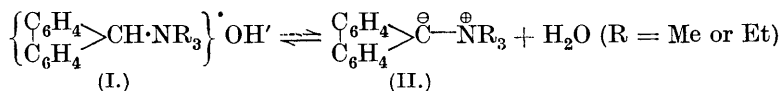


XCV.—*Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part IX. Isolation of a Substance believed to contain a Semipolar Double Linking with Participating Carbon.*

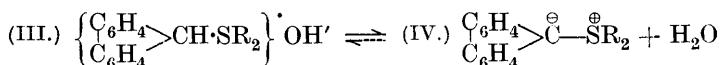
By CHRISTOPHER KELK INGOLD and JOE ARTHUR JESSOP.

IN Part VI it was noted (J., 1929, 2357) that, whilst fluorenyl-9-trimethylammonium and fluorenyl-9-triethylammonium bromides are colourless, the aqueous solutions of the corresponding hydroxides are coloured; and the suggestion was made (p. 2359, footnote) that

in either case the hydroxide (I) might be in equilibrium with an anhydride (II) which, since it contains unshared carbon electrons, would probably be coloured and highly reactive. The special structural feature of (II) is the semipolar double linking with carbon at its negative end, and since no compound containing a semipolar double bond between carbon and another element has hitherto been described, attempts were made to isolate the coloured substance :



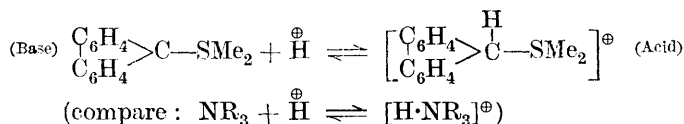
At the outset it was obvious that (II) could not be present in high concentration, for if it were it should be precipitated; it was not precipitated and the coloured solution was strongly alkaline. Probably the low concentration and the instability of the compound (see Part VI) conspired to defeat the attempts at isolation. We reflected, however, that (II) is analogous to the trialkylamine oxides, $\overset{\ominus}{\text{O}} - \overset{\oplus}{\text{N}}\text{R}_3$, which have low thermal stability and a strong tendency to combine with water to form trialkylhydroxylammonium hydroxides, $\{\text{OH} \cdot \text{NR}_3\}' \text{OH}'$, analogous to (I); and, further, that dialkylsulphoxides, $\overset{\ominus}{\text{O}} - \overset{\oplus}{\text{S}}\text{R}_2$, have much higher thermal stability and exhibit very little tendency to effect an analogous union with water. It followed that a study of the corresponding fluorenyl-sulphonium compounds (III and IV) might reveal an equilibrium much more favourable to the form which it was desired to isolate, and that the anhydride (IV), despite its negative carbon, might possess sufficient thermal stability to permit of isolation :



The initial difficulty here was to prepare a fluorenyl-9-dialkyl-sulphonium salt. 9-Bromofluorene and dimethyl sulphide showed little tendency to combine either in ether or in benzene or without a solvent; furthermore, attempts to prepare 9-fluorenyl mercaptan by the action of alkali sulphides on 9-bromofluorene led to the formation of 9:9-difluorenyl. At this juncture Richardson and Soper's paper appeared (J., 1929, 1873) in which their cohesion principle was enunciated; perusal of this memoir made it immediately obvious (a) that the combination of 9-bromofluorene with dimethyl sulphide should be strongly catalytically accelerated by a solvent of high cohesion, and (b) that the tendency to thermal decomposition of the required sulphonium bromide, which sets a limit to the temperatures that can be used in its synthesis, would be reduced by such a solvent. Actually, effect (a) was so powerful

that there was no need to make use of the presumed increased stability of the product at high temperatures : we mixed the reagents in nitromethane at the ordinary temperature and observed a rapid and almost quantitative formation of the sulphonium bromide. Several other successful applications of the cohesion principle have since been made in these laboratories, and there can be no doubt about its practical utility in the replacement of empirical by rational technique in synthetic operations.

When a solution of *fluorenyl-9-dimethylsulphonium bromide* was treated with excess of silver oxide, the filtrate was practically neutral. When sodium hydroxide or aqueous ammonia was used instead of silver oxide, *dimethylsulphonium 9-fluorenylidide* (IV; R = Me) was obtained as a yellow crystalline precipitate. It was sufficiently stable to admit of analysis and the determination of its molecular weight in benzene, but after some hours decomposition set in with evolution of dimethyl sulphide. Details relating to the thermal decomposition of the substance are given in the experimental portion, and it will suffice to note here that, although the compound resembles sulphoxides in refusing to form a sulphonium hydroxide by addition of water, it is definitely more basic than are sulphoxides, since it at once reacts with dilute hydrochloric acid, forming the corresponding fluorenyl-9-dimethylsulphonium salt. This is essentially a reversal of the reaction whereby dimethylsulphonium 9-fluorenylidide is formed, and thus it may be said that the constitutional environment of the 9-carbon atom confers on it properties analogous to those of a nitrogen atom :



The probable mechanism underlying this conferment of nitrogen-like properties on carbon is sufficiently indicated in Part VI.

EXPERIMENTAL.

Fluorenyl-9-dimethylsulphonium Salts.—The *bromide*, irregular hexagonal plates, m. p. 133° (Found : Br, 26·4. C₁₅H₁₅BrS requires Br, 26·1%), was prepared, as described in the introduction, in cold nitromethane solution, from which it crystallised. The *picrate*, precipitated by addition of aqueous sodium picrate to a solution of the bromide in water, separated from hot water in needles, m. p. 149—150° (Found : C, 55·6; H, 4·0. C₂₁H₁₇O₇N₃S requires C, 55·4; H, 3·7%).

9 : 9-*Difluorenyl*.—Prior to the above experiments attempts were

made to prepare the same salts by way of fluorenyl mercaptan or sulphide. 9-Bromofluorene and alcoholic sodium hydrogen sulphide were kept together over-night in the cold and the solution was then distilled to half its bulk, poured into water, and made alkaline. 9-Bromofluorene and alcoholic disodium sulphide were similarly kept in the cold and then heated for 2 hours in the steam-bath and poured into water. In each case a crystalline precipitate was obtained which was recrystallised from benzene and identified as 9 : 9-difluorenyl by its m. p. (242—244°) and by analysis (Found : C, 94.8; H, 5.6. Calc. : C, 94.5; H, 5.5%).

Action of Bases on Fluorenyl-9-dimethylsulphonium Bromide : Dimethylsulphonium 9-Fluorenylidide.—(a) *Water.* The sulphonium bromide was heated on a water-bath with water for 2 hours. Dimethyl sulphide was evolved (odour) and 9-fluorenyl alcohol precipitated (m. p. and mixed m. p.). In order to substantiate the obvious explanation of this decomposition, 9-bromofluorene was similarly heated with water; 9-fluorenyl alcohol was then formed in quantity.

(b) *Silver oxide.* On addition of excess of freshly precipitated carbonate-free silver oxide to a cold aqueous solution of the sulphonium bromide, the solution remained practically neutral. Heating the suspension on a water-bath caused the evolution of dimethyl sulphide (odour) and the formation of 9-fluorenyl alcohol (m. p. and mixed m. p.), a large quantity of which separated when the filtrate from the hot suspension was cooled. Extraction of the dried silver oxide residue with benzene yielded a red gum similar in appearance and properties to the non-volatile thermal-decomposition product of dimethylsulphonium 9-fluorenylidide (below).

(c) *Soluble alkalis.* Sodium acetate and sodium carbonate gave no precipitate with an aqueous solution of the sulphonium bromide; but aqueous ammonia, barium hydroxide, and sodium hydroxide yielded *dimethylsulphonium 9-fluorenylidide* as yellow leaflets, m. p. ca. 70—75° (decomp.), on rapid heating, which were washed with water, alcohol, and ether and dried for several hours in a vacuum. It was insoluble in water and ether, slightly soluble in alcohol, and readily soluble in ethyl acetate and benzene (Found : C, 80.3; H, 6.2; *M*, cryoscopic in benzene, 215, 226. $C_{15}H_{14}S$ requires C, 79.6; H, 6.2%; *M*, 226). The compound began to darken and develop the odour of dimethyl sulphide after exposure to the atmosphere for a few hours (sooner if placed in a closed tube), but could be kept in a vacuum for about 24 hours with little if any signs of decomposition. In solution, however, decomposition was more rapid and the above molecular-weight determination requires explanation. Preliminary experiments showed that in benzene at

its freezing point the decomposition began to be perceptible soon after solution, and that for several hours thereafter there was a steady diminution in the apparent molecular weight. The determinations were therefore plotted against time and extrapolated to zero time. A sample, dried in a vacuum for 2 hours, gave values ranging from 196 to 153 and the extrapolated value at the moment of solution was 215. Another preparation, which had been similarly dried for 16 hours, gave values falling from 209 to 183 and the extrapolated result was 226.

Reactions of Dimethylsulphonium 9-Fluorenylidide.—The freshly prepared compound is immediately soluble in cold dilute hydrochloric acid. The solution contains fluorenyl-9-dimethylsulphonium chloride, as is proved by the observations that it yields dimethylsulphonium 9-fluorenylidide on treatment with ammonia, and fluorenyl-9-dimethylsulphonium picrate with aqueous sodium picrate.

The nature of the non-volatile product formed in the spontaneous decomposition which takes place at atmospheric pressure and temperature could not be elucidated. The evolution of dimethyl sulphide, which became perceptible after a few hours, was apparently complete after 4 days, and the residue was a brown amorphous substance which still contained sulphur but could not be crystallised. It was wholly insoluble in hot concentrated hydrochloric acid. By use of benzene and glacial acetic acid and other solvents, various orange and red amorphous products were obtained from it, but none could be crystallised.

Similar results were obtained more quickly by heating, and in this case the dimethyl sulphide was identified by passing the evolved gases through mercuric chloride solution and identifying the precipitated additive compound, $3\text{HgCl}_2 \cdot 2\text{Me}_2\text{S}$, by mixed m. p. and direct comparison. When the same decomposition was carried out in a diffusion-pump vacuum connected to the top of a mercury barometer, dimethyl sulphide condensed on the mercury, the depression of which, allowing for the vapour pressure of the sulphide, showed that no gas of the type of methane or ethylene was evolved; the sulphide was afterwards collected and converted into trimethylsulphonium iodide for confirmatory identification. The resinous residue (Found: C, 88.7; H, 5.4%) contained sulphur and could not be crystallised; on being strongly heated, it gave a crystalline distillate which proved to be fluorene (m. p. and mixed m. p.).

The solubility of dimethylsulphonium 9-fluorenylidide in acids suggested that it should add on methyl iodide. The reaction was tried under various conditions, but the addition, if any, was masked by the separation of dimethyl sulphide and its conversion into

trimethylsulphonium iodide, decomp. 207—210° (Found : I, 62·5. Calc., 62·2%); the remaining product was amorphous.

The investigation has been aided by a grant from the Royal Society, whom we wish to thank.

THE UNIVERSITY, LEEDS.

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