35. *The Interaction of Triphenylmethanol, Fluoren-9-ol, and Diphenylmethanol with Hydrazoic Acid in the Presence of Sulphuric Acid.*

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By reaction with hydrazoic acid in the presence of sulphuric acid, triphenylmethanol yields azidotriphenylmethane, fluoren-9-ol yields phenanthridine and 9-azidofluorene, and diphenylmethanol yields aniline, benzaldehyde, and azidodiphenylmethane. 9-Azidofluorene has been prepared from 9-chlorofluorene; its acid-catalysed decomposition yields phenanthridine, and spontaneous decomposition (on storage or heating) yields 9-iminofluorene.

A mechanism, based on carbonium-ion formation, is proposed for the reaction of di- and tri-arylmethanols with hydrazoic and sulphuric acids.

In order to account for the observed products from the reaction of ketones, carboxylic acids, and olefins with hydrazoic acid in the presence of a strong acid, mechanisms have been proposed in which carbonium ions of the following forms are essential intermediates: for ketones the polarised molecule (I) (Briggs and Lyttleton, *J.*, 1943, 421) and the proton-adduct (II) (Sanford, Blair, Arroya, and Sherk, *J. Amer. Chem. Soc.*, 1945, **67**, 1941; Newman and Gildenhorn, *ibid.*, 1948, **70**, 317; Smith, *ibid.*, p. 320), for carboxylic acids

$$\begin{array}{ccccc} RR'\overset{+}{C}\text{—}\overset{-}{O} & RR'\overset{+}{C}\text{—}OH & R{\cdot}\overset{+}{C}(OH)_2 & R{\cdot}\overset{+}{C}{=}O & Ar_2\overset{+}{C}\text{—}CH_3 \\ (I) & (II) & (III) & (IV) & (V) \end{array}$$

the proton-adduct (III) (Newman and Gildenhorn, *loc. cit.*; Schuerch and Huntress, *ibid.*, 1949, **71**, 2233; Arcus, Kenyon, and Levin, *J.*, 1951, 407) and its dehydro-form (IV) (Newman and Gildenhorn, *loc. cit.*), and for 1 : 1-diarylethylenes the proton-adduct (V) (McEwen, Gilliland, and Sparr, *J. Amer. Chem. Soc.*, 1950, **72**, 3212).

Numerous alkylations effected with di- and tri-arylmethanols have been recorded, and reaction probably proceeds *via* the carbonium ion:

$$RR'R''C^+ + HX \longrightarrow RR'R''CX + H^+$$

Further, di- and tri-arylmethanols form coloured solutions in sulphuric acid, a property attributed to the formation of carbonium ions (Balfe, Kenyon, and Searle, *J.*, 1950, 3309; Gold and Tye, *J.*, 1952, 2172, where earlier references are given), and cryoscopic measurements with such solutions yield van't Hoff *i* factors of approximately 4 (Newman and Deno, *J. Amer. Chem. Soc.*, 1951, **73**, 3644; Gold, Hawes, and Tye, *J.*, 1952, 2167, where earlier references are given), a value attributed (Newman, *J. Amer. Chem. Soc.*, 1941, **63**, 2431) to ionisation according to equation (1). In view of the evidence for the formation of carbonium ions from di- and tri-arylmethanols, it seemed probable that these alcohols would, in the presence of sulphuric acid, react with hydrazoic acid. The reaction with triphenylmethanol, fluoren-9-ol, and diphenylmethanol has been investigated; a preliminary note has appeared (*Chem. and Ind.*, 1951, 701).

The reaction with triphenylmethanol yielded azidotriphenylmethane; it is considered that the carbonium ion, formed as in (1), reacts with hydrazoic acid to give the proton-adduct of the azide (2), which releases a proton to yield the free azide (3).

$$RR'R''C{\cdot}OH + 2H_2SO_4 \longrightarrow RR'R''C^+ + H_3O^+ + 2HSO_4^- \quad . \quad . \quad . \quad . \quad (1)$$

$$RR'R''C^+ + HN_3 \longrightarrow RR'R''C{\cdot}NH{\cdot}\overset{+}{N}{\vdots}N \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$RR'R''C{\cdot}NH{\cdot}\overset{+}{N}{\vdots}N \xrightarrow{\text{Alternatively}} \begin{cases} H^+ + RR'R''C{\cdot}N_3 \quad . \quad . \quad . \quad . \quad . \quad . & (3) \\ N_2 + RR'C{:}\overset{+}{N}HR'' \quad . \quad . \quad . \quad . \quad . \quad . & (4) \end{cases}$$

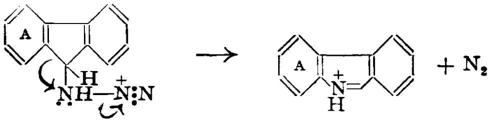
$$RR'C{:}\overset{+}{N}HR'' \longrightarrow H^+ + RR'C{:}NR'' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$RR'C{:}NR'' \xrightarrow{\text{Acid hydrol.}} RR'CO + R''{\cdot}NH_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Azidotriphenylmethane has been prepared by the action of nitrous acid on triphenylmethylhydrazine (Wieland, *Ber.*, 1909, **42**, 3026) and by the interaction of triphenylmethyl perchlorate with sodium azide (Lifschitz and Girbes, *Ber.*, 1928, **61**, 1488). Wieland found azidotriphenylmethane to be remarkably stable: it decomposed at about 180° when heated (Senior, *J. Amer. Chem. Soc.*, 1916, **38**, 2718, decomposed the azide at 225° and isolated benzophenone and aniline after hydrolysing the product) and, when the azide was added to sulphuric acid, a temperature of about 200° was required to effect appreciable decomposition. The azide is stable under the conditions of the present reaction, from which it was the main product.

The reaction with fluoren-9-ol yielded phenanthridine. In this instance the proton–azide adduct, formed as in (2), is considered to rearrange with loss of nitrogen to give the proton-adduct of an imine (4); loss of a proton yields the base (5), which is here a stable heterocycle, and reaction terminates at this stage. From one experiment, which gave a relatively low yield of phenanthridine, 9-azidofluorene was isolated, and this compound has also been prepared from 9-chlorofluorene and sodium azide. Reaction of 9-azidofluorene with sulphuric acid at 25° gave phenanthridine in good yield. On long storage or on heating, 9-azidofluorene decomposed to give 9-iminofluorene; this reaction, which is being further investigated, may proceed by a free-radical mechanism. It is concluded that the entity which undergoes rearrangement during the hydrazoic–sulphuric acid reaction is the proton-adduct of the azide and not the free azide.

The Schmidt reaction with (+)-α-phenylpropionic acid proceeds with a high retention of asymmetry and, probably, of configuration (Campbell and Kenyon, *J.*, 1946, 25), indicating the mechanism to be an intramolecular exchange of bonding at one face of the migrating carbon atom. From this result, together with the fact that the phenanthridine arises by a ring-expansion, the act of rearrangement, above, is considered to be intramolecular:



Electronic sharing between the migrating carbon atom of the ring A and the CH–NH fragment is continuous, and the four electrons initially present as the A–CH bond and the nitrogen lone-pair appear finally as the A–$\overset{+}{\mathrm{N}}$H bond and the π-electrons of the $\overset{+}{\mathrm{N}}$H=CH bond.

The reaction with diphenylmethanol yielded benzaldehyde and aniline. The products are considered to arise from hydrolysis (6) of the imine formed by reactions (1)—(5); this course for the reaction is in accord with the observation of Schmidt and Klavehn (D.R.-P. 583,565) that benzylideneaniline is produced by the reaction of thionyl chloride with a solution of diphenylmethanol in benzene containing hydrazoic acid. Azidodiphenylmethane has been isolated from the neutral, non-aldehydic fraction of the reaction products. Attempts to prepare the azide in larger quantity by interaction of diphenyl methyl chloride and sodium azide gave specimens which had suffered considerable loss of nitrogen. Reaction of the azide so prepared, and of the fraction containing the azide, with sulphuric acid at 25° yielded, in each case, aniline and benzaldehyde.

Equations (1)—(6) are proposed for the course of the reaction with di- and tri-arylmethanols; the stabilities of the compounds from the successive stages control the proportions in which these compounds appear in the final product from individual alcohols.

Improved preparations of the hydrazones of benzophenone and fluorenone are recorded.

EXPERIMENTAL

96% Sulphuric acid was used except where otherwise stated.

The Hydrazoic Acid–Sulphuric Acid Reaction.—(a) *With triphenylmethanol.* To a suspension of sodium azide (4·2 g.) in chloroform (13 ml.), cooled in ice, sulphuric acid (9 ml.) was slowly added with stirring. The ice was replaced by a water-bath maintained at 25°, and a solution of triphenylmethanol (10 g.) in chloroform (40 ml.) added during 1 hour. Stirring was continued for ½ hour, ice (75 g.) was then added, and the mixture was kept overnight and filtered. The aqueous layer was extracted with ether. The combined ether and chloroform solutions were washed with water and dried (Na_2SO_4), and the solvents evaporated; addition of a little alcohol caused the separation of a solid (7·7 g.), which, recrystallised from alcohol, yielded azidotriphenylmethane, white needles (6·5 g.), m. p. 64° (Found: C, 80·0; H, 5·5; N, 14·5. Calc. for $C_{19}H_{15}N_3$: C, 80·0; H, 5·3; N, 14·7%). Wieland, and Lifschitz and Girbes, *locc. cit.*, record m. p. 64° and 65°. The filtrate from the above product yielded a small quantity of a 2 : 4-dinitrophenylhydrazone having m. p. 236—237° alone and when mixed with benzophenone 2 : 4-dinitrophenylhydrazone. The acid aqueous solution (above) was made alkaline with sodium hydroxide solution and extracted with ether; the extract yielded azidotriphenylmethane (0·2 g.).

(b) *With fluoren-9-ol.* To hydrazoic acid–sulphuric acid solution (from sodium azide, 2·7 g.; chloroform, 12 ml.; and sulphuric acid, 6·1 ml.), at 25°, a suspension of fluoren-9-ol (4·3 g.; m. p. 154—155°; Bachmann, *J. Amer. Chem. Soc.*, 1933, **55**, 772) in chloroform (23 ml.) was added in small portions during 20 minutes; stirring was continued for 1 hour, and crushed ice (100 g.) was then added. The mixture was warmed to 50°, stirred for 40 minutes, kept overnight, and filtered. The chloroform layer was shaken mechanically for 30 minutes with N-sulphuric acid (50 ml.) and washed with water. The aqueous part of the reaction mixture was shaken with chloroform (15 ml.). The two acidic aqueous solutions were combined and made alkaline with sodium hydroxide solution, warmed (to coagulate the precipitate), cooled and filtered. The phenanthridine so obtained crystallised from light petroleum (b. p. 60—80°) as rectangular plates, m. p. 106—107° [*mercurichloride*, buff needles, m. p. 195—198° (Found: Hg, 40·5; Cl, 21·3. $C_{13}H_9N,HCl,HgCl_2$ requires Hg, 40·4; Cl, 21·4%) (Pictet and Ankersmit, *Annalen*, 1891, **266**, 147, and Sielisch and Sandke, *Ber.*, 1933, **66**, 433, record m. p. 197° and 195—207°, but no analysis); picrate, m. p. 245° (Found: C, 56·3; H, 3·0; N, 13·6. Calc. for $C_{19}H_{12}O_6N_4$: C, 55·9; H, 3·0; N, 13·7%) (Pictet and Ankersmit, *loc. cit.*, give m. p. $\nless$220°)]. Evaporation of the combined chloroform solutions, above, yielded a non-basic oil. The yields from repetitions of hydrazoic acid–sulphuric acid reactions, despite efforts to maintain identical conditions, varied considerably. There was obtained: phenanthridine (i) 2·55 g., (ii) 1·94. g, (iii) 2·98 g.; non-basic material (i) 1·00 g., (ii) 1·64 g., (iii) 0·84 g. The non-basic material (ii) deposited crystals which on recrystallisation from aqueous alcohol yielded 9-*azidofluorene* (Found: C, 75·3; H, 4·4; N, 20·4. $C_{13}H_9N_3$ requires C, 75·3; H, 4·4; N, 20·3%), m. p. 41° and m. p. 43° when mixed with a specimen of m. p. 44—45° prepared as below.

Concentrated hydrochloric acid (200 ml.) containing fluoren-9-ol (22 g.) was boiled for 5 minutes. The solid product, recrystallised from light petroleum (b. p. 60—80°), yielded 9-chlorofluorene (20·5 g., 85%), needles, m. p. 90—91°. A solution of 9-chlorofluorene (20 g.) in methanol (60 ml.) was heated under reflux with sodium azide (10 g.) for 4 hours, then poured into water, and extracted with ether; the extract was washed with aqueous sodium hydroxide, and with water, dried (Na_2SO_4), and evaporated, giving a solid which yielded 9-azidofluorene (16 g., 77%), needles, m. p. 44—45° (from aqueous alcohol), readily soluble in chloroform, hot alcohol, or hot benzene, sparingly soluble in ether, light petroleum (b. p. 40—60°), or carbon disulphide. After 2 months 9-azidofluorene had become yellow and recrystallisation from ligroin (b. p. 100—120°) gave 9-iminofluorene, pale yellow needles, m. p. 124° (Found: C, 87·0; H, 5·1; N, 7·0. Calc. for $C_{13}H_9N$: C, 87·1; H, 5·1; N, 7·8%). Pinck and Hilbert (*J. Amer. Chem. Soc.*, 1934, **56**, 490) record m. p. 124°. The imine (1·0 g.) was heated under reflux for 30 minutes with sulphuric acid (30%; 40 ml.) and yielded fluorenone (0·87 g.), m. p. 83° alone or mixed with an authentic specimen. 9-Azidofluorene was gently heated above its m. p., vigorous decomposition occurring with formation of a solid which on recrystallisation from ligroin yielded the imine.

To 9-azidofluorenyl azide (4·9 g.) in chloroform (35 ml.), at 25°, sulphuric acid (6·1 ml.) was added dropwise, with stirring which was continued for a total of 30 minutes. Crushed ice (100 g.) was added and the mixture treated as described under (*b*), yielding phenanthridine (i) 3·5 g., (ii) 3·1 g., m. p. 106° alone or mixed with an authentic specimen (mercurichloride, m. p. 195—197°, mixed m. p. 195—198°). Evaporation of the final chloroform solution yielded an amorphous solid, (i) 1·0 g., (ii) 0·9 g., containing sulphur but not nitrogen, m. p. >300°.

(c) *With diphenylmethanol.* A solution of diphenylmethanol (10 g.) in chloroform (20 ml.) was allowed to react with a hydrazoic acid–sulphuric acid (from sodium azide, 5·5 g.; chloroform 17 ml.; and sulphuric acid, 9·2 ml.), with subsequent addition of ice (100 g.) and warming, as described for fluoren-9-ol. Next morning the mixture was filtered from sulphur-containing material. The chloroform layer was shaken mechanically for 30 minutes with N-sulphuric acid (40 ml.). The acidic extract was combined with the aqueous part of the reaction mixture and extracted with ether. The aqueous layer was then made alkaline with sodium hydroxide solution and thrice extracted with ether, the extracts were washed with water, dried (Na_2SO_4), and evaporated, yielding aniline, b. p. 183°, n_D^{25} 1·5800 (benzoyl derivative, m. p. and mixed m. p. 161°). The chloroform and ether solutions were combined and evaporated, and the residue was shaken mechanically for 1 hour with a solution prepared as follows: sufficient water was added to sodium carbonate decahydrate (25 g.) to cover the crystals, and sulphur dioxide was passed until the solution was saturated. Chloroform (20 ml.) was added to the mixture, which was then filtered and separated. The solid bisulphite compound together with the aqueous solution was warmed with sulphuric acid (40%; 45 ml.) until the evolution of sulphur dioxide ceased; after cooling, the mixture was twice extracted with ether and the extract dried (Na_2SO_4). Evaporation of the ether yielded benzaldehyde, b. p. 178° (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 236°). In a control experiment 83% of the benzaldehyde originally present was isolated by this method. The chloroform extract of the bisulphite reaction mixture gave on evaporation a neutral liquid. There were obtained: aniline (i) 1·07 g., (ii) 2·05 g.; benzaldehyde (i) 0·48 g., (ii) 0·65 g.; neutral product (i) 8·4 g., (ii) 7·0 g. The neutral products were combined; distillation of a portion (2·5 g.) yielded *acidodiphenylmethane* (1·7 g.), b. p. 135°/4 mm., n_D^{22} 1·5883 (Found: C, 74·7; H, 5·3; N, 20·3. $C_{13}H_{11}N_3$ requires C, 74·6; H, 5·3; N, 20·1%). Another portion (5·0 g.) was dissolved in chloroform (12 ml.) and allowed to react with sulphuric acid (4 ml.) as described for 9-azidofluorene; crushed ice (100 g.) was added and the product kept overnight. It was separated as described above and yielded aniline (0·93 g.), benzaldehyde (0·90 g.), and neutral product (0·83 g.).

Two experiments were carried out as described under (*c*) except that 90% sulphuric acid (12·2 ml.) was used and diphenylmethanol (9·2 g.) in chloroform (20 ml.) was added during 1 hour and stirring continued for ½ hour; there were obtained: aniline (i) 1·6 g., (ii) 2·18 g.; benzaldehyde (i) 0·68 g., (ii) 1·15 g.; neutral product (i) 6·6 g., (ii) 4·3 g.

A solution of diphenylmethyl chloride (30 g.) in ethyl alcohol (99%; 45 ml.) (methanol and aqueous acetone were less satisfactory) was heated under reflux for 4 hours with sodium azide (15 g.). There was obtained impure azidodiphenylmethane (24 g.), b. p. 116—118°/1 mm., n_D^{21} 1·5702 (Found: C, 80·6; H, 6·9; N, 9·1%; Cl, 0), which by interaction with sulphuric acid, as described for the neutral product from (*c*), yielded aniline, benzaldehyde, and a neutral liquid product.

Benzophenone (19 g.), hydrazine hydrate (100%; 7 g.), and butyl alcohol (20 ml.) were heated under reflux for 3 hours. On cooling, a solid separated which on recrystallisation from alcohol (99%) yielded benzophenone hydrazone (11 g., 55%), rods, m. p. 99°. Fluorenone (8 g.), hydrazine hydrate (100%; 3·2 g.), and methanol (3 ml.) were heated under reflux on a water-bath for 5 minutes; the solid product, recrystallised from methanol, yielded fluorenone hydrazone (7·5 g., 89%), yellow needles, m. p. 148—149°. These preparations appear more satisfactory than, respectively, that of Curtius and Rauterberg (*J. pr. Chem.*, 1891, **44**, 194; *Org. Synth.*, 1944, **24**, 53) which employs ethyl alcohol in an autoclave for benzophenone hydrazone, and that of Wieland and Roseeu (*Annalen*, 1911, **381**, 231) which uses ethyl alcohol for fluorenone hydrazone and, as we have confirmed, yields fluorenone azine as a major product.

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