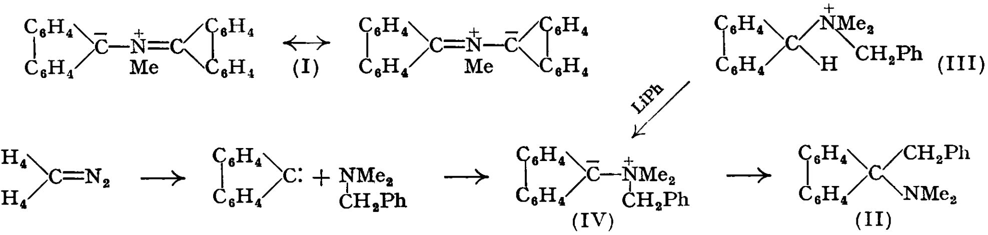
911. *A New Reaction of Aliphatic Diazo-compounds.*

By W. R. BAMFORD and T. S. STEVENS.

It is shown that aliphatic diazo-compounds react with certain tertiary amines, giving nitrogen and a base believed to be produced by the reactions :

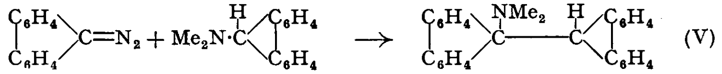
$\mathrm{R_2C{=}N_2 \longrightarrow R_2C\colon + N_2;\quad R_2C\colon + NMe_2R' \longrightarrow R_2\overset{-}{C}{-}\overset{+}{N}Me_2R' \longrightarrow R_2R'C{\cdot}NMe_2}$.

STAUDINGER and MEYER (*Helv. Chim. Acta*, 1919, **2**, 608) showed that aliphatic diazo-compounds do not combine with tertiary amines as they do with phosphines; diphenyldiazomethane when heated with triethylamine undergoes the same decomposition to benzophenone azine as when heated in other solvents. If the first product of decomposition of the diazo-compound is the uncharged diphenylmethylene radical $\mathrm{Ph_2C\colon}$, it is conceivable that this will co-ordinate, reversibly, with the amine, giving $\mathrm{Ph_2\overset{-}{C}{-}\overset{+}{N}Et_3}$, although in the end its fate is to combine with unchanged diazo-compound, yielding the azine. A case might then be found in which the dipolar ion would be stable or would undergo irreversible change to a significant product. We failed to effect the combination of diazofluorene with fluorenone methylimine to give the specially stabilised compound (I);

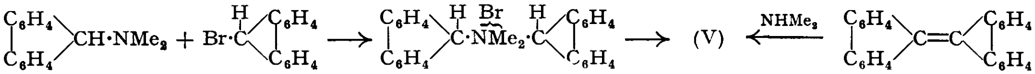


but diazofluorene and benzyldimethylamine afforded a considerable amount of 9-benzyl-9-dimethylaminofluorene (II). Wittig and Felletschin (*Annalen*, 1944, **555**, 133) obtained the same compound from (III) *via* the unstable (IV).

Diazofluorene reacted similarly with fluorenyldimethylamine :

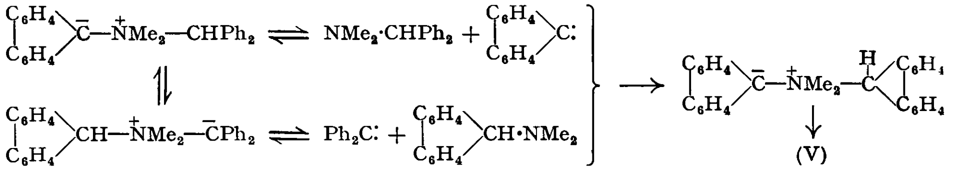


The same product was obtained from bromofluorene and fluorenyldimethylamine in presence of alkali :



and its properties agreed with those recorded by Pinck and Hilbert (*J. Amer. Chem. Soc.*, 1935, **57**, 2401) for the product of addition of dimethylamine to difluorenylidene.

Diazofluorene did not react in a similar way with fluorenylmorpholine, and with (diphenylmethyl)dimethylamine gave only the base (V). This curious result could be accounted for as follows :

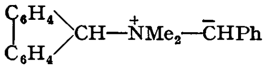


The same product was obtained from diphenyldiazomethane and fluorenyldimethylamine. Fluorenyl bromide with (diphenylmethyl)dimethylamine, and diphenylmethyl bromide with fluorenyldimethylamine, at 100°, gave in each case the base (V). In order to avoid analytical uncertainties arising from the similarity in composition of fluorenyl and diphenylmethyl compounds, experiments with nitrofluorene compounds were projected, but 9-bromo-2-nitrofluorene gave only dinitrodifluorenylidene with (diphenylmethyl)dimethylamine. With benzyldimethylamine and fluorenyldimethylamine the products of rearrangement of the normal quaternary salts were obtained.

Phenyldiazomethane and fluorenyldimethylamine afforded the base (VI) isomeric with (II), suggesting that prototropic change of the intermediate (VII) to the more stable (IV) is slower than the rearrangement. For comparison, (VI) was synthesised by direct combination of dimethylamine with benzylidenefluorene, the expected direction of addition being that involving attachment of the nitrogen atom to the α-carbon atom of the benzylidene group.

(VI) 

$$\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>CH\cdot CHPh\cdot NMe_2$$

 (VII)

$$\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>CH{-}\overset{+}{N}Me_2{-}\overset{-}{C}HPh$$

No analogous interaction was observed with the following pairs of reactants: phenyldiazomethane with benzyldimethylamine or (diphenylmethyl)dimethylamine; diphenyldiazomethane with (diphenylmethyl)dimethylamine; diazoacetophenone with fluorenyldimethylamine; diazodeoxybenzoin with benzyldimethylamine. The failure with the last two diazo-compounds may be attributed to their tendency to decompose to ketens: $Ph\cdot CO\cdot CR{=}N_2 \longrightarrow N_2 + Ph\cdot CR{=}C{=}O$; with benzyldimethylamine, however, diazoacetophenone gave a little of the expected product, $Ph\cdot CO\cdot CH(NMe_2)\cdot CH_2Ph$.

It is difficult to analyse the effect of structure on the incidence of this reaction. Foreseeable influences are complicated, and from the nature of the compounds studied, steric considerations may be important. It is noteworthy that the diphenylmethyl grouping appears in general to be unfavourable.

The reaction offers a possible synthetic route to α-dimethylamino-acids: $R\cdot NMe_2 + N_2{=}CH\cdot CO_2Et \longrightarrow R\cdot\overset{+}{N}Me_2\cdot\overset{-}{C}H\cdot CO_2Et \longrightarrow NMe_2\cdot CHR\cdot CO_2Et$; but fluorenyldimethylamine gave with ethyl diazoacetate only a trace of amphoteric material after hydrolysis, and with diethyl diazomalonate none at all.

An experiment of a similar type with a sulphur compound, $Ph_2C{=}N_2 + Ph\cdot CH_2\cdot SMe \longrightarrow Ph_2\overset{-}{C}\cdot\overset{+}{S}Me\cdot CH_2Ph \longrightarrow Ph_2C(SMe)\cdot CH_2Ph$, gave no decisive result. The corresponding oxygen compound reacted thus: $2Ph_2C{=}N_2 + 2Ph\cdot CH_2\cdot OMe \longrightarrow 2N_2 + (Ph_2CH)_2 + (Ph\cdot CH\cdot OMe)_2$, suggesting that diphenylmethylene radicals had abstracted hydrogen atoms from the ether and both univalent radicals had then dimerised.

EXPERIMENTAL

In each experiment the diazo-compound was added portionwise to the base, at such a temperature, varying from below 100° for phenyldiazomethane to 150° for diazofluorene, that a steady reaction was maintained without further external heating.

Diazofluorene (Nenitzescu and Solomonica, *Org. Synth.*, 1935, **15**, 62) *and Benzyldimethylamine.*—The filtered ethereal solution of the melt was extracted with hydrochloric acid, and the basic material, not volatile in steam, crystallised from methanol (30%). It was identical (mixed m. p. of base and picrate) with 9-benzyl-9-dimethylaminofluorene prepared from benzylfluorenyldimethylammonium bromide (Marrian, Thesis, Glasgow, 1941).

Diazofluorene and 9-*Fluorenyldimethylamine.*—The base was prepared by Wittig and Nagel's method (*Chem. Ber.*, 1950, **83**, 109); the procedure of Ingold and Jessop (*J.*, 1929, 2361) gave appreciable quantities of 9-dimethylamino-9 : 9′-difluorenyl. The basic material from the interaction of diazofluorene and fluorenyldimethylamine was fractionally crystallised from methanol; the least soluble fraction crystallised from benzene–ligroin in colourless rhombs (45%), m. p. 214—216° (Found: C, 90·1; H, 6·3; N, 3·7. Calc. for $C_{28}H_{23}N$: C, 90·0; H, 6·2; N, 3·8%). The same (mixed m. p.) dimethylaminodifluorenyl was obtained by refluxing 9-bromofluorene with 9-fluorenyldimethylamine in alcoholic potassium hydroxide for 1 hour. The *picrate* crystallised from alcohol in yellow needles, m. p. 208—209° (Found: N, 9·1. $C_{28}H_{23}N,C_6H_3O_7N_3$ requires N, 9·3%).

9-*Fluorenylmorpholine* was prepared from bromofluorene (2·4 g.) and morpholine (1·7 g.) in ether. After 15 hours the precipitated hydrobromide, m. p. 241° (decomp.) after crystallisation from water, was basified with ammonia; the free base (55%) crystallised from ligroin in prisms, m. p. 149° (Found: 81·0; H, 6·8; N, 5·9. $C_{17}H_{17}ON$ requires C, 81·2; H, 6·8; N, 5·6%).

Diazofluorene and (*Diphenylmethyl*)*dimethylamine.*—The base was obtained (94%) when a solution of diphenylbromomethane (5 g.) and dimethylamine (2 g.) in nitromethane (10 c.c.) was kept overnight and the basic material isolated in the usual way. The basic product not volatile in steam, from the reaction between diazo-compound (4 g.) and base (2 g.), crystallised from benzene–ligroin in rhombohedra (Found: C, 90·1; H, 6·1; N, 3·8%); it was identical (mixed m. p. of bases and picrates) with authentic 9-dimethylamino-9 : 9′-difluorenyl.

Diphenyldiazomethane and Fluorenyldimethylamine.—Benzophenone (50 g.), 90% hydrazine hydrate (20 c.c.), and ethylene glycol (50 c.c.) were refluxed for 6 hours. The hydrazone, deposited on cooling, was crystallised from alcohol (yield 85%) and oxidised with mercuric oxide in ligroin in presence of potassium hydroxide pellets (Staudinger, Anthes, and Pfenninger, *Ber.*, 1916, **49**, 1932). The basic products of the reaction between diphenyldiazomethane (2 g.) so prepared and fluorenyldimethylamine (1 g.) were fractionally crystallised from methanol, giving 9-dimethylamino-9 : 9′-difluorenyl, identified by mixed m. p. of base and of picrate. On one occasion a small quantity of material was isolated, as needles (from methanol), m. p. 135—136° (Found: C, 89·5; H, 6·7. $C_{28}H_{25}N$ requires C, 89·6; H, 6·7%). In attempts to prepare 9-fluorenyldiphenylmethyldimethylamine, $(C_6H_4)_2CH{\cdot}CPh_2{\cdot}NMe_2$, for comparison, 9-diphenylmethylenefluorene (Kaufmann, *Ber.*, 1896, **29**, 73) was heated with dimethylamine at 120° for 3 hours and kept at room temperature for 3 days, but was recovered unchanged.

Experiments with 9-*Bromo*-2-*nitrofluorene.*—This compound (Anantakrishnan and Hughes, *J.*, 1935, 1607), heated with (diphenylmethyl)dimethylamine (2 mols.) at 80° alone or in benzene, or kept for several weeks in cold nitromethane, gave only dinitrodifluorenylidene, red needles, m. p. >360° (Found: N, 7·1. Calc. for $C_{26}H_{14}O_4N_2$: N, 6·7%). Bromonitrofluorene (1 g.) was refluxed for 48 hours with fluorenyldimethylamine (1·45 g.) in benzene, and the basic products were crystallised from methanol. The least soluble fraction, crystallised from benzene–ligroin, formed pale-yellow prisms, m. p. 224° (decomp.), regarded as 9-*dimethylamino*-9-*fluorenyl*-2-*nitrofluorene* (Found: C, 80·3; H, 5·5; N, 6·7. $C_{28}H_{22}O_2N_2$ requires C, 80·3; H, 5·3; N, 6·7%). The picrate, prepared in alcohol, melted at 204—206° (decomp.). Bromonitrofluorene (1 g.) and benzyldimethylamine (0·95 g.) were kept at room temperature for 2 weeks. The basic material, extracted by hot hydrochloric acid and liberated by ammonia, crystallised from *cyclo*hexane in yellow prisms, m. p. 174°, probably 9-*benzyl*-9-*dimethylamino*-2-*nitrofluorene* (Found: C, 76·7; H, 5·9; N, 8·3. $C_{22}H_{20}O_2N_2$ requires C, 76·7; H, 5·8; N, 8·1%). The picrate, from alcohol–acetone, had m. p. 235—238° (decomp.).

Phenyldiazomethane and *Fluorenyldimethylamine.*—Benzaldehyde hydrazone (Curtius and Franzen, *Ber.*, 1902, **35**, 3236), b. p. 150°/15 mm., afforded the diazo-compound by Staudinger and Gaule's method (*Ber.*, 1916, **49**, 1897); this was also prepared from benzylurethane (Basterfield, Woods, and Wright, *J. Amer. Chem. Soc.*, 1926, **48**, 2372) *via* the nitroso-compound (Hantzsch and Lehmann, *Ber.*, 1902, **35**, 903). The basic products of the reaction between phenyldiazomethane (3 g.) and fluorenyldimethylamine (1·5 g.) were crystallised from methanol and from benzene–ligroin, giving 9-α-*dimethylaminobenzylfluorene* (40%), m. p. 164° (Found: C, 88·0; H, 7·3; N, 4·7. $C_{22}H_{21}N$ requires C, 88·2; H, 7·1; N, 4·7%). The *picrate* formed prisms (from alcohol), m. p. 188—189° (Found: N, 10·3. $C_{22}H_{21}N,C_6H_3O_7N_3$ requires N, 10·6%). The same base (mixed m. p.) was synthesised by heating 9-benzylidenefluorene (Thiele and Henle, *Annalen*, 1906, **347**, 290) with excess of dimethylamine at 110° for 3 hours; the product was extracted by dilute hydrochloric acid and liberated by ammonia.

Diazoacetophenone and Benzyldimethylamine.—The diazo-compound (Bradley and Robinson, *J.*, 1928, 1316) (0·7 g.) and base (2 g.) gave, after steam-distillation of unchanged benzyldimethylamine, a small quantity of ω-benzyl-ω-dimethylaminoacetophenone, prisms (from methanol), identified with an authentic specimen by mixed m. p.s of the base and of the picrate.

Benzoylphenyldiazomethane (Nenitzescu and Solomonica, *loc. cit.*) reacted vigorously with benzyldimethylamine, giving mainly diphenylketen.

Ethyl Diazoacetate and Fluorenyldimethylamine.—The ester (4 g.) and amine (2 g.) yielded a deep brown, uncrystallisable mixture of bases, after removal of fluorenyldimethylamine by steam-distillation. This mixture was refluxed for 2 hours with 20% potassium hydroxide solution, and then yielded on neutralisation only a small quantity of pale brown, sparingly soluble, microcrystalline, amphoteric material, m. p. 205—210° (decomp.). A similar experiment with diethyl diazomalonate [prepared from diethyl aminomalonate (Cerchez, *Bull. Soc.*

chim., 1930, **47**, 1279, 1282) by the method of Womack and Nelson (*Org. Synth.*, 1944, **24**, 56)] gave only a trace of basic material other than the original amine.

Diphenyldiazomethane and Benzyl Methyl Sulphide.—After interaction of the diazo-compound (8 g.) and the sulphide (4 c.c.; Thomson and Stevens, *J.*, 1932, 71) the mixture was distilled, giving successively unchanged sulphide, a series of deep blue fractions, and tetraphenylethylene. These intermediate fractions lost their colour (possibly that of thiobenzophenone) on storage, and more quickly when dissolved in alcohol or ligroin. Analysis suggested that a fraction, b. p. 130—135°/1—1·5 mm., was a mixture (Found: C, 80·6; H, 6·9; S, 6·3%). This material was instantly decolorised when warmed on the water-bath with 100% hydrogen peroxide in acetic acid; after 3 hours the solution was poured into water and the *product* crystallised from aqueous methanol: long prisms, m. p. 130—132° (Found: C, 68·1; H, 5·6; S, 10·9%; *M*, 302. $C_{17}H_{16}O_3S$ requires C, 68·0; H, 5·4; S, 10·7%; *M*, 300). Sulphuric acid also was produced. The product was insoluble in water, acid, and alkali.

Diphenyldiazomethane and Benzyl Methyl Ether.—The product from the reaction of the diazo-compound (6 g.) and benzyl methyl ether (6 c.c.) was treated with ether, and a mixture of tetraphenylethylene and benzophenone azine was filtered off. The filtrate deposited more solid on concentration, and was then distilled, giving (1) benzyl methyl ether, (2) a fraction, b. p. up to 140°/0·5 mm., and (3) a fraction, b. p. 140—165°/0·5 mm. Fraction (2) gave colourless, nitrogen-free prisms, m. p. 140°, from ethyl alcohol [Found: C, 79·6; H, 7·4; OMe, 23·8%; *M*, 230. Calc. for $C_{14}H_{12}(OMe)_2$: C, 79·3; H, 7·5; OMe, 25·6%; *M*, 242]. Hydrobenzoin dimethyl ether melts at 140—142° (Irvine and Weir, *J.*, 1907, **91**, 1390). Recrystallisation of fraction (3) from alcohol gave tetraphenylethane, m. p. and mixed m. p. 210° (Found: C, 93·2; H, 6·5. Calc. for $C_{26}H_{22}$: C, 93·4; H, 6·6%).

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THE UNIVERSITY, SHEFFIELD, 10.

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