XCIV.—*Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part VIII. The Methylenic and Paraffinic Degradations of Sulphones.*

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The following scheme summarises the three known ways in which a radical may be eliminated as a hydrocarbon in the thermal degradation of an " onium " hydroxide. The table also indicates the conclusions which have been reached with regard to the characteristics of the ejected radical which favour each mode of elimination and the changes necessitated in the electron-groups (Hanhart and Ingold, J., 1927, 997; Ingold and Vass, J., 1928, 3125; Fenton and Ingold, J., 1929, 2342; Ingold and Jessop, *ibid.*, p. 2357).

		Eliminated radical.		Valency octets of	
Elimination reaction.	Eliminated as	Structural requirement.	Facilitation by electron-sink at	" onium " element.	hydrocarbon radical.
(1) Olefinic	R *minus* H_β	H_β	C_β	Preserved	Preserved
(2) Methylenic	R *minus* H_α*	H_α	C_α	Preserved	To *sextet*
(3) Paraffinic	R *plus* H_α	—	C_α	To *decet*	Preserved

* The bivalent carbon compound may polymerise or isomerise.

Reaction (1), which preserves all octets, is common to ammonium and phosphonium hydroxides. In the former series, when the constitutional conditions inhibit (1) and strongly favour (2) and (3), the observed reaction is (2), and not (3); this is connected with the presumed inability of nitrogen to enlarge its octet (Sidgwick). In the latter series, when (1) is suppressed, the observed reaction is not (2), but (3); it is inferred that the phosphorus octet has a considerable tendency towards enlargement. Fenton and Ingold have shown (J., 1928, 3127; 1929, 2338; preceding paper) that sulphones in the presence of alkali undergo reaction (1); it remained to discover which type of decomposition, (2) or (3), would supervene when (1) was inhibited. The answer, contained in this paper, is that both occur; and that sulphone sulphur apparently shares, on the one hand, the tendency of phosphonium phosphorus to enlarge its electron group, and, on the other, the ability of ammonium nitrogen to deplete the electron group of a neighbouring carbon atom:

$$\begin{array}{llll} R_4N^{\cdot} + OH' \longrightarrow (1) & (2) & — \\ R_4P^{\cdot} + OH' \longrightarrow (1) & — & (3) \\ R_2SO_2 + OH' \longrightarrow (1) & (2) & (3) \end{array}$$

The following table summarises the observations. In two of the sulphones examined, no α-hydrogen atom was present and methylenic degradation was therefore impossible; these underwent paraffinic decomposition. In the remaining five examples an α-hydrogen atom was present, and both reactions were shown to proceed side by side, with the exceptions that in one case the evidence for paraffinic degradation, and in another the evidence that the same decomposition occurs in a second direction, is incomplete (indicated by parentheses in the table). It should also be mentioned that whereas the extrusion of methylene and benzylidene was diagnosed by the recovery of ethylene and stilbene respectively, the bis-*oo'*-diphenylylene-ethylene into which fluorenylidene would be expected to pass was not isolated as such, but as diphenyl-*o*-carboxylic acid, into which the unsaturated hydrocarbon is known to pass in the presence of alkali under the conditions employed.

	Sulphone $RR'SO_2$.		Group eliminated as hydrocarbon.	
	Group R.	Group R′.	Reaction (2).	Reaction (3).
H_α absent	Phenyl	Phenyl		Phenyl
	p-Tolyl	9-Phenyl-9-fluorenyl		Phenylfluorenyl
H_α present	*p*-Tolyl	9-Fluorenyl	Fluorenyl	Fluorenyl
	Benzyl	Benzyl	Benzyl	(Benzyl)
	Phenyl	Benzyl	Benzyl	Benzyl
	Methyl	Benzyl	Benzyl	Benzyl
	Methyl	*p*-Tolyl	Methyl	Methyl (*p*-tolyl)

In the above series methylenic elimination (reaction 2) has been observed with three groups, namely, fluorenyl, benzyl and methyl. In the ammonium hydroxide series, apparently only the first of these is capable of this form of extrusion : stilbene and ethylene have never been proved to arise in the decompositions of ammonium hydroxides containing only benzyl or methyl groups. Furthermore, the direction of the methylenic decomposition of benzylmethylsulphone shows that the reaction is more prone to occur with the benzyl than with the methyl group. Hence the complete order of facility of methylenic extrusion is 9-fluorenyl > benzyl > methyl; which is the order of anionic stability, as the theory of the reaction demands (Fenton and Ingold, J., 1929, 2342; Ingold and Jessop, *loc. cit.*). This statement will be understood to relate only to *one* of the several factors which it would be necessary to envisage in a *general* discussion of bivalent carbon stability.

As regards the paraffinic degradation of sulphones (reaction 3), it need be stated only that the order in which the radicals examined tend to this form of elimination is consistent with that found in connexion with the thermal decomposition of phosphonium hydroxides. Actually the relation, fluorenyl > simple aryl, is additional; but it constitutes a further confirmation of the view that tendency to ejection increases with the anionic stability of the group.

EXPERIMENTAL.

Preparation of Sulphones.—9-Bromofluorene (10 g.) was heated for 15 minutes on the steam-bath with a solution prepared from sodium *p*-toluenesulphinate dihydrate (12 g.) and alcohol (20 c.c.) Sodium bromide separated, and the mixture was evaporated to dryness, and the residue heated for 1 hour at 100° in a stream of dry air to dehydrate the excess of sodium salt. The dried product was extracted repeatedly with boiling benzene until the extracts failed to crystallise on cooling. *9-Fluorenyl-*p*-tolylsulphone* separated in iridescent plates (12·5 g.), m. p. 226—227° (Found : C, 75·2; H, 5·2. $C_{20}H_{16}O_2S$ requires C, 75·0; H, 5·0%).

9-Hydroxy-9-phenylfluorene was prepared as described by Ullmann and Wurstemberger (*Ber.*, 1904, **37**, 73), and purified by crystallising it twice from carbon tetrachloride (compare Kliegl, *Ber.*, 1905, **38**, 288), crushing the solvated crystals, and air-drying the powder over-night at 40°. The product had m. p. 85—87° and, notwithstanding the observed efflorescence, appeared still to contain solvent of crystallisation. A warm solution of the product (18 g.) in glacial acetic acid (18 c.c.) was treated with a warm solution (18 c.c.) of hydrogen bromide in the same solvent (600 g./l.), and the non-homogeneous mixture was rapidly stirred until solid appeared and then heated at 80° for 0·5 hour. The product (20 g.) obtained by filtering the cooled solution and washing the precipitate with cold glacial acetic acid had m. p. 99—100°, and, after crystallisation from ligroin, m. p. 101—101·5° (compare Staudinger, *Ber.*, 1906, **39**, 3060). A further quantity (1 g.) was recovered by adding a limited amount of water to the acetic acid solution.

When this bromide was treated with an alcoholic solution of hydrated sodium *p*-toluenesulphinate, as in the preceding preparation, the product was 9-ethoxy-9-phenylfluorene. Sodium *p*-toluenesulphinate (8 g.), dried at 100°, was therefore boiled for 40 hours with a solution of the bromide (12 g.) in dry benzene (50 c.c.). The suspension was filtered while hot, and the residue extracted with hot benzene until it became completely soluble in water.

The 9-*phenyl*-9-*fluorenyl*-p-*tolylsulphone*, which was crystallised twice (8·0 g.), separated from benzene in needles or stout prisms, m. p. 211—212° (Found: C, 78·7; H, 5·3. $C_{26}H_{20}O_2S$ requires C, 78·8; H, 5·1%).

Decomposition with Potassium Hydroxide.—The reactions were carried out by the general method illustrated in the earlier papers by Fenton and Ingold.

The degradation of diphenylsulphone has already been described by Otto (*Ber.*, 1886, **19**, 2425), who observed the formation of phenol as a main product but did not record the production of benzene. Under corresponding conditions we find that both benzene (identified as the *m*-dinitro-derivative) and phenol (benzoyl derivative) are formed in quantity, and that, at temperatures below that at which benzenesulphinic acid would be largely decomposed, this acid is absent but benzene is formed and benzenesulphonic acid and phenol are also present. The initial fission products are therefore benzene and benzenesulphonic acid, not phenol and benzenesulphinic acid.

The volatile products from the decomposition of 9-phenyl-9-fluorenyl-*p*-tolylsulphone (6 g.) consisted of toluene (0·3 g.; 2 : 4-dinitro-derivative) and 9-phenylfluorene (0·1 g.; sublimed under reduced pressure as needles, m. p. and mixed m. p. 146—147°). The aqueous extract of the non-volatile portion yielded a small amount of cresol (qualitative tests), which was extracted with ether after the solution had been treated with carbon dioxide, and *p*-toluenesulphinic acid (1·5 g., m. p. and mixed m. p. 88—89°), which was similarly extracted after acidification. The non-volatile product which was insoluble in water consisted of a brown resin : this was converted into a pale yellow powder by boiling with dilute aqueous ammonia and extracted several times with boiling alcohol, which removed most of the colouring matter. The dried substance (free from nitrogen and sulphur) separated in a solid form resembling lycopodium when its solution in hot chloroform–acetic acid was cooled, but the material, which decomposed above 300° and did not reduce cold permanganate in moist benzene–acetone, did not appear to be crystalline : the microscope revealed small clusters of nearly spherical particles. Considering the difficulties of purification, the analysis [Found : C, 94·0 ; H, 5·4 ; *M*, by Rast's method, 932. $(C_{19}H_{12})_4$ requires C, 95·0 ; H, 5·0% ; *M*, 960] appears to show that the *substance* is a hydrocarbon. Its formation seems analogous to that of the product $(C_{19}H_{14})_x$ obtained by Nef by the action of triethylamine on triphenylmethyl bromide (*Annalen*, 1899, **309**, 168). The 9-phenylfluorene required for comparison was prepared from 9-bromo-9-phenylfluorene (2 g.) and thin amalgamated aluminium foil (2 g.) in moist ether (50 c.c.). After being kept for 2 hours at the ordinary temperature, the solution was filtered, dried, and evaporated, and the residue crystallised from alcohol, from which the hydrocarbon separated in feathery needles, m. p. 146—149°. Its solution in ether is strongly fluorescent.

The volatile decomposition products from 9-fluorenyl-*p*-tolylsulphone on fractionation yielded toluene (25%, identified as 2 : 4-dinitro-derivative) and fluorene (43%), and a further 2% of fluorene was obtained by sublimation at 100° from the brown resin (6% of the weight of the sulphone) constituting the benzene-soluble portion of the non-volatile residue. The aqueous extract of the residue yielded cresol (10%, identified as benzoate), which was extracted with ether after the solution had been treated with carbon dioxide. Acidification of the residual aqueous solution yielded a white precipitate, m. p. 110—112°, consisting of diphenyl-2-carboxylic acid (yield, 15%) : it crystallised from ether–ligroin in stout prisms and its solution in concentrated sulphuric acid yielded pure fluorenone (m. p. and mixed m. p.) on dilution with water. This establishes the identity of the acid, which was confirmed by comparison with a specimen obtained from fluorenone, and also with one prepared by the action of hot concentrated potassium hydroxide solution on bis-*oo'*-diphenylylene-ethylene. Extraction of the acid filtrate with ether yielded *p*-toluenesulphinic acid (20%), m. p. 89—89·5° (the recorded m. p. of this acid is 85°, but our numerous specimens all had m. p. 89°).

Phenylbenzylsulphone yielded liquid and solid hydrocarbons, of which the latter was identified as stilbene (m. p. and mixed m. p.; yield, 48%). The liquid hydrocarbons, b. p. 80—105°, were heated in a closed tube with 3% permanganate solution for 4 hours; benzene was then recovered by distillation and converted into its dinitro-derivative, and the presence of toluene in the original mixture was diagnosed by the isolation of benzoic acid by ether-extraction of the decolorised, filtered, and acidified aqueous solution. The alkaline residue from the decomposition yielded sulphur dioxide and phenol.

Dibenzylsulphone yielded toluene, stilbene, and sulphur dioxide.

Benzylmethylsulphone yielded the same products together with methanesulphinic acid and a very small amount of gas. The methanesulphinic acid was isolated as its *silver* salt by the method previously described for propanesulphinic acid (J., 1929, 2340) except that aqueous alcohol was used for the precipitation and crystallisation (Found: C, 6·6; H, 1·75. CH_3O_2SAg requires C, 6·4; H, 1·6%).

p-Tolylmethylsulphone yielded toluene (yield, *ca.* 25%; identified as 2 : 4-dinitro-derivative), *p*-cresol (*ca.* 30%; identified as benzoate), *p*-toluenesulphinic acid (18%; m. p. and mixed m. p.), and a gas which was swept over with nitrogen and shown to contain methane (13%), ethylene (27%), and a substantial quantity of hydrogen.

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