A STUDY OF CERTAIN ORGANIC COMPOUNDS OF SULPHUR.

T H E S I S

presented by

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THE DECOMPOSITION OF BENZENESULPHONHYDRAZIDES.

Précis.

A NEW METHOD FOR THE CONVERSION OF AN ACID TO THE CORRESPONDING ALDEHYDE:- The applicability of the following series of reactions:-

$$R.COOH \longrightarrow R.CO.NH.NH.SO_2.Ph \xrightarrow{\text{alkali}} RCHO + N_2 + Ph.SO_2K$$

as a general method for the conversion of acids to the corresponding aldehydes has been investigated.

The method was found to be in general effective for the conversion of aromatic acids (benzoic, p-chlorobenzoic, anisic, piperonylic, salicylic, and m-nitrobenzoic; but not p-nitrobenzoic) to the aldehyde, but failed in the case of acids of the aliphatic series (acetic, isobutyric and diphenylacetic).

A NEW PREPARATION OF 1:3:5-TRINITROBENZENE:- The same type of benzenesulphonhydrazide decomposition has been successfully applied as a simple means of conversion of picryl chloride to 1:3:5-trinitrobenzene, in the following two stages:-

$$C_6H_2(NO_2)_3Cl \longrightarrow C_6H_2(NO_2)_3NH.NH.SO_2Ph \xrightarrow{\text{alkali}} C_6H_3(NO_2)_3 + N_2 + Ph.SO_2K$$

A NEW METHOD FOR THE CONVERSION OF AN ACID TO THE CORRESPONDING ALDEHYDE.

INTRODUCTION.

A number of methods for the conversion of an acid to the corresponding aldehyde has been recorded in the literature. Of these, probably the most useful is that of Rosenmund (*1*), involving catalytic reduction of the (mono- or di-basic) acid chloride with hydrogen in an inert solvent. Good yields of both aliphatic and aromatic aldehydes have been obtained in this way. Another method, less satisfactory as regards yields, but also of fairly wide application, is that first recorded by Limpricht (*2*) in the aliphatic, and Piria (*3*) in the aromatic, series, utilising dry distillation of a mixture of the calcium salt of the acid with calcium formate; and later improved by Krafft (*4*), first by dilution of the mixture with calcium carbonate and distillation in vacuo, and later by the use of the corresponding barium salts. Sabatier and Mailhe (*5*) obtained good yields in many cases by passing the mixed vapours of the acid and formic acid over manganese dioxide at 300 - 360°. Most of the other recorded methods are suited mainly to specific types of

acid, such as Weil's (6) reduction of aromatic ortho-hydroxy acids with sodium amalgam in presence of boric acid; the electrolytic reduction of oxalic to glyoxylic acid, Tafel and Friedrichs (7); Fischer's (8) reduction of mono- and di-basic polyhydroxy acids via the lactone in acid solution; and Neuberg's (9) reduction of amino acid hydrochlorides with sodium amalgam. Other methods which have been adopted include reductions of various derivatives of the acid, such as iminoethers (Henle (10)); thioanilides (Ciusa (11)); amidines (Merling (12)); and imide chlorides (Staudinger (13)).

A further possible method for this conversion was suggested by the probable instability of the structure R.CO.N:NH. No organic compound of the fundamental structure R.N:NH has so far been isolated. Thus, for example, Chattaway (14) has shown that treatment of phenylhydrazine with certain oxidising agents yields benzene and nitrogen. By analogy, one might expect that the aldehyde R.CHO, together with nitrogen, would result from a reaction of which the structure R.CO.N:NH was a theoretically possible product.

The scheme first proposed to test the validity of this idea may be outlined thus:-

$$2RCOCl \longrightarrow RCO.NH.NH.COR \xrightarrow{O} RCO.N = N.CO\,R$$

$$\downarrow HOH$$

$$RCHO + N_2 \leftarrow [RCON{=}NH] + RCOOH$$

The recovery of one molecule of acid after the hydrolysis stage, and hence a maximum possible conversion (acid to aldehyde) of 50%, is an obvious theoretical drawback; but it was on account of practical difficulties in the oxidation of the diacylhydrazine to the azo compound that this scheme was abandoned.

A method which could in theory yield 100% conversion was suggested by the fact that under certain conditions the elements of the aryl sulphinic acid may be abstracted from an arylsulphonhydrazide by the action of alkali; for example, Escales (15) has shown that benzenesulphonphenylhydrazide (I), when treated with alkali, yields benzene, benzenesulphinic acid and nitrogen, probably via the unstable intermediate (II):-

$$\underset{(I)}{Ph.NH.NH.SO_2.Ph} \xrightarrow{KOH} Ph.SO_2K + \underset{(II)}{[Ph.N{:}NH]} \longrightarrow PhH + N_2$$

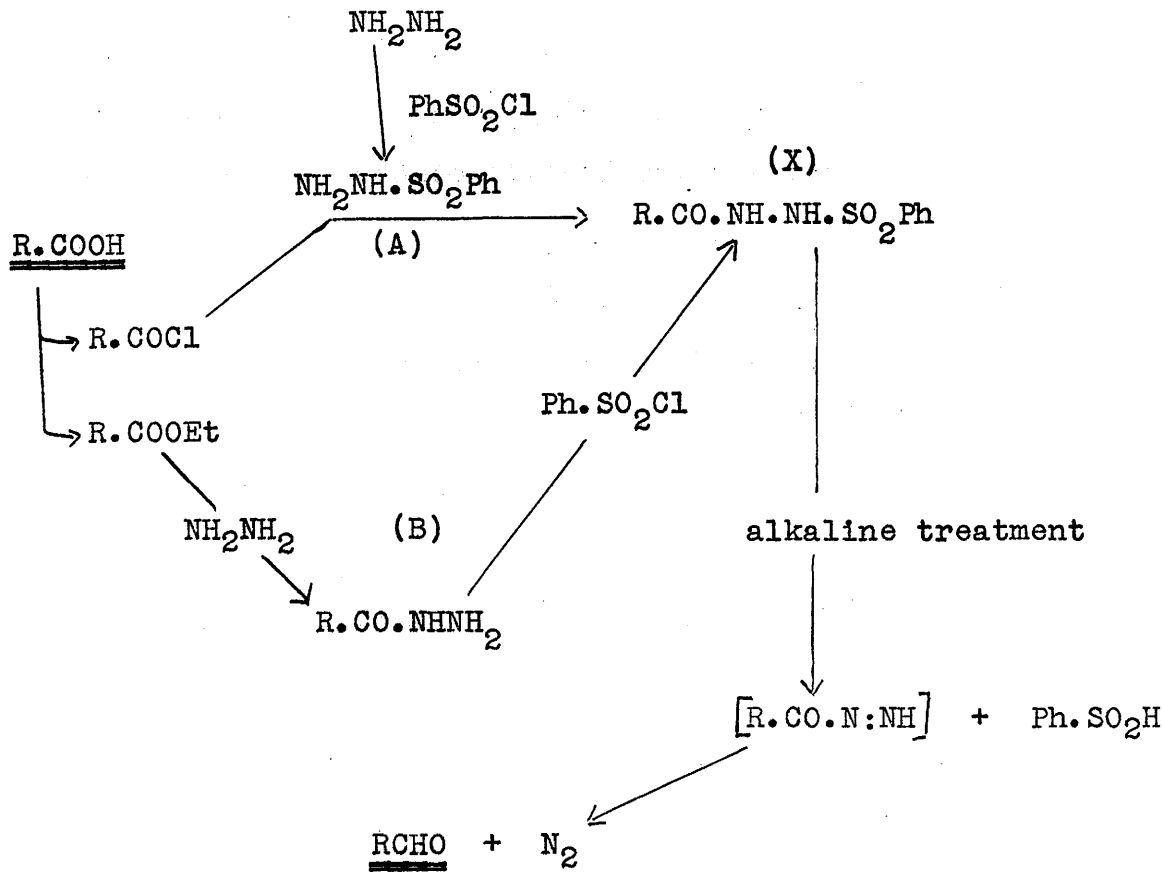
Again, p-toluenesulphon-uns.-benzylphenylhydrazide, on alkaline treatment (see page 67), yields benzaldehyde-phenylhydrazone and sodium p-toluenesulphinate, the

question as to whether the removal of the toluene-sulphinic acid precedes or succeeds the intramolecular rearrangement involved being immaterial here. It was therefore thought that it might be possible in the same way to remove the elements of benzenesulphinic acid from an acylbenzenesulphonhydrazide (III), with the resultant development of the desired unstable intermediate (IV):-

$$\underset{\text{(III)}}{R.CO.NH.NH.SO_2.Ph} \longrightarrow PhSO_2H + \underset{\text{(IV)}}{[RCO.N{:}NH]} \longrightarrow RCHO + N_2$$

A preliminary investigation of the behaviour of benzoylbenzenesulphonhydrazide (R = Ph in III), on decomposition with alkali, showed that benzaldehyde and benzenesulphinic acid were in fact produced. The decomposition of this particular hydrazide was therefore investigated in some detail, with successful results, and the reaction was subsequently extended to a number of other acylbenzenesulphonhydrazides, with varying degrees of success.

The following theoretical scheme indicates the possible means of conversion of acid to aldehyde by this method:-



It should be noted that the route (A) to the compound (X) involves the radical R.CO' of the acid in two steps, whereas route (B) involves three steps. For reasons which will be defined later, the method involving the extra step was found preferable as a general rule.

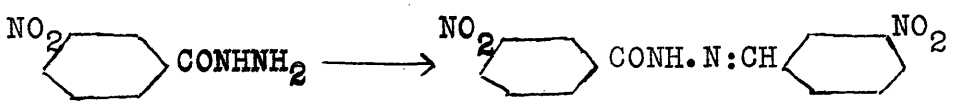
DISCUSSION OF EXPERIMENTAL WORK.

The possibility of utilising this acylbenzenesulphonhydrazide decomposition for the preparation of the corresponding aldehyde was examined in the case of the acids listed below. In each case, where R represents the acyl radical concerned, the compound R.NH.NH.SO_2Ph, or a close analogue, was synthesised and decomposed under conditions detailed later, with the following results:

Aldehyde obtained from	No aldehyde obtained from
(a) benzoic acid.	(g) p-nitrobenzoic acid. [Note 1]
(b) p-chlorobenzoic acid.	(h) cinnamic acid. [Note 2]
(c) anisic (p-methoxybenzoic) acid.	(i) acetic acid.
(d) piperonylic (3:4-methylene dioxybenzoic) acid.	(j) isobutyric acid. [Note 3]
(e) salicylic acid.	(k) diphenylacetic acid.
(f) m-nitrobenzoic acid. [Note 1]	(l) gallic acid. [Note 4]

NOTE 1. The complete failure to obtain p-nitrobenzaldehyde as against the comparative success in obtaining m-nitrobenzaldehyde is rather remarkable, but recalls the experience of Curtius and Melsbach (16), who found that whereas m-nitrobenzhydrazide on prolonged standing in weakly alkaline

solution yielded m-nitrobenzal-m-nitrobenzhydrazide,

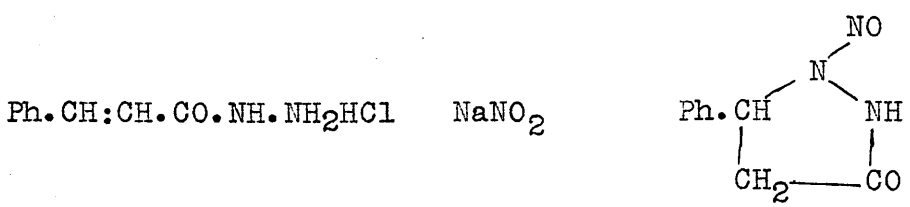


the corresponding o- and p-nitrobenzhydrazides underwent no analogous reaction.

NOTE 2. By the action of benzenesulphonyl chloride on cinnamoyl hydrazine there was obtained a compound which gave rather a high nitrogen percentage to agree well with the formula:

$$Ph.CH:CH.CO.NH.NH.SO_2Ph$$

and which on decomposition failed to yield any cinnamaldehyde. Mückermann (17) found that sodium nitrite reacted with cinnamoylhydrazine hydrochloride to form an N-nitroso ring compound, N-nitroso phenylpyrazolidone:



Possibly benzene sulphonyl chloride behaves with cinnamoyl hydrazine in an analogous manner, which would account for the failure to obtain cinnamaldehyde on decomposition, if not for the high nitrogen percentage.

NOTE 3. All three conversions attempted in the aliphatic series yielded negative results.

NOTE 4. The failure in the case of gallic acid was a failure not to decompose, but to synthesise, the intermediate sulphonhydrazide.

For the reason previously indicated (page 6), namely, the saving of a step, it was at first hoped to prepare the various acylbenzenesulphonhydrazides by the interaction of the appropriate acyl chloride with benzenesulphonhydrazide. This method was, however, found very liable to lead to the formation of di-acylbenzenesulphonhydrazides (see experimental work in the benzoic, anisic, and diphenylacetic acid series), which is most undesirable from the point of view of conversion of acid to aldehyde, since the primary action of alkali on the di-acyl compound was found to be the removal of one acyl group by hydrolysis, to give the mono-acyl compound, one molecule of acid being returned unchanged for each two molecules used. Thus

$$2\ RCOOH \longrightarrow (RCO)_2N.NH.SO_2Ph \xrightarrow{HOH} RCONH.NH.SO_2Ph + RCOOH$$

For this reason the alternative route to the hydrazide (acid ⟶ ester ⟶ acylhydrazine ⟶ acylbenzenesulphonhydrazide) was ultimately adopted, except in a case such as that of triacetylgallic acid, where the preparation of the acylhydrazine does not seem feasible.

The acylbenzenesulphonhydrazides have been given the symmetrical structure, with no free $-NH_2$ group, since it was found that benzoylbenzenesulphonhydrazide did not react with benzaldehyde in boiling alcoholic solution.

A considerable number of decompositions of the various acylbenzenesulphonhydrazides was carried out, generally by the use of alkaline carbonates in ethylene glycol solution. Ethylene glycol was chosen as solvent on account of its (a) high boiling point, (b) ability to dissolve alkaline carbonates, and (c) miscibility with water. A number of small scale experiments with solvents such as pyridine, quinoline and cyclohexanol, and with sodium borate, sodium acetate or organic bases in place of alkaline carbonates, gave results which were not encouraging.

In general, the decomposition was carried out by dissolving the acylbenzenesulphonhydrazide in hot ethylene glycol, adding from 1 to 5 equivalents of alkaline carbonate in the solid form to the solution at a temperature of from 80° to about 160°, and maintaining the mixture at the specified temperature for a definite time. The reaction was stopped by the addition of a relatively large bulk of hot water and the resulting mixture was cooled, extracted with ether, and the aldehyde recovered from the ethereal solution and estimated as the 2:4-dinitrophenylhydrazone. (The recovery of the alkali-soluble

salicylaldehyde was effected by steam distillation from the acidified reaction mixture, with subsequent isolation as the dinitrophenylhydrazone in the usual manner).

The decomposition could also be conveniently brought about by steam distillation of a solution of the acylbenzenesulphonhydrazide in aqueous sodium carbonate, where feasible, i.e., where:-

(i) the acylbenzenesulphonhydrazide was found to decompose sufficiently readily at the relatively low temperature involved, and

(ii) the aldehyde in question was

(a) sufficiently volatile in steam,

(b) insoluble in alkali.

The use of the acyl<u>dichloro</u>benzenesulphonhydrazide in place of the acylbenzenesulphonhydrazide was found in the case of the benzoyl series to give a decomposition temperature lower by about 30°, and slightly improved yields of aldehyde, but the latter advantage was not borne out in the salicoyl series. On account of the lower decomposition temperature, however, the use of the dichloro compounds would appear preferable in cases where it was proposed to prepare the aldehyde by steam distillation of the hydrazide in alkaline solution; apart from this, the dichloro would appear to possess little advantage over the unsubstituted compound.

The following general observations may be made on the tabulated results of the decompositions of benzoylbenzenesulphonhydrazide (page 16):

(a) The quantity of solvent (5 to 20 parts) had little effect on the yield.

(b) Sodium carbonate as alkali gave slightly better results than the potassium salt.

(c) The optimum temperature was about 160° (compare cases A, B, and C). Prolonged heating at a high temperature gave poor results (case F).

(d) Considerable excess of alkali was necessary (compare cases C, D and E).

EXPERIMENTAL.

Benzenesulphonhydrazide was prepared as described by Curtius and Lorenzen (18). Yield 85 - 90%, m.p. 100 - 103°.

A. BENZOIC ACID SERIES.

Benzoylbenzenesulphonhydrazide:-

(i) From benzhydrazide:- Benzenesulphonyl chloride (3.8 c.c.) was added slowly to a stirred, cooled solution of benzhydrazide (4 g.) in pyridine (25 c.c.). After 2 hours the solution was poured into a mixture of crushed ice and dilute hydrochloric acid, and the pale yellow precipitate filtered off, washed with dilute hydrochloric acid and water, and recrystallised from alcohol (80 c.c.). Colourless prismatic needles (7 g.), m.p. 192 - 194° (decomp.). (Found: N, 10.4. $C_{13}H_{12}O_3N_2S$ requires N, 10.2%).

(ii) From benzenesulphonhydrazide:- Benzoyl chloride (26.8 c.c.) was added slowly (40 mins.) to a stirred, ice-cooled solution of benzenesulphonhydrazide (40 g.) in pyridine (100 c.c.). After further brief stirring, the solution was poured into a mixture of crushed ice and dilute hydrochloric acid, with vigorous stirring.

The amorphous product was collected and washed, first with water, then with alcohol. Yield, crude, 55 g. Recrystallisation from rect. spirit gave a first crop, in 2 hours, of colourless prismatic needles (30 g.), m.p. 191 - 193°, not depressed on admixture with the product from the method (i) above. On standing for 2 days the mother liquor deposited a further crop of the same product, together with colourless silky needles. By repeated warming, filtration, and recrystallisation, the more readily soluble fine needles were obtained as an apparently homogeneous product, m.p. 192 - 194° (decomp.), depressed on admixture with benzoylbenzenesulphonhydrazide, but not with dibenzoylbenzenesulphonhydrazide (vide infra.).

Attempted condensation of benzoylbenzenesulphonhydrazide with benzaldehyde:-

Benzoylbenzenesulphonhydrazide (1 g.) and benzaldehyde (0.39 g.) were refluxed for one hour in alcohol (10 c.c.). On cooling, there crystallised prismatic needles (0.83 g.), m.p. 192 - 194°, not depressed on admixture with benzoylbenzenesulphonhydrazide; and benzaldehyde (0.25 g.) was recovered as the dinitrophenylhydrazone. No condensation product was found.

Dibenzoylbenzenesulphonhydrazide:- Benzoylbenzenesulphonhydrazide (1.1 g.) and benzoyl chloride (0.72 g.)

were kept in pyridine (10 c.c.) at 40° for 4 hours. The mixture was then poured into water and ligroin, with vigorous shaking. The precipitated solid was filtered off and recrystallised from alcohol, giving colourless silky needles, m.p. 198 - 200° (decomp.). (Found: N, 7.4. $C_{20}H_{16}O_4N_2S$ requires N, 7.4%).

Hydrolysis of dibenzoylbenzenesulphonhydrazide:-
In warm alcoholic solution with the addition of conc. ammonium hydroxide, dibenzoylbenzenesulphonhydrazide was rapidly quantitatively converted to benzoylbenzenesulphonhydrazide (m.p. and mixed).

Benzoyl-2:5-dichlorobenzenesulphonhydrazide:-
2:5-dichlorobenzenesulphonyl chloride (10 g.) (Stewart (*ref*)) was added in small portions to a stirred, cooled solution of benzhydrazide (5.5 g.) in pyridine (25 c.c.). The mixture was left at room temperature for 2 hours and then poured with vigorous stirring into a mixture of ice and dilute hydrochloric acid. The orange precipitate was collected, well washed with water, and recrystallised from alcohol with the addition of animal charcoal. The product was obtained in very good yield as colourless prismatic needles, m.p. 186 - 188° (slight decomp.). (Found: N, 8.4.

$C_{13}H_{10}O_3N_2Cl_2S$ requires N, 8.1%). This dichloro compound is much more readily soluble in alcohol than is the corresponding unsubstituted compound.

Decompositions of benzoylbenzenesulphonhydrazide:-

	Wt. of hydrazide (g.)	Vol. of ethylene glycol (c.c.)	Oil bath temp. at addn. of alkali (°C)	Time of reaction (secs.).	Alkali		Yield of Aldehyde (%)
					Compound	Equivs.	
A	1	10	90	4000	Na_2CO_3	6	30
B	5	25	130	1000	K_2CO_3	4	40
C	1	12	160	75	Na_2CO_3	5	73
D	1	5	160	40	Na_2CO_3	2	60
E	1	5	165	60	Na_2CO_3	1+	46
F	3	15	140 rising to 180	1000	K_2CO_3	4	10
G*	1	10	110	500	Na_2CO_3	4	74
H*	1	steam-distilled from aqueous			Na_2CO_3	6	65
J	14	100	155	180	Na_2CO_3	5	62 ‡

* In these cases benzoyl 2:5-dichlorobenzenesulphonhydrazide was used.

‡ In this case the benzaldehyde was isolated, redistilled, and weighed as such. In every other case the benzaldehyde was estimated as the dinitrophenylhydrazone.

B. p-CHLOROBENZOIC ACID SERIES.

Ethyl p-chlorobenzoate:- was prepared as described by Van Raalte (20).

p-Chlorobenzhydrazide:- was prepared from ethyl p-chlorobenzoate as described by Kahl (21). Yield, ca. 90%, m.p. 155 - 157°.

p-Chlorobenzoyl-2:5-dichlorobenzenesulphonhydrazide:- 2:5-dichlorobenzenesulphonyl chloride (2.45 g.) was added in small portions to a stirred, cooled solution of p-chlorobenzhydrazide (1.7 g.) in pyridine (15 c.c.). After standing for one hour the mixture was poured into crushed ice and dilute hydrochloric acid. A theoretical yield of orange coloured amorphous solid was obtained, and was twice recrystallised from alcohol, with the addition of animal charcoal, giving colourless prisms, m.p. 234 - 237° (decomp.). (Found: N, 7.5. $C_{13}H_9Cl_3O_3N_2S$ requires N, 7.4%).

Decomposition of p-chlorobenzoyl-2:5-dichlorobenzene-sulphonhydrazide.

Wt. of hydrazide (g.)	Vol. of ethylene glycol (c.c.)	Oil bath temp. at addn. of alkali (°C)	Time of reaction	Alkali		Yield of Aldehyde (%)
				Compound	Equivs.	
1	10	80 rising to 110	1000	Na_2CO_3	5	77

C. ANISIC ACID SERIES.

Anisic acid:- was obtained in excellent yield by the permanganate oxidation of anisaldehyde under the conditions described in Organic Syntheses (22) for the preparation of piperonylic acid from piperonal.

Ethyl anisate:- was prepared according to the method of Curtius and Melsbach (23), b.p. 150 - 155° at 25 m.m.

Anisoyl hydrazine:- was prepared from ethyl anisate as described by Curtius and Melsbach (23). Yield, 80%, colourless needles, m.p. 133 - 134°.

Anisoylbenzenesulphonhydrazide:-

(i) from anisoylhydrazine:- Benzenesulphonyl chloride (4 g.) was added slowly (30 mins.) to a stirred, cooled

solution of anisoyl hydrazine (4 g.) in pyridine (25 c.c.). After 15 mins. stirring, the solution was poured into a mixture of ice and dilute hydrochloric acid. The precipitated lemon-yellow solid was recrystallised from alcohol, with the addition of animal charcoal. Yield, 90%, colourless prisms, m.p. 187 - 189° (decomp.). (Found: N, 9.2. $C_{14}H_{14}O_4N_2S$ requires N, 9.2%).

(ii) from benzenesulphonhydrazide:- Anisoyl chloride (made by boiling the acid with excess thionyl chloride in carbon tetrachloride solution, and purified by distillation in vacuo) (3 g.) was added to benzenesulphonhydrazide (3 g.) in pyridine (25 c.c.). Heat was evolved. The mixture was left overnight and poured into ice-dilute hydrochloric acid. The gummy product was dissolved in hot alcohol (70 c.c.), and water (30 c.c.) was added. Crystals and gum were deposited overnight in the refrigerator. The crystals, recrystallised twice from alcohol, gave prisms, m.p. 180 - 187° (decomp.). (Found: N, 9.3. $C_{14}H_{14}O_4N_2S$ requires N, 9.2%). The gum and mother liquors gave successive crops of needles from alcohol, m.p. after two recrystallisations, 135 - 145° (decomp.). A nitrogen analysis (Found: N, 7.6) indicated that the needles were probably a crude

mixture of mono-anisoylbenzenesulphonhydrazide (requires N, 9.2%) with the corresponding di-anisoyl compound (requires N, 6.4%).

Decompositions of Anisoylbenzenesulphonhydrazide:-

Wt. of hydrazide (g.)	Vol. of ethylene glycol (c.c.)	Oil bath temp. at addn. of alkali (°C)	Time of reaction (secs.)	Alkali		Yield of Aldehyde (%)
				Compound	Equivs.	
1	10	160	120	Na_2CO_3	6	70
1	10	150	120	Na_2CO_3	6	77

D. PIPERONYLIC ACID SERIES.

Piperonylic acid:- was prepared from piperonal as described in Organic Syntheses (*22*).

Methyl piperonylate:- was obtained by refluxing piperonylic acid (10 g.) with methyl alcohol (100 c.c.) and conc. sulphuric acid (.7 c.c.) for 12 hours. Yield, 75%, m.p. 51 - 52°.

Piperonoylhydrazine:- Methyl piperonylate (5 g.) was refluxed for 2 hours with 50% hydrazine hydrate (5.6 c.c) and rect. spirit (6 c.c.). The white needles (4 g.) which

separated on standing overnight were filtered off, washed with a little ice-cold alcohol, and dried in vacuo: m.p. 170 - 171°. Excess alcohol was distilled off from the combined filtrate and washings, and the residue was refluxed for a further 2 hours. On cooling, a further 0.6 g. of product crystallised. Total yield, 4.6 g., 92%. Recrystallisation twice from alcohol, with the addition of animal charcoal, gave small colourless needles, m.p. 171 - 172°. (Found: N, 15.7. $C_8H_8O_3N_2$ requires N, 15.6%).

Piperonoylbenzenesulphonhydrazide:- Benzenesulphonyl chloride (1.8 c.c.) was added slowly (40 mins.) to a stirred, cooled solution of piperonoylhydrazine (2.5 g.) in pyridine (30 c.c.). The resulting solution was poured into a mixture of crushed ice and dilute hydrochloric acid. The pale yellow amorphous solid which separated was filtered off, washed with water and a little alcohol, and recrystallised from alcohol with the addition of animal charcoal. Yield, 90%, stout colourless prisms, m.p. 166 - 168°. (Found: N, 8.8. $C_{14}H_{12}O_5N_2S$ requires N, 8.8%).

Decompositions of Piperonoylbenzenesulphonhydrazide:-

Wt. of hydrazide (g.)	Vol. of ethylene glycol (c.c.)	Oil bath temp. at addn. of alkali (°C)	Time of reaction (secs.)	Alkali		Yield of Aldehyde (%)
				Compound	Equivs.	
0.5	10	155	150	Na_2CO_3	6	87
1	10	157	120	Na_2CO_3	10	86

E. SALICYLIC ACID SERIES.

Salicoylhydrazine:- was prepared from methyl salicylate as described by Kahl (24), m.p. 146 - 147°.

Salicoylbenzenesulphonhydrazide:- Benzenesulphonyl chloride (6.9 g.) was added (15 mins.) to a stirred, cooled solution of salicoylhydrazine (6 g.) in pyridine (40 c.c.). After a further 30 mins. stirring the solution was poured into a mixture of ice and dilute hydrochloric acid. The pale buff oily precipitate was collected, well washed first with dilute hydrochloric acid, then with water, and dried. Yield, crude 95%, m.p. 155 - 157°. Recrystallisation from benzene gave colourless micro-crystals, m.p. 161-162°; and from alcohol, colourless silky needles, m.p. 161 - 162°. (Found: N, 9.8. $C_{13}H_{12}O_4N_2S$ requires N, 9.6%).

Salicoyl-2:5-dichlorobenzenesulphonhydrazide:-

2:5-dichlorobenzenesulphonyl chloride (9.8 g.) was added in small portions to a stirred, cooled solution of salicoylhydrazine (6 g.) in pyridine (40 c.c.). The resulting mixture was poured into ice- dilute hydrochloric acid, the precipitated solid being filtered off and washed, first with dilute hydrochloric acid, and then with water. The product was dissolved in warm, dilute sodium hydroxide solution, stirred with animal charcoal, filtered and acidified. The orange-yellow precipitate (10 g., m.p. 203 - 210°), on washing with hot alcohol, in which it was soluble only with difficulty, gave a residue of m.p. 224 - 227° (decomp.). Recrystallisation from alcohol, with the addition of animal charcoal, gave colourless needles, m.p. 229 - 230° (decomp.). (Found: N, 7.8. $C_{13}H_{10}Cl_2O_4N_2S$ requires N, 7.8%).

Decompositions of Salicoylbenzenesulphonhydrazide:-

Wt. of hydrazide (g.)	Vol. of ethylene glycol (c.c.)	Oil bath temp. at addn. of alkali (°C)	Time of reaction (secs.)	Alkali		Yield of aldehyde (%)
				Compound	Equivs.	
1	20	154	70	Na_2CO_3	5	33
1	10	155	180	Na_2CO_3	4	54
1	20	155	180	Na_2CO_3	5	55
1	10	150	400	Na_2CO_3	5	40
1	10	20 rising to 160	2000	Na_2CO_3	4	30
* 1	5	150	150	Na_2CO_3	7	33
* 1	5	160	40	Na_2CO_3	4	42

* In these cases salicoyl-2:5-dichlorobenzenesulphonhydrazide was used.

F. m-NITROBENZOIC ACID SERIES.

Methyl m-nitrobenzoate:- was obtained by the nitration of methyl benzoate as described in Organic Syntheses (25). Yield, 85%, m.p. 75 - 76°.

m-Nitrobenzhydrazide:- was prepared from methyl m-nitrobenzoate in good yield by the method of Curtius and Trachmann (26): m.p. 153°.

m-Nitrobenzoylbenzenesulphonhydrazide:- Benzenesulphonyl chloride (4.5 g.) was added slowly to a stirred, cooled solution of m-nitrobenzhydrazide (5 g.) in pyridine (25 c.c.). The solution was poured into a mixture of ice and dilute hydrochloric acid, when a pale yellow solid, m.p. 210 - 215° (decomp.) was precipitated. This was recrystallised several times from glacial acetic acid, giving colourless fibrous needles, m.p. 222 - 223° (decomp.). (Found: N, 12.9. $C_{13}H_{11}O_5N_3S$ requires N, 13.1%).

Decompositions of m-nitrobenzoylbenzenesulphonhydrazide:-

Wt. of hydrazide (g.)	Vol. of ethylene glycol (c.c.)	Oil bath temp. at addn. of alkali (°C)	Time of reaction (secs.)	Alkali		Yield of aldehyde (%)
				Compound	Equivs.	
1	20	155	120	Na_2CO_3	6	30
1	20	155	75	Na_2CO_3	6	42

G. p-NITROBENZOIC ACID SERIES.

p-Nitrobenzoylbenzenesulphonhydrazide:- p-Nitrobenzoyl chloride (Organic Syntheses (27)) (11.5 g.), benzenesulphonhydrazide (10.6 g.), and pyridine (30 c.c.) were kept at 50° for an hour, and the resulting solution was cooled and poured into a mixture of ice and hydrochloric acid. After vigorous stirring the gummy product solidified and was filtered off and washed, first with water, then with a little alcohol. Recrystallisation from alcohol, with the addition of animal charcoal, gave colourless silky needles, m.p. 196 - 199° (decomp.). (Found: N, 13.1. $C_{13}H_{11}O_5N_3S$ requires N, 13.1%).

Decompositions of p-nitrobenzoylbenzenesulphonhydrazide:- No p-nitrobenzaldehyde was obtained on several attempted decompositions of this sulphonhydrazide, using the same general methods as were found successful in the series A to F above. The only product isolated was a crude buff amorphous solid, softening at 220°, but not completely melted at 290°.

H. CINNAMIC ACID SERIES.

Methyl cinnamate:- was prepared by refluxing cinnamic acid (12 g.) with methyl alcohol (25 c.c.) and conc. sulphuric acid (.7 c.c.) for 6 hours. Yield, 11 g., 85%, m.p. 35 - 36°.

Cinnamoylhydrazine:- was prepared by the method of Mückermann (28) but using methyl cinnamate in place of the ethyl ester. Yield, 40%, m.p. 96 - 98°.

"Cinnamoylbenzenesulphonhydrazide":- Benzenesulphonyl chloride (2.8 c.c.) was added slowly to a stirred, cooled solution of cinnamoylhydrazine (3.8 g.) in pyridine (15 c.c.). After 15 minutes stirring the mixture was poured into ice - dilute hydrochloric acid, giving a pale orange solid in 60% yield. Recrystallisation from alcohol with the addition of animal charcoal gave colourless rhombs, m.p. 169 - 171° (decomp.). (Found: N, 9.7, 9.8. $C_{15}H_{14}O_3N_2S$ requires N, 9.3%).

Decompositions of "cinnamoylbenzenesulphonhydrazide":- The same general treatment as was found successful for the production of the aldehyde in the series A to F failed in this case to lead to the formation of cinnamaldehyde, on several attempts. A brown oil, with an aroma suggestive of higher hydrocarbons, but containing no aldehyde, was produced.

I. ACETIC ACID SERIES.

Acetylbenzenesulphonhydrazide:- was prepared from benzenesulphonhydrazide as described by Curtius and Lorenzen (29).

Decomposition of Acetylbenzenesulphonhydrazide:- Several decompositions were carried out in a small distilling flask, the vapours produced being led by means of a gentle air stream directly into an alcoholic solution of dinitrophenylhydrazine sulphate. Ethylene glycol, cyclohexanol, and naphthalene were tried as solvents, but in no case was any acetaldehyde detected.

J. ISOBUTYRIC ACID SERIES.

Methyl isobutyrate:- was prepared by refluxing isobutyric acid with excess methyl alcohol in the presence of a little conc. sulphuric acid. It was found that the resulting ester formed a constant boiling mixture with methyl alcohol; so the isolation of the ester was carried out by pouring the reaction mixture into a large volume of dilute sodium carbonate solution and separating the top (ester) layer, which was then washed with water and dried over calcium chloride to remove residual methyl alcohol. The ester distilled at 90 - 95°.

Isobutyrylhydrazine:- was prepared by the method of Stollé and Gutmann (30) by refluxing methyl isobutyrate (12 g.) with 100% hydrazine hydrate (10 c.c.) for 70 hours. Isobutyryl hydrazine (8.5 g., 70%) was obtained on cooling as a white crystalline mass, m.p. 100 - 102°. (Note:- Curtius and Hambsch (31) record an excellent yield with 3 hours refluxing by the use of anhydrous hydrazine.).

Isobutyrylbenzenesulphonhydrazide:- Benzenesulphonyl chloride (6.5 g.) was added slowly to a stirred, cooled solution of isobutyryl hydrazine (4 g.) in pyridine (25 c.c.). After a further 15 mins. stirring, the mixture was poured into ice - dilute hydrochloric acid. The deep cream

coloured precipitate was filtered off, washed and dried. Yield, crude, 7.6 g., 86%, m.p. 156 - 157°. Recrystallisation from alcohol with the addition of animal charcoal gave colourless rhombs, m.p. 157 - 158°. (Found: N, 11.7. $C_{10}H_{14}O_3N_2S$ requires N, 11.6%).

Decompositions of isobutyrylbenzenesulphonhydrazide:- Several decompositions were carried out in a small distilling flask, the vapours being led by a gentle air stream directly into an alcoholic solution of dinitrophenylhydrazine sulphate. Ethylene glycol and quinoline were tried as solvents, but in no case was any butyraldehyde detected.

K. DIPHENYLACETIC ACID SERIES.

Diphenylacetic acid:- was obtained by the reduction of benzilic acid (Organic Syntheses (32)).

Ethyldiphenylacetate:- was prepared by refluxing diphenylacetic acid in alcoholic solution with the addition of a little conc. sulphuric acid.

Diphenylacethydrazide:- was prepared in good yield by the method outlined by Stollé and Schmidt (33) by refluxing ethyl diphenylacetate with an equal weight (i.e. a large excess) of 100% hydrazine hydrate, and twice

its weight of absolute alcohol, at 150° (oil bath temp.) for 8 hours. After the excess alcohol was distilled off, the residue cooled to a colourless mass which was filtered off and washed with a little ice-cold alcohol: m.p. 133 - 134°.

Diphenylacetylbenzenesulphonhydrazide:-

(i) from diphenylacethydrazide:- Benzenesulphonyl chloride (1.6 c.c.) was slowly added to a stirred, cooled solution of diphenylacethydrazide (3 g.) in pyridine (20 c.c.). After further stirring the solution was poured into a mixture of ice and dilute hydrochloric acid, when the crude product was precipitated in 90% yield. Recrystallisation from alcohol, with the addition of animal charcoal, gave colourless plates, m.p. 191 - 193°. (Found: N, 7.8. $C_{20}H_{18}O_3N_2S$ requires N, 7.7%).

(ii) from benzenesulphonhydrazide:- A much less pure product, probably containing some di-diphenylacetylbenzenesulphonhydrazide, was obtained by treating diphenylacetylchloride with benzenesulphonhydrazide in pyridine solution. M.p. 187 - 189°, after three recrystallisations from alcohol, not depressed on admixture with the product from method (i).

Decompositions of diphenylacetylbenzenesulphonhydrazide:-

No diphenylacetaldehyde resulted from several attempts to

decompose this hydrazide by the same general methods as were found successful in the series A to F above.

L. GALLIC ACID SERIES.

Triacetylgalloyl chloride:- was prepared by refluxing for 15 minutes a mixture of triacetylgallic acid (20 g.) and thionyl chloride (28 c.c.). On removal of the excess thionyl chloride in vacuo there was obtained a theoretical yield of triacetylgalloyl chloride, m.p. 100 - 103°.

Triacetylgalloylbenzenesulphonhydrazide:- All attempts to obtain this compound by the interaction of triacetylgalloylchloride and benzenesulphonhydrazide in pyridine solution failed. The products were gums and white solids, melting over a range of from about 35° to 110°, from which homogeneous compounds could not be obtained.

A NEW PREPARATION OF 1:3:5-TRINITROBENZENE.

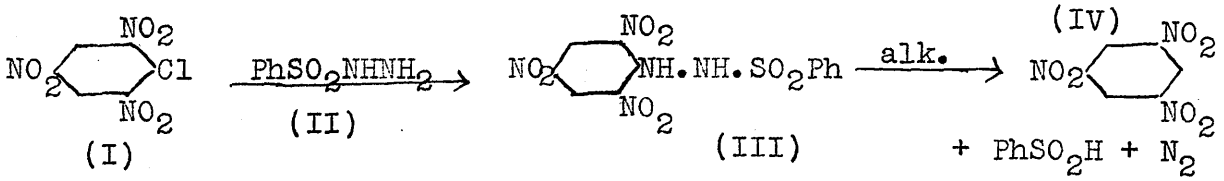
INTRODUCTION.

Most of the methods hitherto recorded for the preparation of 1:3:5-trinitrobenzene have either not been economical, or have required somewhat dangerous operations, such as the nitration, under severe conditions, of m-dinitrobenzene (Hepp, and others (34) (35)); treatment of trinitrotoluene with fuming nitric acid at 180° (Claus, Becker (36)); and oxidation of trinitrotoluene to trinitrobenzoic acid, and subsequent elimination of carbon dioxide from the latter (Organic Syntheses (37)). More recently, Lesslie and Turner (38) record a good yield by the reduction of picryl chloride with copper bronze in tetralin at 195°; whilst an unusual preparation is that utilising condensation of trinitrotoluene with p-nitrosodimethylaniline, hydrolysis of the product to trinitrobenzaldehyde and quantitative conversion of the latter to trinitrobenzene by means of alcoholic ammonia (Secareanu (39)).

It has been previously mentioned (page 4) that benzene is produced by the alkaline decomposition of benzenesulphonphenylhydrazide:

$$Ph.NH.NH.SO_2Ph \xrightarrow{KOH} PhSO_2K + PhH + N_2$$

This suggested the decomposition of the analogous benzenesulphon-2:4:6-trinitrophenylhydrazide as a possible convenient source of 1:3:5-trinitrobenzene. Preliminary experiments showed that m-dinitrobenzene was produced by alkaline treatment of benzenesulphon-2:4-dinitrophenyl-hydrazide; and the conversion of picryl chloride to 1:3:5-trinitrobenzene was subsequently carried out rapidly and in quite good yield in the following two stages:-



Both of these stages require only mild conditions, since (I) and (II) condense to (III) very rapidly in hot alcoholic solution, whilst hot aqueous sodium borate solution is sufficiently strongly alkaline to decompose (III) to (IV).

EXPERIMENTAL.

Benzenesulphon-2:4-dinitrophenylhydrazide:- 2:4-dinitrophenylhydrazine (4 g.) was suspended in pyridine (25 c.c.) at 50°, and vigorously stirred during the addition (15 mins.) of benzenesulphonyl chloride (2.8 c.c.). After stirring for two hours at room temperature, the product was poured into dilute sodium hydroxide solution, and filtered from unchanged dinitrophenylhydrazine. The filtrate, on acidification, gave a brownish yellow precipitate which on recrystallisation from alcohol, with the addition of animal charcoal, gave a mixture of lemon yellow laminae, m.p. 196 - 198° (decomp.) (Found: N, 16.4. $C_{12}H_{10}O_6N_4S$ requires N, 16.6%), and fine yellow needles, m.p. 196 - 198° (decomp.) (Found: N, 16.5%), showing no depression with one another, but each depressed on admixture with dinitrophenylhydrazine. In contact with alcohol, the needles gradually changed to laminae at room temperature.

Decomposition:- Sodium carbonate (1 g.) was added to benzenesulphon-2:4-dinitrophenylhydrazide (1 g.) in ethylene glycol (10 c.c.) at 150°. After three minutes, hot water was added and the mixture cooled. The chocolate-brown precipitate (0.34 g.), m.p. 81 - 83°, was recrystallised from alcohol (animal charcoal), giving pale yellow plates, m.p. 90°, not depressed on admixture with m-dinitrobenzene.

Benzenesulphon-2:4:6-trinitrophenylhydrazide:-
Hot alcoholic solutions of picryl chloride (15 g. in 120 c.c.) and benzenesulphonhydrazide (10 g. in 75 c.c.) were mixed and refluxed for a few minutes with shaking. The yellow solid which rapidly separated was filtered off on cooling and washed with hot alcohol. It crystallised from alcohol (1000 parts) in lemon-yellow fibrous needles, m.p. 210 - 220° (decomp.) (Found: N, 18.3. $C_{12}H_9O_8N_5S$ requires N, 18.3%).

Decomposition:- A mixture of benzenesulphon-2:4:6-trinitrophenylhydrazide (9 g.), borax (5 g.) and water (50 c.c.) was heated carefully until the first effervescence was over, and then boiled for 40 minutes. After thorough cooling, the dark brown amorphous solid (crude trinitrobenzene) was collected. Recrystallisation twice from alcohol (animal charcoal) gave pale yellow plates (3 g.), m.p. 121 - 122°, not depressed on admixture with pure 1:3:5-trinitrobenzene.

THE DEGRADATION OF QUATERNARY AMMONIUM SALTS.

Précis.

The intramolecular rearrangement:-

$$\underset{\text{(I)}}{Ph.CO.CH_2\overset{+}{N}(CH_3)_2 \\ | \\ CH_2Ph} \xrightarrow{\text{alkali}} \underset{\text{(II)}}{Ph.CO.\underset{|}{CH}.N(CH_3)_2 \\ CH_2Ph}$$

discovered by Stevens, has since been investigated in detail by Stevens and co-workers, and extended to include cases of (a) other migrating radicals, (b) other accepting radicals, and (c) migrations from atoms other than nitrogen, to carbon and other atoms.

INTRAMOLECULAR REARRANGEMENTS OF SULPHINIC ESTERS:-

The type of intramolecular rearrangement from sulphinic ester to sulphone, represented by the general equation:-

$$\underset{\text{(III)}}{R-O-\overset{+}{S}-\bar{O} \\ | \\ R'} \longrightarrow \underset{\text{(IV)}}{R-\overset{++}{S}(\bar{O})(\bar{O}) \\ | \\ R'}$$

has now been investigated in the case of a number of esters of p-toluenesulphinic acid (R' = p-Ph.CH_3 in III). The results obtained, pending an investigation of the effect on the migration of variations in the structure of the radical R' in III, strongly indicate that,

in accordance with prediction, this class of rearrangement is of the same general type as, but somewhat less facile than, the quaternary ammonium salt rearrangement I⟶II.

INTRAMOLECULAR REARRANGEMENT OF HYDRAZIDES AND RELATED COMPOUNDS. Attempts made by Dunn and Stevens to extend their reaction:-

$$T.SO_2.NH.N\begin{matrix}Ph\\ CH_2Ph\end{matrix} \xrightarrow{\text{alkali}} Ph.CH{:}N.NH.Ph + TSO_2H$$

(V) (VI)

(where T represents the p-tolyl radical) indicated that if this were an intramolecular rearrangement, which is at least doubtful, such rearrangement was not of the type observed in the quaternary ammonium salt series.

The constitution of the compound (V) has now been confirmed by an independent synthesis; but further attempts to extend, and elucidate the mechanism of, the reaction V⟶VI have failed.

DEGRADATION OF QUATERNARY AMMONIUM SALTS.

INTRAMOLECULAR REARRANGEMENTS OF SULPHINIC ESTERS.

INTRODUCTION.

The reaction:-

$$\underset{\text{(I)}}{PhCOCH_2N(CH_3)_2Br \atop \quad | \quad CH_2Ph} \xrightarrow{\text{alkali}} \underset{\text{(II)}}{PhCOCHN(CH_3)_2 \atop \quad | \quad CH_2Ph}$$

discovered by Stevens, Creighton, Gordon and McNicol (*40*) has been studied in considerable detail by Stevens and co-workers (*41*, *42*, *43*, *44*, *45*, *46*, *47*) with respect to:

(a) the kinetics of the reaction,

(b) the effect of the replacement by other radicals of the various radicals attached to the quaternary nitrogen atom in I,

and (c) the effect of the replacement of the quaternary nitrogen system by other systems such as tertiary nitrogen and tertiary sulphur.

When the reaction is carried out with a mixture of the close analogues phenacyl-m-bromobenzyldimethylammonium and p-bromophenacylbenzyldimethylammonium bromides, which separately undergo the reaction with similar velocities, the sole products are ω-m-bromobenzyl-ω-dimethylamino-acetophenone and ω-benzyl-ω-dimethylamino-p-bromoacetophenone,

showing that the reaction is an intramolecular rearrangement.

Among the observations made on the kinetics of the reaction I ⟶ II are the following:-

(1) the reaction only takes place in alkaline media,

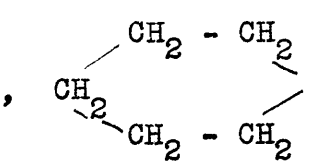
(2) the rearrangement under the influence of sodium alcoholates is unimolecular, and nearly independent of the alkali concentration,

(3) by titration with alcoholic sodium ethoxide, the salt I is shown to contain a very feebly acidic hydrogen atom,

(4) the quaternary iodide and bromide rearrange at the same rate,

but these, and other observations, together with evidence as to the rearrangement of compounds more or less closely related to I, have not as yet enabled the investigators to establish definitely the reaction mechanism.

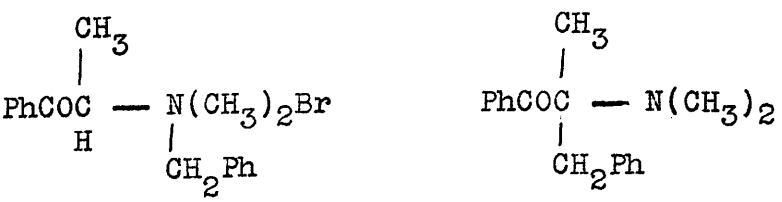
As to the structural requirements of the migrating radical, the rearrangement fails when the benzyl radical in I is replaced by

CH_3-, C_2H_5-, $PhCH_2CH_2$-,  , C_6H_5-

all of which lack an activated methylene group. On the other hand, the α-phenylethyl and benzhydryl radicals migrate some 10,000 times more readily than the benzyl; and the fluorenyl radical migrates so readily that its quaternary salt corresponding to I cannot be prepared. The presence of negative substituents in the m- or p- positions in the benzene ring of the benzyl group markedly accelerates the reaction I $\longrightarrow$ II; whilst all o- substituents show strong acceleration. Facile rearrangement is also observed when the benzyl is replaced by the allyl or the phenacyl radical.

With regard to the effect of varying the radical to which migration takes place,

(1) the accepting radical in I must obviously have at least one alpha hydrogen atom, which is eliminated to accommodate the migrating radical. Rearrangement is effected when only one is present, thus:-



(Note. This requirement, however, does not apply to migrations to oxygen, nitrogen, or sulphur, where the acceptor atom carries an unshared electron pair. Vide infra),

(2) rearrangement is retarded by negative substitution in the benzene ring of the phenacyl group in I,

(3) rearrangement may be effected where the phenacyl group in I is replaced by the acetonyl or the fluorenyl group; as well as by the allyl or benzyl group, but under extreme conditions in the latter two cases,

(4) migration to the methyl, cyanomethyl and carbethoxymethyl groups could not be effected, failure in the last two cases being probably due to hydrolysis.

The facts outlined above appear to show that the migrating and the accepting radical must both be such that if they were united with hydrogen, the hydrogen would have some degree of mobility.

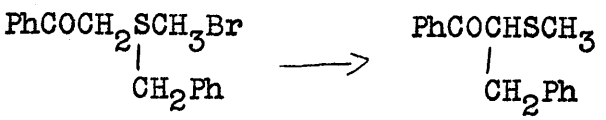
It has further been shown that the quaternary nitrogen system may be replaced by:-

(1) <u>tertiary nitrogen.</u> Thus Stevens (unpublished work) has carried out the rearrangement:

$$PhCOCH_2\underset{\displaystyle CH_2Ph}{\overset{|}{N}}\text{-}Ph \longrightarrow PhCO\underset{\displaystyle CH_2Ph}{\overset{|}{C}}H.NHPh$$

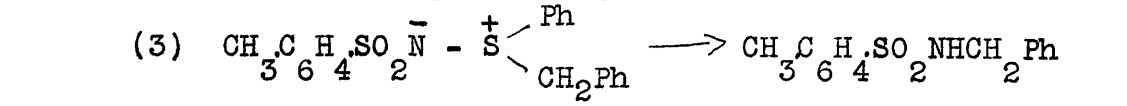
though under more drastic conditions than those required for I $\longrightarrow$ II,

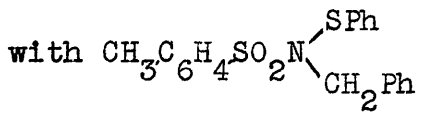
(2) <u>tertiary sulphur</u>. The rearrangement:



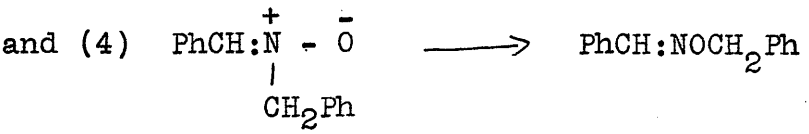
was shown by Thomson and Stevens (44) to proceed very smoothly,

whilst the following rearrangements:-

(3) 

with  as a possible, but not isolated, intermediate

(Dunn and Stevens, unpublished work)

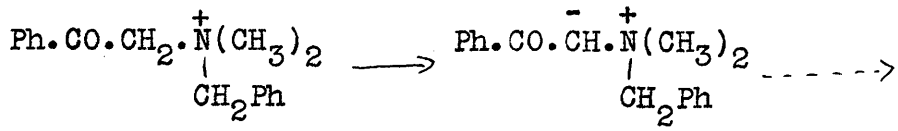
and (4) 

(McGeoch and Stevens, unpublished work)
(cf. Meisenheimer (66))
may well belong to the same general type.

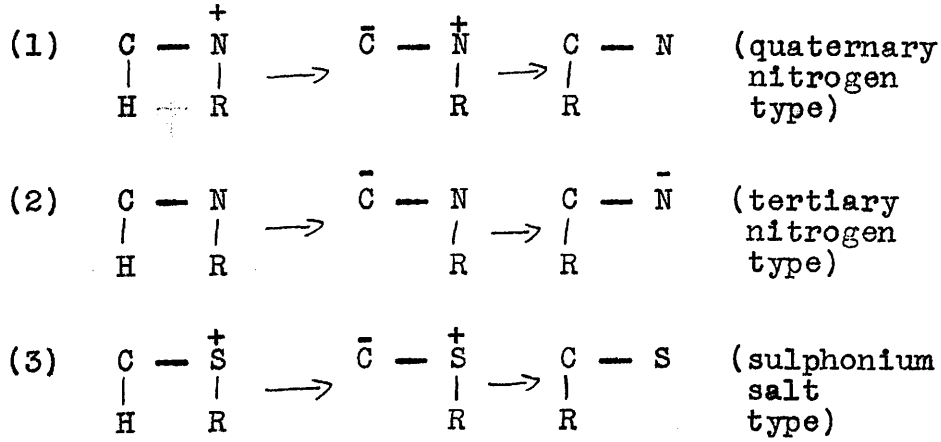
In the present investigation, an attempt is made to realise a similar series of migrations from oxygen to sulphur. In the cases discussed by Stevens and co-workers, and briefly outlined above, generally speaking:-

(A) those involving migration from nitrogen to carbon, and from sulphur to carbon, require alkaline conditions, indicating that salt formation at the reactive methylene group, and hence the freeing of a pair of electrons to accommodate the migrating radical, is a necessary preliminary to rearrangement.

Thus the first stage in the rearrangement in the quaternary nitrogen series would be the formation of a "zwitterion":-



On this basis the essential rearrangements in these cases may be represented thus:-



whereas

(B) those involving migration from sulphur to nitrogen and from nitrogen to oxygen do not require alkaline conditions, the structure of the initial compound being such that the accepting atom can accommodate the migrating radical by means of an already unshared electron pair. In these cases the essential rearrangements may be represented:-

(4) $\bar{N} - \overset{+}{S}(R) \longrightarrow N(R) - S$ (sulphilimine type)

(5) $\bar{O} - \overset{+}{N}(R) \longrightarrow O(R) - N$ (amine oxide type)

The observed fact that rearrangement is more facile in the quaternary than in the tertiary nitrogen series, harmonises with the greater stability, as regards electronic structure, of the rearrangement product (1) in the former case as compared with that in the latter (2). For the same reason it is not surprising that rearrangement of the sulphilimine type (4) is found to require much more severe conditions than that of the sulphonium salt type (3).

Kenyon and Phillips (*48*) record an interesting case of the migration of a radical from an oxygen to a sulphur atom, in which <u>laevo</u>-phenylmethylcarbinyl-p-toluenesulphinate (III)

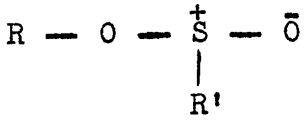
$$Ph.CH(CH_3) - O - \overset{+}{S}(Ph.CH_3) - \bar{O} \longrightarrow Ph.CH(CH_3) - \overset{++}{S}(Ph.CH_3)(=O)(=O)$$

(III) (IV)

is spontaneously converted, slowly at room temperature, and more rapidly on heating, to <u>inactive</u>-α-phenylethyl-p-tolylsulphone (IV). These authors were interested

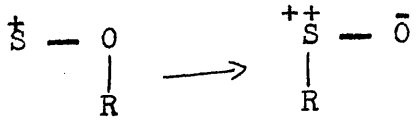
in this reaction mainly from the aspect of the optical instability of the migrating radical, rather than in the intramolecular rearrangement as such.

This type of rearrangement, from sulphinic ester to sulphone, appeared to be very suitable for a study of the migration of radicals from oxygen to sulphur, the instability and difficulty of purification of the sulphinic esters being to some extent compensated by the stability and ease of identification of the sulphones. Accordingly, it was proposed to prepare and investigate the rearrangement of a series of sulphinic esters of the general structure



where R represents the various radicals of which the migration had been studied in the quaternary ammonium salt series*.

The essential rearrangement in such a case may be represented thus:-



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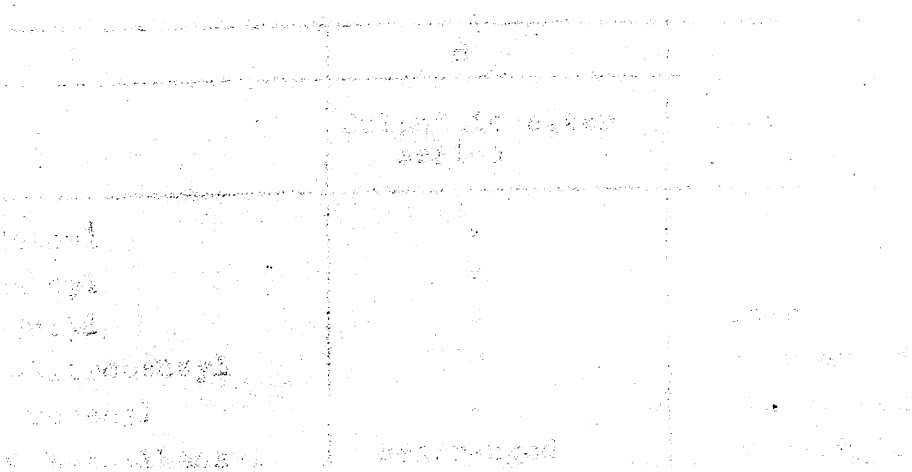
* Before this investigation was begun, Dr. Kenyon was approached, and willingly consented to our attempted extension of the reaction III ⟶ IV on the lines suggested.

From what has been said above, it would appear reasonable to make the predictions that in this type of rearrangement the migration of a radical

(a) would not require alkaline conditions,

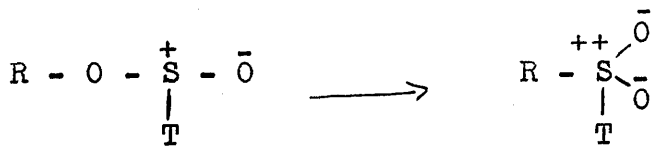
and (b) would probably be less facile than that of the corresponding radical in the quaternary ammonium salt series.

The example recorded by Kenyon and Phillips, and further examples discussed in the following pages, show that the former of these two predictions is fully, and the latter at least apparently, justified by experimental evidence.



DISCUSSION OF EXPERIMENTAL WORK.

The rearrangement of sulphinic ester to sulphone represented by the general equation:



(where T represents the p-tolyl radical)

has been investigated in the case of the group of esters listed in Column A of the table below. Column B indicates whether or not rearrangement was observed in accordance with the above equation. Column C shows whether or not migration of the corresponding radical was observed in the quaternary ammonium salt series previously studied by Stevens and co-workers.

A	B	C
R	Sulphinic ester series	Quaternary ammonium salt series.
(1) Methyl	*	*
(2) Phenyl	*	*
(3) Benzyl	*	rearranged
(4) o-Nitrobenzyl	*	rearranged
(5) Fluorenyl	*	rearranged
(6) α-Methylbenzyl	rearranged	rearranged
(7) αα-Dimethylbenzyl	rearranged	**
(8) Benzhydryl	rearranged	rearranged
(9) 2-Methylbenzhydryl	rearranged	***

* :- No rearrangement observed.
** :- Quaternary ammonium salt could not be prepared.
*** :- Quaternary ammonium salt was not investigated.

The failure to bring about migration of the methyl (1), and of the phenyl (2), radical is common to both series of rearrangements; and a further common feature of both series is that the α-methylbenzyl (6) and benzhydryl (8) radicals are observed to migrate.

In the quaternary ammonium salt series, the velocity of migration of the benzyl radical (3) was very much less than that of the α-methylbenzyl radical (6). In the sulphinic ester series, migration of the benzyl radical (3) could not be effected, whilst the α-methylbenzyl radical (6) migrated fairly readily, and the $\alpha\alpha$-dimethylbenzyl radical (7) very readily. From the point of view of a complete comparison, it is unfortunate that the corresponding $\alpha\alpha$-dimethylbenzyl quaternary ammonium salt could not be prepared; but despite this gap, the observations relative to migration velocities in these cases may be considered to be in good agreement, and to indicate that the rearrangements are of the same general type, but less facile in the sulphinic ester than in the quaternary ammonium salt series; thus

	Migration velocity of
Sulphinic ester series	$[Ph.CH_2-] < Ph.CH(CH_3)- < Ph.C.(CH_3)_2$
Quat. amm. salt series	$Ph.CH_2- < Ph.CH(CH_3)-$ -- ---------

With regard to the behaviour of the o-nitrobenzyl radical (4), in the quaternary ammonium salt series this was observed to migrate with a velocity considerably greater than that of the benzyl but less than that of the α-methylbenzyl radical. In the sulphinic ester series no migration was observed in the case of the o-nitrobenzyl radical, but this may again be simply explained by the fact that rearrangement in this series is less facile than in the quaternary ammonium salt series, and need not be considered as evidence of a fundamental difference in the two rearrangements.

The ease of migration of the benzhydryl (8), and still more of the 2-methylbenzhydryl (9), radical in the sulphinic ester series harmonises well with the observed facts in the quaternary ammonium salt series that (i) the benzhydryl radical migrates with great ease, and (ii) all ortho- substituents in the benzyl radical result in increased velocity of migration.

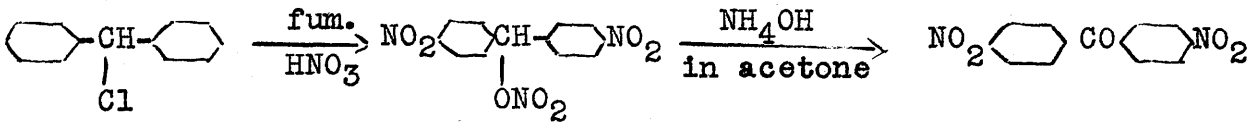
From the eight examples so far discussed, it would seem reasonable to conclude that after due allowance is made for the greater facility of rearrangement in the quaternary ammonium salt than in the sulphinic ester series, and for the impossibility of subjecting the sulphinic esters to severe treatment in an endeavour to

bring about rearrangement, the observations as regards relative migration velocities in the two series are in broad general agreement.

The one case remaining to be considered is that of the fluorenyl radical (5). In the quaternary ammonium salt series this radical was found to migrate with such velocity that the rearrangement product, and not the quaternary salt, resulted from attempts to prepare the latter. In the sulphinic ester series, on the other hand, fluorenyl p-toluenesulphinate can be readily prepared, but has failed entirely to undergo rearrangement to fluorenyl p-tolyl sulphone. No explanation of this anomaly can meantime be suggested.

It has not so far been possible to investigate the effect of variations in the structure of the accepting radical on the course of the rearrangement in the sulphinic ester series; such as, for example, the replacement of the p-tolyl by the p-nitrophenyl radical. Until this has been done, it would be premature to say definitely that the sulphinic ester - sulphone class of rearrangement obeys the same general laws as does the quaternary ammonium salt class, but the facts relative to the migrating radical so far elucidated, and discussed above, strongly indicate that the two rearrangements are of the same general type.

In order to find out whether negative substitution in a benzene ring of the migrating radical accelerated the rearrangement, as had been observed in the quaternary ammonium salt series, the preparation of a mono- or di- nitrobenzhydryl p-toluenesulphinate was contemplated. No mono- or di- nitrobenzhydrols have been recorded, and the preparation of such a compound would appear to be a matter of some difficulty, since (i) direct nitration of benzhydrol is not feasible; (ii) the reduction of a mono- or a di- nitrobenzophenone is similarly impracticable; and (iii) Bauer and Endres (*49*) by the action of bromine on 4:4'-dinitrodiphenylmethane obtained, not 4:4'-dinitrobenzhydryl bromide, but 4:4'-dinitrobenzophenone. Attempts were made to nitrate benzhydryl acetate and benzhydryl chloride, but without success. The latter nitration, however, gave in small yield a compound containing three atoms of nitrogen, no chlorine, and no keto group, and yielding 4:4'-dinitrobenzophenone very rapidly on treatment with ammonia in cold acetone solution. This very surprising result could be accounted for on the assumption that the intermediate compound is 4:4'-dinitrobenzhydryl nitrate, which would be in agreement with the qualitative tests and nitrogen analysis. Thus:-



The combined hydrolysis and oxidation of 4:4'-dinitrobenzhydryl nitrate to 4:4'-dinitrobenzophenone finds a parallel in the hydrolysis by Carlson (50) of benzyl nitrate with alcoholic potash, which resulted in an almost quantitative yield of benzaldehyde and potassium nitrite.

EXPERIMENTAL.

p-Toluenesulphinyl chloride:- was prepared by the action of thionyl chloride on p-toluenesulphinic acid, as described by Phillips (51), and obtained as a pale yellow oil of specific gravity approximately 1.28.

Esters of p-toluenesulphinic acid:- These were all prepared according to the following general method, as used by Kenyon and Phillips (48) for the preparation of phenyl-methylcarbinyl-p-toluenesulphinate.

p-Toluenesulphinyl chloride (1.03 mol.) was added slowly to an ice-cold solution of the appropriate carbinol (1 mol.) in pyridine (1.15 mol.), with continual shaking. When the mixture became inconveniently viscous during the addition of the acid chloride, owing to the quantitative separation of pyridine hydrochloride, anhydrous ether was used as required as a diluent. The reaction mixture was finally further diluted with ether, and the ethereal solution washed twice with dilute hydrochloric acid, five times with dilute potassium carbonate solution, and three times with water, and dried over calcium chloride. The ether was then removed in vacuo, the residue consisting of the ester, generally in almost theoretical yield.

The purification, where possible, and properties of the individual esters are separately described below.

Methyl p-toluenesulphinate:- was obtained as a colourless liquid, b.p. 145 - 150° at 25 m.m., agreeing with the product obtained by Arndt and Scholz (52) by treating toluenesulphinic acid with diazomethane. On thermal treatment, no rearrangement to methyl p-tolyl sulphone (Otto, (53)) was observed.

Phenyl p-toluenesulphinate:- In the preparation of this ester, the ethereal extract, in addition to the usual treatment, was washed with dilute sodium hydroxide, to remove any residual phenol. The product was a very unstable colourless solid, m.p. 51 - 52°, which rapidly decomposed, on keeping and on attempted recrystallisation, to a dark red tar. No rearrangement to phenyl p-tolyl sulphone (Newell (54)) was observed.

Benzyl p-toluenesulphinate:- was obtained as a pale yellow oil, crystallising on strong cooling to a pale yellow solid which became colourless after draining on a chilled porous plate. M.p. 22 - 24° (Found: S, 13.1. $C_{14}H_{14}O_2S$ requires S, 13%). The ester was very readily

soluble in ether and benzene, less soluble in petroleum ether. In petroleum ether solution in a corked test tube, specimens underwent oxidation in the course of a few hours; but in a sealed tube no such deterioration was observed over a period of months. Attempted distillation in vacuo (15 m.m.) led to sudden complete decomposition at ca. 160°.

Benzyl p-tolyl sulphone (Otto (55)) was in no case produced as a result of a number of attempted rearrangements of benzyl p-toluenesulphinate.

The ester was unaffected by heating for 2½ hours on the water bath; or for 30 minutes on the oil bath at 135°. After short heating at slightly higher temperatures (140 to 160°), the ester underwent sudden decomposition to a dark tar, from which, however, no benzyl p-tolylsulphone could be isolated.

Refluxed in xylene solution for 20 hours, progressive decomposition of the ester took place, with the separation of tarry material. On cooling, the solution deposited needles, m.p. 105°, identified as p-toluenesulphonic acid. No benzyl p-tolyl sulphone was isolated.

When refluxed in petroleum ether (100 to 120° fraction) solution for 3 days, in a slow stream of carbon

dioxide, the ester again slowly decomposed to a tar;, but no benzyl p-tolyl sulphone was found.

Refluxing in petroleum ether (80 - 100° fraction) solution for 4 days, in a slow stream of carbon dioxide, led to the same separation of tarry material. The mixture was steam-distilled with the addition of sodium carbonate. The distillate comprised solvent, then benzyl alcohol, and finally a little di-p-tolyl disulphide (m.p. and mixed, 45°), but the aqueous residues contained no benzyl p-tolylsulphone.

Alcoholysis of benzyl p-toluenesulphinate:- Benzyl p-toluenesulphinate (3.7 g.) was refluxed with anhydrous potassium carbonate (4 g.) in abs. alcohol (30 c.c.) for 7 hours. The resulting mixture was steam distilled to remove alcohol and benzyl alcohol, and the residue evaporated to 15 c.c. After the addition of a solution of 2:4-dinitrochlorobenzene (3.5 g.) in acetone (20 c.c.), the mixture was refluxed for 90 minutes, and left overnight in the refrigerator. The solid product was collected, washed with alcohol and water, and dried. Yield 4 g. (83%), m.p. 178 - 181°. Recrystallisation from alcohol gave needles, m.p. 183 - 185°, not depressed on admixture with 2:4-dinitrophenyl-p-tolylsulphone (m.p. 187°).

o-Nitrobenzyl p-toluenesulphinate:- was obtained as a colourless solid, m.p. 58 - 59°. (Found: S, 10.8. $C_{14}H_{13}O_4NS$ requires S, 11.0%). The ester was recovered unchanged after heating for 40 minutes at 115°; more severe treatment led to decomposition; and rearrangement to o-nitrobenzyl p-tolyl sulphone (Tröger and Nolte (56)) was not observed.

[o-Nitrobenzyl alcohol, for the preparation of this ester, was obtained by the Cannizzaro reaction on o-nitrobenzaldehyde, as described by Geigy and Königs (54)].

Fluorenyl p-toluenesulphinate:- A relatively large amount of ether was necessary in the extraction of this ester, owing to its sparing solubility in the cold solvent. Recrystallisation from ether gave colourless prisms, m.p. 107 - 108° (Found: S, 9.8. $C_{20}H_{16}O_2S$ requires S, 10.0%).

In no case was fluorenyl p-tolyl sulphone (Ingold and Jessop (58)) isolated as a result of several attempts to carry out the rearrangement of fluorenyl p-toluenesulphinate.

The ester was recovered unchanged after brief heating in vacuo at 110°. Sudden decomposition resulted from prolonged heating at 110 - 120°, or more rapidly at higher temperatures, giving a dark red viscous liquid which solidified to a glass on cooling. This product, which

when finely divided was pale maroon, gave a good qualitative test for sulphur, and did not effervesce with carbonate solution, became colourless on washing with hot ether, and melted over a range from 160° to 200°. When dissolved in benzene and reprecipitated with petroleum ether, a buff coloured solid was obtained, softening at from 220° to 250°, but incompletely melted by 300°. No fluorenyl p-tolyl sulphone could be isolated, and repeat experiments gave the same result.

When the ester was refluxed in petroleum ether (100 - 120° fraction) for 6 hours in an atmosphere of carbon dioxide, progressive decomposition resulted, with the separation of tarry decomposition products, in which no fluorenyl p-tolyl sulphone was found.

α-Methylbenzyl p-toluenesulphinate:- was obtained as a pale yellow viscous oil which, slowly at room temperature, and more rapidly on heating, deposited crystals of α-methylbenzyl p-tolylsulphone, m.p. 131 - 132° after recrystallisation from alcohol, as described by Kenyon and Phillips (*48*).

αα-Dimethylbenzyl p-toluenesulphinate:- The ester was obtained as a pale yellow, viscous oil. (Found: S, 11.5. $C_{16}H_{18}O_2S$ requires S, 11.7%).

[Specimens of phenyldimethylcarbinol, for the preparation of this ester, were obtained by the action of methyl magnesium iodide on (i) acetophenone, and (ii) ethyl benzoate. Each product contained acetophenone - a surprising result in the latter case - which was removed as the oxime.]

Rearrangement of $\alpha\alpha$-dimethylbenzyl p-toluenesulphinate:- In a sealed tube at room temperature, the ester in the course of a few hours began to deposit $\alpha\alpha$-dimethylbenzyl p-tolylsulphone in the form of clusters of stout needles, m.p. 144 - 145° after recrystallisation from alcohol. (Found: S, 11.5. $C_{16}H_{18}O_2S$ requires S, 11.7%). This conversion to the sulphone was considerably more rapid than in the case of the corresponding α-methylbenzyl ester.

Attempted alcoholysis of $\alpha\alpha$-dimethylbenzyl p-tolylsulphone (used, in place of an independent synthesis, to confirm the constitution):- A mixture of the sulphone (1 g.), anhydrous potassium carbonate (1 g.) and alcohol (10 c.c.) was refluxed for 4 hours. On cooling, unchanged $\alpha\alpha$-dimethylbenzyl p-tolylsulphone (0.8 g.) crystallised from the solution.

Benzhydryl p-toluenesulphinate:- A relatively large amount of ether was necessary in the extraction of this ester, owing to its sparing solubility in the cold

solvent. The crude ester was obtained as a white solid, m.p. ca. 80°, crystallising from ether in colourless prisms, and from alcohol in colourless needles, m.p. 83 - 84°. (Found: S, 9.9. $C_{20}H_{18}O_2S$ requires S, 9.9%). In the crude state, when not thoroughly dry, specimens were found to change spontaneously to benzhydryl p-tolylsulphone, but under ordinary conditions the pure ester was stable.

Rearrangement of benzhydryl p-toluenesulphinate:-

(i) This rearrangement was very strikingly observed on heating the ester in a capillary tube. A clear melt was obtained at 84°; but on further heating, at a temperature of from 130° to 150°, rapid crystallisation took place, and a second m.p. was observed at ca. 185°.

(ii) Benzhydryl p-toluenesulphinate (1 g.) was heated up slowly in vacuo to 120° (oil-bath temperature), when the melt solidified. Heating was continued at 120° for 5 minutes, when the solid product was collected and identified as crude benzhydryl p-tolylsulphone, m.p. 183 - 185°; yield quantitative. Recrystallisation from alcohol gave colourless needles, m.p. 187 - 188°, not depressed on admixture with a specimen prepared as described below.

(iii) Benzhydryl p-toluenesulphinate was rapidly converted to the sulphone on immersion in an oil bath at 140°. The

ester could be recovered unchanged, however, after 3 minutes at 130°, conditions which were found to result in the rearrangement of the corresponding 2-methylbenzhydryl ester.

Benzhydryl p-tolylsulphone:- A solution of benzhydryl chloride (made by passing dry hydrochloric acid gas into benzhydrol in ether) (5 g.) and sodium toluenesulphinate (5 g.) in alcohol (40 c.c.) was refluxed for 3 hours. Benzhydryl p-tolylsulphone separated on cooling, and on recrystallisation from alcohol gave colourless needles, m.p. 188 - 189°. (Found: S, 9.7. $C_{20}H_{18}O_2S$ requires S, 9.9%).

Benzhydryl p-tolylsulphone was recovered unchanged after 3 hours refluxing in methyl alcoholic sodium hydroxide solution.

2-Methylbenzhydryl p-toluenesulphinate:- was obtained as a white solid, m.p. 68 - 70°; very readily soluble in ether, alcohol and benzene, somewhat less soluble in petroleum ether. (Found: S, 9.4. $C_{21}H_{20}O_2S$ requires S, 9.5%).

The 2-methylbenzhydrol for the preparation of this ester was prepared as described by Tschitschibabin (59), by the action of o-tolyl magnesium bromide on benzaldehyde; yield, 60%, m.p. 89 - 90°.

Rearrangement of 2-methylbenzhydryl p-toluenesulphinate:- The ester was heated in vacuo at 120° (oil-bath temperature) for 5 minutes, giving a dark red viscous liquid. The glass which formed on cooling was crushed, washed with ether, and recrystallised from alcohol, giving an almost quantitative yield of 2-methylbenzhydryl-p-tolyl sulphone, colourless rhombs, m.p. 127 - 128°, not depressed on admixture with a specimen prepared as below.

2-methylbenzhydryl p-tolyl sulphone:- A mixture of 2-methylbenzhydrol (2 g.), toluenesulphinic acid (1.4 g.), glacial acetic acid (8 c.c.), and a few drops of conc. hydrochloric acid, was refluxed for an hour. The crystals which slowly deposited on cooling were filtered off and recrystallised from alcohol, giving colourless rhombs, m.p. 127 - 128° (Found: S, 9.3. $C_{21}H_{20}O_2S$ requires S, 9.5%).*

Nitration of benzhydryl chloride:- Benzhydryl chloride (5 c.c.) was added slowly (45 mins.), at 10°, to vigorously stirred fuming nitric acid (20 c.c.), giving a deep red solution. After further stirring (90 mins.) at below 10°, the crystalline material which had separated was filtered off and was obtained as a colourless solid,

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* c.f. preparation of benzhydryl phenyl sulphone, Hinsberg (65).

after washing with water and ether (1.0 g., m.p. 145 - 148°). More of the same product (0.4 g.) was recovered by pouring the acid filtrate into crushed ice, triturating the tarry product with ether, and filtering off the precipitated solid. Recrystallisation from acetone-alcohol gave stout colourless needles, m.p. 154 - 155°. Qualitative tests for halogen gave negative results, and no 2:4-dinitrophenylhydrazone was formed. (Found: N, 13.0; 13.1. 4:4'-dinitrobenzhydryl nitrate, $C_{13}H_9O_7N_3$ requires N, 13.2%).

Other attempted nitrations of benzhydryl chloride under slightly different conditions of time, temperature and concentration, failed to result in the separation of a solid from the nitric acid mixture, but again yielded small amounts of the above product when the tar obtained on pouring the nitration mixture into crushed ice was triturated with ether.

Conversion of this compound to 4:4'-dinitrobenzophenone:- The addition of a little conc. ammonium hydroxide to a solution of this compound in acetone caused the separation, in a very short time, of fine colourless needles. These, after recrystallisation from acetone, had m.p. 185 - 186°, not depressed on admixture with a specimen of

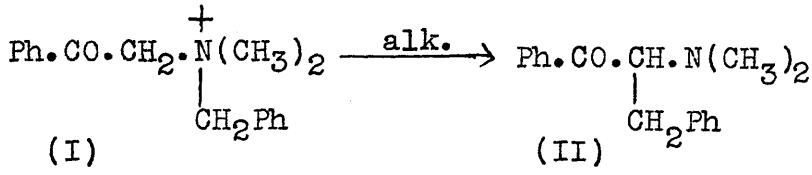
4:4'-dinitrobenzophenone, m.p. 187 - 188°, prepared by the chromic acid oxidation of 4:4'-dinitrodiphenylmethane.

DEGRADATION OF QUATERNARY AMMONIUM SALTS.

INTRAMOLECULAR REARRANGEMENTS OF HYDRAZIDES AND RELATED COMPOUNDS.

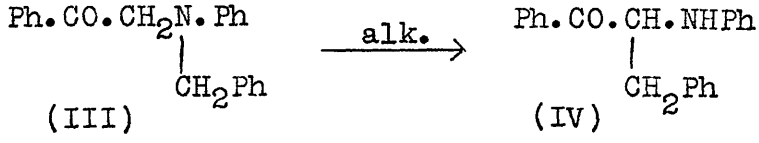
INTRODUCTION.

It has already been mentioned (page 42) in discussing the generality of the intramolecular rearrangement:



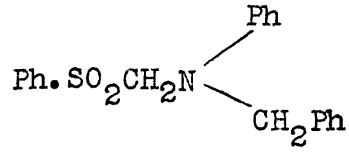
(I) (II)

that the replacement in (I) of the quaternary by the tertiary nitrogen system, to give (III), does not inhibit the rearrangement, which, however, is effected only on much more severe treatment:

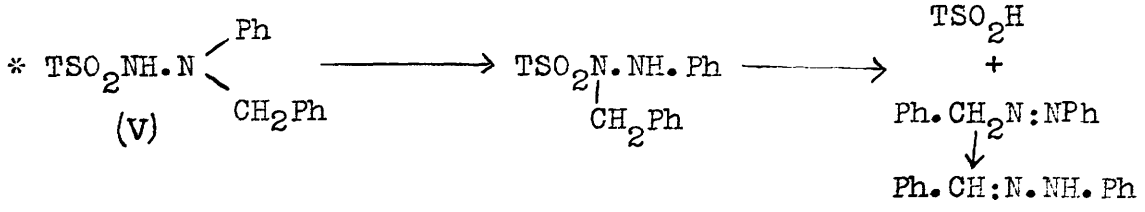


(III) (IV)

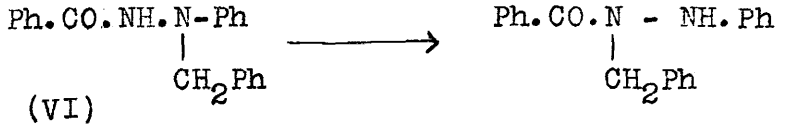
The similarity between the compound (III) and p-toluenesulphon-uns.-benzylphenylhydrazide (V) led to experiments being undertaken with the latter by Dunn and Stevens (unpublished work). The compound



would be more closely analogous to (III) than is (V), but would probably be very difficult to synthesise. On boiling with 8 per cent alkali, (V) was found to yield benzaldehyde phenylhydrazone and p-toluenesulphinic acid, suggesting that migration had taken place, followed by elimination of the elements of p-toluenesulphinic acid from the new hydrazide, with subsequent conversion of the benzene-azo-toluene to the isomeric benzaldehyde phenyl-hydrazone, viz:-



Contrary to their expectations, however, the corresponding benzoyl hydrazide (VI) could not be rearranged, even on heating to 200° with alcohol-free sodium methoxide, a reaction from which it had been hoped to isolate the initial rearrangement product, thus



This suggested that possibly the first action of the alkali

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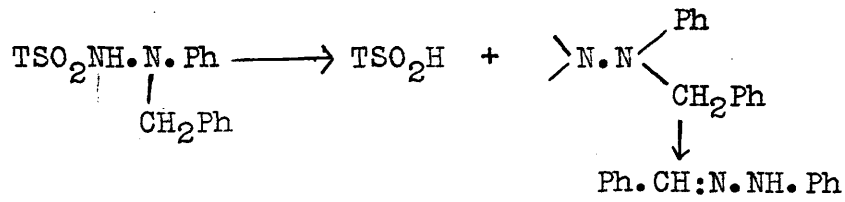
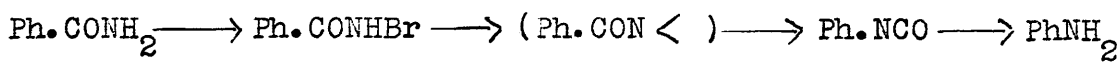
* Throughout this paper the symbol "T" is used to denote the para-tolyl radical.

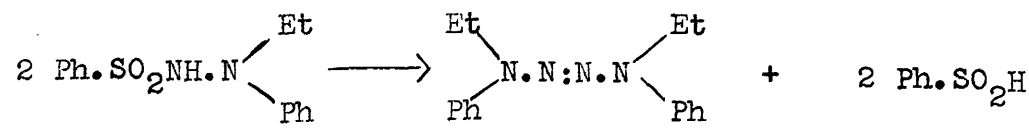
on the compound (V) was to remove the elements of p-toluene-sulphinic acid, followed by rearrangement of the univalent nitrogen compound so formed, viz.:-



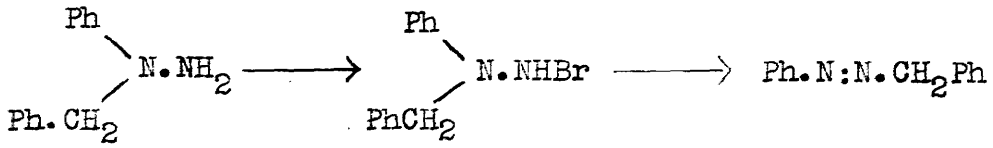
a mechanism analogous to that put forward by Stieglitz for the Hofmann degradation of amides with hypobromite:-



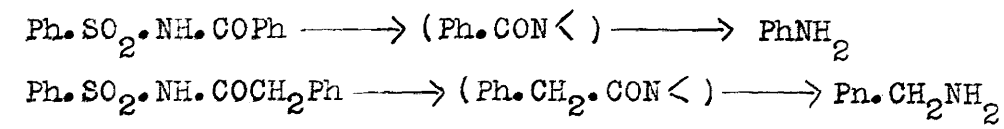
Since the Hofmann rearrangement appears to take place irrespective of the nature of the migrating radical, a similar rearrangement might be expected from any unsymmetrical sulphonhydrazide, if the reaction mechanism is truly analogous. Dunn and Stevens found, however, that benzene-sulphon-uns.-diphenylhydrazide would not undergo rearrangement to give azo-benzene, being stable to aqueous alkali in concentrations up to 30%, and decomposed to diphenylamine on more drastic treatment. Further, the action of 10 per cent aqueous alkali on benzenesulphon-uns.-phenylethyl- or phenylmethyl-hydrazide led to the formation of brown oils from which small amounts of corresponding tetrazones could be isolated:-



In addition, the action of alkaline hypobromite on uns.-benzylphenylhydrazine resulted in the formation of the tetrazone (i.e., simple oxidation) and not in a reaction analogous to the Hofmann rearrangement, viz.:-



Furthermore, if this were the mechanism of the reaction, then on treatment with alkali benzenesulphonbenzamide and benzenesulphonacetamide should give by analogy with the Hofmann rearrangement aniline and benzylamine respectively:-

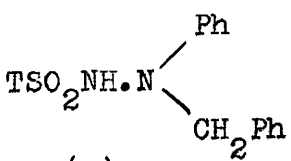


but in concentrations up to 30% alkali had no effect on these compounds, while fusion with alkali led to hydrolysis, with recovery of benzoic and phenylacetic acids respectively.

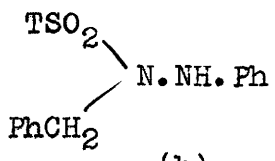
DISCUSSION OF EXPERIMENTAL WORK.

(A) The fact that the attempted rearrangements of these sulphonhydrazides had failed in every case except that of p-toluenesulphon-uns.-benzylphenylhydrazide indicated the desirability of a close examination of this latter compound.

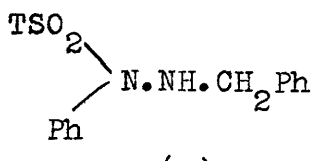
The hydrazide used in the above rearrangement had been prepared by the action of p-toluenesulphonyl chloride on uns.-benzylphenylhydrazine. This benzylphenylhydrazine had been made by the method of Minunni (60), by treating phenylhydrazine with benzyl chloride, a method which might possibly lead to the presence of varying amounts of <u>symmetrical</u> benzylphenylhydrazine in the product, in which event toluenesulphonylation might result in a mixture of



(a)



(b)

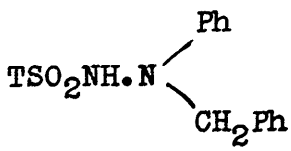


(c)

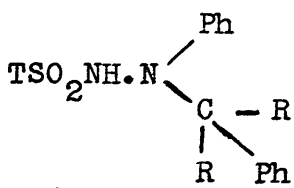
The removal of the elements of toluenesulphinic acid from either (b) or (c) by means of alkali could in theory result in the production of benzaldehyde phenylhydrazone without any intramolecular rearrangement having taken place. A specimen of uns.-benzylphenylhydrazine was

therefore synthesised by the reduction of benzylphenylnitrosamine, yielding a product which could hardly include the symmetrical hydrazine among possible impurities. The resulting uns.-benzylphenylhydrazine was coupled with toluenesulphonyl chloride and the product was found to agree (melting point and mixed) with the compound (V) of Dunn and Stevens, and on alkaline treatment underwent the same conversion to benzaldehydephenylhydrazone and toluenesulphinic acid.

(B) For two reasons, it is extremely desirable to obtain a compound (VII) analogous to (V), but with the two alpha-hydrogen atoms of the benzyl radical replaced by alkyl or aryl groups, viz:-



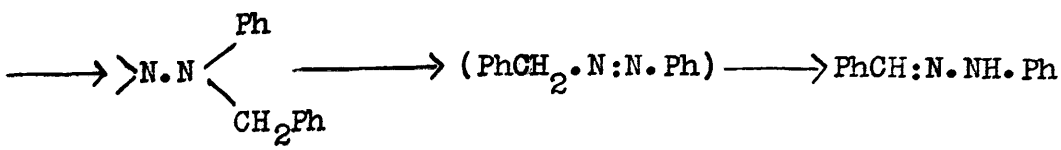
(V)



(VII)

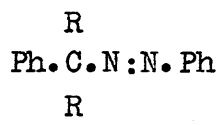
because:-

(i) if the rearrangement with (V) proceeds as follows:-



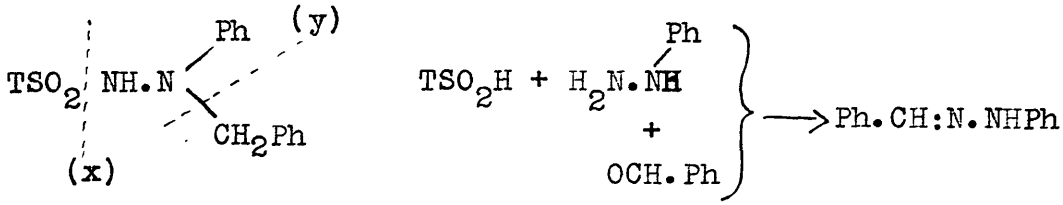
then an analogous reaction with the compound (VII) should

stop at the azo-compound stage, thus:-



isomeric change to a hydrazone being no longer possible. Isolation of an azo-compound would therefore give a valuable clue as to the mechanism.

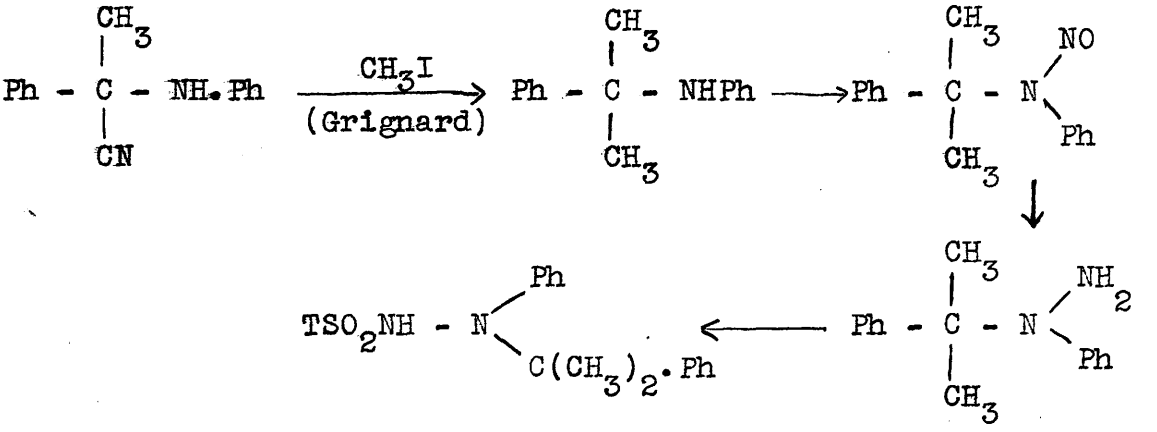
(ii) in a compound such as (V) there are two particular linkages in the molecule at one of which (x) reduction might readily take place and at the other (y) oxidation. Under these circumstances, an intramolecular oxidation-reduction reaction might quite possibly occur, thus:-



on which scheme the isolation of benzaldehydephenyl-hydrazone from the reaction mixture would be readily explained without any migration of a radical. On the other hand, in the compound (VII) the presence of the two substituent groups in the alpha positions in the benzyl radical would render oxidation at the N - C linkage highly improbable.

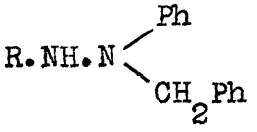
Unfortunately, the attempted synthesis of a compound of the type (VII) has failed. It was hoped to carry out

the synthesis on the following lines:-



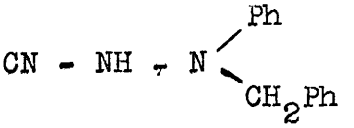
but the Grignard reaction on α-phenyl-α-anilinopropionitrile did not have the desired result.

(C) It has already been shown by Dunn and Stevens (c.f. page 67) that the compound (VIII) appears to undergo facile rearrangement where R represents the TSO_2' radical,



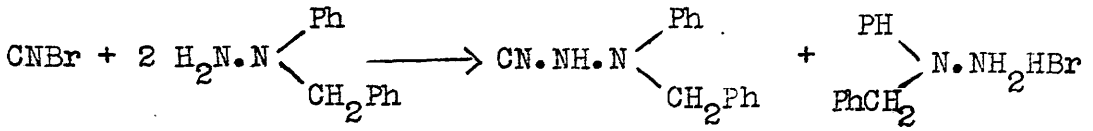
(VIII)

but not where R represents the Ph.CO' radical, suggesting that a necessary condition may be that R.H is an acid. The synthesis of some other compound of the structure (VIII) where R.H is an acid, was therefore called for, and the compound chosen was:-



(IX)

Compounds of this type are, in general, highly unstable, (c.f. Tivoli (61)). An attempt was made to prepare (IX) by the condensation of cyanogen bromide with uns.-benzylphenylhydrazine:



From the reaction mixture an approximately theoretical amount of uns.-benzylphenylhydrazine hydrobromide crystallised out. In view of the known instability of this class of compound, the filtered solution was treated in an attempt to bring about rearrangement without preliminary isolation of the cyanohydrazide, but the only product which could be identified was a relatively small amount of benzaldehyde benzylphenylhydrazone. No benzaldehyde phenylhydrazone was found, nor could any cyanide be detected in the reaction mixture.

EXPERIMENTAL.

Uns.-benzylphenylhydrazine was prepared by the method of Antrick (62), by the reduction of benzylphenylnitrosamine. According to Antrick, the product contained, after purification by distillation in vacuo, varying amounts of benzylaniline. In this case the crude product was found to be approximately 70% benzylaniline. The entire crude yield was therefore distilled in vacuo, dissolved in benzene, and shaken out with successive small amounts of dilute hydrochloric acid, the precipitated hydrochloride and aqueous extracts being collected. The first few extracts were almost pure uns.-benzylphenylhydrazine hydrochloride (m.p. 167°), uns.-benzylphenylhydrazine being a more powerful base than benzylaniline. Extraction was continued until a specimen proved to be a mixed product. The uns.-benzylphenylhydrazine hydrochloride was dissolved in water, made alkaline with sodium hydroxide solution and extracted with ether. After washing the ethereal solution, and drying over sodium sulphate, the ether was distilled off, and the residual uns.-benzylphenylhydrazine distilled in vacuo giving an almost colourless oil (b.p. 207 - 208° at 10 m.m.).

p-Toluenesulphon-uns.-benzylphenylhydrazide:-

A solution of uns.-benzylphenylhydrazine (5.2 g., 2 mols.) and p-toluenesulphonyl chloride (2.3 g., 1 mol.) in benzene (15 c.c.) was refluxed for 6 hours on the water bath, and left overnight. The solid material which separated was collected, well washed with hot water, and recrystallised from alcohol. The first crop consisted of small cubes, m.p. 141°, not depressed on admixture with a specimen of the compound prepared by Dunn and Stevens (m.p. 139 - 141°). A later crop consisted of fine needles, m.p. 140°, not depressed when mixed with the cubic form. A hot alcoholic solution of cubes or needles could be induced to crystallise in either form by appropriate seeding. In the course of a few hours in contact with alcohol the needles changed to cubes.

p-Toluenesulphon-uns.-benzylphenylhydrazide (0.75 g.) was dissolved in 10% sodium hydroxide solution (7.5 c.c.), and alcohol (3.8 c.c.) added. The mixture was refluxed on the water bath, showing turbidity after 2 minutes. Refluxing was continued for 15 minutes, when the alcohol was distilled off, and water (25 c.c.) added. The precipitated solid (0.33 g.) was collected and recrystallised from alcohol, giving colourless needles, m.p. 154 - 155°,

not depressed on admixture with benzaldehydephenylhydrazone, m.p. 157 - 158°. Passing chlorine in the cold into the filtrate made just acid to litmus gave a precipitate which was extracted with benzene, and the benzene solution dried over sodium sulphate. On removal of the benzene there was obtained a solid, m.p. 66°, showing no depression on admixture with pure toluenesulphonyl chloride (m.p. 69°).

α-Phenyl-α-anilinopropionitrile:- was prepared by the method of Bucherer and Grolée (63), by the condensation of aniline hydrochloride, acetophenone, and potassium cyanide.

Attempts to prepare αα-dimethylbenzylaniline by the Grignard reaction on α-phenyl-α-anilinopropionitrile:-

(1) Methyl magnesium iodide was prepared in the usual way from methyl iodide (1.6 c.c.), magnesium (0.6 g.), and dry ether (12 c.c.). To this solution was added rapidly a solution of α-phenyl-α-anilinopropionitrile (1.80 g.) in hot dry toluene (30 c.c.), and the resulting mixture was refluxed on the water-bath for an hour, left overnight, and then decomposed with a mixture of crushed ice and ammonium chloride. The toluene-ether layer was separated and extracted with dilute hydrochloric acid. The acid extract, on making alkaline, gave the calcium hypochlorite test for aniline, but no other base could be detected.

The toluene-ether layer after acid extraction was twice washed with water, dried over calcium chloride, and distilled in vacuo to 40°, to remove ether and toluene. The small amount of solid residue was washed with methyl alcohol and dried, and was found to be unchanged starting material, m.p. 150°, not depressed on admixture with α-phenyl-α-anilinopropionitrile, m.p. 153 - 155°. No other product could be isolated.

(2) Methyl magnesium iodide was prepared in the usual way from methyl iodide (5.7 c.c.), magnesium (2.17 g.) and dry ether (40 c.c.). α-phenyl-α-anilinopropionitrile (4.90 g.) was washed into this solution with dry ether (30 c.c.). After refluxing for an hour the mixture was set aside overnight, then decomposed with a mixture of crushed ice and ammonium chloride, and the aqueous layer separated. The ethereal layer was washed with water, filtered, and extracted with dilute hydrochloric acid. On making alkaline this extract became cloudy, and oily drops separated, again proving to be aniline; no other base could be detected. The ethereal layer after acid extraction was twice washed with water, dried over sodium sulphate, and the ether distilled off. The residue consisted of a small amount of crude unchanged α-phenyl-α-anilinopropionitrile (m.p. and mixed). No other product could be isolated.

(3) Methyl magnesium iodide was prepared in the usual way from methyl iodide (11.60 c.c.), magnesium (4.50 g.) and dry ether (90 c.c.); and α-phenyl-α-anilino-propionitrile (10 g.) was washed with dry ether (150 c.c.) into the cold Grignard solution. The mixture was stirred vigorously in the cold for three hours, left overnight, and decomposed with a mixture of crushed ice and ammonium chloride. The ethereal layer was separated, washed twice with water, and filtered. Half of the ether solution was extracted with dilute hydrochloric acid, but again only aniline could be detected in the extract. The remaining half of the ether solution was dried and dry hydrochloric acid gas was passed in, giving a smeary precipitate containing unchanged starting material, and yielding some acetophenone on steam distillation from a dilute sodium carbonate solution. No other product could be isolated.

Attempted preparation and rearrangement of N cyano N'N' benzylphenylhydrazine:-

A solution of uns.-benzylphenylhydrazine (8.40 g., 2 mols.) in dry ether (17 c.c.) was added with shaking to a solution of cyanogen bromide (64) (2.25 g., 1 mol.) in dry ether (17 c.c.). Colourless needles began to

separate in a few minutes. The mixture was set aside for an hour with occasional shaking, and then filtered. The crystalline residue was identified as uns.-benzylphenylhydrazine hydrobromide by conversion to the hydrochloride (m.p. and mixed, 166°).

To a portion of the filtrate (20 c.c.) was added alcoholic sodium ethoxide (20 c.c.; from a solution of 5 g. sodium in 75 c.c. alcohol), causing the separation of an oil or very fine solid. Most of the ether was distilled off, and the residue refluxed on the water-bath for half-an-hour. After distilling off about half of the remaining alcohol, the mixture was diluted with a large excess of water, when a heavy brown oil separated. This oil was removed and dissolved in hot methyl alcohol containing a few drops of glacial acetic acid. After two days the solution deposited a small amount of yellow crystalline material, m.p. 105°. This melted at 106 - 108° when mixed with benzaldehyde benzylphenylhydrazone (m.p. 108 - 109°). Additional small amounts of the same product crystallised on further standing, but no benzaldehyde phenylhydrazone could be isolated; and the reaction mother liquor gave negative tests for cyanide.

A repetition of the process gave an identical result.

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C.	:	Chemisches Zentralblatt.
C.r.	:	Comptes rendus de l'Académie des Sciences.
G.	:	Gazzetta Chimica Italiana.
J.C.S.	:	Journal of the Chemical Society.
J. pr.	:	Journal für Praktische Chemie.
Org. Synth.	:	Organic Syntheses.
R.	:	Recueil des travaux chimiques des Pays-Bas.

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