amount of SiX^+ produced, is independent of the position of the substituent. Second, no ion corresponding to allyl (*e.g.*, $SiC_2H_5^+$) is formed in any of the cases. This would require a carbon–silicon double bond, the resulting fragments of which are never observed. Third, ions of the general formula $SiC_6H_6X^+$ are observed when methyl or halogen is the substituent corresponding to the structures 21 or 22. A distinction between which of these is present (ineeed, both may be) is not possible at this time. Fourth, anomalies appear in the ortho cases when a particularly stable ion may be formed, for example, **23**, **24**, or **25**. The nitro and the trifluoromethyl derivatives appear to undergo a fragmentation of the aromatic ring which does not occur in the other compounds.

Registry No.—**3**, 69-45-31; **4**, 108-88-3; **8**, 770-09-2; **9**, 1007-26-7; **12**, 768-32-1; **13**, 2060-89-1; **14**, 13183-70-5; **15**, 98-06-6; **16**, 1012-72-2; **17**, 7450-03-5; **18**, 3728-44-7; **19**, 3728-43-6; **20**, 1075-38-3; **23**, 15842-76-9; **24**, 4405-42-9; **25**, 10557-71-8; **26**, 27378-66-1; *o*-fluorobenzyltrimethylsilane, 1833-40-5; *m*-fluorobenzyltrimethylsilane, 772-48-5; *p*-fluorobenzyltrimethylsilane, 706-25-2; *o*-nitrophenyltrimethylsilane, 15290-22-9; *m*-nitrophenyltrimethylsilane, 15290-24-1; *p*-nitrophenyltrimethylsilane, 4405-33-8.

Studies in Boron Hydrides. IV. Stable Hydride Meisenheimer Adducts[1]

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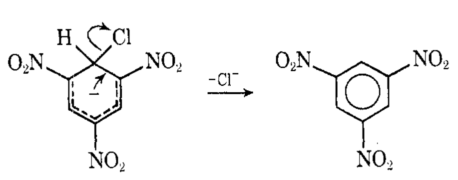
The addition of hydride from the octahydrotriborate ion to 1-substituted 2,4,6-trinitrobenzenes affords a stable C_3-hydride Meisenheimer adduct. Concurrent with this addition reaction is hydride displacement of the C_1 substituent to form 1,3,5-trinitrobenzene. Under the reaction conditions, 1,3,5-trinitrobenzene is reduced to a monohydride Meisenheimer adduct. Displacement of the C_1 substituent by hydride is favored by substituents which can coordinate with the developing B_3H_7 moiety in the transition state.

Severin[2–4] demonstrated that the reduction of nitroaromatic compounds with sodium tetrahydroborate under alkaline conditions produced the dihydro or polyhydro product. Thus, 1,3,5-trinitrobenzene (**1**), and 1-X-2,4-dinitrobenzene (X = Cl, CH_3, H, etc.) afforded 1,3,5-trinitrocyclohexane and 2-X-3,5-dinitrocyclohex-1-ene, respectively. Kaplan[5] has shown that the reduction of 1-X- or 1,3-X,Y-2,4,6-trinitrobenzenes (X,Y = Br, Cl, OCH_3) under identical conditions yields 1,3,5-trinitrocyclohexane as the sole product. This transformation was formulated[5] for 1-chloro-2,4,6-trinitrobenzene as occurring by attack of hydride at C_1 to produce the anion **2** which rearomatizes by loss of chloride to form **1**. Subsequent reduction of **1** affords 1,3,5-trinitrocyclohexane.

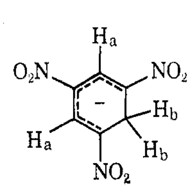


2 **1**

To test this suggested mechanism for the conversion of **1** and mono- and disubstituted trinitrobenzenes to 1,3,5-trinitrocyclohexane, the reaction of these substrates with some hydropolyborate ions which would be weaker hydride donors than tetrahydroborate ion was investigated. By decreasing the formal reduction potential of the hydride donor, it might be possible to interrupt the reduction at an intermediate stage, thereby permitting the isolation of cyclohexadienyl-type products.

Results and Discussion

The reaction of **1** with the *nido*hydropolyborate ions $B_3H_8^-$, $B_9H_{14}^-$, $B_{10}H_{13}^-$, $B_{10}H_{14}^{2-}$, and $B_{10}H_{15}^-$[6] in such solvents as acetone, acetonitrile, dimethyl sulfoxide, and nitromethane resulted in the formation of dark purple solutions which had absorption maxima at 478 and 582 nm. The position of these absorption maxima are similar to those displayed by 1:1 Meisenheimer adducts of **1** with cyanide,[7] thiophenoxide,[8] and sulfite[9] ions, and piperidine.[10] For preparative work, tetramethylammonium octahydrotriborate proved to be the most convenient reducing agent. On mixing chilled acetonitrile solutions of the reactants, glistening, purple-black crystals separated which analyzed for the tetramethylammonium salt of the hydride Meisenheimer adduct **3**.



3

Confirmation of this structural assignment was obtained from the nmr spectrum in dimethyl sulfoxide. This spectrum exhibited lines at $\delta_{Me_4N^+}$ 3.12 (6),[11] δ_{H_b} 3.87 (1.1), and δ_{H_a} 8.24 (1). The line position found for H_a is almost identical with those reported for H_a in the Meisenheimer adducts of **1** with hydroxide

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[1] Part III: A. R. Siedle and T. R. Hill, *J. Inorg. Nucl. Chem.*, **31**, 3874 (1969).

[2] T. Severin and R. Schmitz, *Chem. Ber.*, **95**, 1417 (1962).

[3] T. Severin and M. Adam, *ibid.*, **96**, 448 (1963).

[4] T. Severin, R. Schmitz, and M. Adam, *ibid.*, **96**, 3076 (1963).

[5] L. A. Kaplan, *J. Amer. Chem. Soc.*, **86**, 740 (1964).

[6] The ions $B_6H_6^{2-}$, $B_9H_{19}^{2-}$, $B_{10}H_{10}^{2-}$, and $B_{20}H_{18}^{2-}$ were found to be unreactive.

[7] A. R. Norris, *Can. J. Chem.*, **45**, 2703 (1967).

[8] M. R. Crampton, *J. Chem. Soc. B*, 1208 (1968).

[9] M. R. Crampton, *ibid.*, 1341 (1967).

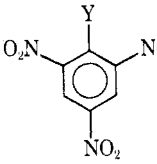
[10] M. R. Crampton and V. Gold, *ibid.*, 23 (1967).

[11] Chemical shifts are in parts per million downfield from internal tetramethylsilane. Relative intensities are in parentheses; H_a is used as reference.

(δ 8.42),[12] ethoxide (δ 8.41),[13] ammonia, and alkyl and dialkylamines (δ 8.32–8.50)[9] in dimethyl sulfoxide solutions. The slight upfield shift found for H_a in the adduct **3**, relative to the average value for H_a, δ 8.4, in the hydroxide, ethoxide, and amido Meisenheimer adducts of **1**, can be attributed to increased shielding of H_a on replacing an electronegative nitrogen or oxygen atom on the ring by hydrogen.

The assignment of H_b to the line at δ 3.87 can not be made by analogy with the reported values[9,12,13] for the "aliphatic" proton in other Meisenheimer adducts as this structural moiety is a methinyl proton, δ 5.8 ± 0.4, whereas in **3**, it is a methylene proton. An upfield shift of about 2 ppm could be expected on going from a methinyl to a methylene proton, and a shift of similar magnitude is found when one compares the methylene protons in 2,2′,4,4′,6-pentanitrodiphenylmethane, δ 4.95, with the methinyl proton of 2,2′,4,4′,6-pentanitrodiphenylchloromethane, δ 7.67.[14]

Having defined **3** as the structure of the hydride adduct of **1**, the reduction procedure was extended to 1-Y-2,4,6-trinitrobenzenes, **4**, with the expectation of isolating a C_1-hydride adduct **5**, the proposed precursor of 1,3,5-trinitrocyclohexane formed in reductions with tetrahydroborate ion.[5] When **4** (Y = Cl) was reduced with tetramethylammonium octahydrotriborate in acetonitrile solution, the nmr spectrum of the isolated purple-black crystals indicated the presence of two components. Lines at δ 8.24 (1.0) and 3.87 (1.2) are coincident with those found for **3**. Two additional lines at δ 8.35 (1.0) and 4.04 (2.2) (Table I) could not be reconciled with the spectrum expected for the C_1-adduct **5** (Y = Cl[9,12,13]), but they did have the proper position and intensity ratio for the C_3 adduct **6** (Y = Cl. The line for the tetramethylammonium cation, δ 3.12, was used as an internal reference in interpreting these spectra by subtracting from its area the contribution due to **3** and normalizing the residual area to the observed area of the H_a line in the adduct **6** (Y = Cl). Thus, the areas of the lines for H_a, H_b, and the tetramethylammonium cation were found to be in the ratio of 1:2.2:13. This agrees well with the calculated ratio, 1:2:12, for the adduct **6** (Y = Cl).



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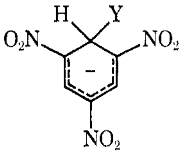

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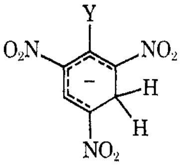


6

When **4** (Y = OCH_3) is reduced under similar conditions, a mixture composed of 65% of the C_3 adduct **6** (Y = OCH_3), and 35% of the adduct **3**. By contrast, *N,N*-dimethylpicramide yields only **3** and 2,4,6-trinitrotoluene forms the C_3 adduct **6** (Y = CH_3) exclusively.

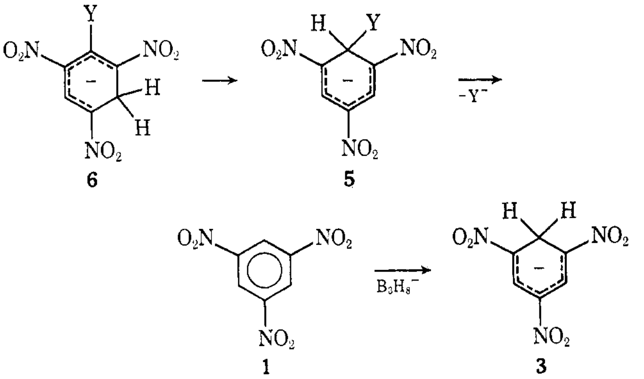
The formation of mixed products from picryl chloride and 2,4,6-trinitroanisole suggested, by analogy with previously observed[15,16] transformations of C_3 Meisenheimer adducts to the C_1 isomers, that hydride initially added at C_3 to form the adduct **6** which during the course of the reaction reverses to **4** and readds hydride at C_1 to form **5**. Though C_1 adducts are reported to be more thermodynamically stable than the C_3 adducts, like the C_3 adducts, they too are in equilibrium with their progenitors.[17] For the adduct **5**, this should involve the loss of the better leaving group, Cl^-, OCH_3^-, or $(CH_3)_2N^-$ rather than H^-, to form **1** which would be subsequently reduced to **3** under the reaction conditions.

TABLE I

PROTON MAGNETIC RESONANCE SPECTRA OF HYDRIDE MEISENHEIMER ADDUCTS[a]

Substrate[b]	δH_a[c]	δH_b[c]	$\delta (CH_3)_4N^+$[c]	% C_3 adduct[g]
Pi-H	8.24 (1)	3.87 (1.1)	3.12 (6.8)	
Pi-Cl	8.35 (1)	4.04 (2.2)	3.12 (13)[f]	75
	8.24 (1)	3.87 (1.2)	3.12 (6)	
Pi-OCH_3[d]	8.35 (1)	3.92 (2.4)	3.12 (12.6)[f]	65
	8.24 (1)	3.87 (1.0)	3.12 (6)	
Pi-$N(CH_3)_2$	8.24 (1)	3.86 (1.2)	3.12 (6)	0
Pi-CH_3[e]	8.38 (1)	3.90 (2.0)	3.12 (13.0)	100

[a] In dimethyl sulfoxide-d_6; δ in ppm downfield from internal tetramethylsilane. [b] Pi = 2,4,6-trinitrophenyl. [c] Relative intensities, H_a = 1, in parentheses. [d] δ_{OCH_3} 3.76 (3.2). [e] δ_{CH_3} 2.58 (4.2); integral not accurate due to some overlap with dimethyl sulfoxide-d_5, δ 2.50. [f] By subtracting the area due to **3** from total and normalizing remainder. [g] Calculated from the areas of the respective H_a lines.



Evidence to support the above reaction sequence could not be obtained. We have observed that the adducts **3** and **6** undergo slow decomposition in dimethyl sulfoxide solution. However, inspection of the nmr spectra of these aged solutions showed neither a change in the ratio of **6** to **3** nor a new line attributable to 1,3,5-trinitrobenzene. These observations tend to rule out the above proposed C_3 to C_1 hydride equilibration. Furthermore, when **4** (Y = Cl or OCH_3) is reduced using a twofold excess of tetramethylammonium octahydrotriborate, the product ratio (**6**:**3**) is unchanged. Thus, the product composition appears to be subject to kinetic rather than thermodynamic control as is observed in reactions leading to the formation of other Meisenheimer adducts.[15,16]

Unlike other nucleophiles, hydride would have to produce the C_1 and C_3 adducts concurrently, by separate nonequilibrating paths, with the former eliminating the C_1 substituent to form **1** which is subsequently reduced to the hydride adduct **3**. A perhaps more attractive route to **3** would not involve the intermediacy of the C_1 adduct **5**, but would require displacement of the

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(12) M. R. Crampton and V. Gold, *J. Chem. Soc.*, 4293 (1964).

(13) R. Foster and C. A. Fyfe, *Tetrahedron*, **21**, 3363 (1965).

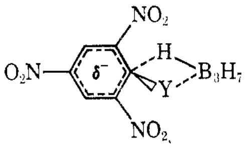
(14) K. G. Shipp and L. A. Kaplan, unpublished results.

(15) K. L. Servis, *J. Amer. Chem. Soc.*, **87**, 5495 (1965).

(16) M. R. Crampton and V. Gold, *J. Chem. Soc. B*, 893 (1966).

(17) The methoxide Meisenheimer adduct of 2,4,6-trinitroanisole is converted to the acetonyl adduct by dissolution in acetone; *cf.* ref 13.

C_1 substituent by hydride to form **1**. In this reaction, the participation of the developing B_3H_7 moiety as an electrophile in the transition state is involved. A reasonable transition state geometry would be **7** in



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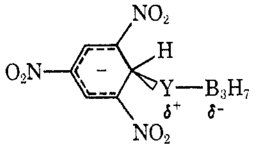

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which B–Y bond formation occurs concurrently with C–H bond formation. Collapse of this transition state to the tetrahedral intermediate **8** is followed by loss of $B_3H_7Y^-$ which results in rearomatization to produce **1**.[18] Relative to rearomatization to **1**, the reversal of **8** to its progenitors should be kinetically disfavored as C–Y bond cleavage should be energetically more favorable than B–Y bond cleavage. For a reaction sequence involving participation of B_3H_7 as an electrophile, the product yield from reaction at C_1 should be, as is observed, a function of the B–Y bond strengths which are in the order B–N > B–O > B–Cl.[19] This ordering is to be contrasted with the ordering of the C_1 substituents as leaving groups in other SN2 displacements at aromatic carbon, Cl > OMe > NMe$_2$.[20] In support of this hypothesis is the observation that 2,4,6-trinitrotoluene forms neither a C_1 Meisenheimer adduct[21] nor the 1,3,5-trinitrobenzene adduct **3**. The lack of hydride attack at C_1 in 2,4,6-trinitrotoluene can be attributed to the inability of the methyl group to coordinate with the developing B_3H_7 moiety in the transition state.

Experimental Section

These reactions involve powerful oxidizing and reducing agents. Precooled solutions should be employed and solvents should not be added to the dry premixed reactants. The reaction mediums from which the Meisenheimer adducts have crystallized should not be further concentrated as an explosion can result.

Reactions were carried out under nitrogen. Acetonitrile was dried by distillation from phosphorus pentoxide. The nitroaromatics used were of a good commercial grade and not purified further. Nmr spectra were obtained with the Varian HA-100 spectrometer at 23487 G and 30°. Chemical shifts reported are accurate to better than ±0.02 ppm.

$(CH_3)_4N^+C_6H_3(NO_2)_3^-$, 3.—Acetonitrile solutions, 0.3 *M*, were prepared from 0.23 g (2 mmol) of tetramethylammonium octahydrotriborate and 0.43 gm (2 mmol) of 1,3,5-trinitrobenzene. The solutions were cooled to about −10° and mixed. After standing for several minutes at this temperature, **3** separated as dark lustrous needles. It was collected by filtration, washed with a small amount of cold acetonitrile, and dried *in vacuo*. The yield was 0.34 g (57%): λ_{max} (CH_3CN) 262 nm (ϵ 15,000), 478 (27,600), 582 (33,500); the infrared spectrum (KBr) exhibited bands at 1325, 1490, 1550 and 1623 cm^{-1}. *Anal.* Calcd for $C_{10}H_{16}N_4O_6$: C, 41.7; H, 5.5; N, 19.4; B, 0.0. Found: C, 41.1, 41.1; H, 5.9, 6.1; N, 17.4, 17.9; B, 0.1.[22]

The order of addition of the reactants did not affect the yield. The Meisenheimer adduct **3** is stable for several days in the solid state, but in solution its decomposition is much more rapid.

$(CH_3)_4N^+C_6H_2CH_3(NO_2)_3^-$, 6 (Y = CH_3).—This compound was prepared from tetramethylammonium octahydrotriborate and 2,4,6-trinitrotoluene as described above: λ_{max} (CH_3CN) 256 nm (ϵ 11,000), 478 (25,000), 580 (34,000);[23] yield 62%. *Anal.* Calcd for $C_{11}H_{18}N_4O_6$: C, 43.7; H, 6.0; N, 18.5. Found: C, 43.5, 43.2; H, 6.1, 6.2; N, 18.2, 18.6.

Reduction of 2,4,6-Trinitroanisole and Picryl Chloride.—The reduction of these substrates with 1 and 3 equiv of tetramethylammonium octahydrotriborate was carried out in acetonitrile solution as described above.

Registry No.—**3**, 27554-58-1; **6** (Y = Cl), 27554-59-2; **6** (Y = OCH_3), 27554-60-5; **6** [Y = $N(CH_3)_2$], 27554-61-6; **6** (Y = CH_3), 27554-62-7.

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[18] An alternate route involves synchronous C–Y bond breaking in the transition state **7**. Collapse of this transition state affords **1** and $B_3H_7Y^-$ directly. We have no preference for either sequence based on the data. However, we do feel that the data, *vide infra*, support the proposal that the B_3H_7 moiety participates as an electrophile in the reaction. The coproduct in these reductions, the species $B_3H_7Y^-$, is isoelectronic with the stable $B_3H_8^-$ and should therefore be capable of being isolated from the reaction. We are continuing our so far unsuccessful attempts to isolate this coproduct.

[19] E. L. Muetteries and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, New York, N. Y., 1968, p 13.

[20] J. Miller, "Aromatic Nucleophilic Substitution," Elsevier, Amsterdam, 1968, p 138.

[21] By analogy with other Meisenheimer systems, the C-1 adduct should be more stable but kinetically less favored.[15,16]

[22] Analysis of these compounds is cometimes difficult as they tend to explode on combustion.

[23] Dilute solutions of these adducts are moisture sensitive and not particularly stable. This makes an accurate determination of their extinction coefficients quite difficult.