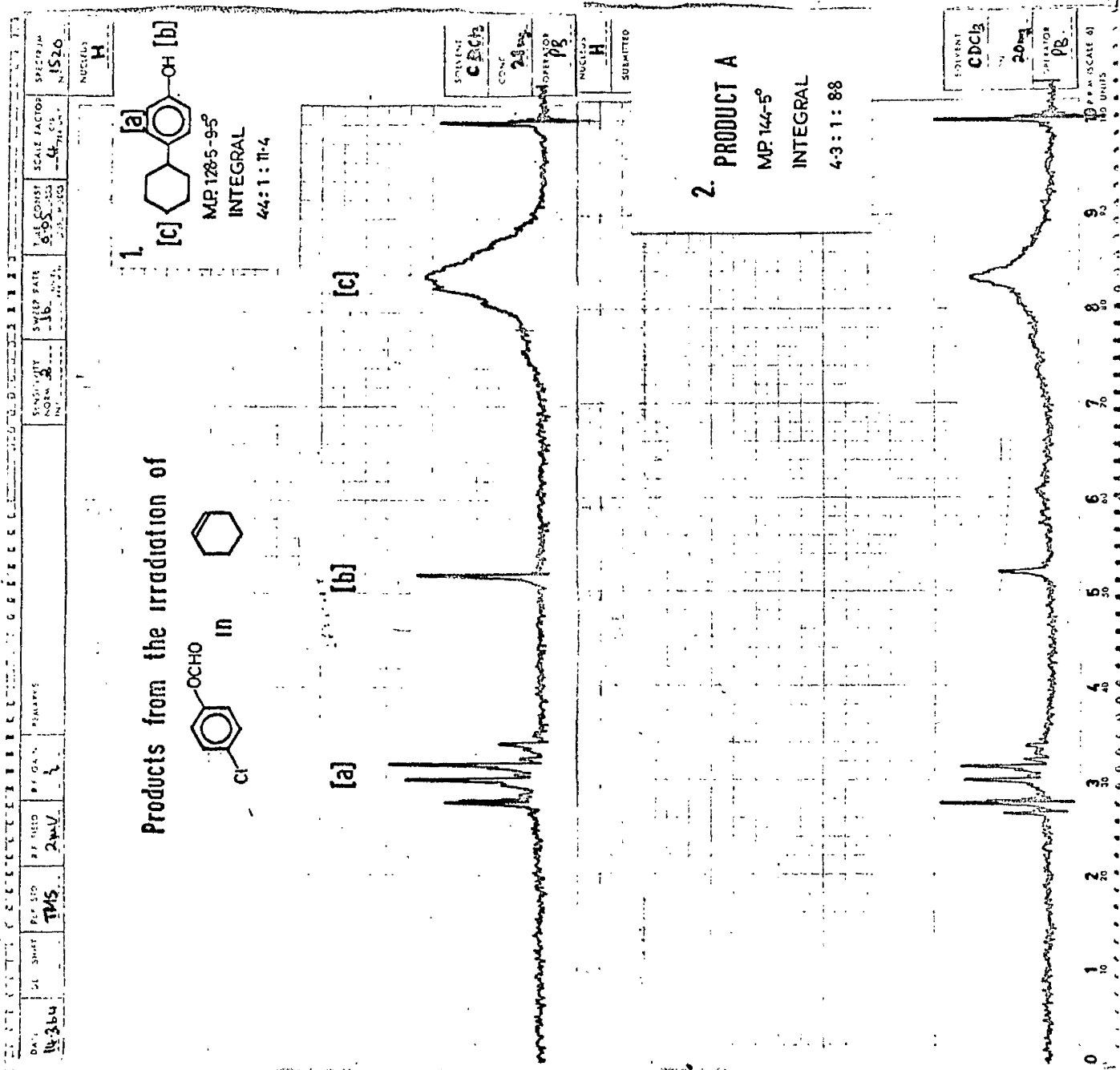
$\tau$  values:- Ph + two shielded protons 2.3-3.2(m);  
 two de-shielded protons 4.08(m); (a) 5.85(q);  
 (b) 8.75(t)



Integral:- 7.3:0.9:2:3.1:  
 3.3

$\tau$  values:- Ph + two shielded protons 2.65-3.15(m); one  
 de-shielded proton 3.85(m); (a) 5.82(q); (c) 8.11(d);  
 (b) 8.72(t)

(t) triplet; (q) quartet; (m) multiplet.



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