Reduction of Aromatic Sulphoxides by Phosphorus Trichloride

By **I. Granoth** and **A. Kalir**, Israel Institute for Biological Research, Ness Ziona
Z. Pelah, Institute for Higher Education in the Negev, Beer-Sheva

Sulphoxides are reduced by phosphorus trichloride to the corresponding sulphides in high yields. No chlorination occurs as in the known ' reduction ' of sulphoxides by phosphorus pentachloride or oxychloride.

SEVERAL agents for the reduction of sulphoxides to sulphides have been recorded in the literature.[1-7] Certain halogen-containing agents of this type, such as phosphorus pentachloride,[8] thionyl chloride,[9,10] phosphorus oxychloride,[10] hydrogen bromide in acetic acid,[11] or hydrochloric acid[12] give halogenated sulphides, possibly through rearrangement of intermediate *S*-halogen compounds. Unlike these agents phosphorus trichloride reduces aromatic sulphoxides in a smooth, exothermic reaction with excellent yields. Nitro-groups present in the aromatic ring are not attacked under the reaction conditions and the simplicity of the procedure recommends the reaction for preparative use.

EXPERIMENTAL

M.p.s were determined on a Kofler hot stage apparatus. The i.r. spectra were measured as KBr discs. The sulphoxides were generally obtained by peracetic acid oxidation of the appropriate sulphides,[14] which were either commercially available or prepared, as reported before.[15] The sulphoxides used are described in Table 1.

The sulphides obtained by reduction of the sulphoxides were identified by comparison of the m.p.s and the i.r. spectra with those of authentic specimens. Diphenyl sulphide, being a liquid, was identified by oxidation to the solid sulphone. The characteristic S=O absorption at 1035—1060 cm.$^{-1}$ permits an easy differentiation between a sulphoxide and a sulphide.

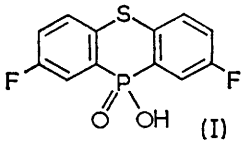
TABLE 1

Diaryl sulphoxides

Substd. sulphoxide	M.p.	Yield	Solvent ‡	Formula	Calcd. (%)					Found (%)					ν(S=O) (cm.$^{-1}$)
					C	H	Br	Cl	S	C	H	Br	Cl	S	
Unsubstd.	71°	80 *	L	$C_{12}H_{10}OS$											1035
4,4′-Me$_2$	92	85 *	E	$C_{14}H_{14}OS$											1040
4,4′-Cl$_2$	145	80 *	E	$C_{12}H_8Cl_2OS$											1045
4-Br,4′-Cl	144	85	E	$C_{12}H_8BrClOS$	45·7	2·5	25·4	11·1	10·2	45·2	2·6	25·9	11·5	10·6	1045
4-Cl,4′-F	76	67	L	$C_{12}H_8ClFOS$ †	56·6	3·1		13·9	12·6	57·7	3·2		14·2	12·3	1045
2-Br,4′-Cl	98	70	E	$C_{12}H_8BrClOS$	45·7	2·5	25·4	11·1	10·2	45·4	2·6	25·3	11·2	10·4	1045
4-NO$_2$,4′-Cl	151	80	E	$C_{12}H_8ClNO_3S$	51·2	2·8		12·6	11·4	51·4	2·8		12·9	11·6	1050
4-BrC$_6$H$_3$,Me	81	82	E	C_7H_7BrOS	38·4	3·2	36·5		14·6	38·7	3·4	36·7		14·1	1040

* Ref. 14. † F, calcd., 7·5, F, found, 7·1%. ‡ L = ligroin, E = ethanol.

4-Bromo-4′-chlorodiphenyl sulphoxide and phosphorus trichloride yield in the presence of aluminium chloride the same phosphonic acid *p*-$ClC_6H_4{\cdot}S{\cdot}C_6H_4$–$PO_3H_2$-*p* which was obtained previously from the parent sulphide.[13] Equally 3,7-difluoro-5-hydroxy-5-oxodibenzo[*b*,*e*]thiaphosphor(V)in (I) was obtained from



(I)

4,4′-difluorodiphenyl sulphoxide and phosphorus trichloride in the presence of aluminium chloride.

The corresponding sulphones do not react with phosphorus trichloride.

Reduction of Sulphoxides with Phosphorus Trichloride.—General procedure. The sulphoxide (0·02 mole) was added gradually to stirred and cooled (ice) phosphorus trichloride (10 ml.). The mixture was held for 18 hr. at room temperature and then decomposed with crushed ice (100 g.). The solid sulphide was washed with water and then crystallized. (Diphenyl sulphide was extracted with chloroform). The yields were in the range 90—98%. The sulphides obtained are described in Table 2.

4-(4-*Chlorophenylthio*)*benzenephosphonic Acid*.—A mixture of 4-bromo-4′-chlorodiphenyl sulphoxide (9·5 g., 0·03 mole), aluminium chloride (5·1 g.), and phosphorus trichloride (12 ml.) was heated under reflux for 6 hr. and then poured onto ice (100 g.). Extraction with a 10% solution of sodium hydroxide left 4-bromo-4′-chlorodiphenyl sulphide, m.p. 106° (from ethanol) (2·1 g.). The basic solution yielded the *phosphonic acid* (4·0 g., 44%) after acidification

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TABLE 2

Diaryl sulphides [a] from the reduction of the sulphoxides

Substd. sulphide	M.p.	Yield	Solvent *	Remarks
Unsubstd.	125° [b]	90	E	Ref. 16
4,4′-Me_2	58	90	E	Ref. 15
4,4′-Cl_2	94	98	E	Ref. 15
4-Cl,4′-F	34	95	80% E	Ref. 15
2-Br,4′-Cl	65	90	E	*c*
4-NO_2,4′-Cl	87	98	E	Ref. 17
(4-BrC_6H_3,Me	39	96	E	Ref. 16)

[a] In the i.r. spectrum of all the products, the S=O absorption was absent. [b] M.p. of diphenyl sulphone. [c] Found: C, 47·8; H, 2·8; Br, 27·1; Cl, 12·0; S, 11·2%. Calc. for $C_{12}H_8BrClS$: C, 48·1; H, 2·7; Br, 26·7; Cl, 11·7; S, 10·7%.

* E = ethanol.

with hydrochloric acid. The acid was identified as its dicyclohexylammonium salt, m.p. 237° (from dimethylformamide) which was identical with a sample obtained from 4-bromo-4′-chlorodiphenyl sulphide.[13]

4,4′-*Difluorodiphenyl Sulphoxide*.—Aluminium chloride (80 g.) was added gradually to an ice-cooled mixture of fluorobenzene (150 ml.) and thionyl chloride (40 g.). The mixture was heated under reflux for 2 hr., and was then cooled and decomposed with crushed ice (800 g.). The product was extracted with chloroform (250 ml.) and finally distilled, b.p. 125°/0·1 mm., to yield an oily distillate (60 g.; 75%) which solidified when scratched, m.p. 48° (from light petroleum), $\nu_{max.}$ 1220 (C–F), 1050 (S=O) cm.$^{-1}$ (Found: C, 61·8; H, 3·2; F, 15·6; S, 13·5%. Calc. for $C_{12}H_8F_2OS$: C, 60·5; H, 3·4; F, 16·0; S, 13·6%).

3,7-*Difluoro*-5-*hydroxy*-5-*oxodibenzo*[b,e]*thiaphosphor*(V)*in* (I).—4,4′-Difluorodiphenyl sulphoxide (23·8 g.) was added gradually to a stirred, agitated, and ice-cooled suspension of phosphorus trichloride (40 ml.) and aluminium chloride (27·0 g.). The mixture was boiled for 24 hr., cooled, and poured onto ice (500 g.). The oily precipitate was taken up in 5% solution of sodium hydroxide, and the clear solution was acidified. The precipitate was washed with ether to yield the crude phosphorin (7·2 g.; 25%), which was identified as the dibenzylammonium salt (prepared in, and recrystallized from, dimethylformamide), m.p. 251°. $\nu_{max.}$ 1250 (C–F), 1195 (P=O) cm.$^{-1}$; $\lambda_{max.}$ (EtOH) 223 (log ε 4·36), 242s (3·85), 264 (4·18), 285s (3·44), and 315 mμ (3·60). (Found: C, 64·7; H, 4·5; P, 6·1%. Calc. for $C_{26}H_{22}F_2NO_2PS$: C, 64·9; H, 4·6; P, 6·4%).

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