952. *The Basic Reductive Fission of Sulphones.*

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Several diaryl and alkyl aryl sulphones are shown to undergo reductive fission by sodium amalgam and boiling ethanol to a sulphinic acid and a hydrocarbon, the latter being derived from the radical of more pronounced electron-releasing character. Dialkyl sulphones appear to be indifferent to this reagent.

THERE is much evidence, summarised by Suter ("Organic Chemistry of Sulphur," John Wiley & Sons, London, 1944, p. 683), that sulphones are unaffected by the usual reducing agents. On the other hand, Mozingo, Wolf, Stanton, Harris, and Folkers (*J. Amer. Chem. Soc.*, 1943, **65**, 1013) showed that diphenyl sulphone (and several other sulphones), when heated with Raney nickel in ethanol, undergoes hydrogenolysis to benzene in 65% yield. Recently Balfe, Dabby, and Kenyon (*J.*, 1951, 385) found that

Products of the reductive fission of sulphones.

Sulphone.	Products. (Yields are given as from 1 g. of sulphone. The sulphinic acids were isolated as their benzyl sulphones.)
$Ph \cdot SO_2 \cdot Me$	$Ph \cdot SO_2H$ (0·75 g.)
$Ph \cdot SO_2 \cdot Ph$	$Ph \cdot SO_2H$ (0·8 g.), C_6H_6 (0·1 g.) [1]
$p\text{-}C_6H_4Me \cdot SO_2 \cdot Ph$	$p\text{-}C_6H_4Me \cdot SO_2H$ (0·5 g.)
$Ph \cdot SO_2 \cdot CH_2Ph$	$Ph \cdot SO_2H$ (0·7 g.), C_7H_7 (0·1 g.) [2]
$Ph \cdot SO_2 \cdot C_6H_3(OMe)_2\text{-}2 : 4$	$Ph \cdot SO_2H$ (0·7 g.), $m\text{-}C_6H_4(OMe)_2$ (0·6 g.) [3]
$p\text{-}C_6H_4Me \cdot SO_2 \cdot C_6H_3(OMe)_2\text{-}2 : 4$	$p\text{-}C_6H_4Me \cdot SO_2H$ (0·5 g.), $m\text{-}C_6H_4(OMe)_2$ (0·6 g.) [3]
$\beta\text{-}C_{10}H_7 \cdot SO_2 \cdot C_6H_3(OMe)_2\text{-}2 : 4$	$\beta\text{-}C_{10}H_7 \cdot SO_2H$ (0·15 g.), $C_{10}H_8$ (0·3 g.), $m\text{-}C_6H_4(OMe)_2$ (0·2 g.) [3]
$p\text{-}MeO \cdot C_6H_4 \cdot CHPh \cdot SO_2 \cdot C_6H_4Me\text{-}p$	$p\text{-}C_6H_4Me \cdot SO_2H$ (0·3 g.), $p\text{-}MeO \cdot C_6H_4 \cdot CH_2Ph$ (0·4 g.) [4]
$p\text{-}MeO \cdot C_6H_4 \cdot CH(C_{10}H_7\text{-}a) \cdot SO_2 \cdot C_6H_4Me\text{-}p$	$p\text{-}MeO \cdot C_6H_4 \cdot CH_2 \cdot C_{10}H_7\text{-}a$ (0·6 g.) [5]
$2 : 1\text{-}MeO \cdot C_{10}H_6 \cdot CHPh \cdot SO_2 \cdot C_6H_4Me\text{-}p$	$2 : 1\text{-}MeO \cdot C_{10}H_6 \cdot CH_2Ph$ (0·6 g.) [6]
$p\text{-}C_6H_4Ph \cdot CHPh \cdot SO_2 \cdot C_6H_4Me\text{-}p$	$p\text{-}C_6H_4Ph \cdot CH_2Ph$ (0·6 g.) [7]
$2 : 4 : 6\text{-}(MeO)_3C_6H_2 \cdot CHPh \cdot SO_2 \cdot C_6H_4Me\text{-}p$	$p\text{-}C_6H_4Me \cdot SO_2H$ (0·3 g.), $2 : 4 : 6\text{-}(MeO)_3C_6H_2 \cdot CH_2Ph$ (0·55 g.)
$2 : 4 : 6\text{-}(MeO)_3C_6H_2 \cdot CH(C_{10}H_7\text{-}a) \cdot SO_2 \cdot C_6H_4Me\text{-}p$	$p\text{-}C_6H_4Me \cdot SO_2H$ (0·2 g.), $2 : 4 : 6\text{-}(MeO)_3C_6H_2 \cdot CH_2 \cdot C_{10}H_7\text{-}a$ (0·7 g.)

$CH_2Ph \cdot SO_2 \cdot Me$, $CH_2Ph \cdot SO_2 \cdot CH_2Ph$, and $n\text{-}C_8H_{17} \cdot SO_2 \cdot C_8H_{17}\text{-}n$ are inert to sodium amalgam.

[1] As $m\text{-}C_6H_4(NO_2)_2$. [2] As $Ph \cdot CO_2H$. [3] As dibromo-derivative. [4] B. p. 171°/22 mm. (lit., b. p. 157°/8 mm.) (Found : C, 84·9; H, 7·0. Calc. for $C_{14}H_{14}O$: C, 84·8; H, 7·1%). [5] M. p. 94° (Found : C, 87·1; H, 6·8. $C_{18}H_{16}O$ requires C, 87·1; H, 6·5%). [6] M. p. 98·5° (Found : C, 87·2; H, 6·4. $C_{18}H_{16}O$ requires C, 87·1; H, 6·5%). [7] M. p. 85·5° (lit., m. p. 85°) (Found : C, 93·5; H, 6·6. Calc. for $C_{19}H_{16}$: C, 93·4; H, 6·6%).

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p-methylsulphonylbenzophenone was converted by sodium amalgam or zinc dust–sodium hydroxide in alcohol quantitatively into diphenylmethanol : $p\text{-}Me\cdot SO_2\cdot C_6H_4\cdot COPh \longrightarrow Ph_2CH\cdot OH$. This unexpectedly smooth fission led us to apply this simple procedure to other sulphones with the object of determining the nature of the second product of fission. From the results given in the Table it appears that the radical of more pronounced electron-releasing character manifests itself as a hydrocarbon whilst the second radical remains attached to sulphur and appears as a sulphinic acid : $R\cdot SO_2\cdot R' + H_2 \longrightarrow R\cdot SO_2H + R'H$. In the case of 2 : 4-dimethoxyphenyl β-naphthyl sulphone the two possible hydrocarbons and one of the two possible sulphinic acids were isolated. Furthermore it seems evident that a necessary condition for this reaction to occur is that the sulphonyl group must be directly attached to at least one aromatic radical.

Some of the sulphones examined were derived from alcohols which readily undergo alkyl–oxygen fission; they were easily prepared by the interaction of the alcohol and sodium toluene-*p*-sulphinate in acid solution.

EXPERIMENTAL

Reductive Fission of p-*Tolyl* 2 : 4 : 6-*Trimethoxydiphenylmethyl Sulphone.*—The sulphone (1 g.) was heated under reflux (4 hours) in ethanol (25 c.c.) with 6% sodium amalgam (25 g.). The solution was decanted and concentrated. On cooling, prismatic rods of 2 : 4 : 6-trimethoxy-diphenylmethane (0·55 g., 88%), m. p. 91—92°, separated. The filtrate contained sodium toluene-*p*-sulphinate and was evaporated on the steam-bath. The trimethoxydiphenylmethane, when recrystallised from ethanol, had m. p 93·5—94·5° alone or when mixed with a specimen obtained from the hydrogenolysis of the corresponding sulphide. The sulphinic acid was characterised as its benzyl sulphone (0·3 g.), m. p. 145—146° alone or when mixed with an authentic specimen. This procedure was applied to several sulphones and the corresponding hydrocarbons and sulphinic acids (isolated as *p*-tolyl sulphones) were obtained.

Preparations.—2 : 4-Dimethoxydiphenyl sulphone was prepared by Burton and Hoggarth's method (*J.*, 1945, 14) as were also 2 : 4-*dimethoxyphenyl* p-*tolyl sulphone*, small rhombs (from ethanol), m. p. 154—155° (Found : C, 61·8; H, 5·5; S, 11·0. $C_{15}H_{16}O_4S$ requires C, 61·7; H, 5·5; S, 10·9%), and 2 : 4-*dimethoxyphenyl* β-*naphthyl sulphone*, needles (from methanol) or plates (from acetic acid), m. p. 135° (Found : C, 65·7; H, 5·0; S, 10·2. $C_{18}H_{16}O_4S$ requires C, 65·9; H, 4·9; S, 9·8%).

Reductive Fission of 2 : 4-*Dimethoxydiphenyl Sulphone.*—The sulphone (2·5 g.) in ethanol (40 c.c.) was heated under reflux (5 hours) with 6% sodium amalgam (30 g.). The decanted solution was distilled in a current of steam. The residue yielded benzyl phenyl sulphone (1·7 g.), m. p. 149—150° alone or when mixed with an authentic specimen. The material obtained by ether-extraction of the steam-distillate was mixed with ethanol (10 c.c.) and bromine (3 g.) dropwise. There separated dibromoresorcinol dimethyl ether (1·4 g.), m. p. 141—142° alone or mixed with an authentic specimen. This procedure was applied to the two dimethoxyphenyl sulphones described above.

Reductive fission of 2 : 4-dimethoxyphenyl β-naphthyl sulphone (2 g.) gave naphthalene (0·6 g.), m. p. and mixed m. p. with an authentic specimen 78—80°; dibromoresorcinol dimethyl ether (0·4 g.), m. p. 140—142°, and *benzyl* β-*naphthyl sulphone* (0·3 g.), plates (from butanol), m. p. 190·5—191·5° (Found : C, 72·3; H, 5·1; S, 11·7. $C_{17}H_{14}O_2S$ requires C, 72·4; H, 5·0; S, 11·4%).