

325. *Some Heterocyclic Quaternary Dichloroiodides.*

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By treatment at a low temperature with sulphuryl chloride in acetic anhydride, six heterocyclic ethiodides were converted into crystalline dichloroiodides. One of these was converted into a quaternary salt by use of zinc in acetic acid and one by use of carbon tetrachloride.

SULPHURYL CHLORIDE can function in various ways, according to the conditions of reaction.¹ It proved a powerful chlorinating agent for alkylpyrroles, whereby aldehydes and acids were synthesised.² It seemed as though its application to six-membered heterocyclic nuclei, having a reactive methyl group, might be of interest, and its behaviour with the ethiodides of quinaldine, lepidine, and 2-methylbenzothiazole was first examined.

Whereas ether was the usual solvent for the pyrroles,² acetic anhydride proved a suitable medium for heterocyclic quaternary salts. When a suspension of an ethiodide in that solvent was treated at a low temperature with a solution of an equimolecular quantity of sulphuryl chloride, it quickly dissolved and a new salt crystallised. The crude products were unstable but, after being washed, could be recrystallised from acetic acid and, when dry, could be kept without apparent deterioration.

In each of the three instances named, analyses showed that two chlorine atoms had been added. The methyl group was not involved since quinoline ethiodide and benzothiazole methiodide behaved similarly. When 2-iodoquinoline ethiodide was treated with two molecular equivalents of sulphuryl chloride, two chlorine atoms were added and, besides, chlorine replaced iodine in the 2-position. Negative results, which were obtained when the starting points were quinaldine ethochloride and 2-methylbenzothiazole ethotoluene-*p*-sulphonate, indicated that the iodine atom was essential. So it was concluded that the products were dichloroiodides.

Attempts to prepare the dichloroiodide of a 4 : 4'-cyanine and of a thiacyanocyanine similarly in acetic anhydride were unsuccessful.

Perhalides of tetra-alkylammonium salts have been prepared by interaction of a halogen, in alcohol or acetic acid, with a quaternary salt;³ tetrachloroiodides of various organic bases have been prepared by the action of iodine and chlorine on a hydrochloric acid solution of the bases.⁴

That the present crystalline compounds are perhalides is confirmed by the ease of removal of halogen. Thus the compound prepared from 2-methylbenzothiazole ethiodide was quickly decolorised by zinc in acetic acid but double salt formation made isolation of quaternary salt difficult. However, excess of sodium hydroxide was used to remove the zinc salt; the resultant methylene base was extracted and was acidified to give a salt.

In decomposing perhalides, the halogen atom which remains attached to the cation is the lightest in the molecule.⁵ As carbon tetrachloride dissolves halogens, it was chosen in studying the dissociation of polyhalides.⁶ The present salt from quinaldine ethiodide was shaken hot with water and carbon tetrachloride; at first iodine was readily removed, but protracted treatment was necessary for its complete removal; the salt in the aqueous layer was quinaldine ethochloride.

EXPERIMENTAL

1-Ethyl-2-methylquinolinium Dichloroiodide.—A suspension of powdered quinaldine ethiodide (2.99 g., 1 mol.) in acetic anhydride (3 c.c.) was cooled with ice-salt, and a cooled solution of sulphuryl chloride (1 mol.) in acetic anhydride (3 c.c.) was added in one lot. A brown colour developed, the solid dissolved, and the colour became lighter. On stirring, crystals separated. They were filtered off (smell of sulphur dioxide) and washed twice with acetic anhydride and five times with absolute ether, and dried in a vacuum-desiccator. On recrystallisation from

¹ Brown, *Ind. Eng. Chem.*, 1944, **36**, 785.² Fischer, Sturm, and Friedrich, *Annalen*, 1928, **461**, 249.³ Chattaway and Hoyle, *J.*, 1923, **123**, 654.⁴ Chattaway and Garton, *J.*, 1924, **125**, 183.⁵ Sidgwick, "The Chemical Elements and their Compounds," Oxford Univ. Press, 1950, Vol. II, p. 1195.⁶ Cremer and Duncan, *J.*, 1931, 2243.

acetic acid (20 c.c. per g.), the 37% yield dropped to 33%. The yellow *dichloroiodide*, both before and after recrystallisation, had m. p. 99—100°, with previous yellowing (Found: C, 39.1; H, 4.05; O, 0; N, 3.8; Cl, 19.45; I, 34.5; S, 0. $C_{12}H_{14}NCl_2I$ requires C, 38.95; H, 3.8; N, 3.8; Cl, 19.15; I, 34.3%). When twice the amount of acetic anhydride was used, the yields were 23% and 20%. When the sulphuryl chloride was added during 3 min., inoculation was necessary to start crystallisation, and the yield of washed salt was only 7%.

1-Ethyl-4-methylquinolinium Dichloroiodide.—Lepidine ethiodide similarly gave the lemon-yellow *dichloroiodide*, m. p. 114° (decomp.) (46% after two crystallisations from acetic acid) (Found: C, 39.2; H, 4.15; N, 3.5; Cl, 18.95; I, 34.2%).

3-Ethyl-2-methylbenzothiazolium Dichloroiodide.—2-Methylbenzothiazole ethiodide similarly gave the bright yellow *ethodichloroiodide*, m. p. 85—86°, the yield being 32% after recrystallisation from acetic acid (Found: C, 31.95; H, 3.4; I, 33.85. $C_{10}H_{12}NCl_2IS$ requires C, 31.95; H, 3.2; I, 33.75%).

1-Ethylquinolinium Dichloroiodide.—From quinoline ethiodide (2.85 g.) and sulphuryl chloride the yield of pale yellow washed *perhalide* was 42%. Twice recrystallised from acetic acid (yield 32%), it had m. p. 100° (Found: C, 36.95; H, 3.65; N, 3.8; Cl, 19.75; I, 35.7. $C_{11}H_{12}NCl_2I$ requires C, 37.1; H, 3.4; N, 3.95; Cl, 19.9; I, 35.65%).

3-Methylbenzothiazolium Dichloroiodide.—From benzothiazole methiodide (2.77 g.), the yield of *perhalide* was 63%, and after two recrystallisations from acetic acid 48%. The pale yellow crystals had m. p. 139° (decomp.), with previous yellowing (Found: C, 27.8; H, 2.6; N, 3.9; Cl, 19.95; I, 36.9; S, 9.05. $C_8H_8NCl_2IS$ requires C, 27.6; H, 2.3; N, 4.0; Cl, 20.35; I, 36.45; S, 9.2%).

2-Chloro-1-ethylquinolinium Dichloroiodide.—2-Iodoquinoline ethiodide (2.06 g., 1 mol.) and sulphuryl chloride (2 mols.) in acetic anhydride (6 c.c.) similarly gave a crude salt (109%) which was crystallised from acetic acid, and washed three times with acetic acid and five times with ether, yielding the pale yellow *perhalide* (57%), m. p. 124° (Found: C, 33.95; H, 3.2; N, 3.5; Cl, 27.6; I, 32.7. $C_{11}H_{11}NCl_3I$ requires C, 33.85; H, 2.85; N, 3.6; Cl, 27.25; I, 32.5%).

Breakdown of 3-Ethyl-2-methylbenzothiazolium Dichloroiodide.—The dichloroiodide (0.75 g., 1 mol.), suspended in acetic acid (15 c.c.), was heated with zinc dust (8 atoms) on the water-bath, with stirring, for 3 min. After filtration hot, the filtrate and washings were treated, with cooling, with sodium hydroxide (20 g.) in water (100 c.c.) and extracted with chloroform. The extract was washed once with water, then extracted with 17% hydrochloric acid (6 × 4 c.c.). The acid extracts were evaporated to dryness on the water-bath and in a vacuum-desiccator. The product (42% yield) was recrystallised from ethanol and then anhydrous acetone (21% yield; as for 2-methylbenzothiazole ethochloride, recrystallised similarly). When the product was heated, it and its mixture with 2-methylbenzothiazole ethochloride behaved like that salt, partly melting about 150° and frothing up to about 180°. When boiled with pyridine and ethyl orthoformate, it gave the same colour as did 2-methylbenzothiazole ethochloride.

Breakdown of 1-Ethyl-2-methylquinolinium Dichloroiodide.—This dichloroiodide (0.37 g.) was shaken with carbon tetrachloride (40 c.c.) and water (40 c.c.), on the water-bath. The aqueous layer became orange and the lower layer deep pink. After cooling, the latter was filtered and the treatment was repeated with fresh solvent (40 c.c.), which became slightly less intensely coloured. The third extract was paler but even the last of eight such extracts was pink. The last extract was left in contact with the aqueous layer for 48 hr. during which its colour deepened. After three further extractions with carbon tetrachloride (3 × 80 c.c.) on the water-bath with stirring for 15 min. both layers were colourless. The final aqueous layer was taken to dryness on the water-bath and in a vacuum-desiccator but the product (100% yield) was brown. It was recrystallised from ethanol (charcoal) by addition of anhydrous acetone. The 29% yield of colourless crystals was of the same order as the yield obtained when quinaldine ethochloride was similarly recrystallised. They were free from iodine, although the crude product gave a faint positive test ($CS_2-H_2SO_4$). The recrystallised salt, quinaldine ethochloride, and their mixture all decomposed at 236° (darkening *ca.* 170°). When heated with pyridine and ethyl orthoformate, the salt gave a blue colour, as did quinaldine ethochloride, thus confirming the identity.

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