An Optically Active Haloform: (+)-Bromochlorofluoromethane

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BROMOCHLOROFLUOROMETHANE, structurally the simplest organic compound capable of optical activity, has been obtained in an optically active form [$[\alpha]_D^{19} = +0{\cdot}20°$ ($t = 1$, $c = 1{\cdot}25$), $\alpha_D = 0{\cdot}25°$ in cyclohexane] by hydrolysis of 1,1,1-bromochlorofluoroacetone with aqueous potassium hydroxide (9N). The halogeno-ketone itself was resolved into its optical antipodes by means of "(−)-menthydrazide" [(−)-menthyl-*N*-aminocarbamate]. The less-soluble menthydrazone was crystallised from dry benzene to a minimum rotation of $[\alpha]_D^{22} = -45{\cdot}4°$ ($l = 1$, $c = 1$, in acetone). On acid hydrolysis this gave the (+)-ketone ($[\alpha]_D^{21} + 0{\cdot}39°$, $l = 1$, homogeneous). The menthydrazone of the (−)-ketone could not be obtained with the same degree of optical purity; the (−)-ketone ($[\alpha]_D^{21}$ $-0{\cdot}29°$) was, however, obtained.

The established methods for the preparation of oxime, hydrazone, semicarbazone, phenylhydrazone, and 2,4-dinitrophenylhydrazone derivatives failed with the ketone.

Earlier reported attempts to obtain conclusive results in the resolution of the haloform by means of its digitonin complex,[1] or by resolution of bromochlorofluoroacetic acid,[2] were also unsuccessful. Attempts at resolution by one of the present authors (M.K.H.) by crystallisation of the tri-*o*-thymotide complex[3] in the presence of iso-octane gave evidence of success but it was not possible to obtain the active haloform in quantitity sufficient for proof of the resolution.

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