Tetrachloropyridine-4-sulphonyl Chloride, a Stable Derivative of Pyridine-4-sulphonyl Chloride

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Summary The title compound was prepared from the corresponding mercaptan, disulphide, or sulphenyl chloride by modification of the usual procedures and was found to be remarkably stable in comparison with pyridine-2- and -4-sulphonyl chloride.

THE generalisation has been made[1] that "imino-conjugated chlorosulphonyl derivatives of the structure $-N{=}C-(C{=}C)_n-SO_2Cl$ are unstable under certain very definite conditions and rearrange to produce sulphur dioxide and the corresponding chloro-derivative." Thus, at room temperature, the 2- and the 4-sulphonyl chloride of pyridine decompose by an S_Ni mechanism[1] to give sulphur dioxide and 2- or 4-chloropyridine respectively. We have prepared tetrachloropyridine-4-sulphonyl chloride (Ia) from the corresponding mercaptan (Ib),[2] disulphide (II), or sulphenyl chloride (Ic)† and have found it to be remarkably stable in comparison with pyridine-2- or -4-sulphonyl chloride. In each case the starting material was dissolved in anhydrous acetic acid, preferably containing anhydrous sodium acetate (1 equiv.), and treated with dry chlorine. After dilution of the resulting mixture with water the sulphonyl chloride (Ia) (*ca.* 95%), m.p. 53—54° was precipitated. Anhydrous conditions are essential, otherwise pentachloropyridine is always the major product. Alternatively, if a solution of (Ib), (Ic), or (II) in anhydrous acetic acid is saturated with

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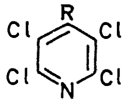
† All new compounds had the correct spectroscopic properties. With the exception of (Ic), which gave the expected products with acetone, aniline, and sodium cyanide, they analysed correctly for C, H, and N.

chlorine and then poured on to ice, the sulphonyl chloride (Ia) is obtained, also in high yield.

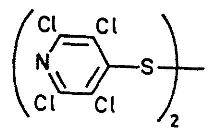
The disulphide (II), m.p. 140—141°, was prepared in 95% yield by treating the mercaptan (Ib) with bromine in acetic acid, and the sulphenyl chloride (Ic), m.p. 59—60° (decomp.), was prepared in 93% yield by treating (Ib) with chlorine in anhydrous carbon tetrachloride.

Tetrachloropyridine-4-sulphonyl chloride (Ia) was found to be stable at ambient temperatures. Moreover, it remained unchanged in acetic acid at 100° for 16 hr. but decomposed to give pentachloropyridine when heated for 16 hr. in boiling light petroleum (b.p. 120—160°). The product of the latter reaction, which may occur by a radical mechanism, still contained a trace of (Ia). The sulphonyl chloride (Ia) was also recovered after being treated with chlorine in acetic acid at room temperature in the presence or absence of hydrogen peroxide or water. At higher temperatures (*e.g.* in boiling acetic acid), however, hydrogen peroxide promoted the loss of sulphur dioxide to give pentachloropyridine.

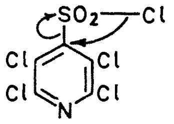
We attribute the stability of the sulphonyl chloride (Ia) to steric hindrance by the two *o*-chlorine atoms which prevent the compound from undergoing an S_Ni rearrangement (III) to give pentachloropyridine. A similar explanation has been advanced recently[3] to account for the reluctance of 4-piperidinotetrachloropyridine to undergo an S_Ni rearrangement *via* its 4-*N*-oxide (IV) to give a hydroxylamine derivative.



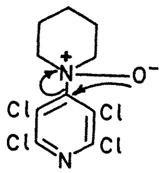
(I)a; R = SO_2Cl
b; R = SH
c; R = SCl



(II)



(III)



(IV)

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[3] S. M. Roberts and H. Suschitzky, *J. Chem. Soc.* (*C*), 1968, 1537; 1969, 1485.