

Preparation of Solutions of Trichloronitrosomethane from Chloroform

By **B. W. Tattershall**, Department of Inorganic Chemistry, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU

Trichloronitrosomethane has been prepared as a solution in chloroform, by irradiation of an equimolar mixture of nitrosyl chloride and chloroform using light from a mercury arc.

PREVIOUSLY described syntheses of trichloronitrosomethane involve a two-stage preparation, starting from methyl trichloroacetate and hydroxylamine,¹ or a three-stage preparation from trichloromethanesulphenyl chloride.^{2,3} The photochemical nitrosation of hydrocarbons by nitrosyl chloride is long established. The application of this method to the synthesis of trichloronitrosomethane from chloroform is now reported.

Trichloronitrosomethane is both photolytically unstable and thermally unstable above room temperature. The similarity of its volatility to that of chloroform prevented the use of a circulatory irradiation apparatus with a trap to remove the unstable product. However, with irradiation only of the gas phase of the mixture, and apparatus designed to favour establishment of equilibrium between gas and liquid, a yield of nitroso-compound of over 12% can be attained, without significant production of by-products. The concentration of nitroso-compound in unreacted chloroform was then >15 mol%, but no method has yet been found satisfactory for the separation of this mixture.

A mixture of chloroform (5 mmol) and nitrosyl

chloride (5 mmol) gave *ca.* 15% yield on irradiation for 54 h, using a 220 W mercury arc external to a 320 ml silica vessel. Irradiation of a mixture containing 13 times these quantities, in the same apparatus, gave only a very low conversion. This may have been limited by the amount of light falling on the mixture, or by the quenching of reactive intermediates in the gas, as a result of the increased pressure of nitrosyl chloride. These restrictions were overcome by use of a 10 l reactor with an immersed 500 W lamp, which enabled the nitroso-compound (21.8 mmol) to be prepared in one overnight irradiation experiment (19.5 h).

EXPERIMENTAL

Apparatus and Procedures.—Compounds were manipulated in a Pyrex glass vacuum system, the stopcocks of which were lubricated with Kel-F No. 90 grease. Pressures were measured by use of a Pyrex spiral gauge.

Irradiation method (1). Reactants were contained in a 25-cm cylindrical silica vessel, i.d. 4 cm, closed by a glass and P.T.F.E. grease-free valve connected through a graded seal. The liquid phase of the reactants was shielded by

¹ I. L. Knunyants and G. A. Sokol'skii, *Doklady Akad. Nauk S.S.S.R.*, 1960, **132**, 602.

² W. Prandtl and K. Sennewald, *Chem. Ber.*, 1929, **62**, 1754; W. Prandtl and W. Dollfus, *ibid.*, 1932, **65**, 754.

³ H. Sutcliffe, *J. Org. Chem.*, 1965, **30**, 3221.

aluminium foil and cooled in a water-bath, while the vessel was irradiated at 30 cm from a Hanovia type 504/4, medium-pressure mercury-arc lamp.

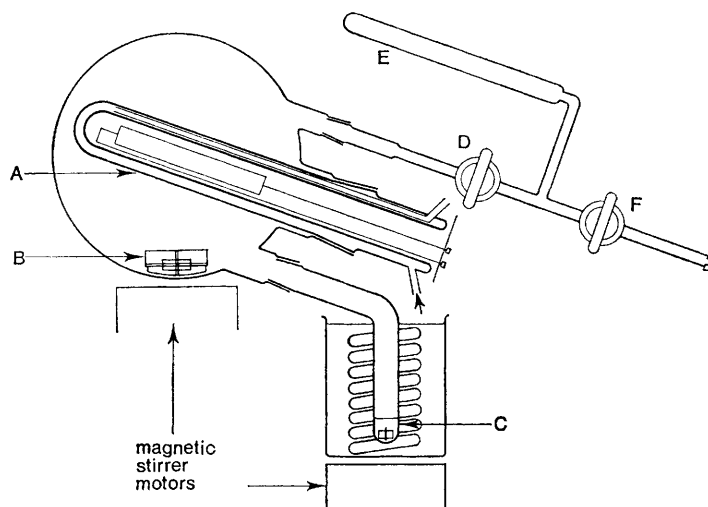
Irradiation method (2). The apparatus (Figure) was made by adaptation of a Hanovia 10 l photochemical reactor with a silica lamp jacket (A). Joints and stopcocks were lubricated with Halocarbon Series 6-00 wax, which is solid at room temperature. The gas stirrer (B) was made of pieces of P.T.F.E. sheet interlocking to enclose a P.T.F.E.-coated magnetic stirring bar. A second stirring bar was put in finger C. The 10 l bulb was surrounded by a perforated-zinc implosion shield and the apparatus was evacuated.

With the necks of the flask vertical and tap D closed, the previously measured reactants were condensed in turn from the vacuum system into finger E, then together into

compound taken [$Aw = Kp$]. When the product mixtures from the irradiations were sampled, the whole product, or a portion taken from it as a liquid in an apparatus involving a glass and P.T.F.E. grease-free needle valve, was completely vaporised at room temperature, and the gas was allowed to mix by diffusion. The gas mixture was expanded into an i.r. cell, and its pressure was measured.

Materials.—Nitrosyl chloride was prepared by the reaction of nitric oxide and chlorine at room temperature, followed by vacuum fractionation. Chloroform was washed successively with sulphuric acid, water, sodium hydroxide solution, and water; it was dried over calcium chloride, then distilled and stored under nitrogen, and finally subjected to vacuum fractionation.

Exploratory Small-scale Irradiation.—A mixture of nitrosyl chloride (5.0 mmol) and chloroform (0.594 g, 5.0 mmol) was



Apparatus for irradiation method (2)

the flask by pouring liquid nitrogen into the lamp pocket while tap F was closed. Both taps were then securely closed. The mixture was allowed to warm to room temperature, and was transferred to finger C by tipping the flask and cooling the finger. The apparatus was then set up as shown in the Figure, so that the gas stirrer rotated near the entrance to the finger containing the stirred liquid phase. The liquid phase was kept dark and at 18–19° by dipping finger C into a shielded water-bath cooled by tap water circulating through a copper coil. The lamp used was a Hanovia type 6744, medium-pressure mercury-arc. Heat from this was dissipated by circulation of water through the lamp jacket from a cooled tank. The lamp jacket was thus maintained at 24–25°, so that the reactants neither condensed onto it, nor were unduly pyrolysed.

Estimation of Trichloronitrosomethane.—The nitroso-compound, in admixture with unreacted chloroform, was estimated spectrophotometrically in the gas phase by measurement of the i.r. absorption at 1619 cm^{-1} , by use of a Perkin-Elmer 125 spectrophotometer. In a calibration experiment with CCl_3NO prepared by a literature method,² and purified by vacuum fractionation, the product of maximum absorbance (A) at 1619 cm^{-1} and the band width (w) in cm^{-1} at half this absorbance was found to vary in an approximately linear manner with the pressure (p) of

irradiated for 54 h, with its shaded liquid phase cooled in ice, by use of method (1). The liquid darkened in 6 h and was green after 18 h. Partial fractionation and i.r. examination of the mixture showed that trichloronitrosomethane had been formed, and that little further change took place on irradiation for a further 17 h with the liquid phase at 22°. Further irradiation (73 h) in the presence of dried sodium fluoride (4.6 g) did not substantially alter the quantity of the nitroso-compound in the product. The mixture was finally treated with water (1 ml) and vacuum fractionated to yield a mixture of trichloronitrosomethane (0.53 mmol, concentration 24 mol%) and chloroform. Other fractions contained further CCl_3NO (0.22 mmol); the total yield was ca. 15%.

Use of Increased Quantities of Reactants in Method (1).—A mixture of nitrosyl chloride (67.4 mmol) and chloroform (8.02 g, 67.1 mmol) was irradiated with the liquid phase at 22°, for 31 h. The yield of CCl_3NO was barely detectable.

Larger Scale Preparation.—A mixture of nitrosyl chloride (168.3 mmol) and chloroform (20.33 g, 170.3 mmol) was irradiated by method (2). Occasional interruption of the irradiation and examination of the i.r. spectrum of the mixture indicated that after irradiation for a total of 19.5 h, little further trichloronitrosomethane was being formed, and the irradiation was terminated. Vacuum fractionation through a trap at –63° condensed a fraction

shown by its i.r. spectrum to contain only the nitroso-compound and chloroform (11.64 g; $M = 126.2$; CCl_3NO estimated: 14.5 mmol at concentration 15.5 mol%). The more volatile fraction, containing nitrosyl chloride, was shaken for 1.5 h with water (60 ml) at room temperature, and the non-aqueous layer dried over magnesium sulphate

at 0°. This product was fractionated to yield a further mixture of the nitroso-compound and chloroform (4.12 g; $M = 128.7$; CCl_3NO estimated: 7.3 mmol at concentration 22.5 mol%). The total yield of CCl_3NO , based on nitrosyl chloride, was 12.9%.

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