Reactions of α-Substituted Polynitrotoluenes. II. The Generation and Reactions of 2,4,6-Trinitrobenzyl Anion

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The reaction of 2,4,6-trinitrotoluene in tetrahydrofuran–methanol solution with aqueous sodium hypochlorite yields 2,2′,4,4′,6,6′-hexanitrostilbene. The intermediate 2,4,6-trinitrobenzyl chloride can be obtained in 85% yield by "short-stopping" the reaction. Reaction conditions can also be adjusted to form 2,2′,4,4′,6,6′-hexanitrobibenzyl rather than the stilbene. Evidence is presented to support the proposal that these reactions are nucleophilic displacements by the 2,4,6-trinitrobenzyl anion or the α-chloro-2,4,6-trinitrobenzyl anion on undissociated nitrobenzyl halides.

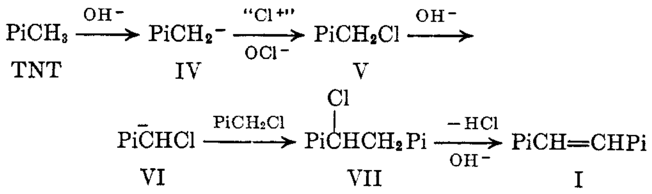
In the first paper in this series[1] we reported an unequivocal synthesis of 2,2′,4,4′,6,6′-hexanitrostilbene (I). The melting point, 316° (dec), and solubility of I differed from those reported by Reich, Wetter and Widmer[2] for a product, mp 211°, obtained from the reaction of 2,4,6-trinitrobenzyl bromide (II) with alcoholic potassium hydroxide. This product was thought to be the stilbene I,[2] but this structural assignment was incompatible with the results of our unequivocal synthesis of the stilbene I.[1] It seemed reasonable to assume that Reich's product was 2,2′,4,4′,6,6′-hexanitrobibenzyl (III)[3] and that this saturated compound would arise from an SN2 displacement by the 2,4,6-trinitrobenzyl anion (IV) on the bromide II. We also assumed the source of the anion IV in Reich's system[2] to be residual 2,4,6-trinitrotoluene (TNT) present in the bromide II as prepared by Reich.[4] The proposed intermediacy of the anion IV[5] in this reaction prompted us to investigate further the reactions of this species.

Results and Discussion

Since it seemed that the anion IV would decay rapidly in solution[6] we decided to generate the species in the presence of the trapping agent. Our first attempts to trap this reactive intermediate, the anion IV, involved its reaction with a "positive-halogen" source. This was accomplished by the rapid addition of a chilled solution of TNT in tetrahydrofuran–methanol to a "5%" aqueous sodium hypochlorite solution at 0–15°. After about 2 min a crystalline solid began to separate from the dark red-brown solution and formation of the solid was complete in 1 hr. This product melted at 316° (dec) and its identity with the stilbene I was proved by the superimposability of the X-ray powder diffraction pattern and infrared spectrum on those of an authentic sample of I.[1]

The formation of the bimolecular product, under conditions where halogenation of carbanions generally occurs, suggested that the stilbene I formed by Scheme I.

SCHEME I



$$\underset{\text{TNT}}{\text{PiCH}_3} \xrightarrow{\text{OH}^-} \underset{\text{IV}}{\text{PiCH}_2^-} \xrightarrow[\text{OCl}^-]{\text{“Cl}^{+}\text{”}} \underset{\text{V}}{\text{PiCH}_2\text{Cl}} \xrightarrow{\text{OH}^-}$$

$$\underset{\text{VI}}{\text{Pi}\bar{\text{C}}\text{HCl}} \xrightarrow{\text{PiCH}_2\text{Cl}} \underset{\text{VII}}{\text{Pi}\overset{\text{Cl}}{\overset{|}{\text{C}}}\text{HCH}_2\text{Pi}} \xrightarrow[\text{OH}^-]{-\text{HCl}} \underset{\text{I}}{\text{PiCH{=}CHPi}}$$

Pi = 2,4,6-trinitrophenyl

If Scheme I is correct, then it should be possible to isolate the carbanion "trapping-product," 2,4,6-trinitrobenzyl chloride (V) or the bimolecular product, α-chloro-2,2′,4,4′,6,6′-hexanitrobibenzyl (VII) by "short-stopping" the reaction. By quenching the reaction mixture in dilute acid *1 min* after mixing the TNT and sodium hypochlorite solutions, an 85% yield of the "trapping-product" V was obtained. This is, indeed, an excellent preparative reaction for the chloride V, replacing the tedious series of reactions which had been the only known route to this compound.[7] By using

$$\text{PiCH}_3 \xrightarrow{\text{Br}_2} \underset{\text{II}}{\text{PiCH}_2\text{Br}} \xrightarrow{\text{H}_2\text{O}} \underset{\text{VIII}}{\text{PiCH}_2\text{OH}} \xrightarrow{\text{PCl}_5} \underset{\text{V}}{\text{PiCH}_2\text{Cl}}$$

sodium hypobromite and modifying the reaction conditions somewhat, trinitrobenzyl bromide II has been prepared in 35% yield. This synthetic route is also preferable to the previous sealed-tube bromination of TNT.[7]

We attempted to extend this halogenation procedure to the carbanions of 2,4- and 2,6-dinitrotoluenes. For these substrates the procedure was totally unsuccessful. This can be attributed to the difference in pK values for the nitrotoluenes.[8] Trinitrotoluene, pK = 14.45,[8] is about five hundred times as strong an acid as 2,4-dinitrotoluene, pK = 17.12.[8] Therefore, in order to generate an equivalent concentration of the 2,4-dinitrobenzyl anion a corresponding increase in basicity would be needed. Adding potassium hydroxide to the standard hypochlorite reaction mixture in an attempt to effect ionization apparently could not overcome the large difference between the pK's of TNT and 2,4-dinitrotoluene. The only isolable product was unreacted dinitrotoluene. The same explanation would apply for the lack of reaction with 2,6-dinitrotoluene, pK = 19.0,[8] which is about a 100-fold weaker an acid than the 2,4 isomer.

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[1] K. G. Shipp, *J. Org. Chem.*, **29**, 2620 (1964).

[2] S. Reich, O. Wetter, and M. Widmer, *Ber.*, **45**, 3055 (1912).

[3] (a) W. Will, *ibid.*, **47**, 712 (1914); (b) A. H. Blatt and A. W. Rytina, *J. Am. Chem. Soc.*, **72**, 403 (1950).

[4] The trinitrobenzyl bromide used in Reich's[2] work was prepared by the bromination of TNT. Since TNT and the bromide II have similar solubilities in organic solvents and not too widely differing melting points, contamination of the bromide by TNT could be expected.

[5] The existence of this intermediate has been suggested by other workers: J. B. Ainscough and E. F. Caldin, *J. Chem. Soc.*, 2407 (1960).

[6] The ultraviolet spectra of moderately concentrated alkaline solutions of TNT exhibit changes over rather short time intervals. Private communication from Dr. T. N. Hall of these laboratories.

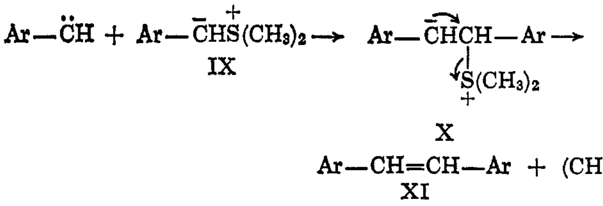
[7] K. L. Ganguly, *Ber.*, **58B**, 708 (1925).

[8] R. Schaal, *J. Chim. Phys.*, **52**, 684 (1955). The pK values for the nitrotoluenes were determined in mixtures of ethylenediamine–water. Though these values do not pertain to the present solvent system, the relative ordering should be about the same.

The formation of the stilbene I as the "long-time" reaction product in the TNT–sodium hypochlorite reaction was not unexpected. It was previously shown that the reaction of trinitrobenzyl chloride with methanolic potassium hydroxide afforded the stilbene I in 30% yield.[1] However, the reaction of aqueous alkali with the chloride V in tetrahydrofuran–methanol solution gave consistently higher yields, 50–52%, of the stilbene I. After normalizing for the yield of the chloride V intermediate, the yield of the stilbene I from the TNT–hypochlorite reaction was essentially identical with that obtained by starting with the chloride V in alkaline THF–methanol.

The initial choice of the tetrahydrofuran, THF, as solvent for TNT in the reaction with sodium hypochlorite appears to have been a fortunate one. Tetrahydrofuran dissolves TNT readily at ambient temperatures, and, in admixture with methanol, provides homogeneous solutions with aqueous sodium hypochlorite. Other solvents that would be expected to fulfill these conditions, *e.g.*, *p*-dioxane, diglyme, diethylene glycol, and acetonitrile, were tried out but with little success. We do not quite appreciate the reasons for the apparent specificity of THF in the reaction, but do note that a similar unique role of THF as a solvent in the preparation of stilbene from benzyl chloride and butyllithium has been attributed to "its superior solvating ability for the metal cation."[9]

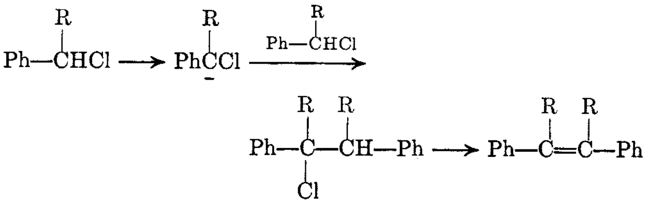
Although we cannot explain the specificity of the tetrahydrofuran in the chlorination reaction, we decided to probe for the mechanism of the conversion of trinitrobenzyl chloride to hexanitrostilbene. The results of kinetic studies of the reaction of 4-nitrobenzyl chloride with alkali to yield 4,4′-dinitrostilbene are consistent with 4-nitrophenylmethylene being formed as an intermediate in the reaction.[10] Though these results ruled out the displacement–elimination mechanism (*cf.* Scheme I) for the formation of 4,4′-dinitrostilbene, they gave no insight as to the mode of formation of the dinitrostilbene from the 4-nitrophenylmethylene. The results of a somewhat analogous kinetic study, the reaction of 4-nitrobenzyldimethylsulfonium ion with hydroxide to yield 4,4′-dinitrostilbene, led Swain and Thornton[11] to suggest that the formation of the stilbene occurs *via* the intermediacy of 4-nitrophenylmethylene which then adds to the carbanion IX to form the carbanion X. Since the carbanion X closely approximates the transition state for a β-elimination reaction, it readily loses dimethyl sulfide to give 4,4′-dinitrostilbene (XI).



$$\mathrm{Ar{-}\ddot{C}H + Ar{-}\bar{C}H\overset{+}{S}(CH_3)_2 \longrightarrow Ar{-}\bar{C}HCH(\overset{+}{S}(CH_3)_2){-}Ar \longrightarrow Ar{-}CH{=}CH{-}Ar + (CH_3)_2S}$$

Ar = 4 – nitrophenyl

However, the isolation of α-chlorobibenzyl from the reaction of benzyl chloride with *n*-butyllithium in THF solution,[9] and 2-chloro-2,3-diphenylbutane from the reaction of α-phenethyl chloride with sodium amide in liquid ammonia[12] can only be explained by a nucleophilic displacement by α-chloro-1-phenylethyl anion on α-phenethyl chloride. When these reactions were carried out with excess base, the corresponding stilbenes were obtained in excellent yields. Because of the remarkable effect of the nitro substituent on the mechanism for the conversion of benzyl halides to the corresponding stilbenes, we have attempted to elucidate the mechanism for the formation of hexanitrostilbene from trinitrobenzyl chloride.



$$\mathrm{Ph{-}CHRCl \longrightarrow Ph\bar{C}RCl \xrightarrow{Ph{-}CHRCl} Ph{-}CRCl{-}CHR{-}Ph \longrightarrow Ph{-}CR{=}CR{-}Ph}$$

Ph = phenyl
R = H or CH_3

A preliminary experiment involving the addition of cyclohexene to the reaction mixture did not give any of the expected methylene trapping product, 7-(2,4,6-trinitrophenyl)norcarane. Additionally, we added a large excess of chloride ion (lithium chloride) to a typical reaction mixture, since the addition of excess chloride ions should increase return of trinitrophenylmethylene to the α-chlorotrinitrobenzyl anion, thereby reducing the rate of formation of the hexanitrostilbene.[13] On quenching the reaction prior to completion we found the yield of hexanitrostilbene to be *greater* than that for an identical reaction carried out in the absence of excess chloride ion. The addition of other salts, sodium chloride, lithium perchlorate, and sodium perchlorate, produced varying yields in similar quenched, incomplete reactions. These effects we interpret as a change in activity coefficient of the reactant species due to the added salts,[14] rather than the expected common ion effect. These results suggested that trinitrophenylmethylene was *not* an intermediate in this reaction.

The strongest evidence we have obtained for the displacement–elimination mechanism came from the results of experiments in which the mole ratio of alkali to trinitrobenzyl chloride was varied while other conditions were maintained essentially constant. We found that changing the mole ratio of alkali to chloride had a pronounced effect on the yield of hexanitrostilbene. The absolute yield of the stilbene I was found to be proportional to the mole ratio of alkali to chloride up to 1 mole of alkali/mole of chloride. For these trials, unreacted chloride could be isolated in those cases where the alkali to chloride ratio was less than unity. After normalizing for the chloride reacted, the yield of the stilbene I was found to be the same in each case and identical with that obtained for an alkali to chloride ratio of unity. By contrast, as the mole ratio of alkali

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[9] D. F. Hoeg and D. I. Lusk, *J. Am. Chem. Soc.*, **86**, 928 (1964).

[10] S. B. Hanna, Y. Iskander, and Y. Riad, *J. Chem. Soc.*, 217 (1961).

[11] C. G. Swain and E. R. Thornton, *J. Am. Chem. Soc.*, **83**, 4033 (1961).

[12] M. S. Kharasch, W. Nudenberg, and E. K. Fields, *ibid.*, **66**, 1276 (1944); C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor, and A. E. Brodhag, *ibid.*, **78**, 1653 (1956). With optically active α-phenethyl chloride and lithium amide in liquid ammonia, optically active 2-chloro-2,3-diphenylbutane was obtained: W. R. Brasen, S. W. Kantor, P. S. Skell, and C. R. Hauser, *ibid.*, **79**, 397 (1957).

[13] This assumes that trinitrophenylmethylene does not react preferentially with α-chlorotrinitrobenzyl anion owing to a high selectivity. The proposed 4-nitrophenylmethylene appears to be extremely selective.[11]

[14] F. A. Long and W. F. McDevit, *Chem. Rev.*, **51**, 119 (1952).

to chloride was increased from unity, the yield of the stilbene I continually decreased until it was negligible at a mole ratio of alkali to chloride of 2.[15]

Of the two mechanisms under consideration, these results are only consistent with the displacement–elimination mechanism.[9,12] If trinitrophenylmethylene is an intermediate in this reaction, we should expect that increasing the concentration of alkali would favor both its formation and subsequent reaction by increasing the concentration of α-chlorotrinitrobenzyl anion.[16] However, if the displacement–elimination mechanism is operating, excess alkali would reduce the concentration of un-ionized trinitrobenzyl chloride. This would decrease the rate of formation of the intermediate α-chlorohexanitrobibenzyl since the rate should be proportional to the product of the concentration of ionized and un-ionized trinitrobenzyl chloride.[17] Because of concurrent side reactions which appear to compete for the α-chlorotrinitrobenzyl anion, trinitrobenzyl chloride is removed from the system in an irreversible manner, thereby reducing the yield of the stilbene I under these conditions. Even under the optimum reaction conditions these side reactions account for about 50% of the trinitrobenzyl chloride.

For those reactions where the mole ratio of alkali to chloride is less than unity, the rate of formation of the intermediate α-chlorohexanitrobibenzyl would be decreased since the concentration product $[\mathrm{ArCH_2Cl}]\cdot[\mathrm{Ar\overset{-}{C}HCl}]$ is smaller than at the optimum yield conditions. In these cases we obtain the same normalized yield of the stilbene I since the concurrent side reactions only compete for the α-chlorotrinitrobenzyl ion and therefore they consume roughly the same fraction of the chloride V as they do at the optimum yield conditions.

We were not able to isolate the intermediate, α-chlorohexanitrobibenzyl, in the displacement–elimination reaction. Our failure was not unexpected considering the known readiness with which even the unnitrated α-chlorobibenzyl eliminates the elements of hydrogen chloride to form the corresponding stilbene.[9] The substitution of nitro groups on the benzene rings will facilitate this reaction as they can stabilize the developing negative charge in the transition state.[18]

Since we apparently effected an SN2 displacement reaction on the trinitrobenzyl chloride substrate by its own anion, we attempted to extend this reaction to other carbanion nucleophiles and different nitrohalide substrates. The first such reaction attempted was that of the trinitrobenzyl anion on trinitrobenzyl chloride. By adding aqueous alkali to a THF–methanol solution of equal molar amounts of TNT and the chloride V, a 1:1 mixture of the stilbene I and the bibenzyl III was obtained. By increasing the proportion of TNT to twice that of the chloride V, thereby increasing the concentration ratio of trinitrobenzyl anion to α-chlorotrinitrobenzyl anion, the ratio of the bibenzyl III to the stilbene I was increased by a factor of 6. A further increase in TNT to three times the chloride V essentially eliminated the stilbene-forming reaction and an 80% yield of hexanitrobibenzyl was obtained. Trinitrobenzyl bromide was found to be an equally good substrate in the reaction with trinitrobenzyl anion to form the bibenzyl III. This result supported our hypothesis that Reich's[2] product from trinitrobenzyl bromide and alkali was, indeed, hexanitrobibenzyl.

$$\underset{\text{IV}}{\mathrm{PiCH_2^-}} + \underset{\text{V}}{\mathrm{PiCH_2Cl}} \longrightarrow \underset{\text{III}}{\mathrm{PiCH_2CH_2Pi}}$$

The reaction of the anion IV with the trinitrobenzyl halides, II and V, to form the symmetrical bibenzyl III has been extended to other nitrobenzyl halides, *e.g.*, 2,6-dinitrobenzyl bromide[19] and 4-nitrobenzyl bromide. In each case the reaction provided a good yield of the corresponding unsymmetrical polynitrobibenzyl, 85% of 2,2′,4,6,6′-pentanitrobibenzyl, and 73% of 2,4,4′,6-tetranitrobibenzyl. Molecular weights and elemental analyses fit the assigned bibenzyl structure,[20] and we were able to rule out the stilbene structure from nmr data,[21] which showed the presence of a methylene signal at $\delta = 3.41$ and 3.20 ppm rather than the vinyl proton signal at $\delta \approx 7.1$ ppm.[22]

Although the nucleophilic displacement of halogen from 2,6-dinitrobenzyl bromide by 2,4,6-trinitrobenzyl anion was successful, an attempt to reverse the substrate–nucleophile functions by treating 2,6-dinitrotoluene with 2,4,6-trinitrobenzyl chloride in the presence of alkali was doomed to failure from the start. As was shown in the chlorination reaction, *vide supra*, it is not possible to attain the alkalinity necessary to generate significant concentrations of the anion of 2,6-dinitrotoluene[8] in this system. Therefore, only the chloride V was converted to its anion which then reacted with the neutral chloride V to form a small amount of hexanitrostilbene.

Further work on the reactions of the trinitrobenzyl anion is continuing and will be the subject of a future communication.

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[15] Under these low yield conditions it was not possible to recover any unreacted chloride. However, a considerable quantity of dark red-brown amorphous material was isolated. Thin layer chromatography showed the presence of at least 12 components. By-products of similar appearance were also isolated under the high yield conditions. We believe that this crude material is a complex mixture of bimolecular reduction products formed in concurrent side reactions. A referee has suggested that the formation of the stilbene I and the bibenzyl III, *vide infra*, could occur *via*

$$\mathrm{Pi\overset{-}{C}HCl} + \mathrm{PiCH_2Cl} \longrightarrow \mathrm{PiCHCl} + \mathrm{PiCH_2Cl\cdot^-}$$

$$\mathrm{PiCH_2Cl\cdot^-} \longrightarrow \mathrm{PiCH_2\cdot} + \mathrm{Cl^-}$$

$$2\mathrm{PiCH_2\cdot} \longrightarrow \mathrm{PiCH_2CH_2Pi}$$

$$\mathrm{PiCH_2\cdot} + \mathrm{PiCHCl} \longrightarrow \mathrm{PiCH_2CHClPi} \longrightarrow \mathrm{PiCH{=}CHPi}$$

radical intermediates. Since 2,4,6-trinitrobenzyl anion does not transfer an electron to oxygen to yield 2,4,6-trinitrobenzyl radical under conditions where *p*-nitrobenzyl anion readily forms *p*-nitrobenzyl radical which subsequently dimerizes to the corresponding bibenzyl (A. J. Moye, Ph.D. Thesis, Iowa State University, 1961), we prefer not to consider the above mechanism as a possible route to these products.

[16] We are assuming here that trinitrophenylmethylene, like 4-nitrophenylmethylene,[11] would be quite selective and react preferentially with α-chlorotrinitrobenzyl anion rather than with hydroxide or other nucleophiles present in the reaction mixture.

[17] We will assume for this discussion that at the optimum yield reaction conditions the ratio of anion to chloride is about unity.

[18] J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 8.

[19] F. Barrow, E. D. Griffiths, and E. Bloom, *J. Chem. Soc.*, **121**, 1716 (1932).

[20] The difference of two hydrogen atoms between stilbene and bibenzyl is not great enough to depend on either molecular weight determination or elemental analyses for characterization.

[21] The authors wish to express their sincere appreciation to Dr. William B. Moniz, U. S. Naval Research Laboratory, Washington, D. C., for making these measurements with a Varian 100-Mc nmr spectrometer and for assisting in this problem.

[22] The vinyl protons in *trans*-stilbene absorb at $\delta = 7.10$ ppm: "Varian Associates NMR Spectra Catalog," Spectrum No. 306.

Experimental Section[23,24]

Materials.—4-Nitrobenzyl bromide, Eastman Kodak Co., 2,6-dinitrotoluene, Aldrich Chemical Co., Inc., tetrahydrofuran, Baker Analyzed Reagent, methanol, Fisher Certified Reagent, and "5%" aqueous sodium hypochlorite, "Clorox," were used as received.

2,6-Dinitrobenzyl bromide was prepared by the method of Barrow, Griffiths, and Bloom.[15] A 65% yield, at best, of a light yellow crystalline product melting at 81° was obtained.[25]

2,2′,4,4′,6,6′-Hexanitrobibenzyl (III). By Nitration of Bibenzyl.[26]—Potassium nitrate (65 g, 0.65 mole) was added to 200 ml of 30% oleum in a 500-ml, three necked, round-bottom flask equipped with a mechanical stirrer and thermometer, keeping the temperature under 60° by the rate of addition, and cooling as necessary. This mixture was heated to 100° with an oil bath and 16 g (0.045 mole) of 2,2′,4,4′-tetranitrobibenzyl[3b] was added in small portions during 0.5 hr. After all of the tetranitrobibenzyl was added the bath temperature was maintained at 100–112° for 1 hr, then raised to 120°, and held there for 28 hr. Well-formed, light yellow needles had formed in the reaction mixture after 20 hr of heating. There was no apparent increase in the amount of product after the longer heating period and 16–20 hr would probably be sufficient time for the reaction. After cooling the mixture the crystalline product was filtered off, washed with 50% sulfuric acid, then thoroughly with water, and dried. It weighed 6.75 g and melted at 215–216°. The mother liquor was poured on to flaked ice; the solid product was collected on a filter, then slurried with 100 ml of 95% ethanol, filtered, and dried. This material weighed 2.53 g. The combined crude yield, 9.28 g, was 46.5% of the theoretical yield. The product was crystallized from glacial acetic acid twice, about 200 ml of acetic acid each time, washed well by slurrying with hot water, and dried: mp 218–220°. *Anal.* Calcd for $C_{14}H_8N_6O_{12}$: C, 37.2; H, 1.79; N, 18.60. Found: C, 37.26, 37.24; H, 1.99, 2.06; N, 18.61, 18.40.

2,4,6-Trinitrobenzyl Chloride (V).—A solution of 10 g of TNT in 100 ml of THF and 50 ml of methanol was chilled to 0° then added quickly, with thorough mixing, to 100 ml of "5%" aqueous sodium hypochlorite which was also chilled to 0°. The mixture was bright cherry red on mixing and the color deepened to a dark red-brown during the 1-min reaction period. The temperature of the mixture was held at 15° or under by chilling in an ice–salt bath.[27] After 1 min, when the temperature began to drop, the reaction was stopped by drowning the mixture in about 1 l. of water containing 10 ml of concentrated hydrochloric acid. A cloudy yellow mixture was formed, from which a waxy crystalline product began to separate almost immediately. Precipitation of product was complete in about 1 hr and the product was filtered off, washed with water, and dried. It weighed 10 g, 85% of the theoretical yield. Recrystallized from benzene–hexane the product formed clear yellow crystals which, on drying, lost solvent of crystallization to form a cream-colored powdery material melting at 85°. The melting point was not depressed on admixture with an authentic sample of trinitrobenzyl chloride,[8] and infrared spectra of the two samples were superimposable.

Various hypochlorites in varying concentrations, 5–12% of sodium hypochlorite, calcium hypochlorite, or potassium hypochlorite, were tried in this reaction. Optimum results were obtained with "5%" sodium hypochlorite which is readily available as commercial household bleaches.

2,4,6-Trinitrobenzyl Bromide (II).—A "0.66 *N*" solution of sodium hypobromite was prepared by adding 5 ml of bromine to a chilled solution of 8.5 g of sodium hydroxide in 100 ml of water, stirring the mixture until all the bromine had reacted and a clear yellow solution formed, and then diluting to 150 ml with water. A solution of 5 g of TNT in 50 ml of THF and 25 ml of methanol was chilled to −10° in an ice–salt bath, then added at once, with rapid stirring, to 50 ml of the sodium hypobromite solution which was chilled to a slush. The temperature of the reaction mixture was kept under 5° during 0.5 min of reaction time and then the bright red mixture was quenched in 500 ml of water containing 10 ml of concentrated hydrochloric acid. An oil separated after about 1 hr, the aqueous layer was decanted from the oil, and the product was washed with ice–water and then extracted with ether. The ether solution was dried over anhydrous magnesium sulfate and filtered, and the ether was removed by evaporation leaving an orange-yellow oily residue. This residue was crystallized twice from benzene–hexane with Darco. It formed pale yellow crystals, which, on drying, lost solvent of crystallization to form a cream-colored powder which melted at 65° and the melting point was not depressed on admixture with an authentic sample of II.[8] Infrared spectra of the two samples were superimposable. The yield of recrystallized product was 2.1 g, 31.5% of the theoretical.

2,2′,4,4′,6,6′-Hexanitrostilbene (I). A. From TNT and Sodium Hypochlorite.—This reaction was carried out as the one described for the preparation of 2,4,6-trinitrobenzyl chloride (V) above, except that after the initial reaction period of 1 min the reaction mixture was allowed to stand at ambient temperature until precipitation of a fine crystalline product, which began to appear within 2 min after mixing the solvents, was complete. This product was filtered off; the filter cake was washed with methanol until the washings were colorless and then dried in an oven at 100°. It weighed 4.2 g, 42% of the theoretical yield. Recrystallized from nitrobenzene or dimethylformamide it formed pale yellow needles which melted at 316° (dec) and the melting point was not depressed on admixture with an authentic sample of I.[1] X-Ray powder diffraction patterns and infrared spectra of the two samples were superimposable.

B. From 2,4,6-Trinitrobenzyl Chloride and Alkali.—A solution of 2.6 g (0.01 mole) of 2,4,6-trinitrobenzyl chloride in 40 ml of THF and 20 ml of methanol was prepared in a small flask. To this solution, at ambient temperature, was added 40 ml of water containing 0.4 g (0.01 mole) of sodium hydroxide. The reaction mixture turned dark red-brown at once and within 0.5 min a very fine crystalline precipitate appeared in the solution. The mixture was allowed to stand for 15 min, then filtered with suction, and the filter cake was washed with methanol until the washings were colorless and dried in an oven at 100°. It weighed 1.12 g, 50% of the theoretical yield. Recrystallized from nitrobenzene, it formed fine yellow needles which melted at 315–316° (dec), and the melting point was not depressed on admixture with an authentic sample of I.[1] The yield of stilbene obtained from this reaction with varying amounts of alkali is shown in Table I.

TABLE I

Mole ratio of chloride to NaOH	% of theoretical yield
1:0.25	11
1:0.50	25
1:0.75	40
1:1.0	50
1:1.5	25
1:2.0	0

With Added Salts.—These reactions were carried out as described in the preceding paragraph except for addition of the salt (0.05 mole in each case) to the aqueous sodium hydroxide solution and quenching of the reaction before completion by the addition of 1 ml (0.01 mole) of concentrated hydrochloric acid 70 sec after the reactant solutions were mixed. Results are shown in Table II. When lithium chloride was added and the reaction was allowed to go to completion, the yield was identical with that from a reaction mixture containing no added salt.

With Cyclohexene.—Since cyclohexene is immiscible with THF–methanol–aqueous sodium hydroxide this reaction was carried out in THF–methanolic potassium hydroxide solution.

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(23) Melting points are uncorrected. Microanalyses were performed by Professor M. H. Aldridge, Department of Chemistry, American University, Washington, D. C.

(24) *Caution!* Many of the compounds herein described are explosive in nature. Appropriate precautions should be taken in handling them.

(25) *Caution!* Although this bromination reaction in a sealed tube was carried out successfully numerous times on a 10–20-g scale, twice the reaction resulted in explosions which completely destroyed the equipment. A glass tube was used in the first case, and the glass may have had a flaw or strain. The second explosion occurred in a stainless steel bomb which was found to have a very thin section of metal at the neck.

(26) The present preparation is reported as an improved procedure over that reported in the literature.[3b]

(27) By keeping the reaction temperature under 15° the side reactions of alkali with TNT as well as the competing reaction of the solvent system, THF–methanol, with hypochlorite are minimized. Analysis of mixtures of the THF–methanol–sodium hypochlorite in proportions used in the reaction showed 25% decomposition of hypochlorite after 3 min at ambient temperature, less than 2% after 2 min at 15°, and only 3% after 15 min at 0°.

Table II

Salt	Yield of I, g
"Control" (no added salt)	0.37
LiCl	0.48
$LiClO_4$	0.44
NaCl	0.29
$NaClO_4$	0.37

A solution of 2.6 g (0.01 mole) of trinitrobenzyl chloride in 25 ml of THF and 15 ml of cyclohexene was prepared. To this solution was added 10 ml of methanol containing 0.56 g (0.01 mole) of potassium hydroxide, at once and with thorough mixing. A crystalline product appeared in the mixture within 1 min. The mixture was allowed to stand at ambient temperature for 1 hr, then filtered, and the filter cake was washed with methanol and water and dried. It weighed 0.81 g, 35.5% of theoretical yield. Recrystallized from nitrobenzene it formed light yellow needles, mp 316° dec.

A "control" reaction using 15 ml of methanol instead of cyclohexene was carried out simultaneously. The yield of crystalline product was 0.8 g, 35.5% of the theoretical.

2,2',4,4',6,6'-Hexanitrobibenzyl (III). From TNT and Sodium Hypochlorite.—A solution of 10 g of TNT in 50 ml of THF and 100 ml of methanol was prepared in a 500-ml wide-mouth erlenmeyer flask equipped with a mechanical stirrer and a 125-ml dropping funnel. A solution prepared by adding 35 ml of "Clorox" to 65 ml of water containing 0.5 g of sodium hydroxide was placed in the dropping funnel and added, with rapid stirring, during 5–10 min, to the TNT solution. The mixture turned dark red-brown and a crystalline product appeared after about 1 min. Formation of the crystalline product was heavy by the end of the addition of the hypochlorite solution and the temperature of the reaction mixture had risen to 35°. The mixture was allowed to stand for 15 min, then filtered with suction, and the filter cake was washed thoroughly with methanol and dried. It weighed 7.9 g, 79% of the theoretical yield. The material was recrystallized by dissolving it in hot acetone with Darco and Celite, filtering the hot solution, adding water to the cloud point, and chilling. It formed faintly yellow needles which melted at 218–220° and the melting point was not depressed on admixture with an authentic sample of III prepared by the nitration of bibenzyl, *vide supra*. X-Ray powder diffraction patterns of the two samples, however, were not superimposable The product formed in the TNT–hypochlorite reaction was a metastable polymorph of the product obtained by the nitration of bibenzyl. This metastable polymorph transformed into the stable form at ambient temperature when placed under 1-nitropropane, a solvent in which it was slightly soluble. When the stable polymorph was heated a solid–solid transition at 105° produced the metastable polymorph.[28]

2,2',4,6,6'-Pentanitrobibenzyl.—A solution of 0.52 g (0.002 mole) of 2,6-dinitrobenzyl bromide and 0.45 g (0.002 mole) of TNT in 10 ml of THF and 5 ml of methanol was prepared. To this solution was added 10 ml of water containing 0.08 g (0.002 mole) of sodium hydroxide, at once and with rapid stirring. The reaction mixture immediately became dark red-brown in color and precipitation of a crystalline product began within 2 min. The mixture was allowed to stand at ambient temperature for 2 hr, then filtered, and the filter cake was washed thoroughly with methanol and dried. It weighed 0.69 g, 86.5% of the theoretical yield. Recrystallized from methyl ethyl ketone–water it formed colorless needles, mp 155–156°. *Anal.* Calcd for $C_{14}H_9N_5O_{10}$: C, 41.50; H, 2.21; N, 17.21; mol wt, 407. Found: C, 41.71, 41.30; H, 2.64, 2.20; N, 17.34, 17.16; mol wt, 395, 400 (acetonitrile solution).

2,4,4',6-Tetranitrobibenzyl.—This compound was prepared from TNT, 4-nitrobenzyl bromide, and sodium hydroxide in the same manner as the pentanitrobibenzyl, above. The reaction produced a 73.6% yield of crude crystalline product. Recrystallized from methyl ethyl ketone–methanol it formed very faintly yellow needles, mp 179–180°. *Anal.* Calcd for $C_{14}H_{10}N_4O_8$: C, 46.40; H, 2.76; N, 15.45; mol wt, 362. Found: C, 46.46, 46.34; H, 2.95, 2.68; N, 15.16, 15.17; mol wt, 365, 357 (acetonitrile solution).

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[28] Dr. J. M. Rosen of these laboratories determined the transition temperature and carried out the transformation of the metastable form into the stable form under solvent.

Aralkyl Hydrodisulfides.[1] V. The Reaction of ^{35}S-Labeled Aralkyl Hydrodisulfides with Triphenylphosphine

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Benzyl or benzhydryl hydrodisulfides-^{35}S ($C_6H_5CH_2{}^{35}SSH$, $(C_6H_5)_2CH{}^{35}SSH$), the sulfenyl sulfur atom of which is labeled with radioactive sulfur, were prepared and allowed to react with triphenylphosphine. Radioactivities of the products, triphenylphosphine sulfide, hydrogen sulfide, aryl-substituted alkanethiol, and diaralkyl disulfide, were measured and compared with those of the corresponding radioactive standard compounds. These data showed that benzyl or benzhydryl hydrodisulfides are attacked by triphenylphosphine both on the sulfenyl and sulfhydryl sulfur atoms. Thus, the mechanisms suggested in a preceding paper are confirmed. The proportions and significance of reaction at sulfenyl and sulfhydryl sulfur atoms are discussed on the basis of the activities of the products.

Hydroperoxides are well known to be attacked on the hydroxy oxygen by triphenylphosphine,[2] to give alcohols and triphenylphosphine oxide.[2,3] A preceding paper[4] reported that triphenylmethyl hydrodisulfide reacts with tertiary phosphine to give the phosphine sulfide and triphenylmethanethiol similarly as hydroperoxides, while benzyl hydrodisulfide and benzhydryl hydrodisulfide give the phosphine sulfide, hydrogen sulfide, the corresponding thiol, disulfide, and hydrocarbon. On the basis of these results, the mechanisms by which hydrodisulfides react with tertiary phosphine were suggested,[4] involving nucleophilic attack of the phosphine on sulfenyl sulfur to yield the phosphine sulfide, hydrogen sulfide, diaralkyl disulfide, and hydrocarbon and competitive attack on sulfhydryl sulfur

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