176. *The Nitration of Halogenoethylenes.*

By Ronald Bertram Burrows and Louis Hunter.

The action of nitrating agents on the solvent halogenoethylenes has been investigated with the object of preparing halogenonitromethanes.

The action of nitric acid of various concentrations appears to cause simultaneous nitration and disruption of the molecule, and halogenonitro-derivatives of methane are formed. The production of dichlorodinitromethane from trichloroethylene by this method may well replace the earlier methods of preparation (Rakshit, J., 1915, **107**, 1115; Gotts and Hunter, J., 1924, **125**, 442). Dichloroethylene, on the other hand, yields mainly chloropicrin, and tetrachloroethylene and tribromoethylene are more or less completely broken up into carbon dioxide and halogen or halogen acid, with formation of only small amounts of lachrymatory substances.

Biltz (*Ber.*, 1902, **35**, 1530) has described the procedure for the addition of nitrogen peroxide to tetrachloroethylene, and the structure of his product has now been confirmed. In only one other instance has a stable addition product been isolated by means of this reagent, *viz.*, *ααβ-tribromo-αβ-dinitroethane* from tribromoethylene. Di- and tri-chloroethylene undergo partial oxidation to oxalic acid, yielding also small amounts of lachrymatory substances of uncertain constitution.

Dipotassium *aci*-tetranitroethane is formed with extraordinary ease by the action of reagents on a great variety of halogenonitro-derivatives of both methane and ethane; *e.g.*, by the action of potash or various potassium salts on bromopicrin (Scholl and Brenneisen, *Ber.*, 1898, **31**, 642), *s*-dichlorotetranitroethane, ααβ-tribromo-αββ-trinitroethane (Hunter, J., 1924, **125**, 1480), hexanitroethane (Will, *Ber.*, 1914, **47**, 963), and *s*-tetrachlorodinitroethane (present investigation). It is evident that, as the majority of these substances are less highly nitrated than the resulting potassium salt, the reactions involve a type of internal nitration seldom met with elsewhere.

EXPERIMENTAL.

The chloroethylenes used were the solvents prepared by the Weston Chemical Co., Ltd., and, with the exception of dichloroethylene, distilled within a range of 2°.

Action of Nitric Acid.—Dichloroethylene. Dichloroethylene (40 c.c.) was cautiously added to a mixture (150 c.c.) of equal volumes of fuming and concentrated nitric acids, and the reaction started by warming. The oil (15 c.c.) obtained on distillation was mainly unchanged dichloroethylene (b. p. about 55°) with a small amount of chloropicrin (b. p. 100—120°).

Trichloroethylene. The action of fuming nitric acid was uncontrollably violent.

Trichloroethylene (60 c.c.) was boiled under reflux with nitric acid (225 c.c., *d* 1·42) for 3 hours. The lachrymatory oil (37 c.c.) obtained on distillation, which was washed with water and dried over sodium sulphate and consisted mainly of dichlorodinitromethane with a small admixture of chloropicrin and unchanged trichloroethylene, was either fractionally distilled, the fraction of b. p. 35—45°/11—12 mm. being redistilled, or treated with an excess of alcoholic potash, the precipitated potassium chlorodinitromethane being removed and treated in aqueous solution with chlorine (Gotts and Hunter, *loc. cit.*, p. 447); 28 c.c. of crude, and 8 c.c. of dichlorodinitromethane of b. p. 40—42°/12 mm., were obtained (Found : Cl, 39·5. Calc. : Cl, 40·6%)

Tetrachloroethylene. No reaction occurred with boiling concentrated nitric acid, and with fuming acid (*d* 1·5) a violent reaction set in with evolution of carbon dioxide, hydrogen chloride, and oxides of nitrogen. The oil which distilled was largely unchanged tetrachloroethylene (b. p. 115—120°) with a very slight lachrymatory residue. No modification of the reaction could be induced by using weaker acid.

Tribromoethylene. This was prepared by the action of aqueous potash (Ward, J., 1930, 2145) on the crude acetylene tetrabromide obtained by passing washed acetylene into aqueous bromine.

Tribromoethylene (20 c.c.) and a mixture (40 c.c.) of equal volumes of concentrated and fuming nitric acids was warmed until reaction commenced. Bromine and oxides of nitrogen were evolved, and an oil distilled (6 c.c.), which, after being washed, was treated with alcoholic potash. The precipitated solid was partly soluble in water (*aci*-nitro-salt); the insoluble portion (2 g.) was pentabromoethane, m. p. 54—55°. Treatment of the yellow aqueous solution with bromine precipitated a pale yellow lachrymatory oil (1 c.c.), which was probably dibromodinitromethane.

Addition of Nitrogen Peroxide.—The nitrogen peroxide was obtained by the distillation of nitric acid and arsenious oxide, the product being collected in a freezing mixture. By redistillation over phosphoric oxide complete oxidation to the peroxide was secured.

Dichloroethylene. Serious explosions result from heating a mixture of this substance and nitrogen peroxide in a sealed tube, even at 30°.

A mixture of nitrogen peroxide (15 g.) and dichloroethylene (10 g.) was left at the ordinary temperature in a boiling-tube closed by a cork carrying a long narrow tube to minimise diffusion. After 24 hours, the solution, which had darkened, was poured into a clock-glass; the excess of nitrogen peroxide and dichloroethylene then evaporated, leaving a pale yellow, crystalline residue of lachrymatory odour. By repeated crystallisation from dichloroethylene, oxalic acid, m. p. 98—100° (Found: equiv., 62·9. Calc. for dihydrate, 63·0), was obtained. The lachrymatory substance could not be isolated.

Trichloroethylene. Nitrogen peroxide (15 g.) and trichloroethylene (10 g.) were heated in a sealed tube at 50° for 6 hours. When the excess of the reactants was allowed to evaporate, a small deposit of oxalic acid was obtained. The resultant oil (7 g.; Cl, 47·5%) was yellow, strongly lachrymatory, and reacted violently with caustic potash and with potassium iodide. The yellow *aci*-salt produced with the latter reagent proved to be dipotassium *s*-tetranitroethane (Found: K, 26·9. Calc.: K, 27·3%. Explosion point, 270°). Only one case is known of a halogenonitromethane yielding an *aci*-salt of a nitroethane under these conditions, *viz.*, bromopicrin (Hunter, J., 1923, **123**, 543). The oil is therefore evidently a chloronitroethane of uncertain constitution.

Tetrachloroethylene. The properties of the addition product, *s*-tetrachlorodinitroethane, prepared according to Biltz (*loc. cit.*) are now described. Towards alkaline reagents it reacts in a manner typical of positive halogen compounds (see Gotts and Hunter, *loc.*

cit.). With alcoholic potash and potassium iodide, a more or less violent action occurs and a yellow explosive organic salt, mixed with chloride, is deposited. Potassium cyanide brings about complete decomposition, yielding carbonate, carbon, and cyanogen chloride.

A solution of tetrachlorodinitroethane (6 g.) in a little alcohol was slowly run into a solution of potassium iodide (12 g.) in water (24 c.c.). Heat was developed, iodine liberated, and a yellow powder (4 g.) containing much chloride precipitated. The solid was removed, washed with alcohol until free from iodine, and recrystallised from water (yield, 1·5 g.). From its appearance, explosion point (270°), and analysis (Found : K, 28·0. Calc. : K, 27·3%), the salt is evidently dipotassium *s*-tetranitroethane. This conclusion was confirmed by its conversion into *s*-dichlorotetranitroethane, m. p. 105° (Hunter, J., 1924, **125**, 1480, gives 107°), by the action of chlorine on its aqueous solution.

When tetrachlorodinitroethane (6 g.) was cautiously heated just above its melting point, oxides of nitrogen were evolved and a liquid distillate collected (3—4 g.). The liquid was weakly lachrymatory and boiled with scarcely any residue between 115° and 120° (b. p. of tetrachloroethylene, 121°). Heating evidently results chiefly in the simple removal of nitrogen peroxide.

Tribromoethylene. Nitrogen peroxide (13 g.) and tribromoethylene (10 g.) were heated in a sealed tube at 40—45° for 8 hours. The product, evaporated in a draught of air, left a residue (1·4 g.), which was well washed with ligroin. The colourless solid obtained, which commenced to decompose at about 120° and melted at 133—134°, was *ααβ-tribromo-αβ-dinitroethane* [Found : Br, 67·9; N, 7·8. $C_2HBr_3(NO_2)_2$ requires Br, 67·2; N, 7·8%]. It was insoluble in water, soluble, often with decomposition, in organic solvents, had the usual lachrymatory properties, and was decomposed by alcoholic potash and by potassium iodide, yielding a yellow organic salt.

Acknowledgment is made to the Chemical Society for a grant in aid of this investigation.

UNIVERSITY COLLEGE, LEICESTER. [*Received, February 25th,* 1932.]