92. *Kationoid Reactivity of Aromatic Compounds. Part V. Fission of Arylsulphones by Means of Sodamide and Piperidine.*

By William Bradley.

Simple arylsulphones undergo fission when treated with a mixture of sodamide and piperidine with formation of an *N*-arylpiperidine and a sulphinic acid. No replacement of nuclear hydrogen by the piperidino-group is observed even when the reaction is carried out in presence of oxygen.

In previous work (Bradley and Robinson, J., 1932, 1254; Bradley, J., 1937, 1091) it has been shown that replacement of nuclear hydrogen by the piperidino-group may occur in aromatic nitro- or carbonyl compounds when these are treated with sodamide and piperidine. When the same reagents are applied to simple arylsulphones, no substitution is observed even when oxygen is present, but fission takes place with formation of an *N*-arylpiperidine and a sulphinic acid :

$$NaNH_2 + NHC_5H_{10} = NH_3 + NaNC_5H_{10}$$
$$^-NC_5H_{10} + Ar{\cdot}SO_2R = Ar{\cdot}NC_5H_{10} + R{\cdot}SO_2^-$$

Diphenylsulphone, phenylbenzylsulphone, and *p*-tolylmethylsulphone are all readily decomposed at the boiling point of piperidine. Diphenylsulphone gives *N*-phenylpiperidine in 75% of the theoretical yield and benzenesulphinic acid, the latter in almost pure condition; phenylbenzylsulphone affords *N*-phenylpiperidine and benzylsulphinic acid; *p*-tolylmethylsulphone gives *N*-*p*-tolylpiperidine and methylsulphinic acid. Methylsulphinic acid was characterised as methylbenzylsulphone (Fromm and de Seixas Palma, *Ber.*, 1891, **24**, 3315). That the Alkyl·CH_2·SO_2 link is more resistant to fission than is the Aryl·SO_2 is substantiated further by the stability of dibenzylsulphone, which was recovered almost unchanged after heating with piperidine and a large excess of sodamide.

The reaction is thus one of a class which includes the formation of amines from sulphonic acids by heating these with sodamide at 230° (Sachs, *Ber.*, 1906, **39**, 3009; cf. Jackson and Wing, *Ber.*, 1886, **19**, 902), and the conversion of sulphonic acids into phenols by fusion with alkali hydroxides. A distinguishing feature of the present reaction is the ease with which it takes place.

The direction of fission in substituted arylalkylsulphones may be determined by the nature of the substituent. An electron-donating group (*e.g.*, OH, NH_2) present in the side chain of an arylalkylsulphone does not affect the normal direction of fission. On the other hand, electron-attracting groups (*e.g.*, SO_2, CN) may cause reversal of the normal direction of fission, the aryl group appearing as a sulphinic acid, and the substituted alkyl group in combination with the reagent. Ethylenebis-*p*-tolylsulphone and aqueous potassium hydroxide afford *p*-toluenesulphinic acid and β-*p*-tolylsulphonylethyl alcohol (Otto, *J. pr. Chem.*, 1884, **30**, 355). Ethylenebisphenylsulphone similarly gave β-phenylsulphonylethyl alcohol and benzenesulphinic acid, but prolonged heating with concentrated alkali failed to hydrolyse the sulphone alcohol (Otto, *ibid.*, p. 321). The same mode of fission was observed when the reagent was ammonia or potassium hydrosulphide. When potassium cyanide was used, however, the intermediate cyano-substituted sulphone was further changed to succinonitrile and succinic acid (Otto, *ibid*, pp. 349, 361).

$$\begin{tikzcd}
Ar{\cdot}SO_2{\cdot}CH_2{\cdot}CH_2{\cdot}SO_2Ar \arrow[r, "KOH"] \arrow[d, "KCN"] & Ar{\cdot}SO_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH + Ar{\cdot}SO_2K \\
(Ar{\cdot}SO_2{\cdot}CH_2{\cdot}CH_2{\cdot}CN) + Ar{\cdot}SO_2K \arrow[r, "KCN"] & Ar{\cdot}SO_2K + CN{\cdot}CH_2{\cdot}CH_2{\cdot}CN
\end{tikzcd}$$

EXPERIMENTAL.

Fission of Diphenylsulphone.—Sodamide (15 g.) was boiled with piperidine (50 c.c.) during 15 minutes and then diphenylsulphone (25 g.) was added to the suspension. There was a rapid evolution of ammonia. The mixture was boiled for 2 hours under reflux, benzene (300 c.c.) added, and then water (75 c.c.) portionwise and with frequent shaking.

The benzene layer, washed with water and dried over potassium hydroxide, gave on distillation a fraction (13·5 g.), b. p. 255—260°/766 mm., which was almost pure *N*-phenylpiperidine. The pure base had b. p. 259°/766 mm.; the picrate crystallised from alcohol in bright lemon-yellow prisms, m. p. 148° (Found: N, 15·0. Calc. for $C_{17}H_{18}O_6N_4$: N, 15·0%). von Braun (*Ber.*, 1904, **37**, 3212; 1907, **40**, 3920) gives b. p. 257—258°/752 mm. and m. p. 148°, respectively.

The alkaline aqueous solution was filtered, cooled in ice, and acidified. An oil separated which quickly solidified. Dried on porous tile, the crude product had m. p. 83°; benzenesulphinic acid has m. p. 83—84° (Otto, *loc. cit.*). When the crude sulphinic acid (7 g.) was heated during 1·5 hours with benzyl chloride (6·5 g.) and a solution of potassium hydroxide (3 g.) in alcohol (30 c.c.), phenylbenzylsulphone (9·5 g., m. p. 148°) was obtained (cf. Knoevenagel, *Ber.*, 1888, **21**, 1695).

p-*Acetamido*-N-*phenylpiperidine*. 6·5 G. of *N*-phenylpiperidine obtained by fission of diphenylsulphone were dissolved in concentrated hydrochloric acid (20 c.c.), the solution cooled to 0° by addition of ice, and a concentrated aqueous solution of sodium nitrite (3 g.) added through a capillary tube with frequent shaking. The solution, at first colourless, became intensely orange-yellow. It was filtered after 30 minutes, and concentrated hydrochloric acid (20 c.c.) added. The heated solution was decolourised with zinc dust (12 g.), cooled, and made alkaline in presence of ether. The ethereal solution was separated, washed with water, mixed with acetic anhydride (20 c.c.), and then evaporated on the water-bath. An oil remained and this was dissolved in alcohol, 5 c.c. of 10% sulphuric acid were added, and the solution kept overnight and then made alkaline. The grey crystalline precipitate was recrystallised from alcohol, giving colourless prisms, m. p. 151—152°, not depressed by *p*-acetamido-*N*-phenylpiperidine obtained from *p*-chloronitrobenzene (Lellmann and Geller, *Ber.*, 1888, **21**, 2286).

p-*Chlorobenzeneazo*-N-*phenylpiperidine*. The diazonium salt prepared from *p*-chloroaniline (2·5 g.) was added to a solution of *N*-phenylpiperidine (3·2 g.) in 5% hydrochloric acid (20 c.c.). A golden-yellow solution was formed, from which sodium acetate (5 g.) precipitated a yellow oil. The *product* solidified and then crystallised from alcohol in golden-yellow plates, m. p. 143° (Found: N, 14·3. $C_{17}H_{18}N_3Cl$ requires N, 14·0%).

When oxygen was passed through a stirred suspension of sodamide (10 g.) in a solution of diphenylsulphone (25 g.) in piperidine (50 c.c.) which was kept for 1 hour at 118—120°, 7 g. of *N*-phenylpiperidine were obtained.

Fission of p-*Tolylmethylsulphone*.—The pure sulphone (7 g.) (Baldwin and Robinson, J., 1932, 1448) and sodamide (5 g.) were added to piperidine (20 c.c.) and gently boiled during 2 hours. Ammonia was evolved almost at once and a brown pasty mass formed. Benzene (50 c.c.) was added and then water (30 c.c.) portionwise.

The pale amber benzene layer was washed with water and dried over potassium hydroxide. On distillation, after benzene and piperidine had passed over, all but a small residue boiled at 274°/763 mm. (5·5 g.). According to von Braun (*loc. cit.*) *N*-*p*-tolylpiperidine has b. p. 268—269°; Lellmann and Just (*Ber.*, 1891, **24**, 2099) state b. p. 262°. The picrate crystallised when the base was added to 10% alcoholic picric acid. It formed bright yellow prisms, m. p. 176° (Found: N, 14·3. $C_{18}H_{20}O_6N_4$ requires N, 14·4%), not depressed by the picrate of *N*-*p*-tolylpiperidine prepared by Lellmann and Just's method.

The alkaline aqueous layer was colourless. When acidified with acetic acid, it decolourised iodine. When it was boiled for 1 hour with benzyl chloride (7 g.), and the solution cooled, an oil was precipitated which rapidly crystallised. After being pressed on porous tile, it separated from alcohol in needles, m. p. 126°, not depressed by benzylmethylsulphone prepared by methylating benzylsulphinic acid (Fromm and de Seixas Palma, *Ber.*, 1906, **39**, 3319).

Fission of Phenylbenzylsulphone.—Sodamide (3 g.) was boiled for 15 minutes with piperidine (20 c.c.), the resulting suspension cooled to 90°, and phenylbenzylsulphone (8·5 g., m. p. 148°) added. There was an immediate reaction in which ammonia was evolved and a solid separated. After 30 minutes' boiling, benzene (50 c.c.) was added and then water (50 c.c.) in small successive amounts.

From the benzene solution there crystallised 3·5 g. of unreacted sulphone, and from the filtered solution *N*-phenylpiperidine, b. p. 255—260°, was obtained. The base afforded 2 g. of the picrate, m. p. 148°.

The alkaline aqueous layer, washed with benzene and then boiled for 1 hour with benzyl chloride (5 g.), gave dibenzylsulphone, which crystallised from alcohol in plates, m. p. 150—151°, not depressed by a specimen prepared by the benzylation of benzylsulphinic acid (Fromm and de Seixas Palma, *loc. cit.*).

Non-fission of Dibenzylsulphone.—The pure sulphone (0·5 g.) was boiled for 1·5 hours with piperidine (10 c.c.) and sodamide (1 g.). The reddish-brown solution obtained, when cooled and diluted with water, gave 0·43 g. of unchanged dibenzylsulphone. In a second experiment 1·5 g. of the sulphone were boiled for 3 hours with piperidine (15 c.c.) and sodamide (3 g.); 1·15 g. of unchanged sulphone were recovered.

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