6b, 34404-77-8; **6c**, 34404-78-9; **7b**, 34404-79-0; **7c**, 34404-80-3; *dl*-**8a**, 30698-38-5; *dl*-**8b**, 34405-36-2; *dl*-**8c**, 34405-37-3; **11a**, 34404-81-4; **11b**, 34404-82-5; **12a**, 34404-83-6; **13a**, 34404-84-7; **13b**, 34404-85-8; **14a**, 34415-49-1; **14b**, 34415-50-4; **15a**, 34404-86-9; **15b**, 34404-87-0.

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Reactions of α-Substituted Polynitrotoluenes. III. 2,4,6-Trinitrobenzyl Anion as a Nucleophile at Aromatic Carbon

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The results of deuterium exchange experiments have shown that 2,4,6-trinitrobenzyl anion is formed from 2,4,6-trinitrotoluene in alkaline tetrahydrofuran–methanol solutions. This carbanion has been utilized as a nucleophile in halogen displacement reactions at aromatic carbon to prepare a series of polynitrodiphenylmethanes.

The previous paper in this series[1] described the preparation of 2,2′,4,4′,6,6′-hexanitrostilbene (**1**) from 2,4,6-trinitrotoluene (**2**) and aqueous hypochlorite in tetrahydrofuran–methanol. It was postulated[1] that, in alkaline media, **2** formed 2,4,6-trinitrobenzyl anion (**3**), which was chlorinated to yield 2,4,6-trinitrobenzyl chloride (**4**). Subsequent reaction of **4** with alkali produced **1**. Evidence to support the intermediacy of **4** in this reaction was obtained by isolating it in 85% yield from a short-stopped reaction.

In the present paper, we present additional evidence for the existence of the anion **3** under our reaction conditions and describe a variety of chemistry based upon its use as a nucleophile in displacement reactions at aromatic carbon. The products of these reactions, polynitrodiphenylmethanes, dissociate in alkaline media to form the corresponding polynitrodiphenylmethide ions. These anions were found to be unreactive in nucleophilic addition reactions.

Results and Discussion

The question of the existence of the anion **3** has been considered by numerous investigators.[2-7] In general, the formation of the anion **3** was disfavored in largely aqueous solvent systems. This conclusion was recently confirmed by Bernasconi,[8] who observed that though the anion **3** is the primary product of the reaction of **2** with alkali in methanol, ethanol, and 50% dioxane–water, there was no evidence to suggest that the anion **3** was present when 10% dioxane–water was used as a solvent.

Since our experimental work[1] had been carried out in tetrahydrofuran–methanol–water, about 1:1:1, our preliminary experiments were designed to determine whether **3** is in fact the primary product formed from **2** upon the addition of alkali. If the anion **3** does form, then in a reaction such as the halogenation of **2**,[1] the formation of **3** should be rate determining.[9a] If halogenation of **3** is rapid relative to its rate of reprotonation by the weak acids water or methanol, then every anion formed will be converted to **4** without returning to **2**. Thus, the conversion of **2** to **4** in a deuterated solvent system should yield **4**-α-H_2.

When **2** in tetrahydrofuran–methanol-*d* was rapidly added to $D_2O–OD^-$ at 0° and the mixture was immediately quenched in DCl–D_2O, the recovered **2** was found to have exchanged 12.4% (nmr) of its methyl protons. Quenching the reaction after a 30-sec equilibration increased the deuterium content of the recovered **2** to 25.5%. However, when the anion **3** was trapped by chlorination[1] in a deuterated solvent system, the halide **4** did not contain any deuterium in the α position. These results are consistent with the proposed slow formation of **3** from **2** (eq 1) followed by a rapid chlorination of the anion **3**.

$$\underset{\mathbf{2}}{\mathrm{PiCH_3}} + \mathrm{OH^-} \longrightarrow \underset{\mathbf{3}}{\mathrm{PiCH_2^-}} + \mathrm{H_2O} \qquad (1)$$

$$\mathrm{PiCH_2^-} + \mathrm{OCl^-} + \mathrm{H_2O} \longrightarrow \underset{\mathbf{4}}{\mathrm{PiCH_2Cl}} + 2\mathrm{OH^-} \qquad (2)$$

$$\mathrm{Pi} = \text{2,4,6-trinitrophenyl}$$

A similar and perhaps rather surprising result was obtained when *p*-nitrobenzyl bromide was used as the substrate molecule for nucleophilic attack by the anion **3**.[1] From this reaction carried out in tetrahydrofuran–methanol-*d*, we obtained an 83% yield of 2,4,4′,6-tetranitrobibenzyl (**5**). The product had not incorporated deuterium at either of the methylene groups (eq 3). The absence of deuterium in the product suggests that the nucleophilic displacement process involving either ionic or ion–radical[9b] intermediates is exceedingly rapid as compared to the recombination of

$$\mathrm{PiCH_2^-} + p\text{-}\mathrm{O_2NC_6H_4CH_2Br} \longrightarrow \underset{\mathbf{5}}{p\text{-}\mathrm{O_2NC_6H_4CH_2CH_2Pi}} \qquad (3)$$

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(1) K. G. Shipp and L. A. Kaplan, *J. Org. Chem.*, **31**, 857 (1966).

(2) K. Bowden and R. Stewart, *Tetrahedron*, **21**, 261 (1965).

(3) E. Buncell, K. E. Russell, and J. Wood, *Chem. Commun.*, 252 (1968).

(4) R. E. Miller and W. F. R. Wynne-Jones, *J. Chem. Soc.*, 2375 (1959).

(5) J. A. Blake, M. J. B. Evans, and K. E. Russell, *Can. J. Chem.*, **44**, 119 (1966).

(6) E. F. Caldin and G. Long, *Proc. Roy. Soc., Ser. A*, **228**, 263 (1955).

(7) K. L. Servis, *J. Amer. Chem. Soc.*, **89**, 1508 (1967).

(8) C. F. Bernasconi, *J. Org. Chem.*, **36**, 1671 (1971).

(9) (a) By analogy with the overall rate of halogenation of other carbon acids: R. G. Pearson and R. L. Dillion, *J. Amer. Chem. Soc.*, **75**, 2439 (1953). Bernasconi[8] reports that the deprotonation of **2** in methanol or ethanol is as slow as in nitroethane. (b) R. G. Kerber, G. W. Urry, and N. Kornblum, *J. Amer. Chem. Soc.*, **87**, 4520 (1965).

3 with protons from the weak acid methanol. We prefer a mechanism involving ionic rather than ion-radical intermediates (eq 4–6) on the following grounds.

$$PiCH_2^- + p\text{-}O_2NC_6H_4CH_2Br \longrightarrow PiCH_2\cdot + p\text{-}O_2NC_6H_4CH_2Br^{-}\cdot \tag{4}$$

$$p\text{-}O_2NC_6H_4CH_2Br^{-}\cdot \longrightarrow p\text{-}O_2NC_6H_4CH_2\cdot + Br^- \tag{5}$$

$$p\text{-}O_2NC_6H_4CH_2\cdot + PiCH_2\cdot \longrightarrow \underset{\mathbf{5}}{p\text{-}O_2NC_6H_4CH_2CH_2CH_2Pi} \tag{6}$$

Though *p*-nitrobenzyl bromide affords an 83% yield of **5**, the corresponding chloro derivative produced only an 8% yield of **5**. Kornblum[9b] has shown that the rate of carbon alkylation of 2-nitropropyl anion by *p*-nitrobenzyl halides, a reaction which proceeds by an ion–radical mechanism, is quite insensitive to the nature of the leaving group. Therefore, the disparity in the yields of **5** obtained from the bromide and the chloride is better fit by an ionic displacement mechanism. Furthermore, the addition of *p*-dinitrobenzene, an electron acceptor that inhibited the carbon alkylation of 2-nitropropyl anion by *p*-nitrobenzyl chloride,[9b] had no effect on the yield of the nucleophilic displacement product **5**. We therefore concluded that under our reaction conditions **2** forms the anion **3**, which can participate in ionic displacement reactions.

Extending the use of the reagent **3** to aryl halides, we observed that, with picryl chloride as the substrate in tetrahydrofuran–methanol solution, a 90% yield of a crystalline solid, mp 232°, was obtained on acidifying the reaction mixture. Its mode of formation and the results of nmr (Table I), molecular weight, and elemental analytical determinations showed the product to have the structure of the expected, but heretofore unknown, nucleophilic displacement product 2,2′,4,4′,6,6′-hexanitrodiphenylmethane (**6**). With other polynitroaryl halides, halide displacement products analogous to **6** were obtained. These results are summarized in Table I.

Inspection of the yield data in Table I for the mono-, di-, and trinitrophenyl halides shows that the yield of polynitrodiphenylmethane is quite sensitive to the number and orientation of the nitro groups attached to the benzene ring of the aryl halide. As the yield of polynitrodiphenylmethane decreases in the order 2,4,6-$(NO_2)_3 \gg$ 2,4-$(NO_2)_2 >$ 2,6-$(NO_2)_2 >>>>$ 3,5-$(NO_2)_2$ or mononitro, an increase in the yield of 2,2′,4,4′,6,6′-hexanitrobibenzyl (**7**), a bimolecular condensation product of **2**, is obtained. Under these reaction conditions in the absence of aryl halide, **2** affords a 41% yield of **7**. Since the relative reactivity of these polynitroaryl halides toward other nucleophiles is in the same order[10–12] as we have observed for **3**, the inability of mononitro-, 3,5-dinitro-, and 2,6-dinitrophenyl (at mole ratio $ArX/PiCH_3 = 0.5$) halides to form any nucleophilic displacement product analogous to **6** can be attributed to a competing reaction of the anion **3** with **2** to form the bimolecular condensation product **7**. The formation of **7** from **3** and **2** probably involves radical ion intermediates and proceeds by a mechanism similar to that suggested for the formation of 4,4′-dinitrobibenzyl from *p*-nitrotoluene in alkaline media.[13]

The system may therefore be described by the following equations.

$$PiCH_2^- + ArX \xrightarrow{k_N} ArCH_2Pi \tag{7}$$

$$PiCH_2^- + PiCH_3 \xrightarrow{k_B} PiCH_2CH_2Pi \tag{8}$$

As the reactivity of the substrate ArX toward nucleophilic reagents increases, the ratio k_N/k_B will increase. Consequently, the product composition should change from **7** to polynitrodiphenylmethane derivative, passing through a region where a mixed **7**–polynitrodiphenylmethane product is obtained as the susceptibility of the substrate to nucleophilic attack increases. Such an intermediate condition was observed when 1-chloro-2,4-dinitrobenzene was used as a substrate. For a molar ratio $ArX/PiCH_3 = 0.5$, a mixture of **7** and 2,2′,4,4′,6-pentanitrodiphenylmethane (**8**) was obtained (Table I). The displacement reaction (eq 7) competed more effectively on increasing the concentration of the halide substrate. When the $ArX/PiCH_3$ ratio was increased to 1.5, a threefold increase in the partial rate factor $k_N[ArX]/k_B[PiCH_3]$, **8** was the only product formed (Table I).

A change in the product composition similar to that obtained by increasing the concentration of the halide substrate could also be obtained by substituting 1-fluoro-2,4-dinitrobenzene for the chloro derivative. With the fluoro derivative at a mole ratio $ArX/PiCH_3 = 0.5$, the sole reaction product was **8** rather than a mixture of **7** and **8** as was obtained with chloride at this reactant ratio. The rate constant ratio k_{ArF}/k_{ArCl} for the reaction of 2,4-dinitrophenyl halides with anionic nucleophiles of the first row elements is much greater than unity.[14] As only a threefold increase in the partial rate factor $k_N[ArX]/k_B[PiCH_3]$ was required to suppress the formation of **7** in the reaction using the chloride substrate, increasing the reactivity of the substrate ArX by certainly more than a factor of 3[14] should produce the same change in the product composition. These results are consistent with the hypothesis that the formation of the polynitrodiphenylmethanes occurs by an S_N2 ionic displacement mechanism with the anion **3** acting as a nucleophile.

The absence of diphenylmethane product with 2-NO_2, 4-NO_2, 3,5-$(NO_2)_2$, and 2,6-$(NO_2)_2$ phenyl halides at mole ratio $ArX/PiCH_3 = 0.5$ (Table I) is understandable from a consideration of the reaction rates for these substrates with methoxide ion in methanol at 50°.[11,15] The relative rates for 2-NO_2, 4-NO_2, 2,6-$(NO_2)_2$, and 2,4-$(NO_2)_2$ chlorobenzenes are in the order 1:3.4:2900:75,000. With a 20–75,000-fold difference between the reactivity of the mononitro and 2,4-$(NO_2)_2$ substrates toward methoxide ion, displacement of halogen from the mononitro derivatives by **3** (eq 7) should not be able to compete with the formation of **7** (eq 8) at either a larger $ArX/PiCH_3$ ratio or by using the more reactive fluoro substrates. However, with

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[10] A. J. Parker and T. O. Read, *J. Chem. Soc.*, 9 (1962).

[11] J. F. Bunnett, *Quart. Rev., Chem. Soc.*, **12**, 1 (1958).

[12] J. Miller, "Aromatic Nucleophilic Substitution," Elsevier, Amsterdam, 1968, Chapters 4 and 5.

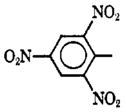
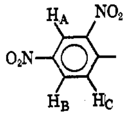
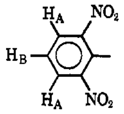
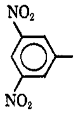
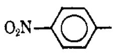
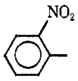
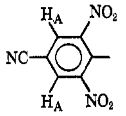
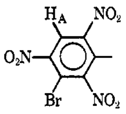
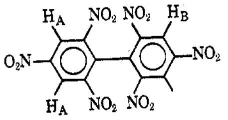
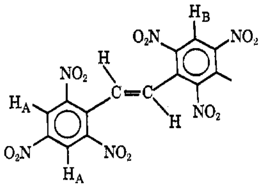
[13] G. A. Russell and E. G. Janzen, *J. Amer. Chem. Soc.*, **84**, 4153 (1962); **89**, 300 (1967).

[14] *Cf.* ref 12, Chapter 5, Section 3b; as examples, k_{ArF}/k_{ArCl} for MeO^- and $p\text{-}O_2NC_6H_4O^-$ with 2,4-dinitrophenyl halides is equal to 890 and 3160, respectively.

[15] Data are not available for the 3,5-$(NO_2)_2$ isomer but it is certainly less reactive than the 2,6-$(NO_2)_2$ isomer and probably less reactive than the 4-NO_2 isomer.

TABLE I

REACTION PRODUCTS, $PiCH_2Ar$, FROM NITROARYL HALIDES AND 2,4,6-TRINITROBENZYL ANION[a]

Ar	X	Yield $PiCH_2Ar$, %		100-MHz Nmr spectrum[b]					
		THF	THF-DMSO	Pi	CH_2	CH	H_A	H_B	H_C
	Cl	90	90	(M) 9.06	5.12				
				(A) 8.70		6.92			
	F	35	84	(M) 9.18	4.78		8.85 (2)	8.38 (4)	7.34 (2)
	Cl	*c*	*c*	(A) 8.42		7.33	8.73 (2)	8.16 (4)	7.25 (2)
	Cl		28[d]						
	Cl		*e*	(M) 9.00	5.02		8.32 (2)	7.84 (3)	
	Cl		35[f]	(A) 8.30		7.13	8.17 (2)	7.61 (3)	
	I	*e,h*	*e*						
	I		*g,h*						
	F		*e*						
	Br		*e*						
	Br		*g*						
	I	*e,h*	*e,h*						
	I		*g,h*						
	Cl		*e,h*						
	Cl	45	54	(M) 9.04	5.09		8.91		
				(A) 8.42[i]		6.96	8.65[i]		
	Br		29[j]	(M) 9.10	5.00		9.05		
				(A) 8.64		6.39	8.95		
	Cl		25	(M) 9.07	5.07		9.29	9.32	
				(A) 8.86		6.08	9.22	9.01	
	Cl	25	71	(M) 9.08	4.99		9.10	9.01[k]	
				(A) 8.62		6.54	9.10	8.94[k]	

[a] Unless otherwise noted, mole ratio $ArX/PiCH_3 = 0.5$. [b] Nmr spectra of neutral molecules (M) in DMSO-d_6. For anion (A) spectra, DMSO-d_6 solutions were partially neutralized with MeO^- in methanol. Changes in δ values for neutral molecules after adding base were less than 0.03 ppm. TMS was used as an internal reference. δ Values are in parts per million, multiplicity of lines in parentheses, $J_{o\text{-HH}} \cong 9$ Hz, $J_{m\text{-HH}} \cong 2$ Hz. [c] Mixture of **7** and **8** isolated. [d] Mole ratio $ArX/PiCH_3 = 1.5$. [e] Only **7** isolated. [f] Mole ratio $ArX/PiCH_3 = 6.0$. [g] Mixture of **7** and **1** isolated from reaction carried out at 60°. [h] Mole ratio $ArX/PiCH_3 = 1.0$. [i] Line assignments are questionable. [j] Only one halogen displaced. [k] Lines for vinyl hydrogens at 7.06 (4) ppm in neutral molecule and 7.03 (1) ppm in anion.

only a 25-fold difference in the reactivity of the 2,6-$(NO_2)_2$ and 2,4-$(NO_2)_2$ substrates toward methoxide ion, the synthesis of 2,2′,4,6,6′-pentanitrodiphenylmethane (**9**) from 1-chloro-2,6-dinitrobenzene was realized by increasing the mole ratio $ArX/PiCH_3$ from 0.5 to 6. Under these conditions, a 12-fold increase in the partial rate factor $k_N[ArX]/k_B[PiCH_3]$, the product composition was changed from **7** to **9** (Table I).

The formation of small amounts of **1** together with the bimolecular product **7** in the reactions carried out at 60° with 2-NO_2, 4-NO_2, and 3,5-$(NO_2)_2$ phenyl halides as substrates probably derives from the oxidation of an intermediate in the conversion of **2** to **7** (eq 8). We have obtained similar product compositions from the reaction of **2** and alkali in the absence of nitrophenyl halides.

The improved yields obtained in a mixed tetrahydrofuran–dimethyl sulfoxide solvent system may be due to an increase in the activity of **3** in the presence of dimethyl sulfoxide. This could be accomplished by either a desolvation of the anion **3**, as dimethyl sulfoxide forms strong hydrogen bonds with both water and methanol, or solvent separation of ion pairs existing in tetrahydrofuran–methanol solution by cation solvation. Similar observations have been noted[16–19] of the effect of dimethyl sulfoxide on the rates and product yields in nucleophilic displacement reactions of nitrophenyl halides.

With a variety of polynitrodiphenylmethanes in hand, we considered the possibility of generating anions from these species for use as nucleophiles. By judicious addition of a solution of sodium methoxide in methanol to dimethyl sulfoxide solutions of the polynitrodiphenylmethanes, intensely colored solutions were obtained. A comparison of the nmr spectra of the solutions prior to and after the addition of base showed that the additional lines in the spectrum of the alkaline solution corresponded in both position and intensity to those of the polynitrodiphenylmethide ion. Unlike alkaline solutions of **2**, partially (about one-half) neutralized solutions of the polynitrodiphenylmethanes were generally stable for at least 24 hr. The nmr spectra of these species are summarized in Table I. When sufficient base was added to neutralize all of the polynitrodiphenylmethane present, the nmr spectrum of the resulting solution became quite complex. The appearance of additional resonances in the aromatic region of the spectrum suggested that, at high base concentrations, the formation of Meisenheimer complexes may be a competing reaction.

We attempted to utilize 2,2′,4,4′,6,6′-hexanitrodiphenylmethide ion as a nucleophile in the addition to formaldehyde. Under reaction conditions in which **2** affords an 85% yield of 2-picrylethanol, 2,2′,4,4′,6,6′-hexanitrodiphenylmethane was recovered quantitatively from the reaction mixture.

Experimental Section

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

Solvents and Reagents.—Solvents used were Baker Analyzed reagent grade. Methanol-*d*, 99% D, and deuterium oxide, 99.8% D, were from E. Merck. The various halonitrobenzenes, 2,6-dinitrochlorobenzene, 4-chloro-3,5-dinitrobenzonitrile and 3,5-dinitroiodobenzene from Aldrich, 2,4-dinitrofluorobenzene, 4-nitrofluorobenzene, and 2-nitrochlorobenzene from J. T. Baker, and picryl chloride, 4-nitrobromobenzene, 4-nitroiodobenzene, and 2,4-dinitrochlorobenzene from Eastman, were used as received. The following were prepared according to literature procedures: 1,3-dibromo-2,4,6-trinitrobenzene,[20] 3-chloro-2,2′,-4,4′,6,6′-hexanitrostilbene,[21] and 3-chloro-2,2′,4,4′,6,6′-hexanitrobiphenyl.[22] Nmr spectra were determined with a Varian HA-100 spectrometer at 30° using internal TMS as a reference.

Equilibration of 2,4,6-Trinitrotoluene (2) with Methanol-*d* and Methoxide.—A solution of 0.01 mol (0.54 g) of NaOMe in 15 ml of D$_2$O was added all at once to a stirred solution of 0.01 mol (2.27 g) of **2** in 30 ml of tetrahydrofuran and 15 ml of MeOD at 0°. The mixture was immediately quenched by adding an excess of DCl in D$_2$O. The precipitated oil was extracted with methylene chloride and dried over magnesium sulfate, and the solvent was removed *in vacuo*. The residue, 1.7 g, shown by tlc to consist only of **2**, was assayed for deuterium uptake by comparing the integral of the methyl group with that of the ring protons. Nmr in chloroform-*d* solution: aryl hydrogen δ 8.83 ppm, integral 54 ± 1 mm (2 H), methyl δ 2.70 ppm, integral 71 ± 1 mm (3 H). Per cent methyl hydrogen exchanged: $100(1 - 71/81) = 12.4$.

Repeating the above procedure, but allowing the reaction mixture to stand for 30 min prior to quenching, gave a dark red oil. This was extracted with 25 ml of benzene to leave a dark red solid that was shown by tlc to be a mixture of **7** and several unidentified products. The benzene extract, containing a mixture of **7** and **2**, was evaporated to dryness *in vacuo*. The residue was taken up in 1:1 benzene–hexane, and, by careful fractional crystallization, 100 mg (later fractions) of pure **2** was obtained for nmr analysis: in chloroform-*d* solution, aryl hydrogen δ 8.83 ppm, integral 22.2 ± 0.6 mm (2 H), methyl δ 2.70 ppm, integral 24.8 ± 0.8 (3 H). Per cent methyl hydrogen exchanged: $100(1 - 24.8/33.3) = 25.5$.

A control experiment in which **2** was dissolved in THF–MeOD–D$_2$O without base and subsequently quenched in DCl–D$_2$O showed that none of the methyl hydrogens had exchanged for deuterium.

Chlorination of 2 in a Deuterated Solvent System.—Clean sodium metal, 0.094 g-atom (2.08 g), was dissolved in 50 ml of D$_2$O under a stream of nitrogen. Dry chlorine gas, 0.079 g-atom (2.80 g), was passed through the resulting solution at such a rate that it was completely absorbed.

To 12.5 ml of the above solution of sodium hypochlorite chilled to 0° was rapidly added with vigorous stirring a solution of 0.0055 mol (1.25 g) of **2** in 12.5 ml of THF and 6.5 ml of MeOD which had been previously chilled to 0°. After 1 min, the dark red mixture was poured into excess DCl–D$_2$O and the precipitated oil was extracted into methylene chloride. After drying over magnesium sulfate and removing the solvent *in vacuo*, the residual red oil was taken up in benzene–hexane (1:1) and concentrated until crystallization commenced. Recrystallization of the crude product from benzene–hexane (1:1) afforded 0.33 g of **4**. Analysis of the product for deuterium uptake by nmr (chloroform-*d*) gave the following results: aryl hydrogen δ 8.91 ppm, integral 30 ± 1 mm (2 H), methylene hydrogen δ 5.09 ppm, integral 29 ± 0.5 mm (2 H); ratio CH$_2$/aryl hydrogen = 0.97.

Preparation of 2,4,4′,6-Tetranitrobibenzyl (5) in a Deuterated Solvent System.—To a stirred solution of 0.005 mol (1.13 g) of **2** and 0.005 mol (1.08 g) of 4-nitrobenzyl bromide in 10 ml of THF and 5 ml of MeOD was added a solution of 0.005 mol (0.27 g) of NaOMe in 10 ml of D$_2$O. After 30 min, the suspended solid was collected by filtration, washed with methanol, and dried. On recrystallizing the crude product (1.5 g, 83%) from methyl ethyl ketone, 1.0 g of **5** was obtained. Deuterium analysis was obtained by nmr spectroscopy (MeCN-d_3): methylene hydrogens δ 3.25 ppm (multiplet), integral 40.0 ± 0.5 mm (4 H), picryl hydrogens δ 8.88 ppm, integral 19.5 ± 0.5 mm (2 H); ratio CH$_2$/picryl H = 2.05.

Reaction of 3 with *p*-Nitrobenzyl Halides. A. General Procedure.—To a well-stirred solution of 0.01 mol of **2** and 0.01 mol of the *p*-nitrobenzyl halide in 50 ml of THF and 25 ml of methanol was added a solution of 0.01 mol (0.40 g) of sodium hydroxide in 60 ml of water. The wine-colored solution was stirred for 30 min, after which the suspended solid was collected on a Buchner, washed thoroughly with methanol, and dried. The unrecrystallized product was assayed by nmr in DMSO-d_6 solution. The following spectra were observed.

	δ, ppm, internal TMS			
Compd	Pi-H	CH$_2$	*o*-Ar H	*m*-Ar H
5	9.07	3.18	7.42, 7.51	8.13, 8.22
7	9.04	3.34		

Assays were calculated by subtracting the average of the integrals for the *o*-Ar H and *m*-Ar H from the total integral for the picryl group. Dividing the remainder by two normalized the integral for **7** to that of **5**. The fraction of **5** present in the mixed product could then be calculated by dividing the integral for the picryl hydrogens of **5** by the sum of the integral for the picryl hydrogens of **5** and the normalized integral for the picryl hydrogens of **7**.

B. ***p*-Nitrobenzyl Bromide.**—Using the general procedure, 2.8 g (77%) of a pale yellow solid was obtained. Nmr analysis showed it to be pure **5**.

C. ***p*-Nitrobenzyl Chloride.**—A 0.54-g yield of crude product

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was obtained. This was found to be a mixture of 54 ± 2% **5** and 46 ± 2% **7**. This is equivalent to an 8% yield of **5**.

D. *p*-Nitrobenzyl Bromide in the Presence of *p*-Dinitrobenzene.—The general procedure was followed except that 0.002 mol (0.34 g) of *p*-dinitrobenzene was added to the solution of **2** and *p*-nitrobenzyl bromide prior to the addition of alkali. The crude product, 2.7 g (75%), was shown by nmr to consist only of **5**.

E. *p*-Nitrobenzyl Chloride in the Presence of *p*-Dinitrobenzene.—The same procedure was followed as in D. The product, 0.63 g, was a mixture of 58 ± 2% **5** and 42 ± 2% **7**. This is equivalent to a 10% yield of **5**.

2,2′,4,4′,6,6′-Hexanitrodiphenylmethane (**6**) was prepared by rapidly adding with vigorous stirring a solution of 0.02 mol (1.32 g) of potassium hydroxide (85%) in 10 ml of methanol to 0.02 mol (4.54 g) of **2** in 50 ml of THF at ambient temperature. Immediately after the addition of alkali, 0.01 mol (2.48 g) of picryl chloride in 25 ml of DMSO[23] was added to the dark red solution. The reaction mixture turned dark blue upon the addition of picryl chloride. After stirring for 30 min, it was quenched in 750 ml of water containing 25 ml of 12 *M* hydrochloric acid. The yellow-orange solid that separated was collected by filtration and washed with hot methanol until the washings were essentially colorless. The residue, 4.0 g (91%), was recrystallized by dissolving it in 35 ml of MeCN, treating the solution with Darco G-60 charcoal, and then adding 50 ml of methanol to the filtrate. On cooling, almost colorless needles of **6**, mp 232° dec, were obtained.

Anal. Calcd for $C_{13}H_6N_2O_{12}$: C, 35.6; H, 1.4; N, 19.2; mol wt, 438. Found: C, 35.5; H, 1.5; N, 18.9; mol wt, 430, 439 (osmometer, MeCN).

2,2′,4,4′,6-Pentanitrodiphenylmethane (**8**) was prepared from 0.02 mol (4.54 g) of **2** and 0.01 mol (1.86 g) of 2,4-dinitrofluorobenzene. The crude product, 3.3 g (84%), was shown by tlc to be a single species. Recrystallization from MeCN–MeOH as described above gave yellow crystals, mp 208–210° dec.

Anal. Calcd for $C_{13}H_7N_5O_{10}$: C, 39.7; H, 1.8; N, 17.8; mol wt, 393. Found: C, 39.5, 39.6; H, 2.0, 1.7; N, 17.7, 17.6; mol wt, 388 (osmometer, MeCN).

With 0.01 mol (2.02 g) of 2,4-dinitrochlorobenzene and 0.02 mol (4.54 g) of **2**, the crude product was shown to be a mixture of **7** and **8** by tlc. Using 0.03 mol (6.06 g) of 2,4-dinitrochlorobenzene and 0.02 mol (4.54 g) of **2**, the crude product, 2.7 g (35%), was shown to be pure **8** by tlc.

2,2′,4,6,6′-Pentanitrodiphenylmethane (**9**) was prepared by the procedure described for the preparation of **6** using 0.12 mol (24.3 g) of 2,6-dinitrochlorobenzene and 0.02 mol (4.54 g) of **2**. A 2.75-g (35%) yield of **9** was obtained. After recrystallization from MeCN–MeOH, the product, pale yellow needles, melted at 188–190° dec.

Anal. Calcd for $C_{13}H_7N_5O_{10}$: C, 39.7; H, 1.8; N, 17.8. Found: C, 39.9, 39.6; H, 2.0, 1.9; N, 18.2, 18.2.

From a reaction mixture consisting of 0.01 mol (2.02 g) of 2,6-dinitrochlorobenzene and 0.02 mol (4.54 g) of **2**, there was obtained 3.25 g (36%) of pure **7**. No **9** could be detected in the crude product from this reaction by tlc techniques.

4-Cyano-2,2′,4′,6,6′-pentanitrodiphenylmethane was prepared by the procedure described for the preparation of **6** from 0.01 mol (2.28 g) of 4-chloro-3,5-dinitrobenzonitrile and 0.02 mol (4.54 g) of **2**. The crude product, 2.25 g (54%), was recrystallized from MeCN–MeOH to yield pale yellow needles, mp 205° dec. The product is very sensitive to light.

Anal. Calcd for $C_{14}H_6N_6O_{10}$: C, 40.2; H, 1.5; N, 20.1. Found: C, 40.7, 40.7; H, 1.6, 1.5; N, 20.0, 19.7.

3-Bromo-2,2′,4,4′,6,6′-hexanitrodiphenylmethane was prepared from 0.01 mol (3.71 g) of 1,3-dibromo-2,4,6-trinitrobenzene and 0.02 mol (4.54 g) of **2**. The red-brown oil that separated upon quenching the reaction mixture was triturated with methanol until it solidified. The crude product, 15 g (29%), was dissolved in acetone and treated with Darco G-60 charcoal, and an equal volume of methanol was added to the filtrate. The resulting solution was heated on a hot plate to remove the acetone, whereupon fine needles of the product, mp 170–172° dec, were obtained.

Anal. Calcd for $C_{13}H_5BrN_6O_{12}$; C, 30.2; H, 1.0; Br, 15.5; N, 16.3. Found: C, 31.0, 30.8; H, 1.8, 1.5; Br, 15.5, 15.5; N, 16.2, 16.1.

3-(2,4,6-Trinitrobenzyl)-2,2′,4,4′,6,6′-hexanitrostilbene was prepared from 0.02 mol (4.54 g) of **2** and 0.01 mol (4.85 g) of 3-chloro-2,2′,4,4′,6,6′-hexanitrostilbene as described previously for the preparation of **6**. The crude product was triturated with methanol and then dissolved in 50 ml of THF and treated with Darco G-60 charcoal. After adding 50 ml of methanol to the hot filtrate, the product, 4.8 g (71%), separated as almost colorless crystals, mp 210–211° dec.

Anal. Calcd for $C_{21}H_9N_9O_{18}$: C, 37.2; H, 1.3; N, 18.8. Found: C, 37.5, 37.7; H, 1.6, 1.5; N, 19.0, 18.4.

3-(2,4,6-Trinitrobenzyl)-2,2′,4,4′,6,6′-hexanitrobiphenyl was prepared from 0.02 mol (4.54 g) of **2** and 0.01 mol (4.58 g) of 3-chloro-2,2′,4,4′,6,6′-hexanitrobiphenyl by the procedure described for **6**. After triturating the crude product with methanol until the extracts were almost colorless, the residue was dissolved in acetone and treated with Darco G-60 charcoal. After addition of an equal volume of methanol to the filtrate, the product, 1.7 g (25%), mp 255–256° dec, separated as pale yellow rods.

Anal. Calcd for $C_{19}H_7N_9O_{18}$: C, 35.1; H, 1.1; N, 19.4. Found: C, 34.9, 34.2; H, 1.6, 1.2; N, 19.2, 18.8.

Registry No.—**2**, 118-96-7; **3**, 34403-92-4; **5**, 5180-52-9; **6**, 32255-27-9; **7**, 5180-53-0; **8**, 32255-28-0; **9**, 32255-29-1; 4-cyano-2,2′,4′,6,6′-pentanitrodiphenylmethane, 32255-30-4; 3-bromo-2,2′,4,4′,6,6′-hexanitrodiphenylmethane, 32255-31-5; 3-(2,4,6-trinitrobenzyl)-2,2′,4,4′,6,6′-hexanitrostilbene, 32255-32-6; 3-(2,4,6-trinitrobenzyl)-2,2′,4,4′,6,6′-hexanitrobibenzyl, 34404-00-7.

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[23] For those runs in the absence of DMSO, it was replaced with an equivalent volume of THF.