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TRANSFORMATIONS

IN

THE BENZOSUBERONE SERIES

BY

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THESIS SUBMITTED TO

THE UNIVERSITY OF GLASGOW

FOR

THE DEGREE OF DOCTOR OF PHILOSOPHY

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SUMMARY

This investigation concerned transformations in the benzosuberone series, directed to the formation of non-benzenoid aromatic compounds related to benzotropone (VIII) having, however, the oxygen atom attached to the six membered ring (IX). Several routes were attempted to obtain the substituted benzotropilidenes required as intermediates.

(p-methoxyphenyl) valeric acid could not be cyclised to m-methoxybenzosuberone. Different methods gave either the starting material or polymers. Ultimately this ketone was synthesised by a different and tedious route of little practical value.

Unsuccessful attempts were made to introduce a functional group (nitro) at the m-position in 1:2 benzocycloheptene 3:7-dione; in contrast it was found possible to introduce (in low yield) a keto group at the 7-position in m-nitrobenzosuberone side products were also isolated and indentified.

Dehydrogenation of m-hydroxybenzocycloheptene was also investigated and found impossible with conventional agents, as the starting material was recovered except in the case of triphenylmethylperchlorate which gave a red pigment of unconfirmed structure. This lead to investigation of the

stability and the effects on triphenylmethylperchlorate on various solvents.

The best route to m-hydroxybenzotropilidene was found to proceed from the p-acetoxybenzosuberone, which was photobrominated and dehydrobrominated to the olefin (XXIII R = OAc). The latter on borohydride reduction followed by dehydration gave m-hydroxybenzotropilidene; which on treatment with triphenylmethylperchlorate gave the required tropylium salt. However, on basification of the salt the ketone (IX) could not be purified, although its presence was inferred by its colour, and by reconversion to the parent tropilidene. The corresponding acetoxy and hydroxy benzotropone was synthesised by standard procedures.

Reduction of 1:2-(3':6'-dihydroxybenzo)-cycloheptene-3:7-dione gave unexpected and interesting results at variance with recently published Polish work on the subject, but this diketone could not be converted to the corresponding dihydroxybenzotropilidene.

ACKNOWLEDGEMENT

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Discussion:-

Experimental:-

Transformations in the benzosuberone series

The original term aromatic (meaning pleasant smelling) has no significance in modern chemistry. At present, aromatic compounds include many not covered by the definition given by Loschmidt[1] in 1861 as 'compounds containing the benzene nucleus'. It was recognised from the very beginning that there are some fundamental chemical differences between benzenoid compounds and simple olefinic compounds. Thus benzenoid compounds have some especial properties associated with them like:-

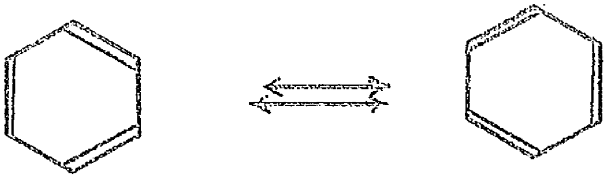
a) Stability to many chemical reagents.

b) Failure to add reagents at the double bonds.

c) Substitution by electrophilic reagents.

d) Especial properties of substituent groups
   e.g. Phenol is acidic

One of the first efforts to explain the behaviour of benzene was made by Kekule[2], who proposed the structure of benzene as (I) and that the resonance between (Ia and Ib) accounted for the features outlined above.



Ia Ib

The advent of more refined physical measurements revealed that most so called aromatic compounds exhibited at least some of the following physical properties.

a) C=C bond distance is intermediate between olefinic C=C (1.34 Å) and saturated C-C (1.54 Å) e.g. benzene (1.39 Å).

b) The rings are planar or nearly planar.

c) High resonance[x] energy (heat of combustion or heat of hydrogenation).

d) Light absorption at comparatively long wavelength.

e) Polarisability (ring current in n.m.r.[3] spectra was a later development).

N.B. The chemical properties are a function of the excited state of the molecule, while the physical properties especially the resonance energies are associated with the ground state of the molecules.

Of striking significance was the theory of the aromatic sextet postulated by Armit and Robinson[4] in 1925.

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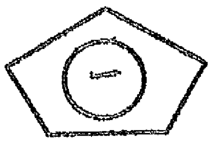
[x] The word stabilisation would perhaps be more accurately applied here.

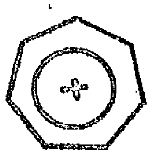
This theory of aromaticity was important in the sense that it explained not only the aromaticity of benzene and six membered heterocyclic compounds but also the absence of aromaticity in cyclobutadiene and cyclo-octatetraene.

Now by improved technical methods, resonance energies could be measured and the agreement between the calculated and the observed values proved the adequacy of this approach. Thus at this time measured resonance energy was supposed to be the criterion of aromaticity.

The modern conception of aromaticity was introduced by Huckel[5,6] based on molecular orbital theory. The π electrons of a closed conjugated system were regarded as common to all carbon atoms. With this theory he fully explained the stability of the then known compounds and also showed theoretically that five and seven membered rings having a conjugated system and bearing a negative and positive charge as C_5H_5 (II) and C_7H_7 (III) respectively could be aromatic and probably stable.



II

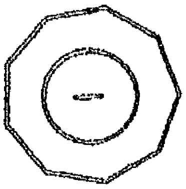


III

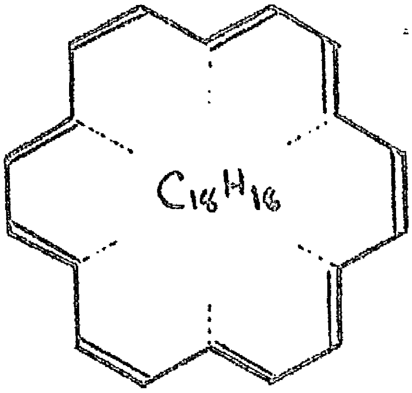
This statement was found true for the cyclopentadienyl anion

II (known by Thiele[7]) and in 1954 Doering and Knox[8] confirmed the predicted properties of tropylium cation III. Huckel went a little further to suggest that aromatic properties were in general to be expected in monocyclic conjugated polyolefinic structures having $(4n+2)\pi$ electrons (n is an integer). The predictions of Huckel were found reasonably accurate even for the cyclononane-tetraenyl anion (IV) recently discovered by Katz and Garatt~~e~~[9].

According to Elvidge and Jackman[10], the essential feature is a ring of atoms so linked that π electrons are delocalised right round the ring. They defined an aromatic compound therefore as a compound which will su~~b~~stain an induced ring current.

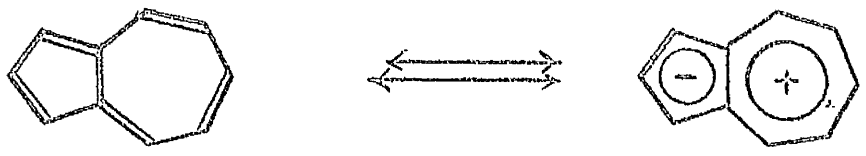


IV



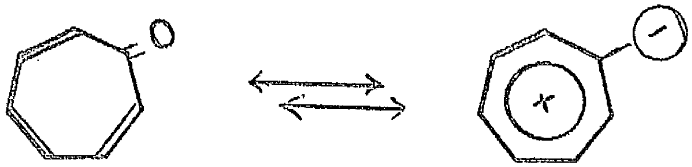
The recent n.m.r. studies on (18) annulene[11,3] that obeyed the Huckel rule and had exhibited aromatic character, indicated two n.m.r. signals, at room temperature; one in the aromatic region ($\overset{1.1}{1.7}\,\tau$) and the other in the non-aromatic region (11.3 τ). But at low temperature ($\overset{-60}{-30}$°C) the bands were further separated (.72τand12.99τ). This increased separation of the band at low temperature is indicative of an increased ring current. Thus Sondheimer et. al.[12] proposed "the existence of a single n.m.r. band in the non-aromatic region cannot be considered as evidence for lack of aromaticity, unless it is shown that there is no change on cooling".

A most interesing non-benzenoid aromatic structure is azulene (V)[13] which may be considered as the combination of (II and III); it is highly coloured and quite stable.



Va Vb

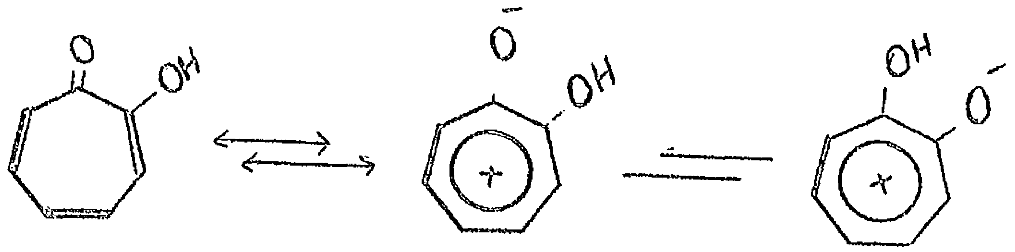
Much work has been lavished on seven membered ring "aromatic" compounds, many of which may be regarded as substituted derivatives of tropone. The parent tropone (VI) was investigated by Dauben and Ringold[14] in 1951.



VIa VIb

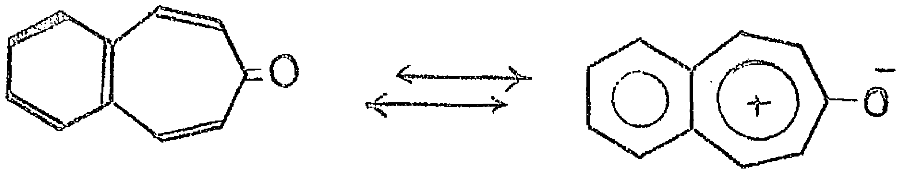
The aromatic character of tropone (VIa and VIb) however is not very prominent and has indeed been disputed by Buchanan and Lockhart[15] on the basis of chemical behaviour. Tropone (VI), in fact forms a semicarbazone and 2:4 dinitrophenylhydrazone[16]. However on the basis of physical character it may partly be, an aromatic compound (e.g. structure VIb). The following physical measurements indicated delocalisation of the π electrons in a closed seven membered ring. The C=C bond length was shown to be 1.41 Å[17] and the dipole moment was found to be 4.30D[18,19], while the dipole moment in cycloheptanone was only 3.04D[20].

But tropolone (VII, α-hydroxytropone)[21] exhibited perfectly aromatic behaviour in the chemical sense as well as the physical.



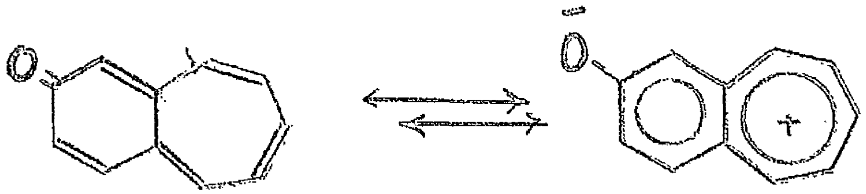
VIIa VIIb VIIc

It was quite stable, underwent nitrosation, nitration, sulphonation, halogenation and azocoupling just like a phenol. The X-ray study of the copper salt by Robertson[22] showed the structure of tropolone to be a planar regular heptagon, having an average bond length 1.40 Å. Reviews on tropone and tropolone have been published[23,24].



VIIIa VIIIb

The first benzotropone (4:5-benzotropone VIII) was synthesised as early as 1910 by Thiele[25], and much later 2:3-benzotropone was obtained by Buchanan[26] in 1959, from benzosuberone[27].

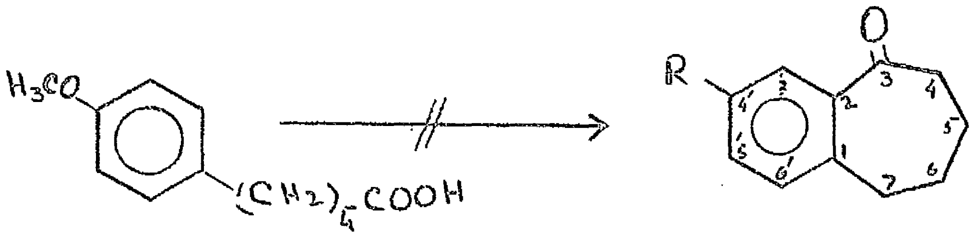


IXa IXb

The object of the present work was to remove the oxygen (in principle) from the seven membered ring to the benzene ring and to see whether the product (IX) shows any resemblance to the analogous tropone (VIII). In a model structure (IX) requires a slight distortion of sp^2 bond angles, but it seems possible to have a flat molecule allowing delocalisation of electrons. A problem of this type has also been recently discussed by G.R. Proctor[28].

The synthesis of such a molecule seemed to require as penultimate intermediate substituted benzotropilidenes, for which various routes have been investigated based on benzocycloheptenones.

Attempted cyclisation of p-methoxy phenyl valeric acid



X XI

It was desired to obtain the benzosuberone (XI, R=OCH$_3$) for the following reason. Bromination at an allylic position was first studied by Wohl[29] (using N-bromoacetamide) and was further developed by Ziegler[30] (using N-bromosuccinimide) and is now called the Wohl-Ziegler reaction. The extensive use of this reagent was discussed by Horner and Winkelmann[31]. Buchanan[26] had observed the allylic substitution of bromine at the 7-position in benzosuberone (XI, R=H). Considering the structure (XI, R=OCH$_3$) it seemed reasonable to suppose that in this case also N-bromosuccinimide might be expected to cause bromination in the 7 position, since the electron releasing effect of a methoxy group on position 3' and 5' (being counteracted by the carbonyl group) might not cause nuclear substitution. From the brominated methoxy benzosuberone one could envisage simple processes leading to the corresponding hydroxy benzotropilidene.

To start with, anisol was condensed with glutaric anhydride[32] by Friedel and Crafts' method[33,34], and the p-methoxy benzoylbutyric acid was isolated in much improved yield. It was quantitatively reduced to the corresponding p-methoxy phenyl valeric acid by an improved Clemmensen's reduction.

The literature contains a number of examples of cyclisation[35-31] to a position meta to an electron releasing group, though the yields were not good. However the cyclisation of p-methoxy phenyl valeric acid was not found possible with various reagents, and generally the starting material was isolated. Polyphosphoric acid behaved differently and gave two main products, depending upon the reaction temperature. When the cyclisation was attempted at 90-100°, the main product (m.p. 120°) was a ketone, confirmed by infrared spectroscopy and the formation of 2:4 dinitrophenylhydrazone.

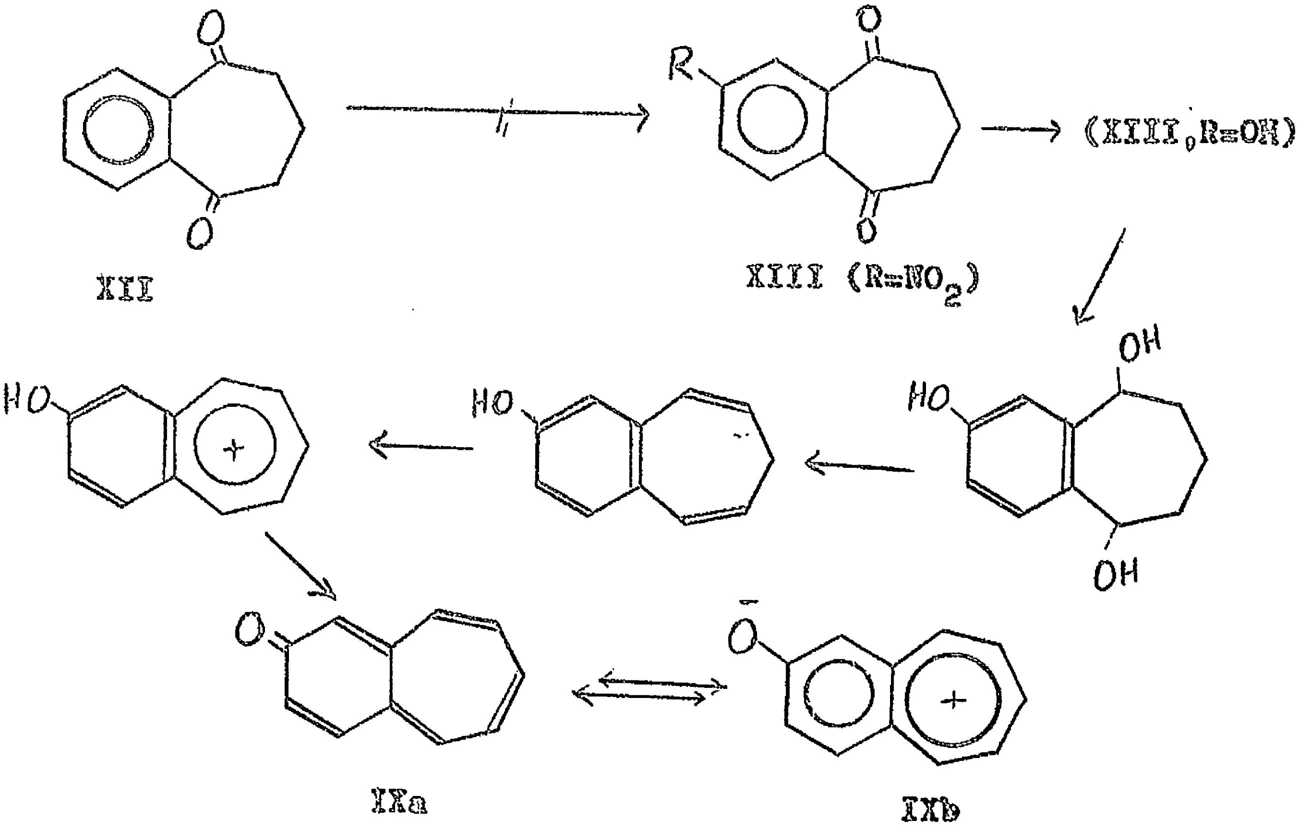
Elementary analysis gave the desired empirical formula $C_{12}H_{14}O_2$, but molecular weight 637 indicated it to be a polymer. Similarly, if the reaction was carried out at low temperature (60-80°) the main product was a gum. Elementary analysis indicated it to be $C_{12}H_{16}O_2$ (molecular weight 406). It underwent polymerisation even on chromatography on neutral deactivated alumina after which when crystallised from alcohol, it solidified (m.p. 96°) and the molecular weight was found to be 750. The same type of trouble was reported during the cyclisaion of δ.O. methoxy phenyl valeric acid by Shlomo Bien[39].

Since the 4' methoxy benzosuberone (XI, R=OCH$_3$, was not available by this route, it was synthesised by an other route in the following way:-

Benzosuberone was nitrated to its nitroderivative (XI, R=NO$_2$), was then reduced, diazotised and hydrolysed to the corresponding hydroxy benzosuberone (XI, R=OH) after the method of Smith and Berry[40]. The hydroxy compound was then methylated with dimethyl sulphate in presence of chloroform to the required 4'-methoxy-benzosuberone (XI, R=OCH$_3$). This route was not found very promising as it involved many steps and the overall yield was poor.

Transformations of benzocycloheptene-3:7-dione

Availability of benzocycloheptene-3:7-dione (XII, synthesised by Dieckman[41] in 1899) and the facile nitration[40] of benzosuberone, mentioned previously made the following scheme very attractive.



XII

XIII (R=NO_2)

IXa

IXb

In 1951 Johnson et. al.[42] claimed to have improved Dieckman's method[41], for the synthesis of the said diketone (XII). Great difficulty was experienced in isolating the required product according to their method for the following reasons:-

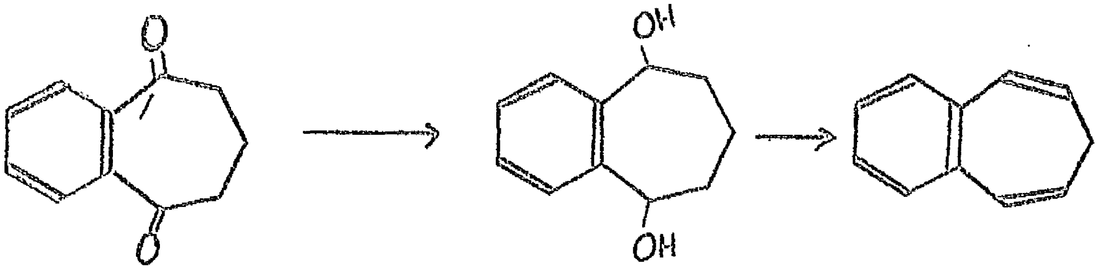
(i) Much unreacted sodium was found in the reaction mixture and the addition of sulphuric acid (25% aq.) seemed to be very dangerous.

(ii) Excess of sodium could not be destroyed by alcohol, as there was every possibility that the ketone might be reduced.

(iii) If water was used (in nitrogen atmosphere) the intermediate diketo ester might be decomposed in strong caustic soda on standing for some time to some unknown material as reported by Dieckman[41].

However, the diketone (XII) was finally synthesised from diethylphthalate and diethyl glutarate by the original Dieckman's method[40], using a mechanical stirrer during the reaction. The intermediate diketo ester was isolated, hydrolysed and decarboxylated to the required diketone (XII); giving a very good quality product and better yield than reported by Johnson et. al.[42] or Dieckman[41]. Full details are reported in the experimental section.

It was first shown that the conversion of diketone (XII) to benzotropilidene (XV) via the diol (XIV) was a practical proposition, before trying to synthesise any substituted benzocycloheptene-3:7-dione (XIII).

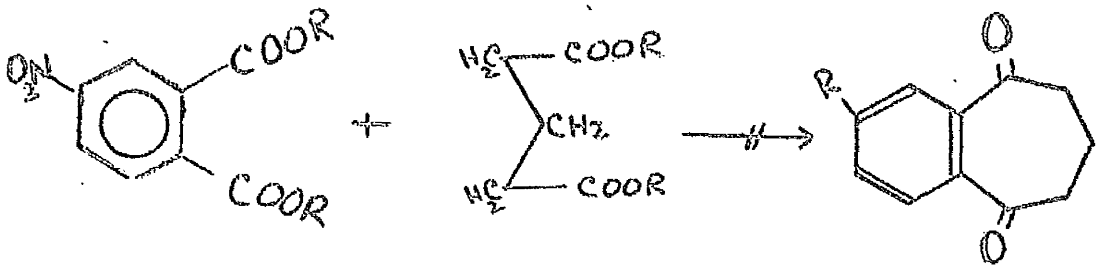


XII XIV XV

The diketone (XII) was reduced with sodium borohydride giving only (trans) 1:2-benzocycloheptene-3:7-diol (XIV). It was recently reported that reduction of the said ketone with potasium borohydride gave trans and cis diol[43]. The alcohol (XIV) was dehydrated to 1:2-benzocyclohept-1:3:6-triene (XV)[44].

Nitration of the diketone (XII) was not found possible. Most probably the two carbonyl groups made the benzene nucleus extremely deactivated towards nitration even with fuming nitric acid or with mixtures of fuming nitric acid and sulphuric acid. At low temperatures the starting material was recovered, while at room temperature some of it had decomposed.

The successful condensation of phthalic ester and glutaric ester in presence of metallic sodium to 1:2-benzocycloheptene-3:7-dione (XII) suggested the possibility of similar condensation of 4-nitrophthalic ester and glutaric ester to give the corresponding nitro diketo ester (XIII, $R=NO_2$)



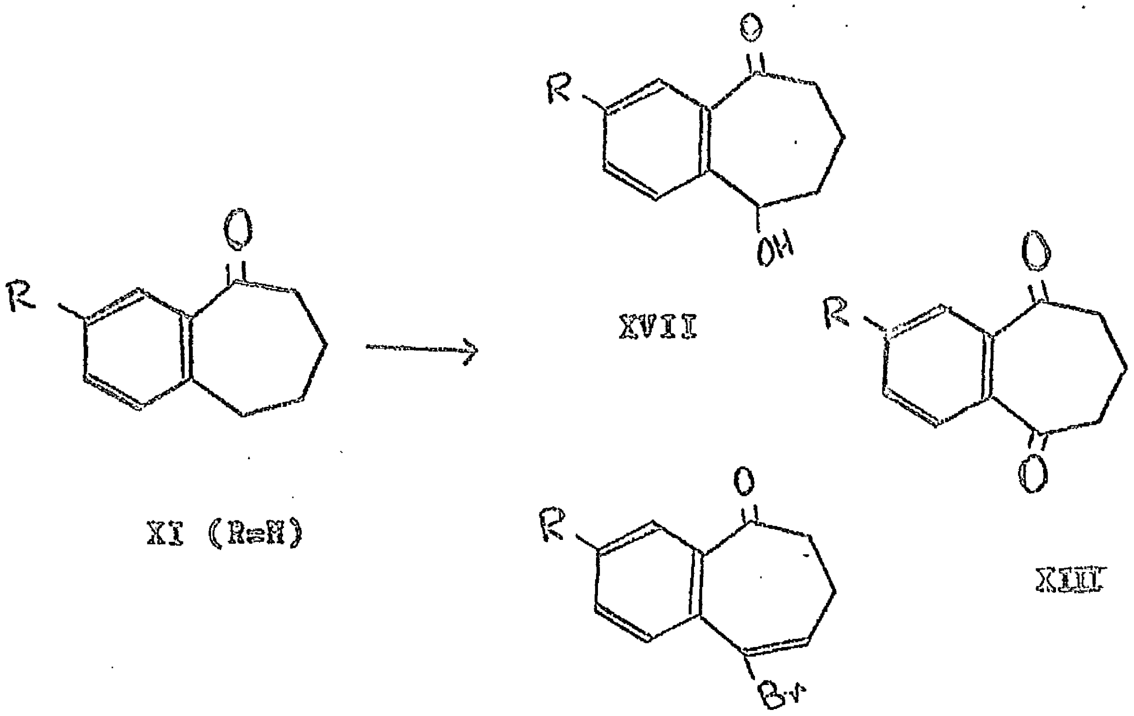
XIII (R=NO_2)

Condensation was attempted under the conditions adopted for (XII) and surprisingly the starting material 4'-nitrophthalic ester) and its hydrolysed product (4-nitrophthalic acid) were isolated. This is hard to explain, since one would not have expected the nitro group to deactivate both the ester groups to attack by carban-ions.

Transformations in the benzosuberone series

As it has been previously explained, the nitration of 1:2-benzocycloheptene-3:7-dione (XII) was not found possible, so other syntheses of substituted benzocycloheptene-3:7-diones were then studied. The allylic bromination described earlier seemed a promising tool; accordingly the effect of two moles of N-bromosuccinimide on benzosuberone was examined first as a model experiment.

On surveying the literature it was found that introduction of more than one bromine atom to the same carbon atom (allylic to an olefin) is quite possible. For example toluene when treated with two moles of N-bromosuccinimide gave a gem-dibromo derivative[45]; ortho and p-xylene on similar treatment with two moles and four moles of N-bromosuccinimide gave dibromo and tetrabromo derivatives[45,47]. Thus it was expected that the treatment of benzosuberone (XI, R=H) with two moles of N.bromo-succinimide should produce 1:2-benzo-7:7-dibromocycloheptene-3-one, which might be hydrolysed to the required diketone (XIII, R=H).



XI (R=H)

XVII

XIII

XVI

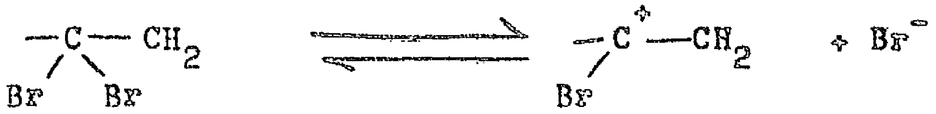
When benzosuberone (XI, R=H) was photobrominated with two moles of N-bromosuccinimide in dry carbon tetrachloride the weight of the bromo-compound indicated it to be a dibromo-compound. One of the conventional methods for hydrolysing gem-dibromo compounds to ketones involves conversion to the gem-diacetate (by treatment of with silver acetate) followed by hydrolysis. When the above dibromo compound was treated with silver acetate followed by acid hydrolysis, it gave mainly the vinyl bromide type compound (XVI, R=H). Hydrolysis of the dibromo compound with acetone and water gave more interesting results.

(i) The main product (~50%) was vinyl bromide type compound (XVI, R=H). The structure was confirmed by infrared spectroscopy and by elementary analysis.

(ii) The alcohol (XVII; R=H; ~40%) confirmed by infrared spectrum, elementary analysis and by n.m.r. spectroscopy, that indicated aromatic signal at 2.7 τ (area4), tertiary proton, a triplet at 5.3 τ (area 1); hydroxyl, 6.2 τ (1); aliphatic protons at 8 τ (6).

(iii) A small quantity (~10%) of the required diketone (XIII; R=H). It was identified by comparison of infrared spectra and by m.p. and mixed m.p. with the genuine sample of 1:2-benzocycloheptene-3:7-dione.

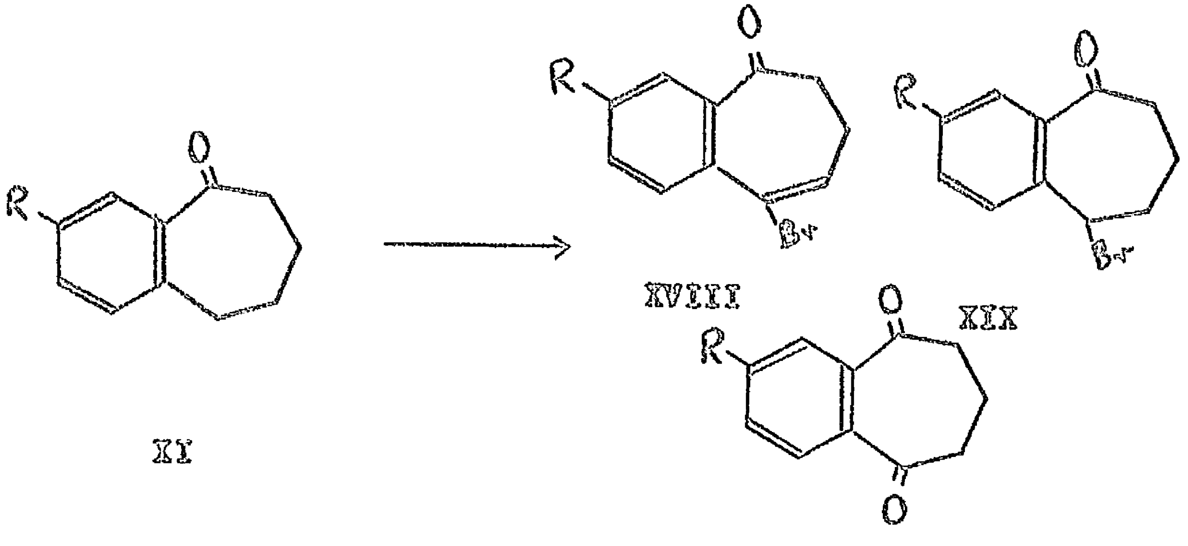
From the above experiment it was quite evident that both bromine atoms entered at 7 position (allylic to olefin). Hydrolysis of the gem-dibromo compound with excess of aqueous acetone 1:1 (almost neutral) most probably proceeded by a first order mechanism[48].



After the formation of carbonium ion there are two competitive reactions. (a) The elemination of a proton which is quite favoured in this environment. (b) The nucleophilic attack of the hydroxyl ion at the positive centre. The latter process might lead to the formation of the gem-diol and then to a ketone. In this reaction the elimination was predominant, and was comparable with the results of Oliver and Weber[49], who showed the reaction of gem-dibromide was 200 times faster than that of vic-di-bromide, when reacted with aqueous acetone.

Inspite of the poor yield of diketone (XIII, R=H), it seemed worthwhile to examine halogenation of substituted benzosuberones (XI, R=NO_2) especially when a vinyl-type bromide could conceivably be utilised as it represents partial oxidation of the molecule.

In fact the bromination of m-nitrobenzosuberone (XI, R=NO_2) with two moles of N-bromosuccinimide went quite smoothly and a colourless dibromo derivative (in expected yield) was obtained. On hydrolysis with aqueous acetone (1:1) three products were isolated.



XI

XVIII

XIX

XII

(i) 1:2-(4'nitrobenzo)-7-bromocyclohept-1:6-diene-3-one (XVIII)$R=NO_2$;~64%); n.m.r. studies indicated:- the aromatic proton (3') sharp band at 1.5τ, the other two aromatic protons at ~2τ and the olefinic gave a triplet at ~3τ while the four aliphatic protons had bands at ~7.4τ, ratio (1:2:1:4)

(ii) Bromoketone (XIX; $R=NO_2$),1:4-(4'-nitro-benzo)-7-bromocycloheptene-3-one (~24%), showed n.m.r. bands for aromatic at ~2τ (area 3), tertiary proton (triplet) at ~4.5τ (area 1) and aliphatic protons had bands at ~7.4τ (area 6).

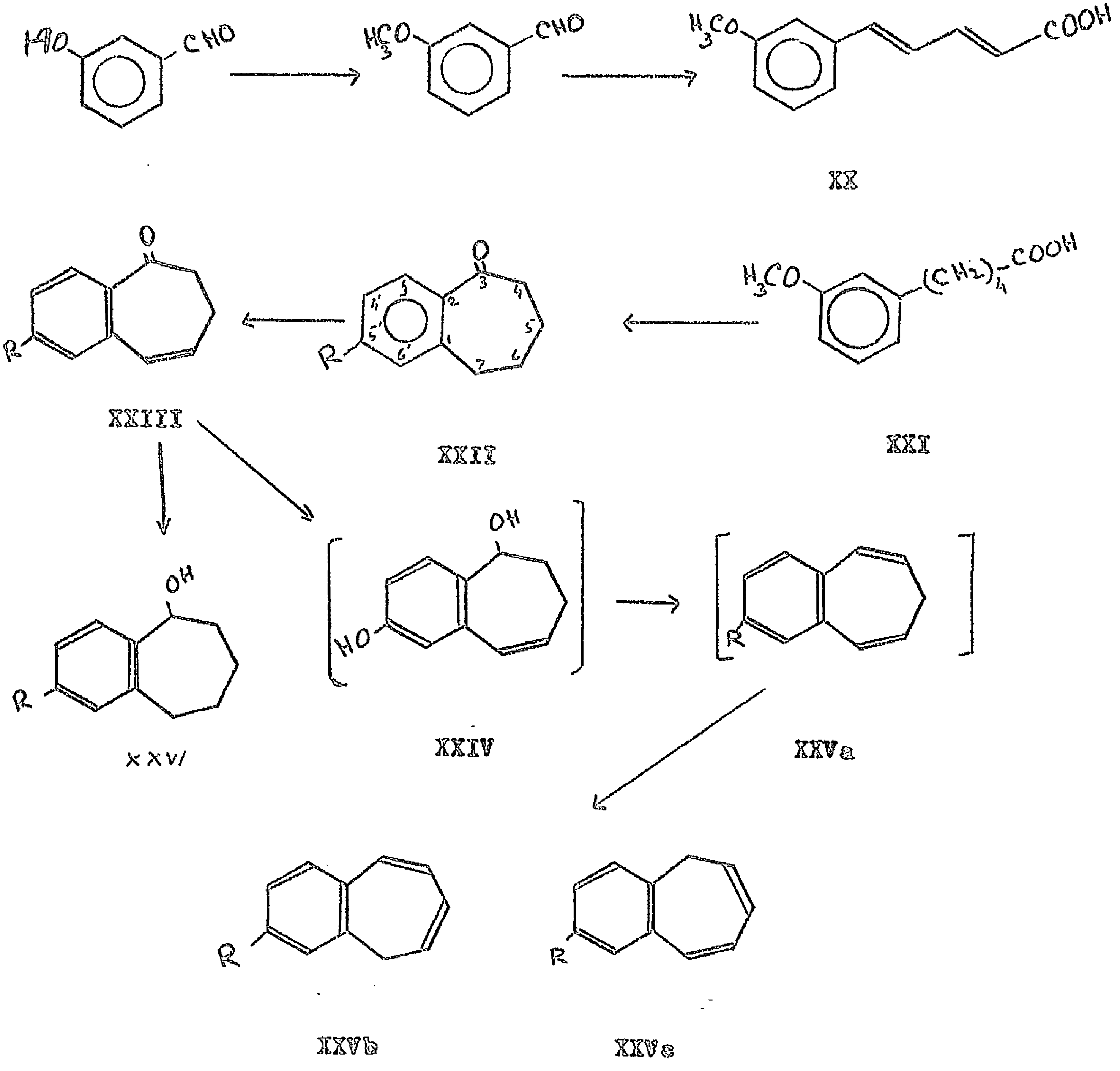
(iii) The required ketone (XII;$R=NO_2$) 1:2-(4'-nitrobenzo) cycloheptene-3:7-dione (~12%) was confirmed by infrared, elementary analysis, and n.m.r. spectroscopy indicated aromatic signals at $\sim 1.7\tau$, four protons adjacent to the carbonyl groups had bands at $\sim 7\tau$ and the other two aliphatic protons at $7.8\ \tau$ and their ratio was (3:4:2).

The resistance to hydrolysis of the mono-bromo-compound (XIX, $R=NO_2$) may be expected due to the presence of a strong electron attracting (nitro) group at the para position, which decreases the tendency of unimolecular carbon bromine bond breaking[50]. This process seems likely to be the rate determination step in aqueous acetone.

It was interesting that apparently in both benzosuberones mentioned above, about 25% of the material produced must have been the mono-bromide. This may be due to the consumption of N-bromosuccinimide caused by reaction of the latter with hydrobromic acid, released thermally from the dibromide. Two pieces of evidence support this possibility. Firstly bromine has been seen in the condenser above reaction vessel and secondly thin layer chromatography showed that the crude dibromide from benzosuberone contained several substances, one of which was probably the vinyl bromide, though it was not expedient to separate it at that stage

Transformations basedon 5'-hydroxy-benzosuberone

Failure in the previous schemes le~~a~~d to the following proposal, which in fact was successfully carried to the hydroxy benzotropilidene (XXV).



Methylation of m-hydroxy benzaldehyde was attempted with methyl iodide on ion exchange resin[51], in expectation of better yield and pure product. However, the yield was not very encouraging. So the most conventional methylating agent dimethyl sulphate was employed in the usual way in alkaline medium[62,53]. It was known that etherification with alkyl or aryl halide or sulphate is generally influenced by the solvent[54]. A non ionic solvent such as benzene etc. gives nuclear substituted products; while ionic solvents like alcohol etc. give ethers. However the above phenol was etherified almost quantitatively with dimethyl sulphate using chloroform as solvent[55].

As early as 1901 Lapworth[56] realised that properties like those possessed by α-hydrogen activated by a neighbouring carbonyl or other competent group, should be shown by γ-hydrogen if connected through an intervening α,β. ethylenic linkage. He demonstrated the condensation of ethyl oxalate with γ position of ethyl crotonate under the influence of sodium ethoxide. Condensation of benzaldehyde and of some substituted benzaldehydes with ethylidene malonic ester to the corresponding cinnamylidene malonic ester were reported by Horton[57] et. al. in 1952; and the yields were further improved by Horton and Pitchforth[58] in 1960. In the present case the m-methoxy benzaldehyde was condensed with methyl crotonate according to the method supplied by Dreiding[59], and the condensed ester was hydrolysed to give an excellent yield of m-anisylidene crotonic acid (XX). The latter was hydrogenated in presence of Adam's catalyst, but on a larger scale, Raney nickel[60] was found best at 80-90°C/125 ~~atm~~ atmospheric pressure to give m-methoxy phenyl valeric acid, (XXI), originally obtained by Horton by the other route[58].

There are numerous examples of cyclisation to ortho or para positions in presence of electron releasing groups. The cyclisation of m-methoxy phenyl valeric acid was reported by Horton[58] who used polyphosphoric acid, but we obtained a poor yield by this method, on the other hand conversion of the acid to its acid chloride followed by Friedel and Crafts' reaction with stannic chloride gave 71% yield of cyclic product (XXII, $R=OCH_3$). The m.p. was found to be 62°, while that reported was 54-58°.

There are many demethylating agents, and all are Lewis acids. Over the last few years, boron halides have been reported to be very good demethylating agents[61-63]. Expecting the easily handled boron tribromide might give a pure product and noting that it was successfully employed by Bonner[64] on 2 methoxy cyclohexanol; it was reacted with the methoxy compound (XXII; $R=OCH_3$).

but the latter was found unaffected. It could not be demethylated with hydrobromic acid. The commercially available anhydrous aluminium bromide demethylated the ether (XXII, R=OCH$_3$) but the yield was low and the quality of the product was poor. However, freshly prepared aluminium bromide[65] gave quantitative yield of colourless phenol (XXII, R=CH)

The acetate (XXII; R=OAc) was photobrominated with one mole of N-bromosuccinimide which presumably caused substitution at the 7 position (allylic to the double bond), as on dehydrobromination with collidine, the product gave 1:2-(5'-acetoxy-benzo)-cyclohept-1:6-diene-3-one (XXIII, R=OAc). It could not be completely purified by chromatography over silica, as the product was always contaminated with starting material (confirmed by mass spectrography)

The acetoxy compound (XXIII, R=OAc) was hydrolysed to the corresponding phenol (XXIII, R=OH) over neutral deactivated alumina if chromatographed slowly, but ultimately it was rapidly chromatographed over neutral deactivated alumina, distilled and crystallised giving a refined product. The structure was confirmed by infrared spectroscopy, elementary analysis and by the n.m.r. spectrum, which indicated aromatic protons at 2 to 3 τ, vinyl protons at ~3.6 τ; aliphatic methylenic protons at 7 τ to 8.1 τ, while O-~~meth~~Ac.yl protons at 7.8 τ (singlet) and the ratio was (3:2:4:3). Catalytic (Adam's catalyst) hydrogenation of (XXIII, R=OAc) gave the alcohol (XXVI, R=OAc).

Reduction of the ketone (XXIII; R=OAc) with sodium borohydride presumably gave the phenolic alcohol (XXIV, R=OH) since on dehydration it gave hydroxy benzotropilidene (XXV; R=OH) as a colourless crystalline material, which rapidly decomposed in air with the appearance of a pink colour. The n.m.r. spectrum was found very interesting. It indicated the expected signals:- aromatic protons at 2 to 3.5 τ, vinylic protons 4.1 τ, but the methylene protons gave unexpectedly a doublet at 7.1 τ, though from the structure (XXVa, R=OH) the methylenic protons having two neighbouring vinylic protons should give a triplet, as it was observed in the n.m.r. spectrum of benzotropilidene (XV). On the basis of this doublet it was expected that most probably the molecule (XXVa; R=OH) might have rearranged to (XXVb or XXVc; R=OH).

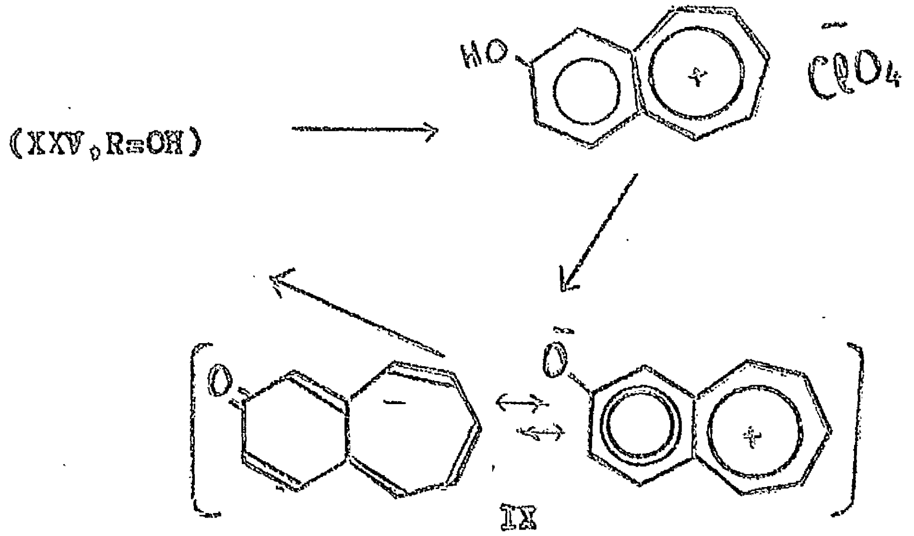
The second point that was noted in the n.m.r. spectrum of (XXV, R=OH) that there was no obvious hydroxyl signal, and the ratio (8:2) of these bands (aromatic, vinylic and aliphatic protons) indicated that the hydroxyl proton was obscured by the vinylic protons. However the hydroxyl group was recognised by infrared spectroscopy.

To provide confirmatory evidence for the phenolic tropilidene (XXV; R=OH) it was decided to prepare the acetate (XXV; R=OAc), which was unexpectedly a thick liquid. The infrared spectrum established the ester peak and the n.m.r. indicated the methyl peak at 7.8 τ. (singlet area 3); a doublet of methylene protons (area 2); vinylic protons 3.8 τ (area4) and aromatic signals 3 τ (area 3).

In order to dehydrogenate or oxidise the molecule (XXV;R=OH), firstly the conventional oxidising agents such as moist silver oxide (extensively used for the preparations of quinones), active manganese dioxide[66-68]; and Fremy's salt[69,70] were tried on this hydroxy tropilidene and unaffected starting material was recovered.

A number of dehydrogenating agents such as selenium, selenium dioxide, sulphonyl chloride have been employed in the synthesis of tropylium salts from tropilidenes[24], but triphenyl methyl bromide and triphenyl methyl perchlorate[71] gave almost quantitative yields. Triphenyl methyl fluoroborate and perchlorate were used by Bonthrone and Reid[72] on dihydroaromatic compounds, from which they isolated either the aromatic compound or its perchlorate if the cation was stable.

The hydroxy tropilidene (XXV;R=OH) was treated with 1 mole of triphenyl methyl perchlorate (prepared by Dauben's method)[73] in dry methylene chloride, when a greenish hydroxy benzotropylium perchlorate (XXVII) was isolated. Basification of the tropylium salt gave a reddish substance, extracted with methylene chloride, but this could not be purified since it decomposed on removal of the solvent.



IX

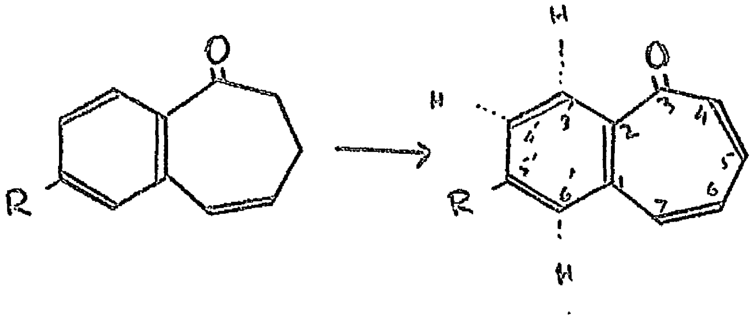
A similar reactivity in a tropylium salt was also reported by Doering, while Nozoe et. al.[74] reported in 1960 that tropylium salt underwent decomposition even on slow neutralisation in aqueous solution with sodium bicarbonate. The only evidence for the expected ketone (IX) was that the crude red material when reduced with sodium borohydride gave back the starting phenol (XXV; R=OH).

The unstability of the molecule (IX) reminded one of the most recent comment by Hafner[75]. "A high degree of delocalisation, that is a strong ring current of electrons does not always guarantee benzene like stability and reactivity".

The unstability of the molecule might be due to a highly ionic character caused by the strongly electron attracting carbonyl group and the electron releasing effect of the tropylium ring. Thus the ionic molecule is fully exposed to any ionic reagent.

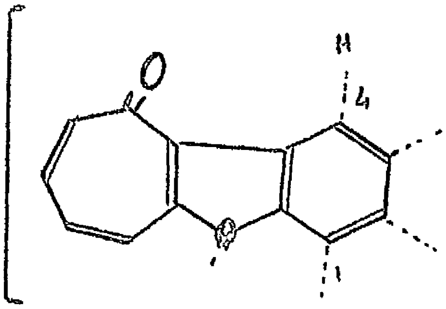
To stabilise the molecule it may be suggested that if the carbonyl group is made sterically hindered (by tertiary butyl groups ortho to the carbonyl) perhaps the approach of an electrophilic reagent would be prevented. It also seems possible that a hydroxyl group ortho to the carbonyl group may stabilise the molecule due to hydrogen bonding, particularly if it be in the 5' position, since the resulting molecule has a plane of symmetry[76] which may be significant.

Since the starting material (XXIII;R=OAc) was at hand, it seemed useful to synthesise the hitherto unknown acetoxy tropone and hydroxy tropone (XXVIII;R=OAc , OH) and particularly to examine the n.m.r. spectrum.



XXIII

XXVIII



XXIX

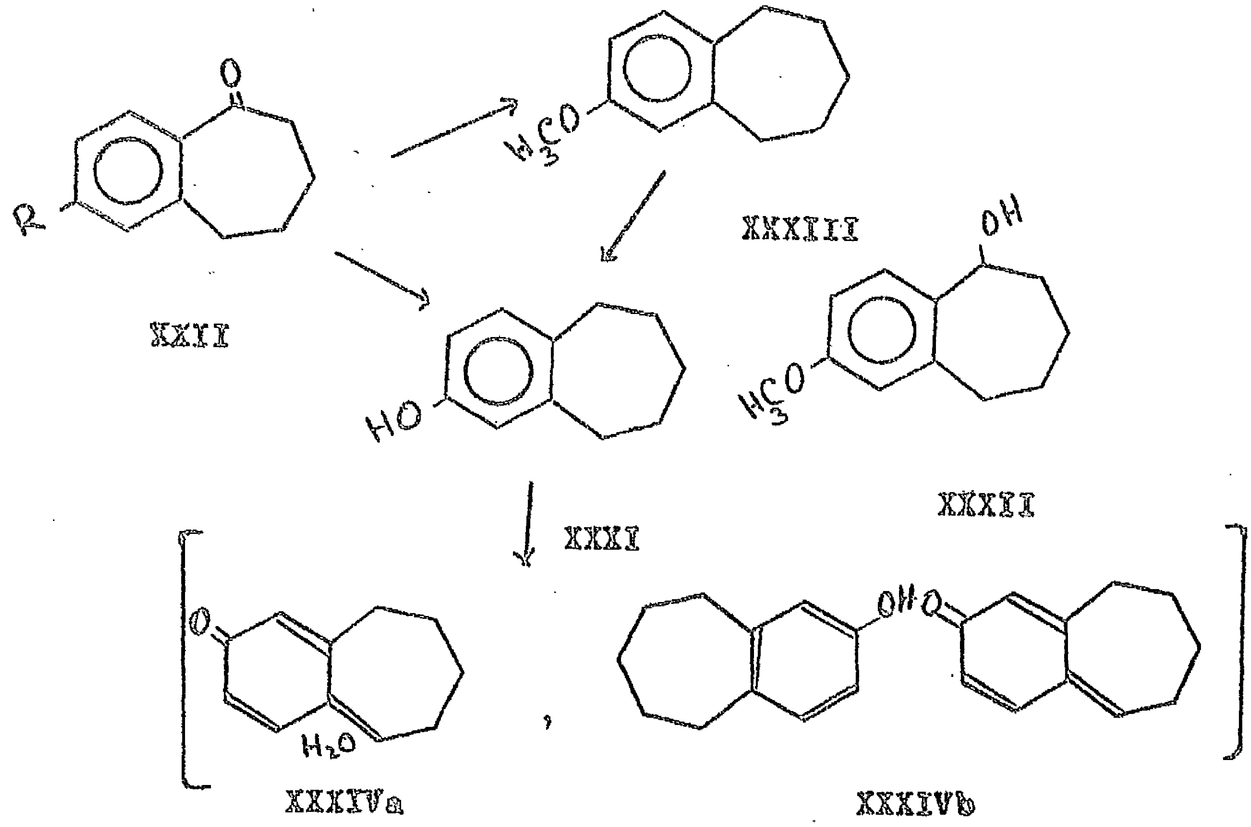
1:2-(5'-acetoxy-benzo)-cyclohept-1:6-diene-3-one (XXIII, R= OAc) was photobrominated with 1 mole of N-bromo succinimide to give presumably the 5-bromo derivative which was dehydrobrominated with collidine and the previously unknown acetoxy tropone (XXVIII, R=OAc) was isolated, it was hydrolysed to the corresponding hydroxy tropone (XXVIII, R=OH).

A tropone formulated as (XXIX) was recently obtained by Rodger[77] and exhibited a signal at very low yield ($\tau = 1.5$) which had to be attributed to the proton (4), since no other explanation was forthcoming. This figure is low even for a proton ortho to a carbonyl group.

However in the present work also a doublet was obtained at 1.37 τ, which is entirely consistent with it being caused by the proton at carbon atom (3'). Moreover a study of the spectra of the ketone (XXII) and (XXIII) showed that the proton at carbon (3') became steadily more deshielded as the unsaturation in the 7 membered ring increased. Thus one might hazard the opinion that, as the negative charge on the carbonyl oxygen increases, so the signal due to the ortho aromatic proton may move to lower field.

Attempted dehydrogenation of m-hydroxybenzosuberane

The successful dehydrogenation of dihydro aromatic and heterocyclic compounds by Bonthrone and Reid^{72,78} with triphenyl methyl perchlorate tempted one to try the reagent on more saturated compounds like m-hydroxybenzosuberane (XXXI; R=OH).



Reduction of the methoxy ketone (XXII, $R=OCH_3$) with lithium aluminium hydride in tetrahydrofuran at reflux temperature gave the expected alcohol (XXXII) but when very concentrated solution in tetrahydrofuran was used, the main product was found to be the phenol (XXXI) together with a small quantity of the alcohol (XXXII).

This type of reduction of carbonyl group to methylene together with demethylation is not well known, but the same type of reaction was observed by Proctor during the reduction of 4',5'-dimethoxybenzosuberone[78]. In order to further confirm the structure of the phenol (XXXI) the methoxy ketone (XXII) was reduced by Clemmensen's method to the ether (XXXIII), which was easily demethylated with aluminium bromide to the required phenol (XXXI). It appeared that lithium aluminium hydride in concentrated solution (tetrahydrofuran) at reflux temperature may generally be used for such reductions. Also 6:7-dimethoxytetralone[79] was prepared from (3:4-dimethoxy-phenyl)butyric acid, and when it was refluxed with lithium aluminium hydride in a small quantity of tetrahydrofuran it gave 6:7-dihydroxytetralin.

Selenium dioxide has been extensively used for introducing an oxygen adjacent to a carbonyl group or olefin or simply as a dehydrogenating agent to introduce a new double bond[80,81]; but m-hydroxybenzosuberone was uneffected when refluxed with selenium dioxide.

Palladised charcoal has been used in the presence of hydrogen accepting reagents (sulphur cyclohexene etc.)[82,83,84] and also used alone for dehydrogenation in azulene series[85] and in tropolone synthesis[86] m-hydroxybenzosuberone was uneffected with palladised charcoal even at 300°C.

Iodine in nitrobenzene has been successfully employed in azulene series by Treibs[13], but was found with out effect on hydroxybenzosuberone.

Triphenyl methyl perchlorate was expected to have some effect on a phenol even if only tritylates the nucleus. When reacted with the reagent in methylene chloride, m-hydroxybenzosuberone gave a deep red amorphous substance (m.p. $<$ 350°C) soluble in most of the organic solvents like benzene, chloroform, alcohol etc. giving beautiful dark red solutions with characteristic peaks in the visible spectrum. It was diamagnetic, elementary analysis that indicated it to be possibly a hydrated (XXXIV,a) $C_{11}H_{14}O_2$, but its molecular weight determination (275) was higher for the monomer (178); and the high m.p. 350°, deep colour suggested a quinhydron type structure (XXXIV b). However, the structure is still obscure and it could not be reduced to any recognisable product.

Proctor[87] obtained similar pigments from 4',5'-dihydroxybenzosuberone and triphenyl-methyl-perchlorate in methylene chloride. This whole work was repeated and the pigments obtained gave very deep coloured solutions which could not be reduced to starting material.

It was striking in this respect that 6:7-dihydroxy-tetralin gave no soluble deep coloured pigment with triphenylmethyl perchlorate, so perhaps the bond angles in the saturated ring are important. Certainly no coloured materials were obtained from p-cresol, but time did not permit a full investigation of this and other phenols.

When m-hydroxybenzosuberone was treated with triphenylmethyl perchlorate in aceto nitrile, a white substance (m.p. 205 - 6°C) was isolated. It contained nitrogen, and analysis gave the emperical formula as $C_{15}H_{19}ON$. This lead to the performance of the blank tests to investigate the stability of the reagent and the effect of different solvents on it.

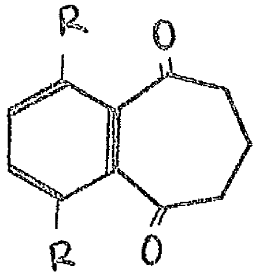
Triphenyl methyl perchlorate (prepared by Dauben's method[73]) was found quite stable . For example, a sample of triphenylmethyl perchlorate kept under dry ether in the refrigerator for about three months, when treated with water at room temperature gave the expected triphenyl-~~methyl~~ carbinol, but the same sample with methylene chloride after twelve hours gave triphenylmethane and a dark red substance with no characteristic m.p. It gave very poor infrared and ultraviolet spectra, While with methyl-cyanide only triphenyl-methane could be isolated.

Triphenyl-methyl perchlorate when refluxed with acetic acid, also gave triphenyl-methane, but the reagent on treatment with liquid sulphurdioxide and then with water gave triphenylcarbinol.

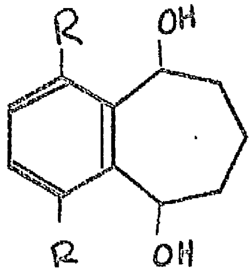
These results are interpreted to show that triphenylmethyl perchlorate may abstract hydrogen slowly from methylene chloride, methyl cyanide and acetic acid. The nature of reactionsbetween the perchlorate and hydroxybenzosuberone in aceto nitrile and in methylene-chloride are still obscure. Presumably in the successful dehydrogenation studied by Reid and co-workers[72,78] the reaction between the substrates and triphenyl methyl perchlorate were much more rapid than reaction involving the solvent.

Reduction of 3':6'-dihydroxy-benzocycloheptene-3:7-dione

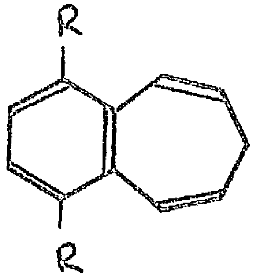
In 1953 Thomson synthesised the above diketone (XXXV, R=OH)[88] by the convenient condensation of hydroquinone and glutaric acid in aluminium chloride and sodium chloride melt. An unsuccessful attempt had been made to synthesis the corresponding tropolone by dehydrogenation[89]. It seemed worthwhile to make an attempt to reduce both the carbonyl groups of the diketone (XXXV, R=OH) to the diol (XXXVI, R=OH) which on dehydration would be expected to yield the corresponding tropilidene (XXXVII, R=OH).



XXXV



XXXVI



XXXVII

The conventional reducing agents such as metallic hydrides, Clemmensen's reduction and catalytic hydrogenation gave unexpected but interesting results at variance with recently published Polish work[90].

The results of catalytic hydrogenation of the diketone (XXXV, R=OH) were found to depend very much on the catalyst as follows:-

(i) Hydrogenation in presence of a small quantity of Adam's catalyst (~1% by weight) in ethanol at room temperature and pressure, using a magnetic stirrer gave predominantly the trihydroxy monoketone (XXX~~C~~VIII, R=OH). The structure was confirmed by infrared spectroscopy and by elementary analysis. Although the n.m.r. spectrum (in deutero pyridine) was not very well defined (due to poor solubility), it clearly indicated the aromatic protons at 2.9τ, the bonded phenolic proton at 1.2τ and most probably the other phenolic proton presented the band at 2.4τ, while the tertiary aliphatic proton gave the expected triplet centred at 3.8τ, the other alcoholic proton was at 4.2τ and remaining aliphatic protons gave a band around 7.6τ. However the corresponding triacetate (XXXCIII, R=OAc) was confirmed by all these methods, in particular the n.m.r. spectrum showed three separate singlets (each area 3) attributable to the 3 different acetyl groups.

(ii) Under similar conditions, Adam's catalyst (3% by weight) gave a mixture of the trihydroxy ketone (XXXVIII, R=OH) and the dihydroxy mono ketone (XXXIX, R=OH) with a little starting material (XXXV, R=OH). The structure of (XXXIX, R=OH) as 1:2-(3':6'-dihydroxy-benzo)-cyclohept-1-ene-3-one was confirmed by infrared spectroscopy, elementary analysis and also by n.m.r.

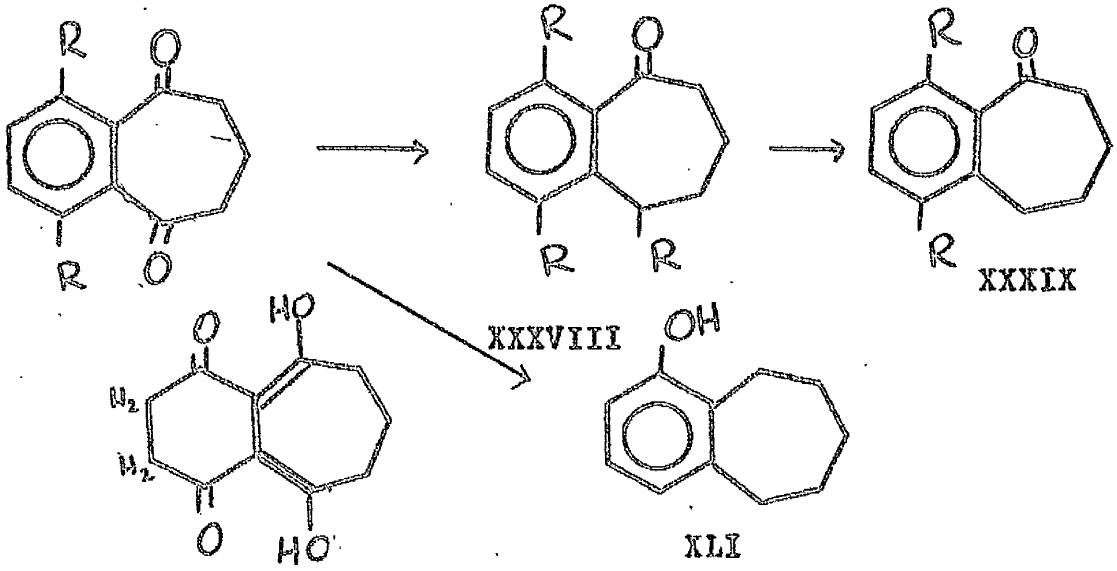
spectroscopy. The structure was also supported by its diacetate (XXXIX, R=OAc) which was proved to be 1:2-(3':6'-diacetoxy-benzo) cyclohept-1-ene-3-one by all these spectroscopic methods and by elementary analysis.. It was significant that the n.m.r. spectrum of this acetate showed two singlets ascribable to the acetyl groups.

(iii) It was observed that in the presence of a little aqueous copper sulphate solution in the above experiment, the hydrogenated product was the dihydroxy ketone (XXXIX, R=OH). Most probably it was due to the acidic medium caused by the hydrolysis of the copper sulphate, under which the alcohol (XXXVIII, R=OH) formed was easily dehydrated to the olefin (XLVI, R=OH) which was readily reduced to (XXXIX, R=OH).

(iv) If excess of Adam's catalyst (5% by weight) was used under similar conditions to those above, it yielded the dihydroxy ketone (XXXIX, R=OH) together with a white amorphous material (m.p. 224°), the elementary analysis indicated it to be $C_{15}H_{21}O_3$ and hydroxy peak was observed in the infrared spectrum, but the structure could not be ascertained.

(v) Hydrogenation in presence of palladised charcoal (3%) under the same conditions yielded exclusively the dihydroxy mono ketone (XXXIX, R=OH).

(vi) Raney nickel was found uneffective under the above conditions and the starting material was recovered.

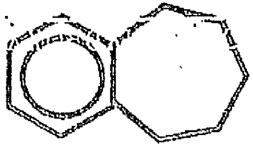


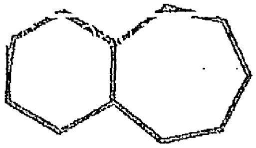
XXXVIII

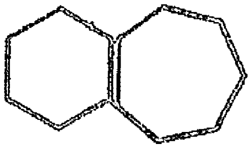
XXXIX

XL

XLI


XLII


XLIII


XLIV

The striking feature of all these reductions was that no compound like (XXVI, R=OH) could be isolated. Hahn and Madeya-Kolkowska recently published[90] that the Clemmensen reduction of the diketone (XXXV, R=OH) yielded the dihydroxy diketone (XL, m.p. 178°). It was thought surprising that Clemmensens method should have reduced the benzene ring and that the double bond migrated from the six membered ring to the seven membered ring. However, the molecule (XL) has some resemblance to our trihydroxy ketone (XXXVIII, R=OH, m.p. 174°); both have the same molecular formula

($C_{11}H_{12}O_4$) and have more or less similar solubility characteristics.

A Clemensen reduction was carried out on the above diketone (XXXV, R=OH), but a compound like (XL) could not be isolated, contrary to the Polish worker; the products isolated were:-

(i) A mono basic phenol (XLI) which had a hydroxyl peak in the infrared spectrum and the n.m.r. spectroscopy revealed aromatic protons at 3.1 τ (area 3), phenolic protons at 5.1 τ (area 1) the four aliphatic protons were at 7.1 τ (area 4) and the remaining aliphatic protons were at 8.2 τ (area 6); while elementary analysis gave the expected molecular formula ($C_{11}H_{14}O$).

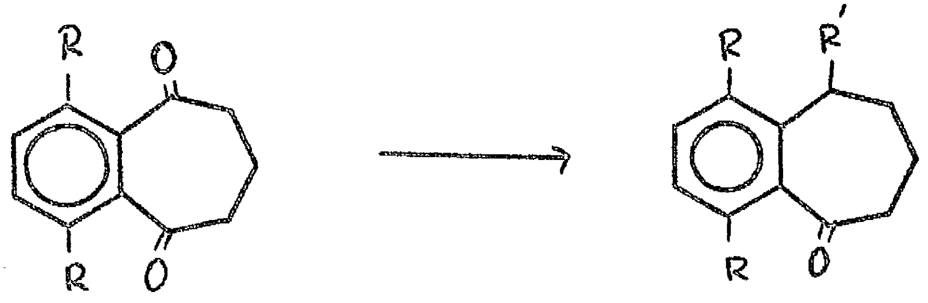
(ii) The other product was a hydrocarbon mixture as its infrared spectrum failed to reveal any functional group and elementary analysis indicated it to be ($C_{11}H_{18}$). Vapour phase chromatography indicated it to be a mixture of three closely related substances. A plausible explanation is that the mixture contains (XLII), (XLIII) and (XLIV).

Sodium borohydride reduction of the diketone (XXXV, R=OH) in ethanol at room temperature gave a white material of obscure structure as elementary analysis indicated it to be ($C_3H_3O_2$), though the hydroxyl group was recognised in its infrared spectrum, lack of solubility prevented n.m.r. spectroscopic study.

The effect of lithium aluminium-~~boro~~hydride was also tried on this diketone in ether solution, but no recognisable products were obtained, indeed the crude yield was very low.

It seemed desirable to examine the reduction of the diacetoxy derivative of the above diketone (XXXV, R=OAc) and to see whether the diol (XXXVI, R=OH or OAc) is available. Thus the diacetate (XXXV, R=OAc) was prepared in the usual fashion with acetic anhydride in pyridine, it had m.p. 175° (recently reported m.p. 169-170°C)[91].

Hydrogenation of diacetate (XXXV, R=OAc) in presence of Adam's catalyst in ethanol at room temperature and pressure gave the diacetoxy mono hydroxy ketone (XLV, R=OAc, R'=OH). The structure was confirmed by infrared and n.m.r. spectroscopy which showed an aromatic band at 3.15τ, tertiary aliphatic proton at 3.5τ, while the hydroxy proton seemed to be obscured by aliphatic protons which showed a band around 7.3τ and the six acetoxy protons had two sharp peaks at 8.0τ and 8.4τ. Elementary analysis gave the expected molecular formula $C_{15}H_{16}O_6$; and on acetylation the same triacetate was obtained as that previously described (XXXVIII, R=OAc).



XXXV

XLV

Polish workers have recently reported[91] that by the reduction of dimethoxy diketone (XXXV,R=OMe) with potasium borohydride at -30° in dioxane, the mono ketone (XLV,R=OMe,R'=OH) was obtained.

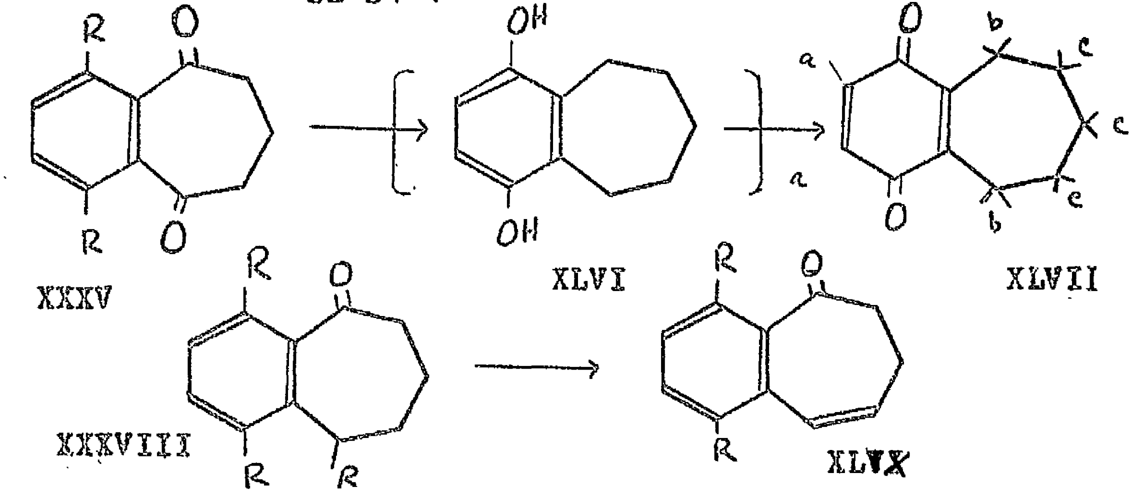
Sodium borohydride reduction of the diacetoxy diketone (XXXV,R=OAc) in ethanol at room temperature gave a dark brown gum which on distillation gave a golden yellow product thought to be (XLVII). The infrared spectrum revealed carbonyl absorption but no hydroxyl peak, while n.m.r. spectroscopy clearly indicated a sharp singlet at 3.3τ for (a) protons (area 2), the b protons were at 7.5τ (area 4) and protons (c) had bands at 8.2τ (area 6).

The formation of a quinone with a reducing agent seemed to be an abnormal reaction, but most probably the reagent only reduced the carbonyl groups to the methylene group, and the alkaline solution hydrolysed the acetate yielding the intermediate hydroquinone (XLV) which underwent subsequent air oxidation to produce the quinone (XLVII).

Both the trihydroxy ketone (XXXVIII,R=OH) and triacetoxy ketone (XXXVIII,R=OAc) when dissolved in acetone and treated with hydrochloric acid (diluted with water after sometime) gave a golden yellow material, m.p. 121-123°C. The infrared spectrum showed hydroxyl absorption and elementary analysis showed it to be $C_{14}H_{16}O_4$.

The n.m.r. spectrum was not well defined, but indicated the bonded hydroxy protons at -2.5τ and at $-1.75\ \tau$ the aromatic band at $3\ \tau$, vinylic band at 4τ and the remaining aliphatic protons were at $7.6\ \tau$. The area for aliphatic protons was more than expected for the molecule (XL~~VIII~~IX, R=OH). However the formula $C_{14}H_{16}O_4$ indicated that acetone had condensed with the molecule in some way, which is perhaps not surprising, since the condensation of acetone with catechol, resorcinol and quinol under similar conditions had already been reported[93,94].

When the trihydroxy ketone (XXXVIII, R=OH) was dissolved in ethanol and concentrated hydrochloric acid was added, the product obtained (after 20 hrs.) was a pale yellow material (m.p. 96°), which was expected to be (XLVIII, R=OH) but elementary analysis indicated it to be $C_{12}H_{14}O_4$.



XXXV XLVI XLVII

XXXVIII XLIX

However analysis of the corresponding acetate[13] did not confirm this molecular formula (XL~~VIII~~IX, R=OAc) and ~~the~~ lack of time prevented a thorough examination of the problem. Dehydration of these derivatives is not a facile process, since it was also found that phosphorus pentoxide in benzene was without effect on the diacetoxy-mono-hydroxy ketone (XXXVIII, $R=OAc$, $R'=OH$). Use of polyphosphoric acid led to decomposition.

ATTEMPTED CYCLISATION OF δ(P- METHOXY PHENYL) VALERIC ACID

γ(p-Methoxy-benzoyl)-butyric acid

Glutaric anhydride (28 g.) and anisole(100 g.) were cooled over ice, when powdered aluminium chloride (75 g.) was added with mechanical stirring, that was continued for 5 hours at 0°C. After standing for two days at room temperature, the mixture was powdered into ice and hydrochloric acid (excess). The organic material was extracted with benzene, which was shaken with dilute sodium hydroxide (10% aqueous). The alkali extract on acidification gave the required product (49.3 g., 90%) which was obtained from water as a colourless material m.p. 139°C (reported 138° - 39°C)^{32}.

δ(p-Methoxy-phenyl)-valeric acid (X)

The above keto acid (40 g.) toluene (200 ml.) amalgamated zinc(50 g.) and hydrochloric acid (100 ml. in portions) were refluxed together for 48 hrs. Completion of reduction was confirmed by infrared spectroscopy. The organic layer was separated and the solvent was evaporated under vacuum giving the required acid (35.5 g.). It had m.p. 117 - 18°C (literature m.p. 118°C)^{32}.

Attempted cyclisation of (p-methoxy phenyl) valeric acid.

(i) With hydrofluoric acid

Anhydrous hydrofluoric acid (~20 ml.) was condensed in a polythene flask containing the above acid (1 g.). The contents were shaken and kept at -30°C for 3 hrs. and then left standing at room temperature to allow the hydrofluoric acid to evaporate. It gave the starting material (1 g.) as the m.p. and mixed m.p. was found to be 117°C.

(ii) (p-Methoxy-phenyl)-valeric acid (5 g.) in dry benzene (200 ml.) was refluxed with phosphorus pentachloride (4 g.) for 1 hr. The contents were cooled on ice and anhydrous stannic chloride (4 ml.) in dry benzene (50 ml.) was added in portions with shaking and cooling on ice. After standing over-night at room temperature the mixture was poured into ice and hydrochloric acid (excess) and extracted with benzene. The unreacted acid (4.2 g.) was recovered from the alkaline extract.

(iiia) With polyphosphoric acid at $98-100^\circ$

Freshly prepared polyphosphoric acid [phosphorus pentoxide (250 g.), 85% O-phosphoric acid (173 ml.)] was heated over a water bath ($98-100^\circ$C), while δ-(p-methoxy-phenyl)-valeric acid (6 g.) was added in portions over 2 hrs. with swirling, the contents were further heated for 3 hrs. and left standing over night. After dilution with cold water, the organic material was extracted with benzene, washed with dilute sodium hydroxide (10% aqueous) dried over sodium sulphate and the solvent was evaporated in vacuo, giving a neutral product (3.8 g.), crystallised from carbon tetrachloride, it had m.p. 120°C. [Found C,75.25, H,7.7; mol. wt. 637 (in nitrobenzene); $C_{12}H_{14}O_2$ requires C,75.75, H,7.4%].

(iiib) Cyclisation with polyphosphoric acid at 70-80°

δ-(p-Methoxy-phenyl) valeric acid (9 g.) was added in portions to polyphosphoric acid (500 g.) with mechanical stirring. The temperature was kept at 70-80°C and stirring was continued for 4 hrs. After standing over-night the mixture was treated with cold water (excess) extracted with benzene and washed with dilute alkali. The neutral material obtained from benzene was a gum (6 g.). It was chromatographed over silica and elution of benzene gave two main products.

(i) Solid ($\sim$2 g.) crystallised from carbon tetrachloride. It had m.p. 120°C, mixed with the previous sample, The m.p. did not depress.

(ii) Gum ($\sim$4 g.) b.p. 250/.05 m.m., ν max 1727, 1669 (diketone or keto ester) cm.$^{-1}$ (liquid film). (Found C,74.6; H,8.3; molecular wt. 406; $C_{12}H_{16}O_2$ requires C,74.95; H,8.4%).

When this gum was crystallised from ethanol it gave a solid product, m.p. 96-97°C; infrared was not much different from that of starting material, ν max 1724, 1653 cm.$^{-1}$ (nujol). [Found c, 75.15, H, 8.4; mol. wt. 750 (in benzene); $C_{12}H_{15}O_2$ requires C, 75.35, H, 7.9%].

1:2(4'Methoxy-benzo)-cyclohept-1-ene-3-one (XI, R=OCH_3)

1:2 (4' Hydroxy benzo) cyclohept-1-ene-3-one was prepared from benzosuberone by nitration followed by catalytic hydrogenation to the amino ketone, then diazotised and hydrolysised according to the reported method by Smith and Berry[40].

The above phenolic ketone (.3 g.) was treated with dimethyl sulphate and sodium hydroxide (10 ml., 15% aqueous) in the presence of chloroform. The chloroform extract was washed with water, dried over sodium sulphate and the solvent was evaporated, giving the required product (.31 g.), which was distilled at 120-124° /.4 m.m. ν max. 1687 (- C=O) 1267 (=C-O-C) cm.$^{-1}$ (liquid film). It was also confirmed by n.m.r. spectroscopy, which indicated the aromatic proton adjacent to the carbonyl group at 2.3 τ (area 1), and the rest, aromatic protons gave bands at 3.1 τ (area 2). The methoxy protons gave a sharp band at ~~7.8~~ 6.2 τ (area 3), and the rest, aliphatic protons were observed at 7.3 τ (area 4) and at 8.2 τ (area 4). (Found C, 75.2; H, 7.35; $C_{12}H_{14}O_2$ requires C, 74.75; H, 7.4%).

TRANSFORMATIONS IN BENZOCYCLOHEPT-1-ENE-3:7-DIONE

1:2(Benzo)4:6-diethoxycarbonyl-cyclopent-1-ene-3:7-dione

The procedure described in the literature[41,42] was modified as follows:-

Diethyl-glutarate (75 g.), diethyl-phthalate (85 g.)[95], sodium (18 g. wire) and ethanol (100ml.) were heated under reflux, with mechanical stirring in an oil bath (120-30°C) for 3½ hrs. The products were poured in portions into dilute sulphuric acid (20% 2 l.) under nitrogen and the organic material was extracted with ether. It was washed with sodium bicarbonate solution (saturated) from which the acid material (21.28 g.) was obtained. The ether extract was then shaken with sodium hydroxide (10% aqueous) and the required diester was obtained by acidification and extraction with ether, giving a white crystalline product (88.5 g.). It had m.p. 86-87°C. (reported m.p. 87°C)[41].

1:2-Benzocycloheptene-3:7-dione (XII)

1:2(Benzo)4:6-diethoxy-carbonyl-cycloheptene-3:7-dione (82 g.) in ethanol (200 ml.) was refluxed with sulphuric acid (28% 1.5 l.) for 44 hrs. After dilution with water (excess), it was extracted with ether, washed with sodium bicarbonate solution (saturated) and with sodium hydroxide (10% aqueous), [to remove the unhydrolysed ester (2.2 g.)] and finally it was washed with water. After drying the neutral extract, the solvent was evaporated giving the solid diketone (XII;R=H; 30.5 g.) it had m.p. 45°C (reported 45-46°).

Attempted nitration of 1:2-benzocycloheptene-3:7-dione

(i) The ketone (3 g.) was poured in portions into fuming nitric acid (10 ml. d. 1.42) at 10°C. The mixture was shaken for 5 mins. and left standing over ice for 30 minutes. The mixture was diluted with cold water and extracted with ether, dried over sodium sulphate and evaporated, it gave the starting material (2.74 g.) m.p. and the mixed m.p. 44-45°.

(ii) When the same experiment was carried out in fuming nitric acid (10 ml. d. 1.5) impure starting material (2.1 g.) and some acid material (0.4 g.) were recovered.

1:2-Benzocyclohept-1-ene-3:7-diol (XIV,R=H)

1:2-Benzocycloheptene-3:7-dione (1 g.) in ethanol (100 ml.) was treated with sodium borohydride (2 g.) and left standing. After 3 hrs. the solution was diluted with water, acidified with hydrochloric acid and the organic material was extracted with methylene chloride. It was dried and the solvent was evaporated giving the required alcohol (XIV;R=H; 0.92 g.), crystallised from chloroform, it had m.p. 185°C. (Found C, 73.9; H,8.2 $C_{11}H_{14}O_2$ requires C,74.1; H,7.9%)

1:2-Benzocyclohept-1:3:6-triene (XV,R=H)

1:2-Benzocycloheptene-3:7-diol (2.86 g.) was refluxed with toluene (150 ml.) containing traces of p-toluene sulphonic acid, using a water separator, for 12 hrs. After washing with water, the toluene was evaporated in vacuo, giving the required olefin (XV, R=H, 2.16 g.) b.p. 40-45°C/11 m.m. (Found C, 92.6; H, 7.5. $C_{11}H_{10}$ requires C, 92.9; H, 7.1%). The n.m.r. spectrum showed the methylenic protons adjacent to the two vinylic protons as a triplet at 7.6 τ, and these two protons a sextet at 4.4 τ, while other two vinylic protons gave doublet at 3.5 τ, the aroma~~c~~tic protons were at 2.9 τ. Their area was in order of (2:2:2:4).

TRANSFORMATION IN BENZOSUBERONE SERIES

γ-Benzoyl-butyric acid[96]

Glutaric anhydride (22 g.) in dry benzene (100 ml) was added slowly to a suspension of anhydrous aluminium chloride (60 g.) in dry benzene (250 ml.) with mechanical stirring, that was continued for further 4 hrs. after the addition of the anhydride was finished. The mixture was poured into ice and hydrochloric acid (excess) and the required acid (27.3 g. 90.5%) was obtained in the usual way. It had m.p. 126-127°C (reported 127°C).

δ-Phenyl-valeric acid

Benzoyl butyric acid (22 g.), zinc (washed with ether acetone and finally with water) amalgamated with mercuric chloride, toluene (200 ml.) and hydrochloric acid, were refluxed together for 24 hrs. Completion of the reduction of the ketone was confirmed by examination of the infrared spectrum. The required acid (19.5 g.) was obtained from the organic layer, which had m.p. 57°.

1:2-Benzocycloheptenone-3-(Benzosuberone)(21)

δ-Phenyl-valeric acid (12 g.) was added in portions to hot (98-100°C) freshly prepared polyphosphoric acid [phosphorus pentoxide (320 g.) was added to ortho-phosphoric acid (175 ml.)]

with occasional swirling. The mixture was further heated on the steam bath for 3 hours, and left standing for two days. The complex was poured into cold water, and extracted with benzene. The latter was washed with sodium hydroxide (10% aqueous) and finally with dilute acid, dried and evaporated, giving the required product (9.02 g., 84%).

Reaction of 1:2-benzocycloheptenone-3 with N-bromosuccinimide (2 mol.

1:2-Benzocycloheptenone-3 (2 g.) in dry carbon-tetrachloride (200 ml.) N-bromosuccinimide (4.5 g., 2 mol.) and traces of benzoyl peroxide were refluxed by the heat of a 150 w. lamp for 6 hrs., till all the N-bromosuccinimide was consumed. The suspension was filtered off, and the solvent of the filterate was evaporated giving the brominated product (3.9 g.).

Hydrolysis of the brominated product

(a) The bromo compound (2 g.) was refluxed with acetone (200 ml.) and water (200 ml.) for 13 hrs. Acetone was evaporated and the organic material was extracted with chloroform, dried, and evaporated in vacuo giving a residue (2.6 g.), which was chromatographed on silica, eluated with benzene and with benzene/chloroform mixture. Three main products were obtained.

(i) Benzene eluate gave 1:2-benzo-7-bromocyclohept-1,6 diene-one-3 (XIII, $\sim$1.2 g.) distilled at $120-124^{\circ}$/.5 m.m. (Found C,56.30; H,4.25; Br,34.20; $C_{11}H_9BrO$ requires C,55.7;

H, 3.8; Br, 33.75%).

(ii) Benzene/chloroform (3/1) eluate gave benzocyclohepten-3:7-dione (VIII, ~.15 g.) crystallised from petroleum ether (b.p. 60–80°C) had m.p. and mixed m.p. 42°C with material obtained by the literature method (34).

(iii) Benzene/chloroform (1/1) eluate gave 1:2 benzocyclohepten-3-one-7-ol (XIV, ~ 0.5 g.), distilled at 120°C/.3 m.m. ν max. 3434(OH), 1648 (>C=O) cm.$^{-1}$ (liq.film). (Found C, 74.70; H, 7.10; $C_{11}H_{12}O_2$ requires C, 74.9, H, 6.8%)

Reaction of 1:2-(4'-nitro-benzo)-cyclohept-1-ene-3-one with N-bromosuccinimide (2 mol.).

1:2-(4'-Nitro-benzo)-cycloheptene-3-one (2 g., prepared by literature method)^{40} dry carbon tetrachloride (200 ml.) N-bromosuccinimide (3.7 g. 2 mol.) and traces of benzoyl peroxide were refluxed over a 150 w. lamp for 3½ hrs. till all the N-bromosuccinimide was consumed. The succinimide was filtered off, and the solvent was evaporated in vacuo. The residue was hydrolysed by refluxing with acetone (200 ml.) and water (200 ml.) for 28 hrs. Acetone was evaporated in vacuo and the organic material was extracted with chloroform, dried and evaporated giving a gum (3.1 g.) which was chromatographed on silica and eluated with benzene and then with benzene/chloroform. Three main substances were isolated in the following order:-

(i) 1:2-(4'-nitro-benzo)-7bromo-cyclohept-1:6-diene-3-one (XVI; R=NO_2; 1.6 g.) crystallised from petroleum ether (b.p. 60-80°C), it had m.p. 123°C. (Found C, 47.05; H, 3.05; Br, 27.55; N, 4.8; $C_{11}H_8BrNO_3$ requires C, 46.85; H, 2.85; Br, 28.1; N, 4.95%). The n.m.r. spectrum showed the signals for aromatic protons at 2.6 τ (area 3), vinylic proton showed a triplet at 3 τ (area 1) and the rest of the aliphatic protons gave bands at 7 τ (area 4).

(ii) 1:2 (4' nitro benzo) 7bromocyclohept-1-ene-3-one (XVII, R=NO_2; 0.6 g.) crystallised from petroleum ether (b.p. 60-80°C), it had m.p. 82-83°C. (Found C, 46.05; H, 3.9; Br, 27.65; N, 4.9; $C_{11}H_{10}NO_3$ requires C, 46.45; H, 3.5; Br, 28.15; N, 4.95%). The n.m.r. spectroscopy indicated the aromatic protons at 2 τ (area 3) vinylic proton had a triplet at 5.4 τ (area 1) and the methylenic protons had bands at 7.3 τ (area 6).

(ii) 1:2 (4' nitro benzo) cyclohept-1-ene-3:7-dione (XVIII, R=NO_2; 0.3 g.) crystallised from petroleum ether it had m.p. 114°C. (Found C, 59.55; H, 4.4; N, 5.9; $C_{11}H_9NO_4$ requires C, 60.25; H, 4.15, N, 6.3%).

Attempted condensation of 4-nitrophthalate esters with glutaric esters

Dimethyl 4-nitro phthalate[97,98] (20 g.) dimethyl glutarate (13.5 g.) and sodium (2.2 g. wire) were heated together under reflux on the oil bath (120-130°C) with mechanical stirring for 6 hrs. After standing over-night the contents were poured in portions into dilute sulphuric acid (20% aqueous) under nitrogen. The organic material was extracted with ether and washed with sodium hydroxide (10% aqueous). The neutral material from ether was found to be the starting material (15.8 g.) confirmed by infrared, m.p. and mixed m.p. 64-65°C .

The acidic material (3.1 g.) obtained from the alkaline extract, after acidification, was found to be 4 nitrophthalate acid; crystallised from ether it had m.p. and mixed m.p. 164-165°C.

TRANSFORMATIONS BASED ON 5'-HYDROXY-BENZOSUBERONE

m-Methoxy-benzaldehyde

(i) Methylation of m-hydroxy-benzaldehyde by ion-exchange resin

m-hydroxy benzaldehyde (14 g.) in benzene (150 ml.) absorbed over resin[(134 g.) amberlite. I.R.A. 410 activated by sodium hydroxide solution (5% aqueous)] was treated with methyl iodide (9.9 ml.) in benzene (100 ml.). The contents were left standing for 52 hours. The benzene was separated and washed with sodium hydroxide (10% aqueous) and finally with dilute hydrochloric acid. The neutral benzene extract was dried over sodium sulphate and the solvent was evaporated. The residual oil (8.6 g.) was distilled at 96°C/.3 m.m. to yield the required product. Unreacted phenol (5.2 g.) was also recovered.

(ii) Methylation with dimethyl sulphate

m-hydroxy benzaldehyde (87 g.) dissolved in potasium hydroxide (200 ml. 20%) was warmed (50-60°C) while dimethyl sulphate (60 ml.) and potassium hydroxide solution (100 ml. 20%) were added at the rate of one or two drops of each per second with mechanical stirring under reflux. Stirring was continued for a further 6 hrs., after the addition was completed. The neutral material was extracted in the usual fashion, giving the required product (43.2 g. 62%). Unreacted pheonl (24.5 g.) was recovered.

(iii) Methylation with dimethyl sulphate using chloroform as a solvent.

m-hydroxy benzaldehyde (200 g.) dissolved in chloroform (500 ml.) and potasium hydroxide (250 ml. 24% aqueous) were treated with dimethyl sulphate (170 ml.) and potasium hydroxide (250 ml. 24% aqueous) as above (ii). The required product (206 g., 94%) was extracted with chloroform. The recovered unreacted phenol (3.1 g.) was of very poor quality.

(iv) (m-Anisyledene)-crotonic acid (XX)

m-Methoxy benzaldehyde (194 g.) and methyl crotonate (215 g.) in t-butanol (500 ml.) was added dropwise to a solution of potasium t-butoxide in t-butanol [potasium (115 g.) t-butanol (2 l.)] with mechanical stirring, which was further continued for 4 hrs. after the addition was completed. The contents were acidified with hydrochloric acid, and the organic material was extracted with chloroform; dried over sodium sulphate and the solvent was evaporated giving a mixture of the required acid and its ester. It was refluxed with alcoholic potash [potasium hydroxide (80 g.) water (3 l.) ethanol (500 ml.)] over night. The contents were washed with benzene and the required acid (280 g.) was obtained from the alkaline extract, on acidification and extraction with chloroform. It was crystallised from benzene and had m.p. 105-108°C (Found C,63.75; H,6.05; $C_{12}H_{12}O_3$ requires C,63.35; H,5.75%).

(m-Methoxy-phenyl)-valeric acid (XXI)

(m-Anisylodene)-crotonic acid (220 g.) in ethanol (500 ml.) was hydrolysied (Raney nickel) at 80-100°C/125 atmospheric pressure. The product was hydrolysed by refluxing with alcoholic potash [potasium hydroxide (70 g.) water (3 l.), ethanol (500 ml.)] for 12 hrs. The reaction mixture was washed with benzene and the required acid (210 g.) was obtained from the alkaline extract on acidification and extraction with chloroform. It was purified by distillation at 135-145°C/0.2 m.m. giving an oil (160 g.). (Found C,69.60; H,7.80; $C_{12}H_{16}O_3$ requires C,69.20; H,7.70%)

1:2 (5'-Methoxy-benzo)-cycloheptene-3-one VII (R=H, R'=OCH_3)

(m-Methoxy-benzo)-valeric acid (17 g.) dry benzene (200 ml.) and phosphorus pentachloride (15 g.) were refluxed for 30 mins. and then cooled on ice. Anhydrous stannic chloride (10 ml.) in dry benzene (50 ml.) was added in portions, with shaking at 0-5°. After standing over night at room temperature the red complex was poured into ice and hydrochloric acid (excess) and the organic material was extracted with benzene, washed with sodium hydroxide (10% aqueous). The benzene extract was dried and the solvent was evaporated under vacuum when the required product appeared as yellow flakes (11 g. 71%) which were crystallised from petroleum ether (b.p. 60-80°C), had m.p. 62°C νmax. 1667 (C=O), 1247 (ether) cm.$^{-1}$ (nujol). (Found C,76.15; H,7.65; $C_{12}H_{14}O_2$ requires C,75.75; H,7.40%) the 2:4 dinitrophenyl-hydrazone crystallised from ether as a red material m.p. 175-176°C (Found C,57.85; H,5.3 ; N,14.35; $C_{18}H_{18}N_4O_5$ requires C,58.35; H,4.9; N,15.05%).

1:2-(5'-hydroxy-benzo)-cycloheptene-3-one (XXII,R=OH)

The previous ketone (18 g.), dry benzene (200 ml.) and anhydrous aluminium bromide (35 g., freshly prepared) were refluxed for 4 hrs. The reaction mixture was poured with ice and hydrochloric acid (excess). The organic material was extracted with benzene, and the phenol was extracted with sodium hydroxide (5% aqueous) which on acidification gave a white crystalline product (16.5 g.). It was recrystallised from benzene, had m.p. 164-165°C νmax. 3135 (OH), 1631 (C=O); 1140, 1310 (C=OH) cm.$^{-1}$ (nujol). (Found C,74.75; H,6.40; $C_{11}H_{12}O_2$ requires C,74.95, H,6.85%).

1:2-(5'-Acetoxy-benzo)-cyclohepten-3-one (VII,R=H, R'=OH)

1:2-(5'-Hydroxy-benzo)-cycloheptene-3-one (3.7 g.) in dry pyridine (75 ml.) was well cooled on ice, while acetic anhydride (3 ml.) was added dropwise with mechanical stirring, which was continued for 4 hrs. after the addition was finished. The mixture was poured into ice and hydrochloric acid (excess) when the required product (4.7 g.) was obtained. Recrystallised for petroleum ether (b.p. 60-80°C), it had m.p. 72°C, νmax. 1754 (ester), 1667 (C=O) cm.$^{-1}$ (nujol). (Found C,71.4; H,6.75; $C_{13}H_{14}O_3$ requires C,71.55; H,6.45%).

1:2-(5'-Acetoxy-benzo)-cyclohept-1:6-diene-3-one (XXIII,R=OAc)

1:2-(5'-Acetoxy-benzo)-cycloheptenone-3 (10 g.), dry carbon tetrachloride (300 ml.) and n-bromosuccinimide (8.25 g. 1 mol.) with traces of benzoyl peroxide were refluxed over a 150 w. lamp for three hours. After cooling, the succinimide was removed and the filterate was evaporated under vacuum, giving the expected 1:2-(5'-Acetoxy-benzo)- bromocycloheptene-3-one (15 g.). The latter was treated with collidine (200 ml.) on the steam bath for 1 hr., and then refluxed for 15 mins. The collidine hydrobromide was filtered off and was washed with ether. The filterate and the ether washings were poured into ice and hydrochloric acid. The required olefin was extracted with ether, which was washed several times with dilute hydrochloric acid, dried over sodium sulphate and evaporated. The product was rapidly chromatographed on neutral deactivated alumina using benzene as eluent. The resulting dark brown oil (8.88 g.) distilled at 140-145°C/ 0.04 m.m. giving a yellowish gum, which was crystallised from benzene and petroleum ether (b.p. 60-80°C) to a white crystalline product m.p. 49-50°C. (Found C,71.8; H,5.15; $C_{13}H_{14}O_3$ requires C,72.2; H,5.6%).

1:2-(5′-Hydroxy-benzo)-cyclohept-1:6-diene-3-one (XXVII, R=OH)

The above acetoxy compound was hydrolysed by alkali, and the product was crystallised from benzene to buff crystal, m.p. 137°C. It had max. 3136 (OH) 1634, (C=O) cm.$^{-1}$ (Found, C,75.55; H,6.1; $C_{11}H_{10}O_2$ requires C,75.8; H,5.8%) and was again acetylated to the starting material confirmed by infrared spectroscopy and mixed m.p.

1:2-(5′-Acetoxy-benzo)-cyclohept-1-one-3-ol

1:2-(5′-Acetoxy-benzo)-cyclohept-1:6-diene-3-one (1 g.) in ethanol was reduced by catalytic hydrogenation (PtO_2) takes 25ml.^{H}). After dilution with water, the product was extracted with methylene chloride, and evaporated yielding the alcohol (0.1 g.) which was crystallised from petroleum ether (b.p. 60-80°C) as a white solid m.p. 101-102°C ν max. 3300 (OH), 1764 (ester) cm.$^{-1}$ (nujol) no carbonyl peak. It was confirmed by n.m.r spectroscopy which indicated the expected signals; i.e. aromatic at 3 τ, (area 3) tertiary protons 5.1τ(area 1); alcoholic proton at 6.3 τ, the two protons adjacent to hydroxy group at 7.2 τ, the methyl group at 7.52 τ, and the other six aliphatic protons at 8.1 τ

1:2-($5'$-Hydroxy-benzo)-cyclohept-1:3:6-triene XXIII

1:2-($5'$-Acetoxy-benzo)-cyclohept-1:6-diene 3 one (3.3 g.) ethanol (100 ml.) and powdered sodium borohydride (1.5 g.) were shaken together and left standing over night. The excess reagent was decomposed with methanol and finally diluted with water (excess) and acidified with dilute hydrochloric acid. The organic material was extracted with methylene chloride which was dried and evaporated giving 1:2-($5'$-Hydroxy-benzo)-cyclohept-1:6-dienol-3 (2.55 g.) a light yellowish gum. The structure was confirmed by infrared spectroscopy; as ν max. 3226 (OH) cm.$^{-1}$(L. Film) and no carbonyl peak. This alcohol (1 g.) was refluxed with toluene in presence of traces of p-toluene-sulphonic acid for 10 hrs., using a Dean and Stark sep~~o~~arator. The toluene was washed with water, evaporated in vacuo giving the product (0.65 g.) which was obtained from petroleum ether (b.p. 60-80°C) as a white crystalline product m.p. 70-71°C. It turned pink rapidly. (Found C,84.0; H,6.35; $C_{11}H_{10}O$ requires C,83.5; H,6.35%). The acetate (XXV,R=OAc) was obtained in the usual way, it distilled at 120-130°C/3 m.m. to a viscous oil, which became red on standing; ν max. 1754 (ester) cm.$^{-1}$ (L.F.) no hydroxyl leak. The structure was confirmed by n.m.r. spectroscopy; which indicated expected signals of aromatic protons at 3τ, vinylic protons at 3.8.τ The two methylenic protons gave a triplet-

7.87 ; the ratio was (7:2:3).

5'-Hydroxy-benzo-1:2-tropylium perchlorate.

1:2-(5'-Hydroxy-benzo)-cyclohept-1:3:6-triene (270 ml.) in methylene-chloride(5 ml.) was added to a solution of triphenyl-methyl perchlorate (1.5 g.) in methylene-chloride (150ml.) It was shaken and left standing in the refrigerator for 24 hrs. The green crystalline product (240 g.) was filtered from the reacting mixture; and was crystallised from methylene-chloride to light green crystals, m.p. 245-250°C with decomposition. (Found C,51.25; H,3.4; Cl,13.95; $C_{11}H_9ClO_5$, requires C,51.45; H,51.45; H,3.5; Cl,13.45%).

Reaction with Sodium bicarbonate

5'-Hydroxy-benzo-1:2-tropylium perchlorate (0.17 g.) dissolved in acetone and methylene-chloride was treated with sodium bicarbonate (200 ml. 5%). The methylene-chloride was further washed with water, dried over sodium sulphate and evaporated under vacuum; giving a dark red powder (0.07 g.) which turned black in air over several days. The red powder had no characteristic melting point and gave poorly defined infrared, visible and ultraviolet spectra.

Reduction of the pigment (IX)

The red pigment (IX ca. 20 g.) from the above experiment in ethanol (50 ml.) powdered sodium borohydride (ca. 40 g.) was added. The red solution immediately turned colourless. After some time the contents were diluted with water and acidified with hydrochloric acid. The organic material was extracted with methylene chloride, dried and evaporated leaving a brownish residue, which crystallised from petroleum ether (b.p. 60-80°C) as a white solid m.p. 66-68°C alone or mixed with 1:2-(5'-hydroxy-benzo) cyclohept-1:3:6-triene (XXV). The infrared spectra were also shown to be identical.

1:2-(5'-Acetoxy-benzo)-cyclohept-1:4:6-triene-3-one (XXVI) or 1:2-(5'-acetoxy-benzo)-tropone-3.

1:2-(5'-Acetoxy-benzo)-cyclohept-1:6-diene-3-one (XXIII; R=OAc; 1.6 g.) in dry carbon tetrachloride (150 ml.) and N-bromosuccinimide (1.3 g.) with traces of benzoyl peroxide were refluxed on a 150 w. lamp for 2½ hrs. After cooling, the residue was filtered off and the solvent was evaporated giving the bromo compound (2.2 g.). It was heated with collidine (50 ml.) on the steam bath for 2 hrs. and finally refluxed for 5 mins. The collidine hydrobromide was filtered off and was washed with ether. The filterate along with ether washing were poured into ice and hydrochloric acid (excess). The expected tropone was extracted with ether, chromatographed over silica (eluating with benzene) and crystallised from petroleum ether (b.p. 60-80°C);

it had m.p. 68–69°C νmax. 1770 (ester), 1672 (-C=C-), 1639 (C=O)[99] cm.$^{-1}$ (nujol). (Found C,73.35; H,4.56; $C_{13}H_{10}O_3$ requires C,72.9; H,4.7%).

1:2-(5'-Hydroxy-benzo)-cyclohept-1:4:6-triene-3-one (XXVII) or 1:2-(5'-hydroxy-benzo)-tropone-3.

The above acetoxy benzotropone was hydrolysed at room temperature with sodium hydroxide (5% aqueous) and extracted with chloroform after acidification with hydrochloric acid, when crystallised from benzene, it had m.p. 180–181°C (Found C,75.45; H,4.65; $C_{11}H_8O_2$ requires C,76.7; H,4.7%).

It was strange that some of the compounds in this series gave bad analysis, particularly the phenols, and this is one of the phenols, though its mode of formations and other characters confirmed the structure.

DEHYDROGENATION OF M-HYDROXY BENZOSUBERANE

1:2-(5'-Methoxy-benzo)-cycloheptene-1 (XXXIII)

1:2-(5'-methoxy-benzo)-cyclohepten-3-one (XXII;R=OCH_3; 4.88 g.) toluene (200 ml.) amalgamated zinc and hydrochloric acid (concentrated) were refluxed together for 34 hrs. The organic layer was separated, washed with water and evaporated leaving the product, which was distilled at 85-100°/.4 m.m to give a clear thin oil, with no carbonyl peak in the infrared spectrum. (Found C,82.6; H,9.3; $C_{12}H_{16}O$ requires C,82.35; H,8.6%). The structure was also confirmed by n.m.r. spectroscopy and the aromatic protons showed bands at 3.4 τ (area 3), the methyl protons showed a singlet at 6.5 τ (area 3) and the methylenic protons were at 7.3 τ and 8.7 τ (area 4 and 6 respectively).

1:2-(5'-Hydroxy-benzo)-cycloheptene-1 (XXXI).

(1) From the above ether.

1:2-(5'-methoxy-benzo)-cycloheptene-1 (0.2 g.) dry benzene (100 ml.) and anhydrous aluminium bromide (4 g. freshly prepared) were refluxed for 1 hr. and then the reaction mixture was poured into ice and hydrochloric acid (excess) and the organic material was extracted with chloroform. The required phenol (0.13 g.) was obtained from alkaline solution in the usual way from petroleum ether (b.p. 60-80°C) it gave crystals m.p. 68-69°C . Sublimation raised the m.p. to 71-72°C (Found C,81.25; H,8.65; $C_{11}H_{14}O$ requires C,81.45; H,8.7%).

(11)a From 1:2-(5'-Methoxy-benzo)-cycloheptenone-3

The above ketone (10 g.) in dry tetrahydrofuran (40 ml.) was refluxed with lithium aluminium hydride (12 g.) for 10 hrs. and then was poured into ice, acidified with hydrochloric acid and the organic material was extracted with chloroform. From the chloroform extract the phenolic product was separated with sodium hydroxide solution (10%) and was extracted with chloroform on acidification. It was dried and evaporated, giving the required product (5.8 g.), which was crystallised from petroleum ether (b.p. 60-80°C), it had m.p. 69° alone, and mixed with material obtained previously.

(11)b 1:2-(5'-Methoxy-benzo)-cycloheptene-1-ol-3 (XXXII)

The neutral chloroform extract from the above experiment was washed with dilute hydrochloric acid and with water, dried and evaporated giving the product (1.5 g.), which was obtained from petroleum ether (b.p. 60-80°C) as a colourless solid, m.p. 99°C. It had no carbonyl peak, but hydroxy peak was observed in its infrared spectrum. (Found C,75.4; H,8.5; $C_{12}H_{16}O_2$ requires C,74.95; H,8.4%).

6:7-Dihydroxy-tetralin

6:7-Dimethoxy-tetralone[100,101] (4.0 g.), tetrahydrofuran (30 ml.) and lithium aluminium hydride (6 g.) were refluxed for 20 hrs. The mixture was poured into ice, acidified with hydrochloric acid and the organic material was extracted with chloroform. The phenolic product was extracted with alkali and worked up in the usual fashion giving the required phenol (2.1 g.) which crystallised from petroleum ether (b.p. 60-80°C) and had m.p. 126-127°C. (Found C,73.25; H,6.95; $C_{10}H_{12}O_2$ requires C,73.15; H,7.35%).

Attempted dehydrogenation of 1:2-(5'-Hydroxy-benzo)-cycloheptene

(i) With selenium dioxide

1:2-(5'-Hydroxy-benzo)-cyclohept-1-ene (0.41 g.) in glacial acetic acid (50 ml.) was refluxed with selenium dioxide (0.4 g.) and water (5 ml.) for 4 hrs. The organic material was extracted with chloroform, which was washed with water, and then shaken with mercury, filtered, dried and evaporated giving the starting material (.4g.), which crystallised from petroleum ether (b.p. 60-80°C) and had m.p. and mixed m.p. 67-68°C.

(ii) With palladised charcoal

The above phenol (0.32 g.) and palladised charcoal (.3 g.20% Pd./c) were heated together at 300°C for 7 hrs. The product was shaken with methylene-chloride and filtered from the catalyst. The solvent was evaporated giving the starting material (0.3 g.) which had m.p. and the mixed m.p. 68°.

(iii) With iodine in nitrobenzene

1:2-(5'-Hydroxy-benzo)-cycloheptene (1.73 g.)(XXX) nitrobenzene (100 ml.) and a crystal of iodine were refluxed together for 6 hrs. The mixture was shaken with sodium hydroxide (10%) and separated from nitrobenzene. The starting phenol (1.4 g.) was obtained from the alkaline extract on acidification and extraction with chloroform. It crystallised from petroleum ether (b.p. 60-80°C) and had m.p. and mixed m.p. 68°C.

(iv) With triphenyl-methyl perchlorate.

(a) 1:1-(5'-Hydroxy-benzo)-cycloheptene (1.26 g.) in dry methylene-chloride (10 ml.) was added to a solution of triphenyl-methyl perchlorate (10 g.) in dry methylene chloride, it immediately turned red. The contents were left standing in the dark over night. The dark red solution was washed with water, dried and the solvent was evaporated giving a residue (8.5 g.). It was washed with boiling petroleum ether (b.p. 60-80°C) to remove triphenyl-methane and gave a dark violet product (0.76 g.).

It was purified by crystallisation from methylene-chloride and petroleum ether (b.p. 60-80°C), the criterion of purity was the maximum extinction coefficient obtained (visible region, λ max 594 mμ, ε max. 5590, in chloroform), ν max. 3336 (OH), 1618 (-C=O) cm.$^{-1}$ KCl (Found C, 74.85; H, 7.0; mol. wt. 275; $C_{11}H_{12}O$ (H_2O) requires C, 74.90; H, 6.8%).

(b) The above phenol (0.31 g.) in methyl-cyanide (30 ml.) was added to a solution of triphenyl-methyl perchlorate (2 g.) in methyl-cyanide (150 ml.). After standing over night in the dark, the contents were diluted with water (excess) and the organic material was extracted with methylene-chloride, dried and the solvent was evaporated. The residue (1.28 g.) was washed with petroleum ether (b.p. 60-80°C), to remove triphenyl-methane and gave a brownish residue (0.279 g.). The latter crystallised from ethyl acetate to a white powder, m.p. 205-206°C (Found C,73.1; H,7.5; N,5.5; $C_{15}H_{19}N_1O_1$ requires C,73.15; H,7.8; N,5.7%).

Blank tests for solvent effect and stability of triphenyl-methyl perchlorate

Triphenyl-methyl perchlorate made by the method of Dauben was stored approximately six months under dry ether at 0° in the dark.

(i) Triphenyl-methyl perchlorate (1 g.) was shaken with methyl-cyanide (100 ml.) and left standing in the dark for 15 hrs. Water was added, and the organic material was extracted with methylene-chloride, dried and evaporated giving triphenyl-methane (0.69 g.) crystallised from petroleum ether (b.p. 60-80°C) had m.p. and mixed m.p. (88-93°C).

(ii) The perchlorate (1 g.) and glacial acetic acid (75 ml.)

were boiled for five minutes, cooled, and diluted with water (excess) and worked up as above, gave triphenyl-methane (0.7 g.) m.p. and mixed m.p. 90-92°C.

(iii) The same perchlorate (1 g.) when treated with water and worked up in a similar fashion gave triphenyl-carbinol (0.72 g.) of m.p. and mixed m.p. 161-163°C

(iv) Triphenyl-methyl perchlorate (1 g.) was treated with sulphur dioxide, and left 2 hrs. at -60°C, sulphur dioxide was allowed to evaporate at room temperature over night. The residue was washed with water and extracted with methylene-chloride, which was dried and evaporated giving triphenyl methanol (0.7 g.) m.p. and mixed m.p. (62-63°C).

(v) The perchlorate (1.5 g.) was dissolved in methylene-chloride (150 ml.) and left standing in the dark over night. After treatment with water, the organic layer was dried, solvent was evaporated. The residue was washed with boiling petroleum ether (b.p. 60-80°C) and gave triphenyl-methane (0.74 g.) m.p. and mixed m.p. 90°C) and a dark red residue (0.088 g.) it had no characteristic m.p. and gave very poor infrared and ultraviolet spectrum.

REDUCTION OF 1:2-(3':6'-DIHYDROXY-BENZO)-CYCLOHEPT-1-ENE-3:7-DIONE

Reduction of 1:2-(3':6'-dihydroxy-benzo)-cycloheptene-3:7-dione

1:2-(3':6'-dihydroxy-benzo)-7-hydroxy-cyclohept-1-ene-3-one

The above diketone (2 g.) in ethanol (200 ml.) was hydrogenated (~300 ml.) in presence of catalyst (platinum oxide ~25 mg.) at atmospheric pressure. The catalyst was filtered off, and the solvent was evaporated under vacuum, giving a yellowish material (2.1 g.) which was washed with benzene and the required product was crystallised from ether, givng a colourless solid, m.p. 174-175°C; ν max. 3344, 3226 (OH); 1636 (>C=O) cm.$^{-1}$ (nujol). (Found C,63.4; H,5.95; $C_{11}H_{12}O_4$ requires C,63.45; H,5.8%).

The acetate (obtained by the usual fashion with acetic anhydrid in pyridine) crystallised from petroleum ether (b.p. 60-80°C) and had m.p. 132-133°C ν max. 1761, 1748 (ester), 1724 (-C=O) cm.$^{-1}$ (nujol). (Found, C,61.0; H,5.9; $C_{17}H_{18}O_7$ requires C,61.05; H,5.4%).

1:2-(3':6'-diacetoxy-benzo)-cycloheptene-3:7-dione

1:2-(3':6'-dihydroxy-benzo)-cycloheptene-3:7-dione (4.185 g.) in dry pyridine (25 ml.) was cooled on ice, while acetic anhydride (5 ml.) was added dropwise with mechanical stirring for 6 hrs. The contents were poured into ice and hydrochloric acid (excess) and the required acetate (6 g.) was obtained; after recrystallisation from ethanol. ~~They~~ It had m.p. 175° max. 1779 (ester), 1692 (C=O), cm.$^{-1}$ (nujol) (Found C,62.35; H,5.05; $C_{15}H_{14}O_6$ requires C,62.05; H,4.85%).

1:2-(3':6'-diacetoxy-benzo)-7-hydroxy-cycloheptene-3-one

The above diacetoxy diketone (5 g.) in ethanol (200 ml.) was hydrogenated (450 ml.) in presence of platinum dioxide (150 mg.) at room temperature and pressure. The catalyst was filtered off and the solvent was evaporated in vacuo, giving a gum (5 g.). It was chromatographed over silica, elution with chloroform gave a small quantity of starting material confirmed by infrared spectrum, m.p. and mixed m.p. (174°C). The main product was desired product , crystallised from petroleum ether (b.p. 60-80°C) to a white solid m.p. 143-147°C; ν max. 3344 (OH); 1751, 1706 (ester); 1687 (C=O) cm.$^{-1}$ (nujol). (Found 61.8; H,5.55; $C_{15}H_{16}O_6$ requires C,61.65; H,5.15%).

1:2-(3':6'-diacetoxy-benzo)-7-acetoxy-cycloheptene-3-one

was prepared from the above hydroxy compound in the usual fashion and crystallised from petroleum ether (b.p. 60-80°C), had m.p. 132°C, undepressed by the material previously described.

1:2-(3':6'-dihydroxy-benzo)-cycloheptene-3-one

1:2-(3':6'-dihydroxy-benzo)-cycloheptene-3:7-dione (3 g.) in ethanol (~200 ml.) was hydrogenated (~370 ml., 34 hrs.) in presence of palladised charcoal (150 mg. 20%). The catalyst was filtered off and the solution was diluted with water (excess) and extracted with methylene-chloride. It was dried over sodium sulphate and the solvent was evaporated giving a yellow material (2.8 g.). The required material was crystallised from petroleum ether (b.p. 80–100°C) and had m.p. 124–125°; ν max. 3226 (OH); 1613 (–C=O) cm.$^{-1}$ (nujol). (Found C,68.6; H,6.05; $C_{11}H_{12}O_3$ requires C,68.75; H,6.3%).

The corresponding acetate obtained by the conventional method, had m.p. 113–114°C . (Found, 64.5; H,6.05; $C_{15}H_{16}O_5$ requires C,65.2; H,5.85%). Structure was confirmed by n.m.r. spectroscopy.

Hydrogenation in presence of Raney nickel

1:2-(3':6'-dihydroxy-benzo)-cycloheptene-3:7-dione (2 g.) in ethanol (150 ml.) was treated with hydrogen in presence of Raney nickel (150 mg.) at room temperature and pressure. Hydrogen absorption (48 ml.) was observed in 30 hrs. The catalyst was filtered off, and the starting material (2 g.) was recovered on evaporation of the solvent under vacuum.

Reduction with sodium borohydride

(i) 1:2-(3':6'-dihydroxy-benzo)-cycloheptene-3:7-dione (1.04 g.) in ethanol (200 ml.) was treated with sodium borohydride (2 g.) and left standing for 5 hrs. when methanol was added to decompose the excess of reducing agent. The contents were diluted with water, acidified with hydrochloric acid and extracted with chloroform which was dried over sodium sulphate and evaporated, giving a solid product (.6 g.) crystallised from ether, had m.p. $290-295^{\circ}$C νmax. 3448 (OH), 826 () cm.$^{-1}$ (Found C, 50.5; H, 4.75; ($C_3H_3O_2$) requires C, 50.7; H, 4.25%).

(ii) 2:3-Cycloheptene-1:4-benzoquinone

1:2-(3':6'-diacetoxy-benzo)-cycloheptene-3:7-dione (1 g.) in ethanol (~100 ml.) was shaken with sodium borohydride (1 g.). After standing over night the excess of metallic hydride was decomposed with methanol. The contents were diluted with water (excess) acidified with hydrochloric acid and extracted with methylene chloride. The organic solution was dried over sodium sulphate, and the solvent was evaporated giving a dark brown product (0.66 g.) . After distillation at $100-120^{\circ}$C/.5 m.m. the product from petroleum ether (b.p. $60-80^{\circ}$C) was golden yellow crystals, m.p. 82°C, νmax. 1640 (–C=O) cm.$^{-1}$ (nujol) (no hydroxyl peak). (Found C, 74.45; H, 7.35; $C_{11}H_{12}O_2$ requires C, 74.4; H, 6.85%).

CLEMMENSEN'S METHOD

Reduction with ~~lithium aluminium hydride~~

~~Powdered lithium~~ aluminium hydride (2.4 g.) ~~was added~~ ~~to a solution of~~ 1:2-(3':6'-dihydroxy-benzo)-cycloheptene-3:7-

dione (3 g.) was refluxed in toluene with amalgamated zinc (8 g.) and concentrated hydrochloric acid for 20 hrs. The organic layer was separated and the solvent was evaporated giving a liquid (2.14 g.), which was chromatographed over silica with benzene/petroleum ether (b.p. 60-80°C) (1/3) giving two main products.

(i) Hydrocarbon (~1.3 g.) distilled at 60-65/.03 m.m. to a thin colourless liquid, infrared did not indicate any functional group. (Found C, 87.76; H, 11.46; $C_{11}H_{18}$ requires C, 87.92, H, 12.0%). V.P.C. indicated to be a mixture of three substances (XLII, XLIII, XLIV a,b,c, or d).

(ii) 1:2-(3'-Hydroxy-benzo)-cycloheptene (~0.6 g.) crystallised from petroleum ether (b.p. 40-60°C) in needles, m.p. 111-112°C, sublimed m.p. 112°C max. 3289 (OH) 1370, 1247 (C-O-H) cm.$^{-1}$ (nujol) (Found C, 81.15; H, 8.25; $C_{11}H_{14}O$ requires C, 81.45; H, 8.7%).

Reaction of acetone with 1:2-(3':6'-dihydroxy-benzo)-7-hydroxy-cyclohept-1-ene-3-one (XXXVIII, R=OH) in presence of hydrochloric acid

The above alcohol (.5 g.) in acetone (50 ml.) was treated with concentrated hydrochloric acid (5 ml.). After 1 hr. it was diluted with water (excess) when the yellow material (100 mg.) was separated. It was crystallised from petroleum ether (b.p. 60-80°) and it had m.p. 122-124°, $\nu_{max.}$ 3134 (OH), 1639 (C=O) cm.$^{-1}$ (nujol). (Found C,67.7; H,5.5, $C_{14}H_{16}O_4$ requires C,67.7, H,6.5%).

The trihydroxy derivatives (XXXVIII, R=OAc) of the above alcohol under similar conditions gave the same product, as confirmed by infrared, m.p. 122° and mixed m.p. was not depressed (121-122°).

Attempted dehydration of 1:2-(3':6'-diacetoxy-benzo)-7-hydroxyl cyclohept-1-ene-3-one (XLV, R=OAc, R=OH)

(i) The above alcohol (1.8 g.), toluene (200 ml.) and traces of p-toluene-sulphonic acid were refluxed for 12 hrs. using a Dean and Stark separator. The toluene was washed with water and then evaporated giving the starting material (1.4 g.)

(ii) The above alcohol [(XLV, R=OAc; R'=OH), 1.3 g.] was stirred in polyphosphoric acid (200 g., at 100°) for 30 mins., and diluted with water (excess). The organic material was extracted with methylene chloride, dried and evaporated giving a black tar (0.4 g.).

Reaction of ethanol on 1:2-(3':6'-dihydroxy-benzo)-7-hydroxyl cyclohept-1-ene-3-one in presence of hydrochloric acid

The above alcohol [(XXXVIII,R=OH), 2 g.] in ethanol (100 ml.) was treated with concentrated hydrochloric acid (8 ml.). After 24 hrs. the mixture was diluted with water (excess) and the organic material (1.2 g.) was extracted with methylene-chloride in the usual fashion and crystallised from petroleum ether (b.p. 60-80°), it had m.p. 96°, and thin layer indicated it to be a single substance. It showed ν max. 3136 (OH), 1645 (C=O) cm.$^{-1}$ (nujol). (Found C,64.95, H,6.55, $C_{12}H_{14}O_4$ requires C,64.85, H,6.35%).

The corresponding acetate, obtained in the usual way, was purified by chromatography over silica and crystallised from petroleum ether (b.p. 60-80°). It had m.p. 116°. (Found C,64.45, H,5.2, $C_{17}H_{16}O_6$ requires C,64.55, H,5.1%).

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