

232. A Method of Synthesis of Trinitromethane Derivatives.

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The present investigations have shown that aromatic halogenomethyl derivatives react with the silver salt of *aci*-trinitromethane yielding trinitromethane derivatives. They are stable, crystalline, colourless compounds, most probably of the true nitro-type. The reaction also yields varying amounts of unstable, deeply coloured derivatives, probably of the *aci*-trinitromethane type.

A number of trinitromethyl and polytrinitromethyl derivatives were prepared by this method, all of which contained the trinitromethyl group in the side chain of the benzene nucleus. The benzene nucleus itself was in many cases either nitrated or polynitrated.

Improved or new methods for the preparation of a number of intermediary products are also described.

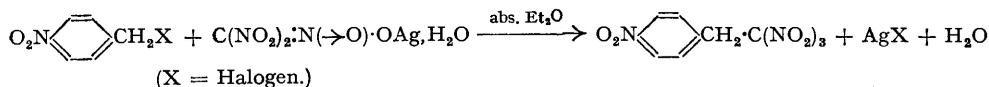
TRINITROMETHANE (nitroform) was first prepared by Schischkoff (*Annalen*, 1857, **101**, 216) by the action of water or alcohol on trinitromethyl cyanide, and later several methods for its preparation from tetranitromethane were described (Hantzsch and Rinkenberger, *Ber.*, 1899, **32**, 635; Chattaway and Harrison, *J.*, 1916, **109**, 171; Macbeth and Orr, *J.*, 1932, 534). A number of addition compounds of trinitromethane, such as its salts with pyridine, piperidine, and dibenzylamine, have also been prepared (Schmidt and Fischer, *Ber.*, 1920, **53**, 1529); they are very unstable and soon decompose on keeping.

Two aliphatic trinitromethane derivatives, *viz.*, 1 : 1 : 1-trinitroethane and hexanitroethane, have been described. Franchimont (*Rec. Trav. chim.*, 1886, **5**, 282) obtained the former by the action of concentrated nitric acid on methylmalonic acid, and it was later prepared (Hantzsch and Rinkenberger, *loc. cit.*) by reaction between silver trinitromethane and methyl iodide, but

this silver salt and iodotrinitromethane failed to give hexanitroethane. All attempts to use higher halogeno-paraffins, such as ethyl or butyl iodide, instead of methyl iodide, with a view to obtain other trinitromethane derivatives failed to yield any pure or stable compound. Will (*Ber.*, 1914, 47, 963) obtained hexanitroethane by the action of concentrated nitric and sulphuric acids on the potassium salt of 1 : 1 : 2 : 2-tetranitroethane.

Ponzo (*Gazzetta*, 1932, 62, 503) obtained aromatic azo-derivatives of trinitromethane [*e.g.*, $p\text{-Cl}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{C}(\text{NO}_2)_3$] by the reaction of ammonium trinitromethane with aromatic diazonium salts. They form yellow or orange crystalline compounds, which rapidly decompose on standing or in solution.

The present investigation has shown that it is possible to prepare stable, crystalline, aromatic trinitromethane derivatives. The synthesis was carried out by reaction of the silver salt of trinitromethane with halogenomethyl derivatives of the aromatic series :



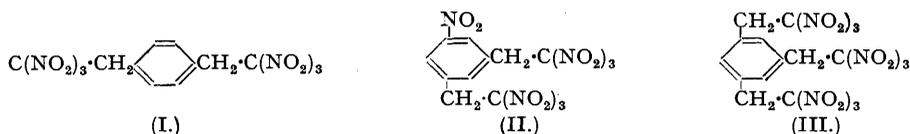
It is noteworthy that the *aci*-trinitromethane group of the silver salt is rearranged to the true nitro-type very probably contained in the stable, colourless trinitromethane derivative. The reaction also yields an unstable, deeply coloured, trinitromethane derivative, probably of the *aci*-trinitro-type, which slowly decomposes with elimination of nitrous fumes. The yield of this unstable compound depends on the working conditions and on the nature of the aromatic group. Substitution of negative groups in the benzene nucleus, especially in the *p*-position, increases the yield of the stable compound.

All the trinitromethane derivatives described in this investigation are very stable : after 3 years' standing in stoppered bottles at room temperature, they showed no change.

(With G. G. ROSE.) The preparation of the 2 : 4 : 6-trinitrobenzyl derivative by the same method proceeds easily, and the yield of the stable compound (presumably of the true nitro-type) is greater (64%) than that of the *p*-nitrobenzyl derivative (45%). In both cases, there was also formed a small amount of an unstable deeply coloured oil, presumably a mono-*aci*-compound or a mixture derived from it by decomposition and secondary reactions.

Attempts to cause reaction between 2 : 4 : 6-trinitrobenzyl bromide and the silver salt of *aci*-trinitromethane were unsuccessful, but the iodide afforded 2 : 4 : 6-trinitro-2' : 2' : 2'-trinitroethylbenzene.

(With W. WILSON.) The same reaction was utilised for the synthesis of some polytrinitromethyl derivatives : *p*-xylylene di-iodide, $\omega\omega'$ -*di*-iodo-5-nitro-*m*-xylene, and $\omega\omega'\omega''$ -*tri*-iodo-*mesitylene* reacted with an ethereal solution of silver *aci*-trinitromethane to yield, respectively, 1 : 4-bis-2' : 2' : 2'-trinitroethylbenzene (I), 5-nitro-1 : 3-bis-2' : 2' : 2'-trinitroethylbenzene (II), and 1 : 3 : 5-tris-2' : 2' : 2'-trinitroethylbenzene (III).



EXPERIMENTAL.

Silver Salt of Trinitromethane.—This preparation has been described by Hantzsch and Rinckenberger (*loc. cit.*), but for the preparation of larger quantities of pure material the following method is better. Silver oxide (freshly prepared, still slightly damp, 265 g.) was cautiously and gradually added to a solution of trinitromethane (180 g.) in ether (1000 c.c.) ; after each addition the mixture was shaken for a short while, and when the addition was complete the mixture was vigorously shaken over-night. The solution was separated by filtration, and the low-boiling material removed under reduced pressure, the ether at room temperature, and the remaining liquid at 42° (bath temp.)/12 mm. The residue was kept at 42°/12 mm. for an hour after it had crystallised and was then pressed on porous plates. A typical yield was 260 g. (*ca.* 70%).

p-Nitrobenzyltrinitromethane.—*p*-Nitrobenzyl bromide (85 g.) was dissolved in dry ether (1800 c.c.), the solution stirred in a water-bath at 20°, and a solution of the silver salt of trinitromethane (109 g.) in ether (600 c.c.) gradually added. After the addition was complete, the stirring was continued for about 2 hours and the mixture was left in the water-bath for 48 hours. The precipitated silver bromide was then filtered off, washed with ether, and dried in a desiccator (76 g. Calc. : 75 g.). The filtrate was concentrated in a high-speed evaporation apparatus at 25° (bath temp.)/12 mm., and the residue, consisting of a red liquid and a solid, was left on the vacuum pump at 30° (bath temp.) for about 15 minutes, and then for 2 hours in a refrigerator. The pale pink crystals were separated by filtration and

pressed on a porous plate (51 g., 45%), m. p. 129° (decomp.). The substance was dissolved in 250 c.c. of boiling absolute alcohol, the solution filtered while hot, and the filtrate kept overnight at 0°. The crystals were separated by filtration, washed with a small amount of cold absolute alcohol, and dried in a desiccator (34 g.). The substance was recrystallised from 200 c.c. of hot absolute alcohol-carbon tetrachloride (25 : 75) (yield 28 g.) and three further similar recrystallisations afforded 17 g. of pure 4-nitro-2' : 2' : 2'-trinitroethylbenzene; white crystals, m. p. 135° (Found : C, 33.7; H, 2.3; N, 19.5. $C_8H_8O_5N_4$ requires C, 33.6; H, 2.1; N, 19.6%).

2 : 4 : 6-Trinitrobenzyl Bromide.—Ganguly's method (*Ber.*, 1925, **58**, 708) was used with some modifications. Repeated crystallisation gave a substance, m. p. 71°, which was almost analytically pure (Found : Br, 26.85. Calc. for $C_7H_4O_6N_3Br$: Br, 26.14%). Ganguly gives m. p. 65° but no analysis.

2 : 4 : 6-Trinitrobenzyl Iodide.—Reich, Wetter, and Widmer's method (*Ber.*, 1912, **45**, 3056) was used. The brown solid was twice recrystallised from hot methyl alcohol, yielding needles, m. p. 87°; yield 47%. In general, the brominated derivative was only once crystallised before being converted into the iodo-compound, as the latter was then considerably easier to purify.

2 : 4 : 6-Trinitro-2' : 2' : 2'-trinitroethylbenzene.—Trinitrobenzyl iodide (105.9 g.) and ether (150 c.c.) were stirred whilst a solution of the silver salt of *aci*-trinitromethane (87 g.) in ether (280 c.c.) was added. The stirring was continued for 18 hours and the mixture filtered. The filtrate on evaporation yielded an unstable red oil which was ignored. The residue, a yellow-brown powder (140 g.), was extracted in portions with chloroform (Sohxlet), and the residues from the extraction were powdered and re-extracted with chloroform. On cooling, the chloroform extracts yielded a light brown, crystalline solid (72 g., 64%), m. p. 151.5–152.5° (decomp.). [The residue insoluble in chloroform was silver iodide (65 g. Calc. : 70 g.).] The brown crystals (72 g.) were dissolved in hot ethyl acetate (220 c.c.), the solution filtered from traces of silver iodide, chloroform (500 c.c.) added to the fairly warm filtrate, and the mixture cooled to 0°; the yellow crystals obtained (62 g.), m. p. 152.5–153.5° (decomp.), were four times recrystallised from hot ethyl nitrate-chloroform (1 : 1 by vol.), and the pure *hexanitro*-compound isolated as faintly coloured, large crystals (38 g.), m. p. 153–154° (decomp.) (Found : C, 25.8; H, 1.3; N, 22.4. $C_8H_4O_{12}N_6$ requires C, 25.5; H, 1.1; N, 22.35%).

Before each crystallisation the substance was finely powdered with an agate pestle and mortar and then dissolved with stirring in the requisite quantity of hot ethyl nitrate (about 150 c.c. to 55 g. of substance); when solution was complete an equal volume of chloroform was added, and the mixture cooled to 0° until crystallisation was complete. By this means prolonged heating, which caused extensive discolouration, was avoided.

ω-Bromo-5-nitro-*m*-xylene.—5-Nitro-*m*-xylene (2 g.) in boiling ethylene dibromide (40 c.c.) was irradiated by a 100-watt tungsten-filament lamp whilst a solution of bromine (4.3 g.) in ethylene dibromide (15 c.c.) was dropped in. After an hour the bromination was complete. Removal of the ethylene dibromide at 75°/20 mm. yielded a dark semi-solid substance, which was recrystallised from petroleum (b. p. 40–60°); yield, 500 mg. of *ω*-bromo-5-nitro-*m*-xylene, m. p. 59.5–60° (Found : C, 9.4; H, 3.4. $C_8H_8O_2NBr$ requires C, 41.7; H, 3.5%).

ωω'-Dibromo-5-nitro-*m*-xylene.—5-Nitro-*m*-xylene (m. p. 71–72.5°; 120 g.), dissolved in boiling ethylene dibromide (450 c.c.), was heated under reflux and irradiated with a 500-watt tungsten-filament lamp whilst a solution of dry bromine (100 c.c.) in ethylene dibromide (100 c.c.) was added fairly rapidly. After the bromine had almost disappeared, the ethylene dibromide was removed in a vacuum, the residue allowed to crystallise, and the crystals separated and washed with ether. Recrystallisation from petrol (b. p. 80–100°) yielded pure *ωω'*-dibromo-5-nitro-*m*-xylene (46 g.), m. p. 105–106.5° (Found : Br, 51.4. $C_8H_6O_2NBr_2$ requires Br, 51.8%).

Both the mono- and the di-bromo-compound were lachrymatory and had skin-irritant properties, and both afforded silver bromide quantitatively on treatment with warm aqueous-alcoholic silver nitrate.

ωω'-Di-iodo-5-nitro-*m*-xylene.—The crude dibromo-compound (above) (62 g.) was added to a solution of sodium iodide (85 g.) in acetone (400 c.c.); after 1 hour's heating under reflux the acetone was distilled off, and the residue washed with water. The product, crystallised from benzene-petroleum (b. p. 40–60°), yielded 53 g. of pure *ωω'*-di-iodo-5-nitro-*m*-xylene, m. p. 136–137° (Found : N, 3.6. $C_8H_6O_2NI_2$ requires N, 3.5%).

5-Nitro-1 : 3-bis-2' : 2' : 2'-trinitroethylbenzene.—(i) *ωω'*-Dibromo-5-nitro-*m*-xylene (m. p. 102–105°; 8 g.) was suspended in ether (100 c.c.) and 48.8 c.c. of a solution of the silver salt of trinitromethane (containing 297.4 g. per l. of ether) were added slowly. After 3 days, the silver bromide (10 g.) was filtered off, the filtrate washed with water, and then desolvated at 30°/20 mm.; the semi-solid residue was triturated with chloroform at 0°, yielding crystals (0.9 g.), m. p. 158–160°. Recrystallisation from chloroform yielded the pure *heptanitro*-compound, m. p. 170–171.5° (slight decomp.) (Found : C, 26.6; H, 1.8; N, 21.8. $C_{10}H_6O_{14}N_7$ requires C, 26.7; H, 1.6; N, 21.8%).

(ii) *ωω'*-Di-iodo-5-nitro-*m*-xylene (50 g.) was suspended in dry ether (500 c.c.), and 280 c.c. of an ethereal solution of the silver salt of trinitromethane (containing 248 g. per l.) were added fairly rapidly at 18–25° with vigorous stirring. After the stirring had continued for 4 hours, the silver iodide (61 g.) was filtered off, and the filtrate washed with water and dried (Na_2SO_4). The ether was removed in a vacuum, and the residue triturated with a little chloroform and the solution filtered after 15 minutes. The product was separated by filtration and washed on the filter with chloroform, yielding a pale pink solid (29 g.), m. p. 160–165° (decomp.). Recrystallisation from chloroform (charcoal) yielded the *heptanitro*-compound (22 g.), m. p. 171–172° (decomp.) (Found : C, 26.5; H, 1.65; N, 21.7%).

p-Xylylene Di-iodide.—This was prepared from the dichloride by double exchange with sodium iodide in acetone solution, the dichloride having been made by chloromethylation of benzyl chloride (Stephen, Short, and Gladding, *J.*, 1920, **117**, 510; Quelet, *Bull. Soc. chim.*, 1933, **53**, 222). Recrystallised from benzene-ethanol, the di-iodide had m. p. 179.5–180° (Found : C, 26.9; H, 2.0. Calc. for $C_8H_8I_2$: C, 26.8; H, 2.2%). Grimaux (*Compt. rend.*, 1870, **70**, 1365; *Annalen*, 1870, **155**, 341) gives m. p. 170°; Finkelstein (*Ber.*, 1910, **43**, 1532), m. p. 174°.

1 : 4-Bis-2' : 2' : 2'-trinitroethylbenzene.—*p*-Xylylene di-iodide (5 g.) was suspended in dry ether

(100 c.c.) and 27 c.c. of a solution of the silver salt of trinitromethane (containing 303.5 g. per l., in ether) were added slowly. After 2 hours' stirring and a further 15 hours' standing, the silver iodide (7 g. Calc. : 6.6 g.) was filtered off, the filtrate washed with water, dried, and desolvated at 30°/20 mm.; the pale yellow semi-solid product was triturated with a little chloroform on a sintered-glass filter, yielding a solid (0.6 g.), m. p. *ca.* 165° (decomp.). Recrystallisation from chloroform yielded white needles of the *hexanitro*-compound, m. p. 190° (decomp.) (Found : C, 29.7; H, 2.3; N, 20.6. $C_{10}H_8O_{12}N_6$ requires C, 29.7; H, 2.0; N, 20.8%).

ωω'ω''-Tri-iodomesitylene.—*ωω'ω''-Tribromomesitylene* (m. p. 98–99°; 1.5 g.) was added to a solution of sodium iodide (3.0 g.) in acetone (30 c.c.); after 30 mins.' heating under reflux, most of the acetone was distilled off, and the residue washed with water and dried, yielding *ωω'ω''-tri-iodomesitylene* (2.1 g.), m. p. 131–133°; crystallised from benzene, needles, m. p. 133° (Found : C, 22.6; H, 1.9. $C_9H_9I_3$ requires C, 22.1; H, 1.9%).

1 : 3 : 5-*Tris-2' : 2' : 2'-trinitroethylbenzene*.—*ωω'ω''-Tri-iodomesitylene* (5.5 g.) was suspended in ether (100 c.c.) and 34 c.c. of a solution containing 287 g. of the silver salt of trinitromethane per l. of ether were added fairly rapidly. After 2 hours' stirring, the product was allowed to stand overnight. The silver iodide (7.3 g. Calc. : 7.8 g.) was filtered off, and the solution washed with water to remove unchanged silver nitroform [the amount of which was determined by conversion into silver chloride (1.3 g.), showing that the reaction was probably about 80% complete]. The ethereal solution was dried and desolvated at 30° in a vacuum, yielding a brown oil mixed with crystals. Trituration with chloroform yielded a white solid (550 mg.), m. p. 198–200° (decomp.). Two crystallisations from chloroform yielded the required *nitro*-compound (250 mg.), m. p. 205–206° (decomp.) (Found : C, 25.4; H, 1.72; N, 22.23. $C_{12}H_9O_18N_9$ requires C, 25.4; H, 1.59; N, 22.22%).

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