Photochemical Nitrosation of Halogenohydrocarbons

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Summary Dichlorofluoronitrosomethane and chlorodifluoronitrosomethane have been prepared by photochemical reaction of nitrosyl chloride with the corresponding chlorofluorohydrocarbons, but trifluoronitrosomethane and nitrosoformyl fluoride could not be made by analogous reactions.

TRICHLORONITROSOMETHANE has been prepared by photochemical nitrosation of chloroform with nitrosyl chloride.[1] The method has now been extended to the preparation of dichlorofluoronitrosomethane and chlorodifluoronitrosomethane from the corresponding partially fluorinated haloforms.

$$\mathrm{RH + NOCl \xrightarrow{h\nu} RNO + HCl}$$

$$(\mathrm{R = CCl_3,\ CCl_2F,\ or\ CClF_2})$$

Dichlorofluoronitrosomethane has previously been made by reaction of dichlorofluoromethanesulphenyl chloride with nitric acid.[2] Chlorodifluoronitrosomethane has been obtained similarly,[2] or by decarboxylation of nitrosyl chlorodifluoroacetate,[3] by irradiation of mixtures of bromo- or iodo-chlorodifluoromethane and nitric oxide,[4] or by treatment of difluoronitroacetic acid with hydrochloric acid.[5]

The present method is a single-stage preparation from materials which are readily and cheaply available commercially. The nitrosyl produced is in each case, however, of similar volatility to the parent halogenohydrocarbon, and is not easily separated from unreacted amounts of this comparatively inert starting material. Work is now in hand on the optimisation of yields of the nitrosyls, on the identification of by-products, and on useful reactions of the product mixtures obtained.

The yields so far obtained of the nitrosyls, starting from equimolar (*ca.* 170 mmol of each) quantities of halogenohydrocarbon and of nitrosyl chloride, have been 12% (as a 19 mol % solution) in 21 h, and 15% (as a 14 mol % solution) in 14·5 h, in the dichlorofluoro- and the chlorodifluoro-cases, respectively. The lamp used was a 500 W medium-pressure mercury arc, immersed in a 10 l reactor containing the gaseous reactants.

Trifluoronitrosomethane could not be made by irradiation of a mixture of fluoroform and nitrosyl chloride. The major products found were nitrogen dioxide, nitrous oxide, and nitrogen, while the fluoroform remained substantially unchanged. Nitrosyl chloride irradiated alone under similar conditions yielded nitrogen dioxide and nitrous oxide, but at a lower rate than in the presence of fluoroform. A similar mixture of nitrosyl chloride with formyl fluoride again gave nitrogen dioxide upon irradiation, but at a much greater rate than in the fluoroform reaction. No nitrosoformyl fluoride, nor any product containing fragments of formyl fluoride, was detected, and the formyl fluoride appeared to be unconsumed.

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