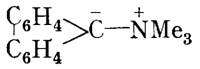
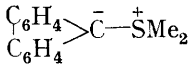
382. *Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part XXIII. Stable Derivatives of the Tercovalent-carbon Compound of Ingold and Jessop.*

By E. D. Hughes and K. I. Kuriyan.

It was observed by Ingold and Jessop (J., 1929, 2357) that solutions of fluorenyl-9-trimethylammonium hydroxide were deeply coloured and it was suggested that the hydroxide might be in equilibrium with an anhydride (I).

(I.) 

$$\left.\begin{array}{l}C_6H_4\\ C_6H_4\end{array}\right>\overset{-}{C}-\overset{+}{N}Me_3$$

 (II.)

$$\left.\begin{array}{l}C_6H_4\\ C_6H_4\end{array}\right>\overset{-}{C}-\overset{+}{S}Me_2$$

Later (J., 1930, 713) the same authors isolated the sulphonium analogue (II), but it was unstable at the ordinary temperature. It was desirable, therefore, to attempt to stabilise this unique compound by the introduction of suitable substituents. Structures of the type $R'R''R'''\overset{-}{C}$ have usually a transient existence, but they should be stabilised by increasing the positive electrical field over the region of the negative carbon atom. We have therefore studied the mono- and di-nitro-derivatives of (II).

The introduction of one nitro-group was effected by using 9-bromo-2-nitrofluorene (preceding paper) as the starting point for the preparation of the sulphonium salt. The action of sodium hydroxide or aqueous ammonia on 2-*nitrofluorenyl*-9-*dimethylsulphonium bromide* or *picrate* gave *dimethylsulphonium* 9-[2-*nitrofluorenylidide*]. This is a purple substance, which can be crystallised from acetone, and kept for several days without decomposition, although eventually a slight odour of dimethyl sulphide is developed. Decomposition can be effected by heating in nitromethane solution: the non-volatile product was 2 : 2′-dinitrobisdiphenylene-ethylene, as was proved by analysis and by oxidation to 2-nitrofluorenone.

The introduction of two nitro-groups into 9-bromofluorene inhibited sulphonium salt formation with dimethyl sulphide. Fluorenyl-9-dimethylsulphonium picrate, however, on direct nitration gave a dinitro-derivative, which was identified as 2 : 7-*dinitrofluorenyl-9-dimethylsulphonium picrate* by heating with hydrogen bromide in acetic acid, and comparing the 9-bromo-2 : 7-dinitrofluorene formed with an authentic specimen (preceding paper). *Dimethylsulphonium* 9-[2 : 7-*dinitrofluorenylidide*], obtained by treating the picrate with alkali, shows no sign of decomposition at the ordinary temperature. In appearance it resembles potassium permanganate both in the crystalline state and in solution, although it is soluble only in organic solvents and not in water alone. Like permanganate also, it acts as its own indicator in volumetric estimation : it reacts instantly with acids, giving colourless 2 : 7-dinitrofluorenyl-9-dimethylsulphonium salts, and the discharge of the purple fluorenylidide colour marks the end-point. Heated in nitromethane solution, it gives dimethyl sulphide and 2 : 2′ : 7 : 7′-*tetranitrobisdiphenylene-ethylene*.

In view of the observations of Ingold and Jessop concerning the relative stability and ease of isolation of ammonium and sulphonium fluorenylidides, it was of interest to examine the corresponding selenonium compound. The action of aqueous alkali or ammonia on *fluorenyl-9-dimethylselenonium bromide* gave a black precipitate, soluble in organic solvents to form purple solutions. It was very unstable, decomposing rapidly with evolution of dimethyl selenide even at room temperature. Search for other stable fluorenylidides is being continued.

EXPERIMENTAL.

2-*Nitrofluorenyl-9-dimethylsulphonium Salts*.—The *bromide* crystallised when 9-bromo-2-nitrofluorene (preceding paper) and dimethyl sulphide were mixed in nitromethane and left over-night at room temperature; it was washed with ether (Found : C, 51·3; H, 4·1. $C_{15}H_{14}O_2NBrS$ requires C, 51·1; H, 4·0%). It decomposed slowly above 130°, giving off dimethyl sulphide, and melted with vigorous decomposition at about 135°, giving 9-bromo-2-nitrofluorene, m. p. 145°, after crystallisation from alcohol. The same products were obtained in an attempt to recrystallise the salt from aqueous alcohol. The corresponding *picrate* was prepared in the usual way with sodium picrate and crystallised from acetone; m. p. 185°, with decomposition into a red liquid (Found : C, 50·6; H, 3·4. $C_{21}H_{16}O_9N_4S$ requires C, 50·4; H, 3·2%).

Action of Bases on 2-*Nitrofluorenyl-9-dimethylsulphonium Salts*.—The action of soluble alkalis on an aqueous, alcoholic, or acetone suspension of the sulphonium salts yielded *dimethylsulphonium* 9-[2-*nitrofluorenylidide*] as a purple precipitate, and a similar but much less complete reaction took place with water alone. The fluorenylidide was prepared in a pure condition as follows : The sulphonium salt was agitated with an excess of concentrated aqueous ammonia, and sufficient acetone added to dissolve the product. The solution was filtered, an equal volume of water added gradually, and the crystalline precipitate obtained was collected, washed with aqueous acetone, and recrystallised from acetone. It formed dark purple needles, easily soluble in nitromethane, ethyl acetate, chloroform, and acetone, giving deep red solutions, sparingly soluble in benzene, carbon tetrachloride, and alcohol, and insoluble in water, ether, and light petroleum (Found : C, 66·5; H, 4·7. $C_{15}H_{13}O_2NS$ requires C, 66·4; H, 4·8%). The nitrofluorenylidide is markedly more stable than its unsubstituted analogue (Ingold and Jessop, *loc. cit.*) as indicated by the fact that the above analysis, made 2 days after its isolation, is satisfactory. On prolonged keeping in a closed vessel, however, it develops a slight odour of dimethyl sulphide. The evolution of sulphide is accelerated by heating; the compound shows no sign of melting at 300°, but the decomposition is accompanied by a change in colour from dark purple to brown. It decomposes slowly in suspension in boiling water and more rapidly in solution in certain organic solvents. It combines immediately with acids, forming 2-nitrofluorenyl-9-dimethylsulphonium salts (compare Ingold and Jessop, *loc. cit.*).

2 : 2′-*Dinitrobisdiphenylene-ethylene*.—The fluorenylidide was dissolved in nitromethane, and the solution boiled. The red colour was rapidly destroyed, dimethyl sulphide was evolved, and decomposition was complete in a few minutes. The reddish compound obtained was insoluble in the usual solvents; crystallised from acetophenone, it had m. p. 300° (compare

Bergmann, Hoffmann, and Winter, *Ber.*, 1933, **66**, 46) (Found : C, 74·9; H, 3·5. Calc. : C, 74·6; H, 3·4%).

Oxidation of 2 : 2′-*Dinitrobisdiphenylene-ethylene.*—The ethylene (1 g.), suspended in glacial acetic acid (10 c.c.), was refluxed with sodium dichromate (5 g.) for 24 hours. The mixture was cooled and the crystalline compound formed was collected and recrystallised from acetic acid; m. p. and mixed m. p. with 2-nitrofluorenone 221°.

2 : 7-*Dinitrofluorenyl*-9-*dimethylsulphonium Salts.*—(a) *Picrate.* Fluorenyl-9-dimethylsulphonium picrate (10 g.) (Ingold and Jessop, J., 1930, 713) was added little by little to nitric acid (25 c.c., *d* 1·5) at − 15°. The temperature was allowed to rise slowly to 0°; the mixture was kept at this temperature for 15 hours and then poured into ice-water. The yellow solid obtained was washed with water, and crystallised from acetone in the presence of a little picric acid; m. p. 180° (decomp. into a red liquid) (Found : C, 46·4; H, 2·9. $C_{21}H_{15}O_{11}N_5S$ requires C, 46·2; H, 2·8%). The orientation of the nitro-groups was effected as follows : The *picrate* (2 g.) was refluxed with hydrogen bromide in acetic acid (30% solution, 10 c.c.) for 30 minutes. The mixture was cooled, and the crystalline product was washed with alcohol and recrystallised from acetone; m. p. and mixed m. p. with 9-bromo-2 : 7-dinitrofluorene (preceding paper) 255—260° (decomp.). The ketone obtained by the oxidation of the bromide with chromic acid in glacial acetic acid was identical in all respects with 2 : 7-dinitrofluorenone.

(b) *Bromide.* Dimethylsulphonium 9-[2 : 7-dinitrofluorenylidide] (below) was dissolved in acetone, and concentrated hydrobromic acid added until the pink colour was destroyed. The white crystalline product was washed with acetone (Found : Br, 20·0. $C_{15}H_{13}O_4N_2BrS$ requires Br, 20·2%). An attempt to recrystallise it from alcohol resulted in the formation of dimethyl sulphide (identified by its additive compound with mercuric chloride) and 9-bromo-2 : 7-dinitrofluorene (identified by direct comparison). When heated alone, it decomposed, evolving dimethyl sulphide, and finally melted with rapid decomposition at about 230°, giving 9-bromo-2 : 7-dinitrofluorene. An attempt to prepare the sulphonium bromide from 9-bromo-2 : 7-dinitrofluorene and dimethyl sulphide in nitromethane solution was unsuccessful.

Dimethylsulphonium 9-[2 : 7-*dinitrofluorenylidide*] was prepared from the above salts as described for the 2-nitro-analogue. It separated from acetone in prismatic crystals resembling potassium permanganate in appearance. It was insoluble in water, alcohol, benzene, ether, light petroleum, and carbon tetrachloride, slightly soluble in chloroform, and readily soluble in acetone, nitromethane, and ethyl acetate, forming deep permanganate-coloured solutions [Found: C, 57·0; H, 3·8; *M* (by titration with acid; cf. p. 1610), 315, 312. $C_{15}H_{12}O_4N_2S$ requires C, 56·9; H, 3·8%; *M*, 316].

Decomposition of Dimethylsulphonium 9-[2 : 7-*Dinitrofluorenylidide*].—The compound evolved dimethyl sulphide above 150° with little change in appearance, but when heated strongly it became brick-red and finally decomposed violently with a flash of light. It appeared to be unattacked by boiling water, and decomposed very slowly in boiling acetone, but in boiling nitromethane the purple colour was rapidly destroyed, dimethyl sulphide was copiously evolved, and orange-coloured 2 : 2′ : 7 : 7′-*tetranitrobisdiphenylene-ethylene* was precipitated. This was crystallised from acetophenone and washed with acetone; m. p. > 300° (Found : C, 61·7; H, 2·5; N, 11·1. $C_{26}H_{12}O_8N_4$ requires C, 61·4; H, 2·4; N, 11·0%). Oxidation with chromic acid in glacial acetic acid as described for the mononitro-analogue gave 2 : 7-dinitrofluorenone, m. p. and mixed m. p. 292°.

Fluorenyl-9-*dimethylselenonium Bromide.*—Dimethyl selenide (1 g.) (Jackson, *Annalen*, 1875, **179**, 1) and 9-bromofluorene (2·5 g.) were mixed in nitromethane (15 c.c.). After 30 minutes, *fluorenyl*-9-*dimethylselenonium bromide* crystallised in almost quantitative yield; recrystallised from nitromethane, it formed white plates, m. p. 134—135° (Found : C, 50·7; H, 4·4. $C_{15}H_{15}BrSe$ requires C, 50·8; H, 4·2%). The corresponding *picrate*, crystallised from alcohol, had m. p. 143° (Found : C, 50·0; H, 3·5; N, 8·3. $C_{21}H_{17}O_7N_3Se$ requires C, 50·2; H, 3·4; N, 8·4%).

When the bromide was refluxed with water for 30 minutes, dimethyl selenide was evolved and 9-fluorenyl alcohol precipitated (compare Ingold and Jessop, J., 1930, 716).

We are much indebted to Professor C. K. Ingold, F.R.S., who suggested the subject, for his advice and encouragement.

UNIVERSITY COLLEGE, LONDON. [*Received, October 3rd*, 1935.]