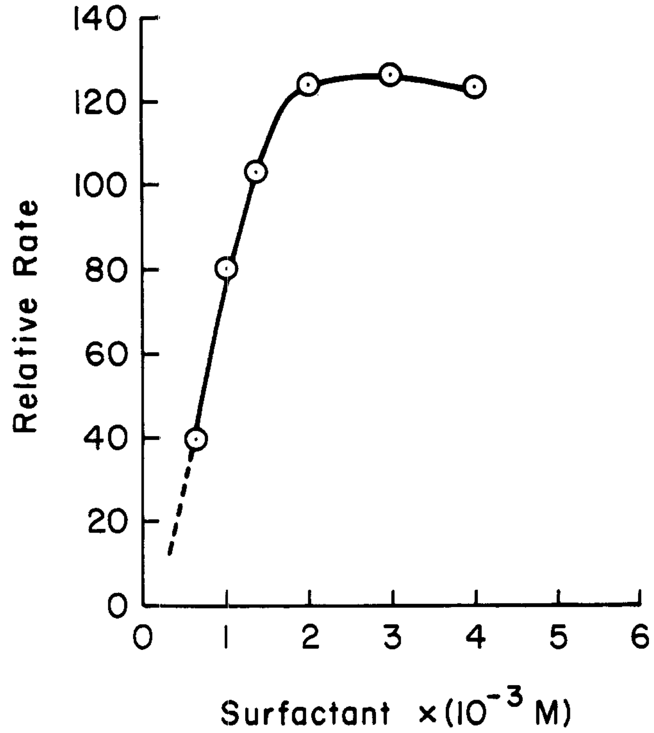

Figure 3. Relative rate for the formation of TNT$^-$ in the reaction of TNT with II as a function of the concentration of hexadecyltrimethylammonium bromide in aqueous solution at 25 °C. Initial concentrations of TNT and II were 2.5×10^{-4} and 1×10^{-3} M, respectively.

factants. The enhanced rate was more pronounced with the cationic surfactant than the nonionic one (cf. 130 vs. 8). The critical micelle concentration of hexadecyltrimethylammonium bromide is 9.2×10^{-4} M.[9] It was observed that the rate was greatly increased above this concentration. For low concentrations of hexadecyltrimethylammonium bromide ($<9 \times 10^{-4}$ M), the reaction rate of TNT with II cannot be detected since precipitation was observed.

Experimental Section

Materials. 2,4,6-Trinitrotoluene was purchased from Eastman Kodak Co. and purified by recrystallizing twice from ethanol. 4-Dodecyldiethylenetriamine and hexadecyltrimethylammonium bromide were also purchased from Eastman Kodak Co. and used without further purification. Alkylphenoxypolyethoxyethanol, Triton X-100, and 3,3′-diamino-*N*-methyldipropylamine were obtained from Rohm and Haas Co. and Jefferson Chemical Co., Inc., respectively.

Reaction Rate Measurements. The reaction rates of TNT with I and II were measured at 25 °C in 1- or 10-cm UV cells by following the absorbance at 525 nm using a Cary 14 spectrophotometer.

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Registry No.—I, 4182-44-9; II, 105-83-9; 2,4,6-trinitrotoluene, 118-96-7.

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Reactions of α-Phenylpolynitrotoluenes. 4. Ortho-Nitro Rearrangements in the Polynitrodiphenylmethanes

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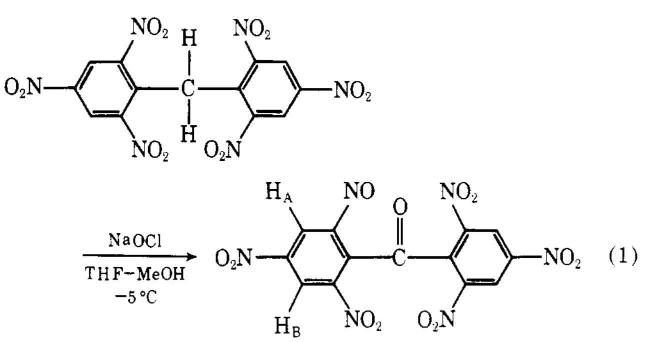
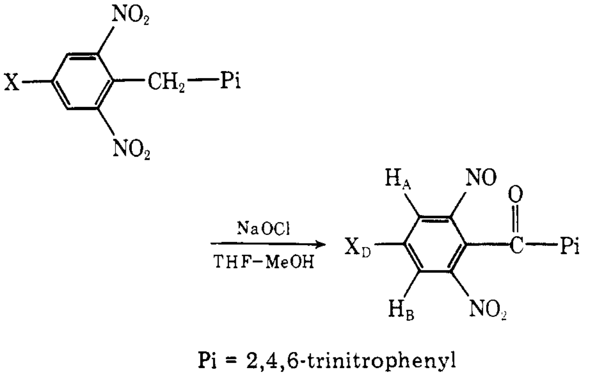
The previous paper in this series[3] described the preparation of some polynitrodiphenylmethanes. In our efforts to synthesize from these compounds tetrakis(polynitrophenyl) ethylenes,[3b] in analogy to the preparation of hexanitrostilbene[3b] from 2,4,6-trinitrotoluene, we investigated their reaction with sodium hypochlorite. The products from these reactions were, however, found to be nitrosopolynitrobenzophenones.

Reaction of 2,2′,4,4′,6,6′ hexanitrodiphenylmethane with sodium hypochlorite in THF-MeOH at −5 °C afforded a green compound in 46% yield, which was identified as 2-nitroso-2′,4,4′,6,6′-pentanitrobenzophenone in 46% yield (eq 1).



(1)

Similarly, 4-substituted pentanitrodiphenylmethanes afforded the corresponding nitroso ketones in 40–50% yield, the results being summarized in eq 2. Proof of structure of the

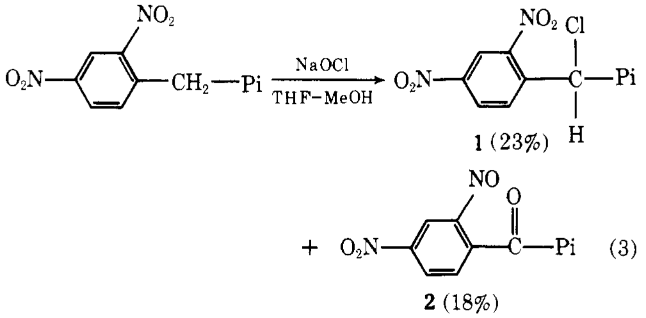


(2)

Pi = 2,4,6-trinitrophenyl
X = H, C≡N

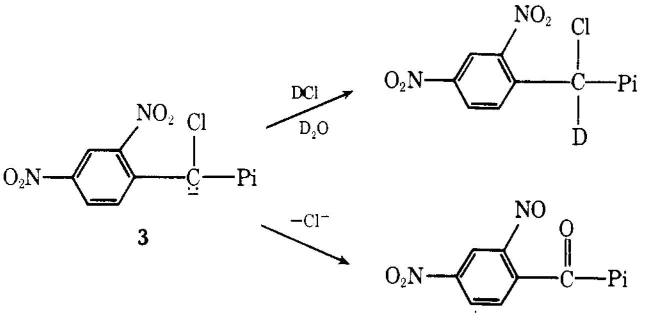
above compounds was obtained by elemental analyses, by NMR measurements, and by IR and mass spectroscopy. Evidence for the carbonyl and nitroso groups came from the infrared spectra in which absorptions in the range 1650–1700 (C=O) and 1550 and 1600 cm^{-1} (NO_2 and NO) were observed; and the fact that all the compounds were emerald green (aromatic nitroso) in color. The NMR spectra show that the 2,4,6-trinitrophenyl (Pi) group remained intact during the course of the reaction (singlet, 2 H, in the region 9.30–9.44 ppm relative to Me_4Si) as previously observed for other picryl derivatives,[3] and that the nitroso group was formed in the other ring (see eq 2). The hydrogens of the ring containing the nitroso function show the expected splitting pattern for nonequivalent hydrogen (see Experimental Section). The mass spectra are also in agreement with the proposed structures as the molecular weights obtained exactly matched the expected theoretical values.

In the case of the 2,2′,4,4′,6-pentanitrodiphenylmethane system, we were able to obtain both the chloro compound **1** as well as the nitroso ketone **2**.

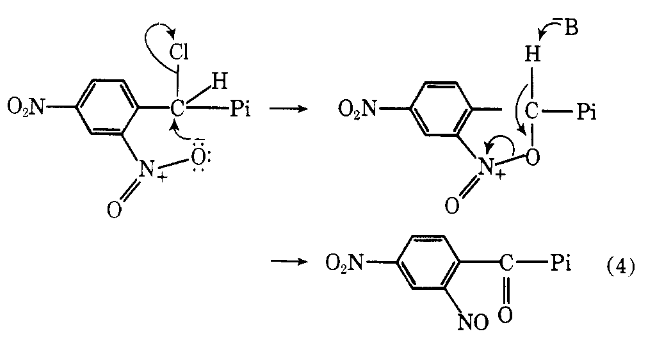


In light of our previous work,[3b] chloro compound formation was not completely unexpected. For example,[3b] 2,4,6-trinitrotoluene (TNT) can be chlorinated with sodium hypochlorite to produce 2,4,6-trinitrobenzyl chloride in 85% yield. The intermediacy of the above chloro compound in the TNT → HNS reaction is well established.[3b] It is worth noting that the yields in the reaction of TNT with sodium hypochlorite to give hexanitrostilbene (HNS), and the yields in the polynitroditan reactions with hypochlorite reported here are of the same order of magnitude, i.e., 40–50%. This similarity, rather than being coincidental, may well arise from a common mechanism for these reactions.

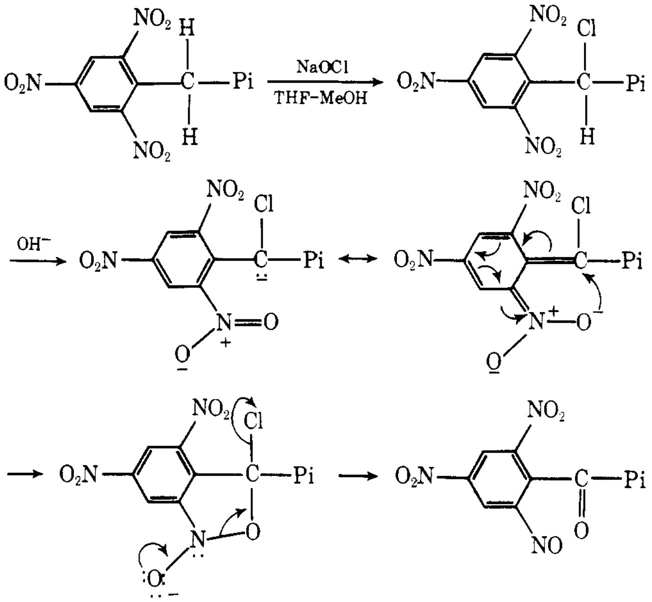
Although chlorination is observed only in the 2,2′,4,4′,6-pentanitroditan system (eq 3), it is probable that initial formation of a chloro compound is a common route to the nitroso ketones in all of the other cases as well. That **1** is indeed an intermediate to the nitroso ketone was established as follows. When 1 equiv of α-chloro-2,2′,4,4′,6-pentanitrodiphenylmethane in THF/MeOH was reacted with 1 equiv of sodium hydroxide, and the reaction was quenched with DCl/D_2O after 3.5 min of stirring, a 23% yield of nitroso ketone was isolated. In addition, unchanged chloro compound was recovered which incorporated 30–35% deuterium as evidenced by mass spectroscopy and NMR. Incorporation of deuterium in the unreacted α-chloro compound suggests the formation of **3** as a reaction intermediate.



A mechanism similar to the one postulated by Dickinson[4] for the reaction of *o*-nitrobenzhydrol with *p*-toluenesulfonyl chloride in pyridine to produce *o*-nitrosobenzophenone is not likely to operate here. Such a mechanism (eq 4) in which the nitro group is assisting the displacement of the chloride ion in the un-ionized intermediate **1** would not account for the incorporation of deuterium in the unreacted **1**.



Scheme I



Experiments with 60 atom % ^{18}O sodium hypochlorite with 2,2′,4,4′,6,6′-hexanitrodiphenylmethane produced 2-nitroso-2′,4,4′,6,6′-pentanitrobenzophenone with no ^{18}O incorporation at all. Only natural abundance, 0.22 ± 0.03 ^{18}O, was found in the formed ketone.

All of these facts, together with known[4,5] literature reports of ortho-nitro oxygen participation, suggest that the following mechanism, as illustrated in Scheme I, is operating.

Experimental Section

Caution! The compounds described in this work are explosives and may detonate on grinding or impact. Appropriate shielding should be used.

The polynitrodiphenylmethanes were prepared according to a procedure described previously.[3] Tetrahydrofuran and methanol, Fisher Certified reagent, and "5%" aqueous sodium hypochlorite, Clorox, were used as received. Melting points were obtained on a Thomas-Hoover 6427-F10 apparatus and are uncorrected. NMR spectra were obtained in nitrobenzene-d_5 on a HA-100 Varian spectrometer. The IR spectra were obtained on a Perkin-Elmer Infracord Model 237.

2-Nitroso-2′,4,4′,6,6′-pentanitrobenzophenone. A solution of 4.4 g (0.01 mol) of 2,2′,4,4′,6,6′-hexanitrodiphenylmethane in 50 ml of THF and 25 ml of methanol was prepared and chilled to −5 °C in an ice-salt bath. This solution was then added rapidly with vigorous magnetic stirring to 20 ml of "5%" aqueous sodium hypochlorite solution, Clorox, which was also chilled to −5 °C. There was a rapid rise in temperature to 15 °C and the initial blue color of the reaction mixture changed almost immediately to a dark red brown. The mixture was stirred at ice bath temperature for 2 min, then for 20 min at ambient temperature, and finally poured into 750 ml of cold water containing 25 ml of concentrated hydrochloric acid. A light yellow precipitate formed which was filtered off, washed well with water, and then extracted with portions of hot methanol until the methanol extracts were light colored. The greenish yellow residue was dried and weighed 3.2 g. It was crystallized by dissolving it in 35 ml of acetonitrile (adding Darco-decolorizing carbon), filtering, adding an equal volume of methanol, and chilling. It formed fine, pale green crystals, mp 215 °C dec. The yield of crystalline material was 2 g or 46% of the theoretical yield. Recrystallization from 70% nitric acid afforded small, chunky, green crystals, mp 220–222 °C dec.

Anal. Calcd for $C_{13}H_4N_6O_{12}$: C, 35.80; H, 0.92; N, 19.26; mol wt, 436. Found: C, 35.26, 35.86; H, 1.05, 1.02; N, 18.68, 19.17; mol wt, 436 (mass spectrometry).

NMR δ 9.44 (Pi), 7.10 (H_A), 9.03 (H_B).

4-Cyano-2-nitroso-2,2′,4′,6,6′-pentanitrodiphenylmethane. 4-Cyano-2,2′,4′,6,6′-pentanitrodiphenylmethane (2.0 g, 0.005 mol) was treated with 15 ml of Clorox as in the preparation of 2-nitroso-2′,4,4′,6,6′-pentanitrobenzophenone, above. The yield of light yellow, crude product was 2.0 g, from which there was obtained 1.15 g of greenish-yellow material after extraction with methanol. Recrystallized from acetonitrile–methanol, it yielded very pale green needles, mp 240 °C dec.

Anal. Calcd for $C_{14}H_4N_6O_{10}$: C, 40.40; H, 0.97; N, 20.19; mol. wt, 416. Found: C, 40.10, 40.21; H, 1.33, 1.26; N, 20.31, 20.04; mol wt, 416 (mass spectrometry).

NMR δ 9.40 (Pi), 6.63 (H_A), 8.52 (H_B).

2-Nitroso-2′,4,6,6′-tetranitrobenzophenone. 2,2′,4,6,6′-Pentanitrodiphenylmethane (4.0 g, 0.01 mol) was treated with 15 ml (ca. 0.01 mol OCl^-) of 5% aqueous sodium hypochlorite in a similar manner to that for 2,2′,4,4′,6,6′-hexanitrodiphenylmethane. The yield of crude product was 1.5 g, which gave upon crystallization from acetonitrile–methanol, 1.0 g of light green crystals, mp 206 °C dec.

Anal. Calcd for $C_{13}H_5N_5O_{10}$: C, 39.89; H, 1.28; N, 17.90; mol wt, 391. Found: C, 40.95, 41.37; H, 1.95, 2.20; N, 17.90, 17.78; mol wt, 391 (mass spectrometry).

NMR δ 9.34 (Pi), 7.91 (H_A), 8.20 (H_B), 6.26 (H_C).

***α*-Chloro-2,2′,4,4′,6-pentanitrodiphenylmethane (1) and 2-Nitroso-2′,4,4′,6′-tetranitrobenzophenone (2).** A solution of 2,2′,4,4′,6-pentanitrodiphenylmethane (4.0 g, 0.01 mol) in 60 ml of THF and 30 ml of methanol was prepared and chilled to −5 °C. This solution was then added rapidly with vigorous stirring to 20 ml of "5%" aqueous sodium hypochlorite solution, Clorox, which was also chilled to −5 °C. There was a rapid rise in temperature to 15 °C, and the initial blue color of the reaction changed almost immediately to a dark red brown. The mixture was then stirred at ambient temperature for 3.5 min, and then poured into 750 ml of cold water containing 25 ml of concentrated hydrochloric acid. A light tan precipitate formed, and was filtered off, washed well with water, and dried. The weight of dried product was 4.2 g. It was triturated at ambient temperature with 9 ml of acetonitrile and filtered. The greenish-yellow filter cake was washed with hot methanol until the extracts were light colored. The remaining material was dissolved in 6 ml of nitromethane and filtered, and upon chilling green crystals formed. The product was filtered and dried and weighed 0.71 g (18%), mp 288–290 °C dec. This first isolated product was identified as the nitrosobenzophenone: NMR δ 9.30 (Pi), 7.15 (H_A), 8.05 (H_B), 6.98 (H_C).

The acetonitrile filtrate obtained above was diluted with methanol and poured into 400 ml of cold, dilute hydrochloric acid. The solid was collected and dried. It was extracted with 9 ml of hot benzene, filtered, and cooled. The crystals which formed were filtered and washed with 10 ml of cold methanol. Analysis by TLC (silica gel, elution with benzene) showed only one zone. The product was recrystallized by dissolving it in 8 ml of acetone, filtering, then adding 20 ml of methanol and 5 ml of water. The red-orange solution was chilled for 0.5 h in an ice–salt bath upon which dark yellow crystals were formed. The weight of the dried crystals was 0.98 g (25%). The compound was identified as *α*-chloro-2,2′,4,4′,6-pentanitrodiphenylmethane.

Anal. Calcd for $C_{13}H_6N_5O_{10}Cl$: C, 36.50; H, 1.41; N, 16.37; Cl, 8.29. Found: C, 36.35, 36.58; H, 1.55; 1.47; N, 16.22, 16.40; Cl, 8.49, 8.48.

NMR δ 9.00 (Pi), 8.90 (H_A), 8.56 (H_B), 8.08 (H_C), 7.67 (H_D).

Reaction of *α*-Chloro-2,2′,4,4′,6-pentanitrodiphenylmethane with Sodium Hydroxide. A solution of *α*-chloropentanitroditan (0.86 g, 0.002 mol) in 10 ml of THF and 5 ml of MeOH was treated with 0.08 g of sodium hydroxide in 2 ml of distilled water. The reaction mixture was stirred for 3.5 min, and then quenched with an aqueous DCl solution until acidic. The precipitate was filtered and then washed with hot MeOH until the extracts were colorless. After drying, 0.18 g of pale green compound remained and was shown to be the nitrosobenzophenone. The methanol extracts were combined and the methanol removed under pressure in a rotary evaporator. The residue, mostly 1, was recrystallized as above and was shown to contain 30–35% deuterium by NMR spectroscopy.

Reaction of 2,2′,4,4′,6,6′-Hexanitroditan with ^{18}O Hypochlorite. The ^{18}O labeled sodium hypochlorite was prepared by carefully dissolving 2 equiv of fresh sodium in water containing 60 atom % ^{18}O. Chlorine gas was bubbled into the $Na^{18}OH$ solution until the theoretical weight corresponding to 1 equiv of Cl_2 had been gained. The experiment was carried out as described above for the unlabeled case.

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Registry No.—1, 61348-80-9; 2, 61348-81-0; 2-nitroso-2′,4,4′,6,6′-pentanitrobenzophenone, 61348-82-1; 2,2′,4,4′,6,6′-hexanitrodiphenylmethane, 32255-27-9; Clorox, 7681-52-9; 4-cyano-2-nitroso-2,2′,4′,6,6′-pentanitrobenzophenone, 61348-83-2; 4-cyano-2,2′,4′,6-6′-pentanitrodiphenylmethane, 32255-30-4; 2-nitroso-2′,4,6,6′-tetranitrobenzophenone, 61348-84-3; 2,2′,4,6,6′-pentanitrodiphenylmethane, 32255-29-1; 2,2′,4,4′,6-pentanitrodiphenylmethane, 32255-28-0.

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(1) Deceased.

(2) National Research Council, NSWC, Postdoctoral Fellow, 1975–1976.

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