

15. *Monothioethylene Glycol. Part IV. Aryl β -Hydroxy- and β -Chloro-ethyl Sulphides.*

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A FURTHER series of substituted aryl β -hydroxyethyl sulphides has been prepared (cf. J., 1927, 1666) and converted into the corresponding chloro-sulphides, the substituents being of as wide a range of polar character as possible.

Of the thiophenols required for the preparations, the *p*-halogenated compounds were obtained from the corresponding amines by the Leuckart reaction through the xanthic esters.

Some of the derived sulphoxides, and a number of the sulphones, are also described.

The vesicant or irritant action of these compounds is slight, but it is very noticeable with the sulphones and particularly in *p*-nitrophenyl- β -chloroethylsulphone.

Each aryl β -hydroxyethyl sulphide was prepared by adding ethylene chlorohydrin to a solution of the thiol in a slight excess of aq. KOH at 60–70° and heating for a short time on the water-bath; the product was removed and dried (K_2CO_3) in Et_2O and recovered. Conversion into the chloro-sulphide was effected by $SOCl_2$ in C_5H_5N and CCl_4 (cf. Part III, *loc. cit.*), but with compounds halogenated in the nucleus fusion with PCl_5 was necessary.

Oxidation to the sulphoxides was carried out with H_2O_2 in AcOH, to the sulphones with aq. $KMnO_4$ in presence of $MgSO_4$. For the synthesis of β -hydroxyethyl sulphones the requisite sulphinic acid was dissolved in aq. KOH, evaporated in vac., and heated for 2–8 hr. at 100–120° with ethylene chlorohydrin. Steam was then passed to remove volatile matter, and the product separated and recrystallised.

Mesityl β -hydroxyethyl sulphide, from *s*-trimethylthiophenol, solidified and formed colourless needles from light petroleum; m. p. 25° (Found: S, 16.5. $C_{11}H_{16}OS$ requires S, 16.3%). It was converted quantitatively into *mesityl β -chloroethyl sulphide*, which crystallised from MeOH in colourless needles with an oblique extinction; m. p. 44° (Found: Cl, 16.55; C, 61.9; H, 7.2. $C_{11}H_{15}ClS$ requires Cl, 16.55; C, 61.6; H, 7.0%). The *sulphoxide* crystallised from light petroleum in small rhomb-shaped crystals with an oblique extinction; m. p. 76° (Found: Cl, 15.1. $C_{11}H_{15}OClS$ requires Cl, 15.4%), and the *sulphone*, when crystallised from dil. MeOH, formed colourless needles with an oblique extinction; m. p. 60.5° (Found: Cl, 14.2. $C_{11}H_{15}O_2ClS$ requires Cl, 14.4%).

p-Chlorophenyl β -hydroxyethyl sulphide, after keeping at 100°/25 mm. for 1 hr., formed a light brown oil (Found: Cl, 19.0. C_8H_9OCIS requires Cl, 18.8%). It was converted by fusion with PCl_5 into *p*-chlorophenyl β -chloroethyl sulphide, which formed large colourless plates with a straight extinction (from light petroleum); m. p. 34° (Found: Cl, 34.2. $C_8H_8Cl_2S$ requires Cl, 34.3%). The corresponding *sulphone* was prepared through the sulphinic acid obtained from *p*-chloroaniline by Gattermann's method, the β -hydroxyethyl sulphone being converted without purification into the β -chloro-sulphone. It separated from light petroleum in minute white prisms with an oblique extinction; m. p. 96° (Found: Cl, 29.9. $C_8H_8O_2Cl_2S$ requires Cl, 29.7%).

p-Bromophenyl β -hydroxyethyl sulphide, prepared similarly, was a dark brown oil (Found: Br, 34.4. C_8H_9OBrS requires Br, 34.3%), converted by PCl_5 into *p*-bromophenyl β -chloroethyl sulphide, large, almost colourless plates, m. p. 39°, from light petroleum (0.1861 g. pptd. 14.79

c.c. $N/10$ - AgNO_3 . $\text{C}_8\text{H}_8\text{ClBrS}$ requires 14.53 c.c.). The *sulphone*, prepared through an oily β -hydroxyethyl sulphone, separated from light petroleum as a microcryst. powder, m. p. 109° (0.1372 g. pptd. 9.58 c.c. $N/10$ - AgNO_3 . $\text{C}_8\text{H}_8\text{O}_2\text{ClBrS}$ requires 9.67 c.c.).

p-Iodophenyl β -chloroethyl sulphide was produced by the action of PCl_5 on the oily hydroxy-sulphide, and crystallised from MeOH in minute plates with oblique extinction; m. p. 54° (0.1503 g. gave 0.1900 g. mixed halides. Found by action of Cl_2 : Cl, 12.3; I, 41.6. $\text{C}_8\text{H}_8\text{ClIS}$ requires 0.1905 g.; Cl, 11.9; I, 42.5%).

2 : 4-Dichlorothiophenol.—The diazonium solution obtained from dichloroaniline (20 g.) in conc. H_2SO_4 (40 c.c.) and H_2O (240 c.c.) at $0-5^\circ$ (8.6 g. NaNO_2 in 60 c.c. H_2O) was mixed with borax (240 g. in 1.5 l. H_2O) and added to potassium xanthate (30 g. in a little H_2O) at $60-70^\circ$. The brown oily xanthic ester was removed in Et_2O , recovered, and hydrolysed (13 g. NaOH in 130 c.c. spirit) for 1 hr., the EtOH distilled off, the solution acidified, and the dichlorothiophenol distilled in steam, being obtained as an oil which solidified; m. p. 20° . It was oxidised by K_3FeCy_6 to 2 : 4 : 2' : 4'-tetrachlorodiphenyl disulphide, colourless prisms, m. p. 82.5° (Found : Cl, 39.9. $\text{C}_{12}\text{H}_6\text{Cl}_4\text{S}_2$ requires Cl, 39.8%), and converted at 120° by BzCl into the benzoate, which crystallised from petroleum in minute, pale brown needles with straight extinction; m. p. 97° (Found : Cl, 25.2. $\text{C}_{13}\text{H}_8\text{OCl}_2\text{S}$ requires Cl, 25.1%). The thiophenol was converted through an oily hydroxy-sulphide into 2 : 4-dichlorophenyl β -chloroethyl sulphide, an almost colourless oil, b. p. $218^\circ/15$ mm. (Found : Cl, 42.9. $\text{C}_6\text{H}_7\text{Cl}_3\text{S}$ requires Cl, 44.1%). [A tendency for β -chloroethyl sulphides to give slightly low values of Cl content after distillation has been previously noticed (e.g., Bennett, J., 1921, 119, 424).] The sulphoxide crystallised from petroleum in colourless needles, m. p. 96.5° (Found : Cl, 41.2. $\text{C}_6\text{H}_7\text{OCl}_3\text{S}$ requires Cl, 41.4%).

From 2 : 5-dichlorothiophenol, m. p. 23° (Gebauer-Fülneegg and Figdor, *Monatsh.*, 1927, 48, 627), which gave a disulphide, forming colourless microscopic prisms, m. p. 81.5° (Found : Cl, 39.8. Calc. : Cl, 39.9%), 2 : 5-dichlorophenyl β -hydroxyethyl sulphide was obtained, colourless plates, m. p. 32° , from dil. MeOH (Found : Cl, 31.8. $\text{C}_8\text{H}_8\text{OCl}_2\text{S}$ requires Cl, 31.8%). 2 : 5-Dichlorophenyl β -chloroethyl sulphide is a colourless oil, b. p. $176^\circ/15$ mm. (Found : Cl, 43.0. $\text{C}_8\text{H}_7\text{Cl}_2\text{S}$ requires Cl, 44.1%). Its sulphoxide crystallised from light petroleum in thin colourless plates with a high double refraction; m. p. 68° (Found : Cl, 41.0; C, 37.1; H, 3.0. $\text{C}_8\text{H}_7\text{OCl}_3\text{S}$ requires Cl, 41.4; C, 37.3; H, 2.7%).

2 : 4 : 6-Trichlorothiophenol was prepared from trichloroaniline, diazotisation being conducted in conc. H_2SO_4 for several days. The solution was diluted and poured into a large excess of potassium xanthate solution slowly at 50° . The thiophenol was subsequently isolated as a colourless solid, m. p. 60° (Found : Cl, 49.7. $\text{C}_6\text{H}_3\text{Cl}_3\text{S}$ requires Cl, 49.9%), readily oxidised to 2 : 4 : 6 : 2' : 4' : 6'-hexachlorodiphenyl disulphide, microscopic white crystals, m. p. 165° , from xylene (Found : Cl, 50.2. $\text{C}_{12}\text{H}_4\text{Cl}_6\text{S}_2$ requires Cl, 50.3%), and furnishing a benzoate, which crystallised from xylene in small colourless elongated plates with a straight extinction; m. p. 170° (Found : Cl, 33.0. $\text{C}_{13}\text{H}_7\text{OCl}_3\text{S}$ requires Cl, 32.8%). By condensation with ethylene chlorohydrin 2 : 4 : 6-trichlorophenyl β -hydroxyethyl sulphide was obtained, which crystallised from light petroleum in colourless prisms with high double refraction and an oblique extinction, m. p. 41° (Found : Cl, 41.2. $\text{C}_8\text{H}_7\text{OCl}_3\text{S}$ requires Cl, 41.4%), and was converted by PCl_5 into 2 : 4 : 6-trichlorophenyl β -chloroethyl sulphide, rhomb-shaped plates with an oblique extinction (from MeOH), m. p. 71° (Found : Cl, 51.4; C, 35.0; H, 2.5. $\text{C}_8\text{H}_6\text{Cl}_4\text{S}$ requires Cl, 51.4; C, 34.8; H, 2.2%).

p-Anisyl β -hydroxyethyl sulphide, from *p*-anisidine, separated from petroleum in minute white plates, m. p. 41° (Found : S, 17.3. $\text{C}_9\text{H}_{12}\text{O}_2\text{S}$ requires S, 17.4%). The derived *p*-anisyl β -chloroethyl sulphide was isolated as a pale yellow oil, b. p. $110^\circ/1$ mm., which darkened and evolved HCl on long keeping (Found : Cl, 17.7. $\text{C}_9\text{H}_{11}\text{OClS}$ requires Cl, 17.5%).

From thio- α -naphthol, an oily β -hydroxyethyl sulphide was prepared and converted at once into α -naphthyl β -chloroethyl sulphide, a pale brown oil which suffered slight decomp. on distillation (Found : Cl, 15.6. $\text{C}_{12}\text{H}_{11}\text{ClS}$ requires Cl, 15.9%). The sulphone was separately synthesised from α -naphthalenesulphonic acid [m. p. 86° , prepared by reduction of the sulphonyl chloride (16 g.) with Na_2SO_3 (60 g.) and NaOH (4 g.) in 200 c.c. H_2O]. α -Naphthyl- β -hydroxyethylsulphone, after crystallising once from dil. MeOH and once from H_2O , formed silvery plates, m. p. 122° (Found : S, 13.5. $\text{C}_{12}\text{H}_{12}\text{O}_3\text{S}$ requires S, 13.6%). α -Naphthyl- β -chloroethylsulphone crystallised from dil. MeOH in stout prisms, m. p. 74° (Found : Cl, 13.9. $\text{C}_{12}\text{H}_{11}\text{O}_2\text{ClS}$ requires Cl, 13.95%). β -Naphthyl β -hydroxyethyl sulphide, from thio- β -naphthol, formed silvery matted plates, m. p. 64° , from light petroleum (Found : S, 15.6. $\text{C}_{12}\text{H}_{12}\text{OS}$ requires S, 15.7%). When allowed to react gently with PCl_5 (1.25 mols.), it yielded β -naphthyl β -chloroethyl sulphide, which

crystallised from EtOH in plates with a high refraction and straight extinction; m. p. 53° (Found: Cl, 16.1. $C_{12}H_{11}ClS$ requires Cl, 15.9%). When the above hydroxy-sulphide was fused with an excess of PCl_5 , nuclear chlorination also occurred with production of *β*-chloro-*β*-naphthyl *β*-chloroethyl sulphide, small crystals (from EtOH), m. p. 52°, depressed to 45° in admixture with the preceding compound (Found: Cl, 28.0. $C_{12}H_{10}Cl_2S$ requires Cl, 27.7%).

From *β*-naphthalenesulphinic acid, *β*-naphthyl-*β*-hydroxyethylsulphone was obtained, which crystallised from warm H_2O in minute silvery plates, m. p. 108° (Found: S, 13.6. $C_{12}H_{12}O_2S$ requires S, 13.6%), and yielded with PCl_5 *β*-naphthyl-*β*-chloroethylsulphone, microscopic crystal aggregates, m. p. 100°, from MeOH (Found: Cl, 13.8. $C_{12}H_{11}O_2ClS$ requires Cl, 13.95%).

p-Nitrophenyl-*β*-chloroethylsulphone, prepared by oxidation of the sulphide (Part III), formed colourless microscopic prisms, m. p. 128° (Found: Cl, 14.0. $C_8H_8O_4NClS$ requires Cl, 14.2%). Phenyl *γ*-chloropropyl sulphide, oxidised with H_2O_2 , yielded a sulphoxide which did not crystallise and was further oxidised with $KMnO_4$ to the *sulphone*, colourless needles (from light petroleum), m. p. 26° (Found: Cl, 16.0. $C_9H_{11}O_2ClS$ requires Cl, 16.2%).

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