829. *Degradation of Quaternary Ammonium Salts. Part IX.* Attempts to Prepare Presumed Intermediates having Co-ordinately Linked Carbon.*

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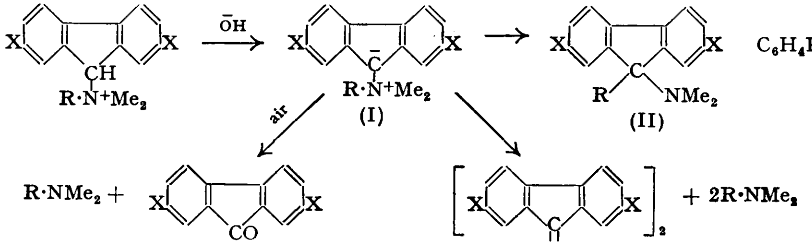
Attempts are described to isolate compounds of the type (I), or to demonstrate their presence. The alkylation of fluorenylidenefluorenylamine, offering a route to (V), could not be effected. This base reacts with nitromethane, giving 9-nitromethylenefluorene. Related work on materials containing the *p*-phenylphenacyl radical is described.

It is believed that the rearrangement,

$$\mathrm{Ph{\cdot}CO{\cdot}CH_2{\cdot}\overset{+}{N}Me_2{\cdot}CH_2Ph} \xrightarrow{\text{Alkali}} \mathrm{Ph{\cdot}CO{\cdot}\overset{-}{C}H{\cdot}\overset{+}{N}Me_2{\cdot}CH_2Ph} \longrightarrow \mathrm{Ph{\cdot}CO{\cdot}CH(NMe_2){\cdot}CH_2Ph},$$

proceeds, as shown, by way of an intermediate zwitterion. When the corresponding rearrangement of benzylfluorenyldimethylammonium salts was observed (S. F. Marrian, Thesis, Glasgow, 1941) to give a red oil which soon lost its colour, changing into 9-benzyl-9-dimethylaminofluorene (II; R = $\mathrm{CH_2Ph}$, X = H), it was natural to assume that the red oil was the unstable zwitterion (I) and to attempt the isolation of such materials in substance. During the progress of this work Wittig and Felletschin (*Annalen*, 1944, **555**, 133) solved the essential problem with the help of organo-lithium compounds as alkaline reagents, and we now present a summary of exploratory experiments and incidental observations.



$\mathrm{C_6H_4Ph{\cdot}CO{\cdot}CH_2{\cdot}NMe_3Br}$
(III)

As Ingold and Jessop (*J.*, 1929, 2357) could not isolate trimethylammonium 9-fluorenylide (I; R = Me, X = H), initial experiments were directed to the analogue (I;

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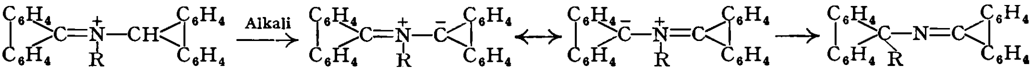
* Part VIII, *J.*, 1934, 279.

R = Me, X = Br) in the hope that it would be more stable and less soluble. Evaporation of a solution of 2 : 7-dibromofluorenyltrimethylammonium hydroxide gave a yellow precipitate which was easily oxidised in the air to dibromofluorenone and on attempted recrystallisation decomposed into trimethylamine and tetrabromodifluorenylidene. It was slightly soluble in water and on additon of hydrobromic acid yielded dibromofluorenyltrimethylammonium bromide. Attempts to combine the yellow compound with methyl iodide gave no decisive result.

Analogous experiments were carried out with trimethyl-*p*-phenylphenacylammonium bromide (III). The bromide gave with alkali a red product which could not be purified. Treatment of (III) with one equivalent each of methyl iodide and sodium methoxide, in the hope of converting any transient zwitterion into the salt $C_6H_4Ph{\cdot}CO{\cdot}CHMe{\cdot}NMe_3I$, yielded only the iodide corresponding to (III). Benzyldimethyl-*p*-phenylphenacylammonium bromide, when treated with alkali in presence or absence of methyl idoide, gave only the rearrangement product (IV) :

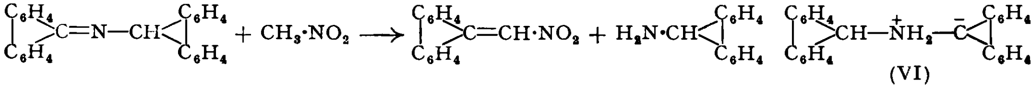
$$Ph{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}\overset{+}{N}Me_2{\cdot}CH_2Ph\}Br^- \longrightarrow Ph{\cdot}C_6H_4{\cdot}CO{\cdot}CH(CH_2Ph){\cdot}NMe_2 \qquad \text{(IV)}$$

It was thought that in a system offering an alternative site for the anionic charge, the postulated intermediate, for example (V), might be more stable :



(V)

This type of structure is the equivalent of that assigned by Staudinger to his nitrenes, which Taylor, Owen, and Whittaker (*J.*, 1938, 206) regard as ethyleneimine derivatives; here the peculiar character of the fluorene system would favour the linear zwitterionic structure. Numerous attempts to prepare quaternary salts of fluorenylidenefluorenylamine by combination with allyl and other alkyl halides and toluenesulphonates failed, and model experiments on the addition of alkyl halides and esters to benzylidenefluorenylamine and fluorenone methylimine were also unsuccessful. Fluorenylidenefluorenylamine, best prepared from 9 : 9-dialkoxyfluorene and fluorenylamine, was also formed when benzylidenefluorenylamine was treated with excess of fluorenylamine. The use of nitromethane as a solvent in experiments with fluorenylidenefluorenylamine led to the production of 9-nitromethylenefluorene, which could not be obtained directly from fluorenone and nitromethane :



(VI)

The *addition* of nitromethane to simpler azomethines is recorded (*e.g.*, Leonard, Leubner, and Burke, *J. Org. Chem.*, 1950, **15**, 979), giving products which yield alkylidenenitromethanes on treatment with acid.

In attempts to prepare the Schiff bases $[{\cdot}C_6H_4]_2 > CH{\cdot}N{:}CH{\cdot}CO{\cdot}Ph$ and $Ph{\cdot}CO{\cdot}CH_2{\cdot}N{:}CH{\cdot}COPh$ from phenylglyoxal and the appropriate amines, the only products obtainable were fluorenylidenefluorenylamine and 2 : 5-diphenylpyrazine respectively.

Pinck and Hilbert (*J. Amer. Chem. Soc.*, 1946, **68**, 2013), observing that difluorenylamine dissolves in liquid ammonia or in alcoholic alkali to deep-blue solutions, attributed the colour to the zwitterion (VI). We have observed a similar colour with fluorenylidenefluorenylamine, less intense colours with difluorenylalkylamines, and none with simple aminofluorenes or fluorenone imines. Benzylideneaminofluorene gives a red colour. A satisfactory interpretation of these colours is lacking.

EXPERIMENTAL

2 : 7 : 9-*Tribromofluorene.*—Bromine (2 mols.), added to 9-bromofluorene (1 mol.) in warm chloroform, caused a vigorous reaction, and the *product* crystallised from chloroform in colourless needles, m. p. 196—197° (Found : C, 38·7; H, 2·0; Br, 59·9. $C_{13}H_7Br_3$ requires C, 38·7;

H, 1·8; Br, 59·5%). By oxidation with potassium dichromate and sulphuric acid in acetic acid it gave 2 : 7-dibromofluorenone (mixed m. p.). Heated at 100° for 6 hours in chlorobenzene with a slight excess of trimethylamine, the tribromofluorene gave 2 : 7-*dibromo*-9-*fluorenyltrimethylammonium bromide* as a precipitate which crystallised from water in prisms, m. p. 210° (decomp.) (Found : C, 41·4; H, 3·7; N, 3·2; Br, 52·4. $C_{16}H_{16}NBr_3$ requires C, 41·6; H, 3·5; N, 3·0; Br, 51·9%) or in hydrated needles (Found : C, 39·5; H, 3·8; Br, 50·1. $C_{16}H_{16}NBr_3,H_2O$ requires C, 40·0; H, 3·8; Br, 50·0%).

Addition of caustic alkali to an aqueous solution of the quaternary bromide gave a yellow precipitate; this could not be freed from bromide ion by filtration and washing, and when dissolved in benzene or carbon tetrachloride quickly decomposed with formation of a high-melting red solid, presumably tetrabromodifluorenylidene. A solution of the bromide was treated with one equivalent of silver sulphate until free from bromide and silver ions, and the sulphate precipitated by an exact equivalent of barium hydroxide. The filtered solution was evaporated in a desiccator over sodium hydroxide, giving a white precipitate which became yellow. This again could not be purified; it was slightly soluble in water and was reconverted into the quaternary bromide on treatment with hydrobromic acid. Attempts to combine it with methyl iodide gave no decisive result. For comparison, the synthesis of the expected product, 2 : 7-dibromo-9-methyl-9-fluorenyltrimethylammonium iodide, was undertaken as follows. By treating 2 : 7-dibromo-9-methylfluoren-9-ol with hydrogen bromide, after Sieglitz and Jassoy (*Ber.*, 1922, **55**, 2032), 2 : 7 : 9-*tribromo*-9-*methylfluorene*, m. p. 190—191°, was obtained (Found : C, 40·5; H, 2·3; Br, 57·4. $C_{14}H_9Br_3$ requires C, 40·3; H, 2·1; Br, 57·5%). When heated with trimethylamine in chlorobenzene at 100° for 4 hours, it gave brownish crystals which formed pale-yellow needles, m. p. 205°, from benzene. This nitrogen-free compound was identical (mixed m. p.) with 2 : 7-dibromo-9-methylenefluorene (Sieglitz and Jassoy, *loc. cit.*).

2 : 7-*Dibromo*-9-*dimethylaminofluorene* was prepared by heating tribromofluorene with dimethylamine in benzene at 70—80° for 3 hours. Isolated *via* the sparingly soluble hydrochloride, the base crystallised from aqueous alcohol in needles, m. p. 80° (Found : N, 4·1. $C_{15}H_{13}NBr_2$ requires N, 3·8%). The *picrate* formed yellow leaflets (from acetic acid), m. p. 225—230° (decomp.) (Found : N, 9·6. $C_{15}H_{13}NBr_2,C_6H_3O_7N_3$ requires N, 9·4%).

Trimethyl-p-*phenylphenacylammonium Bromide*.—*p*-Phenylphenacyl bromide (Carpenter and Turner, *J.*, 1934, 870) combined with trimethylamine in cold benzene; the quaternary bromide, recrystallised from methanol, melted at 230° (decomp.) (Found : C, 61·4; H, 5·8; N, 4·2; Br, 23·8. $C_{17}H_{20}ONBr$ requires C, 61·1; H, 6·0; N, 4·2; Br, 23·9%); the related *picrate*, prepared in methanol, melted at 178° (Found : C, 57·4; H, 4·5; N, 11·5. $C_{17}H_{20}ON,C_6H_2O_7N_3$ requires C, 57·3; H, 4·6; N, 11·6%). A solution of the bromide in a slight excess of 2N-sodium hydroxide became red on being warmed; the mixture was allowed to evaporate on a steam-bath; a smell of trimethylamine became evident, and the dark-red residue, washed free from bromide ion with hot water, contained no nitrogen and melted at 142°. It became discoloured in daylight.

Trimethyl-*p*-phenylphenacylammonium bromide was heated under reflux in a slight excess of methyl-alcoholic sodium methoxide with methyl iodide for several hours. Ether then precipitated from the cooled solution crude trimethyl-*p*-phenylphenacylammonium iodide, which yielded the picrate, m. p. and mixed m. p. 178°. The last m. p. was depressed on admixture with trimethyl-α-methyl-*p*-phenylphenacylammonium picrate prepared as follows. Crystallised from benzene and from alcohol, 4-propionyldiphenyl melted at 96—97°; Long and Henze (*J. Amer. Chem. Soc.*, 1941, **63**, 1939) give 89°; Campbell and Chattaway (*Proc. Roy. Soc.*, 1942, *B*, **130**, 440) give 98°. Bromination in acetic acid at 50° gave the α-bromo-derivative, plates (from alcohol), m. p. 102—103° (Found : C, 61·7; H, 4·4; Br, 27·6. Calc. for $C_{15}H_{13}OBr$: C, 62·3; H, 4·5; Br, 27·7%). The same product was obtained by heating propionyldiphenyl with *N*-bromosuccinimide in a bath at 130° for several hours; it was extracted with carbon tetrachloride and crystallised from alcohol. The m. p. 79—80° is recorded by Collet (*Compt. rend.*, 1897, **125**, 306). The bromo-ketone was heated for an hour at 100° with trimethylamine in benzene; the resulting quaternary bromide crystallised from methanol–ether in needles, m. p. 218° (decomp.), and the derived *picrate*, prepared in methanol, had m. p. 186° (Found : C, 58·2; H, 4·9; N, 11·2. $C_{18}H_{22}ON,C_6H_2O_7N_3$ requires C, 58·1; H, 4·9; N, 11·3%).

Benzyldimethyl-p-*phenylphenacylammonium bromide* was rapidly formed from phenylphenacyl bromide and benzyldimethylamine in warm benzene. Crystallised from methanol–ether, it melted at 207° (decomp.) (Found : C, 67·5; H, 5·7; Br, 19·4. $C_{23}H_{24}ONBr$ requires C, 67·3; H, 5·9; Br, 19·5%). Addition of sodium hydroxide to the hot aqueous solution of the bromide caused rapid separation of a yellow oil, *ω-benzyl-ω-dimethylamino-*p*-phenylacetophenone*, which solidified on cooling and formed yellow crystals (from methanol), m. p. 103—104° (Found : C, 83·9; H, 6·8; N, 4·2. $C_{23}H_{23}ON$ requires C, 83·9; H, 7·0; N, 4·3%). The *methiodide*, prepared in hot methanol, crystallised from methanol–ether in pale yellow flakes, m. p. 194° (Found : C, 61·1; H, 5·4; I, 26·9. $C_{24}H_{26}ONI$ requires C, 61·2; H, 5·5; I, 27·0%). When the quaternary bromide was heated in methanol with sodium hydroxide or methoxide and methyl iodide, it gave only the methiodide of the rearranged product, m. p. 190°.

Fluorenylidenefluorenylamine.—In our hands the method of Ingold and Wilson (*J.*, 1933, 1499) gave yields of only 7%. Slightly better results were obtained by refluxing equimolecular quantities of sodium ethoxide, fluorenylamine hydrochloride, and fluorenone in anhydrous alcohol for 6—7 hours. The deep green colour of the filtered solution faded on cooling, and pale yellow fluorenylidenefluorenylamine separated on cooling. Alternatively fluorenylamine hydrochloride (5 g.) was treated with excess of alkali, and the base dissolved in toluene (70 c.c.). To the toluene solution 9 : 9-dimethoxyfluorene (Schlenk and Bergmann, *Annalen*, 1929, **463**, 199) (5·2 g.) was added and the whole refluxed for several hours. The oily residue from the evaporation of the toluene, taken up in alcohol, afforded crystals of fluorenylidenefluorenylamine (1·7 g.).

The Schiff base did not combine with methyl iodide or sulphate in boiling benzene. Boiled for some hours with methyl sulphate in nitromethane it gave, on concentration after filtration, dark brown crystals of *9-nitromethylenefluorene* which crystallised from benzene in brown needles, m. p. 133—134° (Found : C, 75·9; H, 4·1; N, 5·9. $C_{14}H_9O_2N$ requires C, 75·3; H, 4·0; N, 6·3%). The same substance was produced by heating the base in nitromethane alone; but not from fluorenone and nitromethane, alone or in presence of sodium methoxide or zinc chloride. Prolonged refluxing of fluorenylidenefluorenylamine with allyl iodide, alone or in xylene, gave small quantities of brown solid which could not be purified.

Allyl toluene-*p*-sulphonate (Gilman and Beaber, *J. Amer. Chem. Soc.*, 1925, **47**, 522) distilled at 135—140°/0·5—1·0 mm. without explosion or conspicuous decomposition. The ester (0·6 g.) was refluxed for 5 hours with the Schiff base (0·5 g.) in dry toluene (25 c.c.) with exclusion of moisture. Orange crystals separated which melted at 240° (decomp.). They were identified as *9-iminofluorene toluene-*p*-sulphonate* by analysis (Found : C, 68·0; H, 4·8; S, 9·0. $C_{13}H_9N,C_7H_8O_3S$ requires C, 68·4; H, 4·8; S, 9·1%) and by mixed m. p. of iminofluorene, liberated by sodium hydroxide and crystallised from ligroin. The same product was obtained when the base and ester were heated alone at 100°.

Benzaldehyde and fluorenylamine afforded (Schmidt, *Ber.*, 1908, **41**, 1243) benzylideneaminofluorene (71%) with some fluorenylideneaminofluorene. The latter azomethine is produced in quantity when the former is heated under reflux with excess of aminofluorene in alcohol for several hours. A solution of benzylideneaminofluorene (2 g.) in freshly distilled methyl iodide (4 c.c.) was kept in the dark for several months. The resulting solid was resolved into fractions, m. p. 240—241° (decomp.) and 177° (decomp.), by crystallisation from chloroform–ligroin. The latter, very pale yellow needles, appeared to be *fluorenylmethylamine hydriodide* (Found : C, 52·4; H, 4·3; I, 39·1. $C_{14}H_{14}NI$ requires C, 52·1; H, 4·4; I, 39·3%); the corresponding *picrate*, yellow needles from alcohol, melted at 210° (decomp.) (Found : N, 13·4. $C_{14}H_{13}N,C_6H_3O_7N_3$ requires N, 13·2%). The higher-melting fraction, of variable composition, gave an evanescent blue colour when boiled in alcoholic sodium ethoxide solution; and the basic product of this reaction yielded the picrate, m. p. 210° (decomp.). The same picrate was isolated when the azomethine and methyl sulphate were refluxed in dry ethyl acetate.

9-Methyliminofluorene was prepared by Reddelien's method (*Ber.*, 1921, **54**, 3130) which also afforded much difluorenyl and difluorenylidene. It did not combine with 9-bromofluorene or with phenacyl bromide on long boiling in toluene or under other conditions.

In an attempt to prepare 9-fluorenyl toluene-*p*-sulphonate, fluoren-9-ol (1·8 g.) was fused with toluene-*p*-sulphonyl chloride (2·5 g.) and the finely ground mass shaken for several hours with 5% potassium hydroxide solution. The only isolable product was difluorenyl ether, m. p. 228° (Found : C, 89·8; H, 5·2. Calc. for $C_{26}H_{18}O$: C, 90·1; H, 5·2%). Diazofluorene (2 g.) and toluene-*p*-sulphonic acid (6 g.; dried at 120°) were allowed to react in benzene solution. The washed and dried liquid gave on evaporation a solid evidently containing difluorenylidene. Crystallised from amyl alcohol, this yielded difluorenyl, m. p. and mixed m. p. 245° (Found : C, 94·8; H, 5·4. Calc. for $C_{26}H_{18}$: C, 94·6; H, 5·4%).

Freshly distilled phenylglyoxal (Riley and Gray, *Org. Synth.*, 1935, **15**, 67) was heated under reflux with pure fluorenylamine in alcohol for 30 minutes. The resulting solid crystallised from alcohol in fine yellow needles, identical (mixed m. p.) with fluorenylidenefluorenylamine (Found :

C, 90·8; H, 5·0. Calc. for $C_{26}H_{17}N$: C, 90·9; H, 5·0%). Phenylglyoxal (3·2 g.), ω-aminoacetophenone hydrochloride (3·5 g.), and sodium carbonate (2 g.) were heated on the water-bath for 30 minutes. Alcohol then extracted from the mixture 2 : 5-diphenylpyrazine, m. p. 195°, and no phenacylideneacetophenone could be isolated. Phenylglyoxal did not react with aminoacetophenone hydrochloride in boiling alcohol.

Colour Reactions of Fluorenylamine Derivatives.—A solution of difluorenylamine (0·15 g.) in liquid ammonia (6 c.c.) was deep blue and remained so for over 2 years (cf. Pinck and Hilbert, *loc. cit.*). *Difluorenylmethylamine* gave similarly a pale blue-green colour in liquid ammonia and a blue colour in alcoholic sodium ethoxide. This base was obtained from difluorenylamine (m. p. 201°; 0·4 g.) which was kept for 8 hours with formic acid (1·4 c.c.) and 35% formaldehyde solution (0·9 c.c.) and then heated on the water-bath for 4 hours. Concentrated hydrochloric acid was added in slight excess, the solution evaporated to dryness, and the free base (0·35 g.) liberated and crystallised from benzene–ligroin. It formed large prisms, m. p. 153° (Found: C, 90·2; H, 6·0. $C_{27}H_{21}N$ requires C, 90·3; H, 5·9%). *Allyldifluorenylamine* dissolved in alcoholic sodium ethoxide solution containing a little acetone with a blue-green colour which persisted for several hours. It was prepared by refluxing 9-bromofluorene (1·2 g.) and allylamine (0·6 c.c.) in acetonitrile (3 c.c.) for 30 minutes. The solid hydrobromide gave on basification allyldifluorenylamine, prisms, m. p. 195°, from benzene–ligroin (Found: C, 90·7; H, 5·9. $C_{29}H_{23}N$ requires C, 90·4; H, 5·9%). Fluorenylidenefluorenylamine gave an intense blue colour in warm alcoholic sodium ethoxide, and benzylidenefluorenylamine a red colour. No colours were given by 9-anilino-, 9-methylimino-, or 9-phenylimino-fluorene.

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