186. *Some* p-*Alkoxybenzenesulphonamides and their* N-*Chloro-derivatives.*

By W. E. Hanby and H. N. Rydon.

Eight p-*alkoxybenzenesulphonamides* ($RO\cdot C_6H_4\cdot SO_2\cdot NH_2$; R = n-C_4H_9, n-C_5H_{11}, n-C_6H_{13}, n-C_7H_{15}, n-C_8H_{17}, n-$C_{10}H_{21}$, n-$C_{12}H_{25}$, and n-$C_{16}H_{33}$) have been prepared and converted into the corresponding *sodio-*p-*alkoxybenzenesulphonchloroamides*, $RO\cdot C_6H_4\cdot SO_2\cdot NNaCl$.

In connection with another investigation it was necessary to prepare a series of derivatives of chloramine-B, $Ph\cdot SO_2\cdot NNaCl$, containing aliphatic side-chains of varying length. Of the possible ways in which such side-chains might have been introduced into the chloramine-B molecule the simplest, from the preparative standpoint, appeared to be in the form of *p*-alkoxy-groups; we have accordingly prepared eight *p*-alkoxy-derivatives of chloramine-B containing alkyl groups with from four to sixteen carbon atoms in the chain.

The *sulphonyl chlorides* of the appropriate phenyl alkyl ethers were converted into the *sulphonamides* best by treatment with aqueous ammonia, since the action of ammonium carbonate (Huntress and Carten, *J. Amer. Chem. Soc.*, 1940, **62**, 511) when applied by us to p-n-*hexadecyloxybenzenesulphonyl chloride* gave, not the desired amide, but *bis-*(p-n-*hexadecyloxybenzenesulphon*)*imide*, $(C_{16}H_{33}O\cdot C_6H_4\cdot SO_2)_2NH$.

The compounds *p*-$RO\cdot C_6H_4\cdot SO_2\cdot NH_2$ (R = n-C_4H_9, n-C_5H_{11}, n-C_6H_{13}, n-C_7H_{15}, n-C_8H_{17}, or n-$C_{10}H_{21}$) were converted directly into the required *sodio-*p-n-*alkoxybenzenesulphonchloroamides*, *p*-$RO\cdot C_6H_4\cdot SO_2\cdot NNaCl$, by treatment with alkaline sodium hypochlorite; owing to unfavourable solubility relationships this method failed with *p*-$RO\cdot C_6H_4\cdot SO_2\cdot NH_2$ (R = n-$C_{12}H_{25}$ or n-$C_{16}H_{33}$); these were, therefore, first converted into the p-n-*alkoxybenzenesulphondichloroamides*, *p*-$RO\cdot C_6H_4\cdot SO_2\cdot NCl_2$, which gave the required *sodio-monochloroamides* on warming with sodium hydroxide solution. All these *p*-alkoxy-derivatives of chloramine-B were effective chlorinating agents and, as expected, the solubility in water decreased and the solubility in non-polar solvents increased with increasing chain length of the alkyl group.

Experimental.

The phenyl alkyl ethers used in this work were prepared, in excellent yield, from highly purified specimens of the alkyl bromides (for generous supplies of which we are much indebted to Dr. G. S. Hartley) by reaction with sodium phenoxide in alcoholic solution, essentially as described by Hartley (*J.*, 1939, 1828).

Preparation of p-n-*Alkoxybenzenesulphonamides.*—The appropriate phenyl alkyl ether (1 mol.) was treated gradually with concentrated sulphuric acid (125 c.c. usually sufficed) until the product was completely soluble in hot water (cf. Hartley, *loc. cit.*). The reaction mixture was then warmed with carbon tetrachloride and the lower layer of sulphuric acid run off; addition of light petroleum (b. p. 40—60°) to the carbon tetrachloride layer precipitated the sulphonic acid as an oil which was dissolved in alcohol and neutralised with alcoholic potash. The precipitated potassium salt was filtered off, dried at 100°, and then treated with phosphorus pentachloride (1·5 mols.); after the initial vigorous reaction had subsided the mixture was warmed on the water-bath for a short time and then poured on crushed ice. The precipitated sulphonyl chloride was collected, treated with an excess of warm ammonia solution (*d* 0·880) with hand stirring, and then kept at room temperature overnight. The precipitated sulphonamide was collected and crystallised from aqueous alcohol.

The following were prepared in this way (the quoted yields are based on the phenyl alkyl ether):

p-n-Butyloxybenzenesulphonamide (40% yield), needles, m. p. 108° (Huntress and Carten, *loc. cit.*, give m. p. 103—104°) (Found: C, 52·4; H, 6·5; N, 6·3. Calc. for $C_{10}H_{15}O_3NS$: C, 52·4; H, 6·5; N, 6·1%).

p-n-*Amyloxybenzenesulphonamide* (53% yield), needles, m. p. 96° (Found: C, 54·2; H, 6·7; N, 5·8. $C_{11}H_{17}O_3NS$ requires C, 54·3; H, 7·0; N, 5·8%).

p-n-*Hexyloxybenzenesulphonamide*, short needles, m. p. 100° (Found: C, 56·1; H, 7·7; N, 5·45. $C_{12}H_{19}O_3NS$ requires C, 56·0; H, 7·4; N, 5·4%); *sodium* salt, m. p. 265—270° (decomp.), pearly leaflets from water (Found: C, 51·8; H, 6·9; N, 5·0; Na, 8·2. $C_{12}H_{18}O_3NSNa$ requires C, 51·6; H, 6·45; N, 5·0; Na, 8·2%).

p-n-*Heptyloxybenzenesulphonamide* (65% yield), needles, m. p. 99° (Found: C, 57·6; H, 7·6; N, 5·25. $C_{13}H_{21}O_3NS$ requires C, 57·6; H, 7·7; N, 5·2%).

p-n-*Octyloxybenzenesulphonamide* (65% yield), leaflets, m. p. 104° (Found: C, 58·9; H, 8·3; N, 4·9. $C_{14}H_{23}O_3NS$ requires C, 58·9; H, 8·1; N, 4·9%).

p-n-*Decyloxybenzenesulphonamide* (61% yield), flattened needles, m. p. 107° (Found: C, 61·6; H, 8·8; N, 4·6. $C_{16}H_{27}O_3NS$ requires C, 61·4; H, 8·6; N, 4·4%).

p-n-*Dodecyloxybenzenesulphonyl chloride*, m. p. 37°, needles from light petroleum (b. p. 40—60°) (Found : C, 60·2; H, 8·05; Cl, 9·6. $C_{18}H_{29}O_3ClS$ requires C, 59·9; H, 8·0; Cl, 9·85%). p-n-*Dodecyloxybenzenesulphonamide*, short flattened needles, m. p. 109° (Found : C, 63·4; H, 9·3; N, 4·3. $C_{18}H_{31}O_3NS$ requires C, 63·3; H, 9·1; N, 4·1%).

p-n-*Hexadecyloxybenzenesulphonyl chloride* (95% yield), m. p. 58° (Found : C, 63·5; H, 9·0. $C_{22}H_{37}O_3ClS$ requires C, 63·4; H, 8·9%). p-n-*Hexadecyloxybenzenesulphonamide* (88% yield), m. p. 111° (Found : C, 66·5; H, 9·6; N, 3·55. $C_{22}H_{39}O_3NS$ requires C, 66·5; H, 9·8; N, 3·5%); *sodium* salt, m. p. 310° (decomp.) (Found : C, 63·4; H, 9·2; N, 3·4. $C_{22}H_{38}O_3NSNa$ requires C, 63·0; H, 9·1; N, 3·3%). In another experiment the sulphonyl chloride (265 g.), dissolved in chloroform (30 c.c.), was treated with ammonium carbonate (10 g.) and the mixture evaporated to dryness. The product was ground with water, filtered, and again washed with water and this crude product (23 g.) was crystallised from acetic acid yielding *bis*-(p-n-*hexadecyloxybenzenesulphon*)*imide*, m. p. 89—92° (Found : N, 1·7. $C_{44}H_{75}O_6NS_2$ requires N, 1·8%); this imide (16 g.) was converted, in 85% yield, into the amide, m. p. mixed m. p. 111°, by warming with aqueous ammonia (*d* 0·880; 35 c.c.) and methanol (170 c.c.).

Chlorination of p-*Alkoxybenzenesulphonamides*.—(i) *Lower members.* With the six lowest members of the series the following procedure was used. The sulphonamide (50 g.) was dissolved in 10% sodium hydroxide solution (150 c.c.), warming if necessary. 2N-Sodium hypochlorite (200 c.c.) was then added with stirring; after cooling in ice the product was filtered off, washed with a little water, and crystallised from water.

The Table gives details for the various *sodio*-p-n-*alkoxybenzenesulphonchloroamides* prepared in this way.

Compounds $RO{\cdot}C_6H_4{\cdot}SO_2{\cdot}NNaCl$.

R.	Yield, %.	Cryst. form.	M. p.*	Analysis.
n-Butyl	69	Needles	162°	Found : N, 4·8; Cl, 11·2; available Cl, 22·4. $C_{10}H_{13}O_3NClSNa,2H_2O$ requires N, 4·35; Cl, 11·0; available Cl, 22·1%.
n-Amyl	71	Leaflets	158	Found : N, 4·5; available Cl, 22·4. $C_{11}H_{15}O_3NClSNa,H_2O$ requires N, 4·4; available Cl, 22·3%.
n-Hexyl	96	Needles	160	Found : N, 4·4; available Cl, 21·6. $C_{12}H_{17}O_3NClSNa,H_2O$ requires N, 4·2; available Cl, 21·4%.
n-Heptyl	63	Needles	156	Found : N, 4·3; available Cl, 21·4. $C_{13}H_{19}O_3NClSNa$ requires N, 4·3; available Cl, 21·7%.
n-Octyl	88	Needles	162	Found : N, 4·6; available Cl, 20·6. $C_{14}H_{21}O_3NClSNa$ requires N, 4·1; available Cl, 20·8%.
n-Decyl	71	—	152	Found : C, 49·3; H, 7·1; N, 3·6; available Cl, 18·3. $C_{16}H_{25}O_3NClSNa,H_2O$ requires C, 49·5; H, 7·0; N, 3·6; available Cl, 18·3%.

* All with decomposition.

(ii) *Higher members.* The following procedure was used for the dodecyl and hexadecyl compounds. The finely powdered sulphonamide was treated with excess of filtered bleach paste and excess of glacial acetic acid was added gradually with stirring. After an hour the solid product was collected and re-treated with filtered bleach paste and acetic acid. The product from this second chlorination, the sulphondichloroamide, was crystallised from purified light petroleum (b. p. 40—60°). This product was converted into the sodium sulphonchloroamide by warming (50—70°) for 15 minutes with 10% sodium hydroxide solution (5 c.c./g.); the resulting paste was cooled and filtered, and the sodium salt recrystallised from purified dioxan. The overall yield was about 80%.

The following were prepared in this way :

p-n-*Dodecyloxybenzenesulphondichloroamide*, clusters of needles, m. p. 47° (Found : C, 52·3; H, 7·1; N, 3·3; Cl, 17·6; available Cl, 34·6. $C_{18}H_{29}O_3NCl_2S$ requires C, 52·7; H, 7·1; N, 3·4; Cl, 17·3; available Cl, 34·6%). *Sodio*-p-n-*dodecyloxybenzenesulphonchloroamide*, m. p. 145° (decomp. at 195—200°) (Found : available Cl, 17·8. $C_{18}H_{29}O_3NClSNa$ requires available Cl, 17·9%).

p-n-*Hexadecyloxybenzenesulphondichloroamide*, needles, m. p. 63—64° (Found : C, 56·35; H, 8·2; N, 3·0; available Cl, 29·2. $C_{22}H_{37}O_3NCl_2S$ requires C, 56·65; H, 8·0; N, 3·0; available Cl, 30·4%). *Sodio*-p-n-*hexadecyloxybenzenesulphonchloroamide*, m. p. 215° (decomp.) (Found : N, 2·9; Cl, 7·85; available Cl, 15·5. $C_{22}H_{37}O_3NClSNa$ requires N, 3·1; Cl, 7·8; available Cl, 15·6%).

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CHEMICAL DEFENCE EXPERIMENTAL STATION, PORTON, NEAR SALISBURY.

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