

$m\mu$ and was identical with that of 1,1-dinitroethane in the same solvent mixture. In every run the calculated second-order constant remained constant up to at least 80% reaction when calculated on the basis of complete conversion to 1,1-dinitroethane at infinite time. Exactly the same procedure was used for the deuterated substrate, the 1% difference in molecular weight and the small density difference being neglected. The data obtained in all runs was treated using the first-order integrated equation and the second-order constant evaluated from a knowledge of nitrite ion concentration.

The data given in Table I for the extent of decomposition of 1-chloronitroethane at 30° in the presence of excess 0.1 *N* sodium hydroxide in 50% by volume aqueous ethanol were obtained in the following manner: The proper amount of 1-chloronitroethane was weighed into a 100-ml. volumetric flask and the flask filled to the mark with standard 0.1 *N* sodium hydroxide in 50% ethanol. The flask was immersed in a 30° thermostat and a 5-ml. aliquot of reaction mixture transferred to 25 ml. of a 5% sodium bicarbonate solution after the required time interval had elapsed. A few drops of gum arabic solution was added along with 1 ml. of a 1% potassium chromate solution and the solution titrated to a permanent pink with standard 0.10 *N* silver nitrate solution.

Isolation of 1,1-Dinitroethane as Ammonium Salt.—Ten grams of potassium nitrite (0.117 mole) was dissolved in 75 ml. of water and a solution of 0.313 g. (2.85×10^{-3} mole) of the 1-chloronitroethane described above dissolved in 25 ml. of ethanol was added. The reaction mixture was allowed to stand at room temperature for one hour. An aliquot of this reaction mixture (0.100 ml.) was then taken, diluted to 10 ml. as described above and its absorption spectrum determined. The single peak at 380 $m\mu$ gave an optical density of 1.72 after correction for nitrite ion absorption and indicated that the reaction mixture contained 1.06×10^{-3} mole of 1,1-dinitroethane (37% conversion of 1-chloronitroethane to 1,1-dinitroethane).

A mixture of 15.0 g. (0.216 mole) of hydroxylamine hydrochloride, 25 ml. of concentrated hydrochloric acid and

75 ml. of ether was placed in a 500-ml. flask bearing a reflux condenser, stirrer and dropping funnel and the flask cooled in an ice-bath. The dilute 1,1-dinitroethane solution described above was added slowly from the dropping funnel with vigorous stirring during the course of one-half hour. The resulting colorless mixture was saturated with sodium chloride and the ether layer separated and dried over magnesium sulfate. A saturated solution of ammonia in dry ether was added dropwise to the dry ether solution until ammonium chloride ceased to be precipitated and the yellow color of the ammonium salt of 1,1-dinitroethane began to appear. The solution was then filtered, concentrated to 10 ml. under reduced pressure and extracted with dilute ammonium hydroxide until the aqueous layer was no longer colored. The combined aqueous extracts were cautiously acidified with concentrated hydrochloric acid in the presence of ice and 50 ml. of ether and the ether layer separated, washed three times with water (aqueous layer became light yellow in color on last water wash), dried over magnesium sulfate and evaporated to 5 ml. under reduced pressure; 0.2 ml. of alcohol was added followed by 30 ml. of saturated ammoniacal ether. The precipitated yellow solid was collected on a filter and washed with ether. After air-drying it was found to weigh 65 mg. (4.7×10^{-4} mole) giving a 47% recovery of 1,1-dinitroethane.

The yellow solid sublimed at 127–128°,¹⁰ had an infrared absorption spectrum identical with that of the authentic ammonium salt of 1,1-dinitroethane in a Nujol mull and gave an absorption peak at 380 $m\mu$ in dilute basic solution ($\epsilon = 1.6 \times 10^4$ calcd. on the basis of ammonium salt). The material was further characterized by elemental analysis. Calcd. for $C_2H_7N_3O_4$: N, 30.29; C, 17.46; H, 5.39. Found: N, 30.65; C, 17.52; H, 5.15.

(10) J. S. Belew, C. E. Grabel and L. B. Clapp, *THIS JOURNAL*, **77**, 1110 (1955), report m.p. 90–93° dec. for the ammonium salt of 1,1-dinitroethane. An authentic sample prepared as described above did not melt but sublimed at 128–130° without apparent decomposition. HUNTSVILLE, ALABAMA

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

Nitroalkanes from Conjugated Nitroalkenes by Reduction with Complex Hydrides¹

BY H. SHECHTER, D. E. LEY² AND E. B. ROBERSON, JR.

RECEIVED FEBRUARY 29, 1956

Sodium trimethoxyborohydride, lithium borohydride, sodium borohydride and lithium aluminum hydride are satisfactory reducing agents for converting conjugated nitroalkenes to their corresponding nitroalkanes. The reduction reactions are accompanied by consecutive processes in which the initial reduction products add to the parent nitroolefins to give salts of the corresponding 1,3-dinitroalkanes and related polynitroalkanes of higher molecular weights. The unconjugated nitrocycloalkene, 1-(nitromethyl)-cyclopentene, is not reduced by excess sodium trimethoxyborohydride, even under isomerizing conditions. Excellent procedures have been developed for reducing *D-arabo*-tetraacetoxy-1-nitro-1-hexene with lithium borohydride or sodium borohydride to 1-nitro-1,2-dideoxy-*D-arabo*-hexitol tetraacetate.

An attractive route for synthesis of primary and secondary nitroalkanes involves reduction of the carbon-carbon double bonds of conjugated nitroolefins.³ Catalytic hydrogenation of conjugated^{4a–e} and unconjugated^{4f} nitroolefins to nitroalkanes has been effected successfully; as yet, however, this reaction is unsatisfactory as a general method for pre-

paring saturated nitro compounds. It has been reported that reverse addition of lithium aluminum hydride to 2-nitro-1-phenyl-1-propene^{5a} and to conjugated polyfluoroalkylnitroalkenes^{5b} results in formation of the corresponding nitroalkanes^{5c}; at slightly higher temperatures and with different ratios of reagents, 2-nitro-1-phenyl-1-propene reacts with lithium aluminum hydride to give phenylacetone oxime, *N*-(β -phenylisopropyl)-hydroxylamine and β -phenylisopropylamine.^{5a} Since borohydrides are generally inert to nitro groups^{6a–f} and

(1) Financial support of this research was provided by the Office of Naval Research.

(2) This research has been abstracted principally from a dissertation submitted by Dean E. Ley to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the Ph.D. degree, 1954.

(3) General methods of synthesis of conjugated nitroalkenes are summarized by (a) H. B. Hass and E. F. Riley, *Chem. Revs.*, **32**, 373 (1943), and (b) N. Levy and J. D. Rose, *Quart. Revs.*, **1**, 358 (1947).

(4) (a) A. Sonn and A. Schellenberg, *Ber.*, **50**, 1513 (1917); (b) E. P. Kohler and N. L. Drake, *THIS JOURNAL*, **45**, 1281 (1923); (c) H. Cerf de Mauny, *Bull. soc. chim. France*, [5] **7**, 133 (1940); (d) J. C. Sowden and H. O. L. Fischer, *THIS JOURNAL*, **69**, 1048 (1947); (e) C. D. Hurd, U. S. Patent 2,483,201 (Sept. 27, 1949); (f) K. Alder, H. F. Rickert and E. Windemuth, *Ber.*, **71**, 2451 (1938).

(5) (a) R. T. Gilsdorf and F. F. Nord, *THIS JOURNAL*, **74**, 1837 (1952); (b) D. J. Cook, O. R. Pierce and E. T. McBee, *ibid.*, **76**, 83 (1954); (c) A. Dornow and W. Bartoch, *Ber.*, **87**, 633 (1954).

(6) (a) S. W. Chaikin and W. G. Brown, *THIS JOURNAL*, **71**, 123 (1949); (b) R. F. Nystrom, S. W. Chaikin and W. G. Brown, *ibid.*, **71**, 3245 (1949); (c) H. Shechter, D. E. Ley and L. Zeldin, *ibid.*, **74**, 3664 (1952); (d) H. C. Brown and E. J. Mead, *ibid.*, **75**, 6263 (1953); (e) D. C. Iffand and G. X. Criner, *ibid.*, **75**, 4047 (1953); (f) D. C. Iffand and Teh-Fu Yen, *ibid.*, **76**, 4083 (1954).

TABLE I

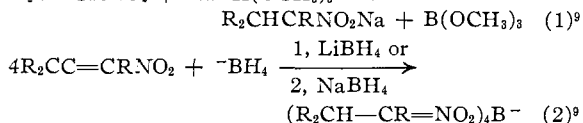
REDUCTION OF CONJUGATED NITROOLEFINS WITH SODIUM TRIMETHOXYBOROHYDRIDE, LITHIUM BOROHYDRIDE, SODIUM BOROHYDRIDE AND LITHIUM ALUMINUM HYDRIDE^a

Reactants	Products	NaBH(OCH ₃) ₃ ^b				LiBH ₄ ^c				NaBH ₄ ^d			LiAlH ₄ ^e			
		Con- ver- sion, %	Temp., °C.	Addn. time, hr.	Re- acn. ^g time, hr.	Con- ver- sion, %	Temp., °C.	Addn. time, hr.	Re- acn. ^g time, hr.	Con- ver- sion, %	Addn. time, hr.	Re- acn. ^g time, hr.	Con- ver- sion, %	Temp., °C.	Addn. time, hr.	Re- acn. ^g time, hr.
CH ₃ CH=CHNO ₂	C ₂ H ₅ CH ₂ NO ₂	82	-70	1.2	0.5	50	-70	3	2							
	C ₂ H ₅ CH(NO ₂)CH(CH ₃)CH ₂ NO ₂	11				2										
C ₂ H ₅ C(NO ₂)=CH ₂	C ₂ H ₅ CH(NO ₂)CH ₃	45	-62	1.2	.5	59	-70	3	2.5	64	3	4				
	C ₂ H ₅ CH(NO ₂)CH ₂ C(CH ₃)(NO ₂)C ₂ H ₅ ^h	35				14										
CH ₃ CH=C(NO ₂)CH ₃	C ₂ H ₅ CH(NO ₂)CH ₃	63	-70	1.1	.6	46	-37	2.5	2.5				53	-65	2.5	3.5
	C ₂ H ₅ C(CH ₃)(NO ₂)CH(CH ₃)CH(NO ₂)CH ₃	11														
(CH ₃) ₂ C=CHNO ₂	(CH ₃) ₂ CHCH ₂ NO ₂ ^h	59 ⁱ	-3	1.4	.6	48 ⁱ	0	0.5	3							
C ₃ H ₇ C(NO ₂)=CHC ₂ H ₅	C ₃ H ₇ CH(NO ₂)C ₃ H ₇	55 ^{h,j}	0	3.0	3.0	65 ^{h,k}	-67	4	4	22 ^l	2	7				
CCl ₃ CH=CHNO ₂	CCl ₃ CH ₂ CH ₂ NO ₂	44	-40	1.1	0.5	85 ^{h,m}	-70	3.5	3.5				44 ⁿ	-70	3.5	3.5
	CCl ₃ CH ₂ CH(NO ₂)CH(CCl ₃)CH ₂ NO ₂	26 ^{o,p}														
CF ₃ CH=CHNO ₂	CF ₃ CH ₂ CH ₂ NO ₂												25 ^q	-40	2	3
	CF ₃ CH ₂ CH(NO ₂)CH(CF ₃)CH ₂ NO ₂												25			
CF ₃ (CH ₃)C=CHNO ₂	CF ₃ (CH ₃)CHCH ₂ NO ₂												55 ^h	-70	1.5	3
C ₃ F ₇ CH=C(NO ₂)CH ₃	C ₃ F ₇ CH ₂ CH(NO ₂)CH ₃	84	-67	2.0	1.0	88	-65	4	4							
C ₃ F ₇ CH=C(NO ₂)C ₂ H ₅	C ₃ F ₇ CH ₂ CH(NO ₂)C ₂ H ₅	91	-60	2.0	1.0	91	-60	4	4				85 ^r	-70	3	3.5
C ₆ H ₅ CH=CHNO ₂	C ₆ H ₅ CH ₂ CH ₂ NO ₂	39 ^s	-40	1.6	0.4	55 ^{h,t}	-70	3	0.25	14	5	1	50, 47 ^u	-40	2.2	3
	C ₆ H ₅ CH ₂ CH(NO ₂)CH(C ₆ H ₅)CH ₂ NO ₂	24 ^{h,v}								24			6, 1.7 ^u			
C ₆ H ₅ CH=C(NO ₂)CH ₃	C ₆ H ₅ CH ₂ CH(NO ₂)CH ₃												43, 31 ^{u,w}	-40	2	3
(C ₄ H ₉ O)CH=CHNO ₂	(C ₄ H ₉ O)CH ₂ CH ₂ NO ₂	28 ^x	-40	1.8	0.9	31 ^h	-73	5	0.25				16 ^h	-55	3	3.5
(C ₁₂ H ₁₇ O ₈)CH=CHNO ₂ ^y	(C ₁₂ H ₁₇ O ₈)CH ₂ CH ₂ NO ₂ ^z					54	0	1.2	2	64	0.75	2				

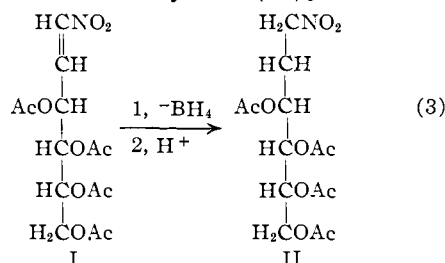
^a All reductions, except as noted, were effected with 50% excess NaBH(OCH₃)₃ and 100% excess LiBH₄, NaBH₄ and LiAlH₄, respectively. ^b Conducted, except as noted, by adding the nitroalkene (0.15 mole) in ethyl ether (25 ml.) to sodium trimethoxyborohydride (0.225 mole) in ethyl ether (125–150 ml.) and tetrahydrofuran (50 ml.). ^c Conducted, except as noted, by adding the nitroolefin (0.15 mole) in ethyl ether (25 ml.) to lithium borohydride (0.075 mole) in ethyl ether (125 ml.) and tetrahydrofuran (25 ml.). ^d The nitroalkene (0.10–0.15 mole) in ethanol (150 ml.) was added at 0° to sodium borohydride (0.05–0.075 mole) in ethanol (50 ml.). ^e Effected, except as noted, upon adding the nitroalkene (0.10 mole) in ethyl ether (25–50 ml.) to the reductant (0.05 mole) in ethyl ether (100–150 ml.) and tetrahydrofuran (0–25 ml.). ^f Based on initial nitroalkene added. In many experiments, the recovery of nitroolefin was appreciable. ^g The reaction mixtures were usually acidified at 0° in 0.75–1.5 hours; salts of nitro compounds which resist Nef hydrolysis may be acidified in shorter periods without excessive losses. ^h The higher boiling products were not characterized. ⁱ Conducted with 10% excess of reducing agent. ^j Slightly contaminated. ^k Yield 74%. ^l Reduction of 4-nitro-3-heptene occurs very slowly and, in this experiment, is quite incomplete. ^m Reaction was effected at one-half the concentration listed in footnote c. ⁿ Conducted with 5% excess reductant. ^o Isolated by crystallization of the concentrated crude reaction product. ^p May exist in 2 *d,l*-modifications. ^q The conversion is not increased by using large excesses of reducing agent, effecting reduction at lower temperatures, or using high dilution techniques. ^r The nitroalkene (0.057 mole) in ethyl ether (25 ml.) was added to the reducing agent (0.01945 mole, 20% excess) in ethyl ether (125 ml.)–tetrahydrofuran (25 ml.). ^s *ω*-Nitrostyrene (0.1 mole) in ethyl ether (50 ml.) and tetrahydrofuran (50 ml.) was added to sodium trimethoxyborohydride (0.1 mole) in ethyl ether (152 ml.) and tetrahydrofuran (25 ml.). ^t *ω*-Nitrostyrene (0.1 mole) in ethyl ether (75 ml.) and tetrahydrofuran (50 ml.) was added to a stirred suspension of lithium borohydride (0.05 mole) in ethyl ether (125 ml.) and tetrahydrofuran (50 ml.). The mixture was then warmed to -15°; the temperature then shot to 18° and poly-*ω*-nitrostyrene separated. ^u Inverse addition. ^v An unidentified white solid of high molecular weight, m.p. 255°, was obtained in 20% conversion; see Experimental. ^w Conducted with 20% excess reductant. ^x A brown glassy solid of high molecular weight, m.p. >350°, was obtained in 47% conversion; the product is similar to that obtained by polymerization of 2-(2-nitrovinyl)-furan with hydroxides. ^y *D-arabo*-Tetraacetoxy-1-nitro-1-hexene. ^z 1-Nitro-1,2-dideoxy-*D-arabo*-hexitol tetraacetate.

yet are nucleophilic reducing agents^{6a-d} similar to lithium aluminum hydride, the present research has been concerned primarily with the reactions of conjugated nitroolefins with sodium trimethoxyborohydride, lithium borohydride and sodium borohydride.^{7,8} A study also has been made of reduction of conjugated nitroalkenes with lithium aluminum hydride^{7,8} in order to develop an additional general method for preparing primary and secondary nitro compounds.

1. **Metal Borohydrides.**—Sodium trimethoxyborohydride, lithium borohydride and sodium borohydride have been found to be excellent reagents for reducing the carbon-carbon double bonds of conjugated nitroalkenes. The reduction reactions (eq. 1 and 2) are of the Michael type⁹ and,



upon acidification¹⁰ and hydrolysis of the products, result in satisfactory general methods for preparing primary and secondary mononitroalkanes. The results of reduction of various α,β -unsaturated nitro compounds are summarized in Table I. Of particular interest is that the carbohydrate derivative, 1-nitro-1,2-dideoxy-D-arabo-hexitol tetraacetate^{4d} (II), may be conveniently prepared (eq. 3) from D-arabo-tetraacetoxy-1-nitro-1-hexene^{4d} (I) by reduction with lithium borohydride (54% conversion) or sodium borohydride (64% conversion).



Reduction of a conjugated nitroolefin by a borohydride is accompanied by consecutive reactions of the Michael type in which the primary reduction product, a salt of a nitroalkane, adds to the initial conjugated nitroolefin to yield a salt of the corre-

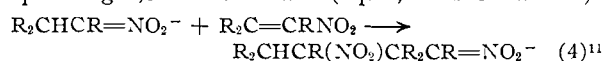
(7) The present research was conducted at essentially the same time as that reported in ref. 5b. The present authors should like to acknowledge the private communications of Drs. Cook, Pierce and McBee concerning the progress of their investigations and to thank L. Friedman for providing the stimulus for inception of many phases of this work.

(8) (a) The general nucleophilic reducing activities of the hydrides investigated in this study are reported to be: $LiAlH_4 > LiBH_4 > NaHB(OCH_3)_3 > NaBH_4$; Technical Bulletin, Metal Hydrides, Inc., Beverly, Mass.; (b) H. C. Brown, E. J. Mead and B. C. Subba Rao, *THIS JOURNAL*, **77**, 6209 (1955).

(9) The mechanics of these reductions apparently involve nucleophilic attack of the trimethoxyborohydride ion and the borohydride ion at the relatively positive end of the carbon-carbon double bond of the conjugated nitroalkene. With the borohydrides addition probably results initially in formation of a metal monoalkanenitronatoborohydride, Li or $Na(R_2CH-CR=NO_2)BH_4$. The intermediate monoalkanenitronatoborohydride ion may then undergo a series of reductive addition reactions with the conjugated nitroolefin to give finally the metal tetraalkanenitronatoboride.

(10) N. Kornblum and G. E. Graham, *THIS JOURNAL*, **73**, 4041 (1951).

sponding 1,3-dinitroalkane (eq. 4,^{11,12} see Table I).



For example, reduction (Table I) of 1-nitro-1-propene with sodium trimethoxyborohydride also gives 2-methyl-1,3-dinitropentane (11%), 2-nitro-1-butene gives 3-methyl-3,5-dinitroheptane (35%) and 2-nitro-2-butene gives 3,4-dimethyl-2,4-dinitrohexane (11%). In order to minimize the competing reactions leading to polynitroalkanes, the nitroalkene was always added to the borohydride (normal addition). Partial control over the forma-

TABLE II
REDUCTION OF 2-NITRO-1-BUTENE WITH SODIUM TRIMETHOXYBOROHYDRIDE^a

Temp., °C.	Addn. time, hr.	Reacn. time, hr.	Moles of NaHB(OCH ₃) ₃ : nitroalkene	^b Recovery, %	2-Nitro-1-butene	3-methyl-3,5-dinitroheptane	Poly-mers ^c
-1 ± 1	1.5 ^d	1.5	1.1	18	9	5	68
-58 ± 2	1.2 ^e	0.5	1.1	17	30	46	7
-63 ± 2	1.2 ^f	0.5	1.5	11	45	35	9

^a Normal addition. ^b The nitroalkene was removed by extraction with aqueous sodium bisulfite; the percentage recovery was calculated by difference. ^c Unidentified polynitro adducts of higher boiling points than that of 3-methyl-3,5-dinitroheptane. ^d A solution of 2-nitro-1-butene (0.15 mole) in ethyl ether (25 ml.) was added dropwise to a stirred suspension of sodium trimethoxyborohydride (0.165 mole) in ethyl ether (125 ml.) and tetrahydrofuran (50 ml.). The solvent volumes were the same in the subsequent experiments. ^e 2-Nitro-1-butene (0.12 mole) was added to sodium trimethoxyborohydride (0.132 mole). ^f See Experimental; 2-nitro-1-butene (0.15 mole) was added to sodium trimethoxyborohydride (0.225 mole).

TABLE III
REDUCTION OF 2-NITRO-1-BUTENE WITH LITHIUM BOROHYDRIDE^a

Temp., °C.	Addn. time, hr.	Reacn. time, hr.	Moles of LiBH ₄ : nitroalkene	^b Recovery, %	2-Nitro-1-butene	3-methyl-3,5-dinitroheptane	Poly-mers ^c
-1 ± 1	1.5	2.5	0.25	45	16	23	16
-52 ± 2	0.8	1.1	.25	67	24	6	3
-69 ± 1	3	5.5	.25	40	39	9	12
-69 ± 1	3	5.5	.52 ^d	8	59	14	19

^a A solution of 2-nitro-1-butene (0.15 mole) in ethyl ether (25 ml.) was added dropwise to a stirred suspension of lithium borohydride (0.0375 mole) in ethyl ether (125 ml.)-tetrahydrofuran (50 ml.). ^b Removed from the reaction product by extraction with sodium bisulfite; the percentage recovery was calculated by difference. ^c Unidentified products of higher boiling points than that of 3-methyl-3,5-dinitroheptane. ^d The amount of reductant added was 0.0788 mole.

(11) These reactions are pictured in this manner because salts of mononitroalkanes add to conjugated nitroalkenes to give salts of the corresponding 1,3-dinitroalkanes (eq. 4); A. Lambert and H. A. Piggott, *J. Chem. Soc.*, 1489 (1947); C. T. Bahner and H. T. Kite, *THIS JOURNAL*, **71**, 3597 (1949). It is possible that the salts of the initial reduction products are transferred to the conjugated nitroalkenes through the agency of methyl borate as $Na(R_2CH-CR=NO_2)B(OCH_3)_3$ and as intermediate alkanenitronatoborides (see footnote 9).

(12) This reaction is analogous to the polymerization of N,N-diethylcrotonamide and to its reductive coupling to N,N,N',N'-tetraethyl-1-ethyl-2-methylglutaramide upon inverse addition of lithium aluminum hydride; H. R. Snyder and R. E. Putnam, *ibid.*, **76**, 33, 1893 (1954).

tion of polynitroalkanes also could be obtained by effecting reduction at lower temperatures. The effects of experimental variables on reduction of 2-nitro-1-butene with sodium trimethoxyborohydride and with lithium borohydride are illustrated in Tables II and III.

The various 1,3-dinitroalkanes obtained in reduction were identified by their quantitative and infrared analyses and molar refractions. The structure of the 3-methyl-3,5-dinitroheptane obtained from reduction of 2-nitro-1-butene was established upon its conversion to 3-methyl-3-nitro-5-heptanone and its 2,4-dinitrophenylhydrazone *via* its sodium salt, the Nef reaction¹³ (41%) and subsequent reaction with 2,4-dinitrophenylhydrazine. The 3-methyl-3-nitro-5-heptanone 2,4-dinitrophenylhydrazone was identical with that obtained from authentic 3-methyl-3,5-dinitroheptane prepared by Michael reaction of 2-nitro-1-butene and 2-nitrobutane.

Selective reduction of a conjugated nitroolefin and competitive addition of the reduction product to the initial nitroalkene are apparently subject to marked steric manifestations. The relatively hindered nitroolefin, 4-nitro-3-heptene, is reduced very slowly at -40° by sodium trimethoxyborohydride, and even after prolonged periods at 0° , reduction is incomplete. Similarly 1,3-dinitroalkanes derivable from competitive Michael additions were absent in reduction of 2-methyl-1-nitro-1-propene and of 4-nitro-3-heptene. Reduction of the relatively unhindered nitroalkene, 2-nitro-1-butene, and subsequent addition of 2-nitrobutane to 2-nitro-1-butene both occur quite rapidly; 3-methyl-3,5-dinitroheptane is usually a major product (35%) of reaction along with 2-nitrobutane. A further aspect of steric factors in reactions of 2-nitro-1-butene and sodium trimethoxyborohydride or lithium borohydride at 0° (Tables I-III) is that significant yields of involatile higher-molecular weight polynitroalkanes (unidentified) are obtained; this suggests that competitive Michael reactions involving the reduction product advance beyond 1:1 addition.¹⁴

Selective reductions of 4,4,5,5,6,6,6-heptafluoro-2-nitro-2-hexene and 5,5,6,6,7,7,7-heptafluoro-3-nitro-3-heptene with sodium trimethoxyborohydride and lithium borohydride occur relatively rapidly and in excellent yields (Table I). There was no evidence in these systems for addition of the reduction product¹⁵ to the initial polyfluoronitroalkene. The much more rapid reduction of 5,5,6,6,7,7,7-heptafluoro-3-nitro-3-heptene at -70° than of 4-nitro-3-heptene, a comparably hindered (but unreactive) nitroolefin,¹⁶ at 0° illustrates the expected

(13) J. U. Nef, *Ann.*, **280**, 263 (1894); K. Johnson and E. F. Degering, *J. Org. Chem.*, **8**, 10 (1943).

(14) The steric influences of substituents on reduction of conjugated nitroalkenes by complex hydrides and on subsequent addition of initial reduction products to the parent nitroalkenes parallel the results obtained from inverse addition of lithium aluminum hydride to substituted N,N-dialkylacrylamides.¹⁴

(15) It has been reported^{5b} that polyfluoronitroalkanes of this type do not undergo the Nef reaction.¹³ It has now been found that the sodium salt of 1,1,1,2,2,3,3-heptafluoro-5-nitroheptane is converted to 5,5,6,6,7,7,7-heptafluoro-3-heptanone by the action of sulfuric acid in 54% yield; see Experimental.

(16) On the basis of the need for excess lithium borohydride to effect rapid and complete reduction of a bulky nitroolefin, it is possible that steric and electrical factors become greatly increased as each alkane-

influence of electron-withdrawing groups in nitroalkenes on the rate of nucleophilic reaction with borohydrides. The electronegatively-substituted nitro compounds: 3,3,3-trichloro-1-nitropropene, ω -nitrostyrene and 2-(2-nitrovinyl)-furan are also rapidly and selectively reduced; ω -nitrostyrene and 2-(2-nitrovinyl)-furan suffer from the disadvantage (see Experimental), however, that they are rapidly and extensively polymerized to high molecular weight adducts *via* Michael processes.¹⁷

Reduction of 1-(nitromethyl)-cyclopentene, a non-conjugated nitroolefin, could not be effected with sodium trimethoxyborohydride under conditions which were satisfactory for reducing conjugated nitroolefins. Attempts were made under reducing conditions to isomerize (base-catalyzed)^{18,19a} 1-(nitromethyl)-cyclopentene to its conjugated exocyclic isomer, nitromethylenecyclopentane, and then effect reduction. In all experiments, however, the unisomerized 1-(nitromethyl)-cyclopentene was recovered (>83%) essentially unchanged.^{19b}

The reactions of 2-nitro-1-butyl acetate with excess sodium trimethoxyborohydride and with lithium borohydride were investigated as a possible simple method for preparing saturated nitro compounds. Since the hydrides are bases, it was deemed possible that acetic acid would be eliminated from 2-nitro-1-butyl acetate²⁰ to give 2-nitro-1-butene; reduction of 2-nitro-1-butene and subsequent acidification were expected to yield 2-nitrobutane. Reaction of 2-nitro-1-butyl acetate with sodium trimethoxyborohydride at $3-5^\circ$ and at

nitronate ion becomes incorporated in the borohydride; the effective reducing activities of the relatively hindered di- and trialkalenitronatoborohydride ions may thus be less than that of the borohydride and the monoalkalenitronatoborohydride ions.

(17) (a) In the present studies the yields of products vary greatly and no reducing agent was found to be universally better than the others. We generally prefer to use lithium borohydride, but perhaps the most important criterion is the availability of a particular hydride. If conversion or yield is of great importance in an investigation it is suggested that each reducing agent be tried under various experimental conditions. (b) Since completion of this study, it has been reported^{8b} that isopropyl alcohol and the dimethyl ether of diethylene glycol are improved solvents for sodium borohydride. These solvents may thus be of real advantage in reduction of nitroolefins with sodium borohydride.

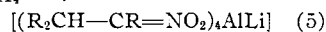
(18) H. Shechter and J. W. Shepherd, *THIS JOURNAL*, **76**, 3617 (1954).

(19) (a) It might be expected that nitromethylenecyclopentane should be an intermediate because of the general stability of *exo* double bonds in cyclopentane ring systems (H. C. Brown, J. H. Brewster and H. Shechter, *ibid.*, **76**, 467 (1954)) and the resonance stabilization resulting from conjugation of the nitro group with the carbon-carbon double bond. (b) Subsequent attempts to isomerize (base-catalyzed)¹⁸ 1-(nitromethyl)-cyclopentene and 1-(nitromethyl)-cyclohexene to their conjugated exocyclic isomers have been unsuccessful. The resistance to extensive isomerization of 1-(nitromethyl)-cyclopentene and 1-(nitromethyl)-cyclohexene to nitromethylenecyclopentane and nitromethylenecyclohexane^{19a} may be related to the relatively greater C-H hyperconjugation in an unconjugated nitroalkylcycloalkene and in particular to the steric requirements resulting from *cis*-interaction of the (coplanar) nitro group in the nitromethylenecycloalkane with the α,α' -methylene hydrogen atoms of the ring (in cyclohexyl systems the interference will result from one of the two equatorial α,α' -hydrogen atoms). It is suggested that (1) *cis* steric effects play important roles in the *exo* and *endo* equilibria of other related unsaturated cyclic compounds and (2) the observed fact that substituted 6-membered rings tend to accommodate *endo* double bonds more readily than do the analogous 5-membered rings may be partly the result of *cis* steric considerations.^{19a}

(20) Bases such as sodium bicarbonate and sodium acetate, etc., will convert vicinal nitro esters of this type to conjugated nitroalkenes.^{3a,b}

40° and with lithium borohydride at 3–4° resulted, however, in reduction of the carboxylic ester²¹ to give 2-nitro-1-butanol (~40%); neither 2-nitro-1-butene nor 2-nitrobutane could be isolated.

2. Lithium Aluminum Hydride.—Conjugated nitroolefins of various representative types are reduced advantageously to primary and secondary nitro compounds (Table I) by lithium aluminum hydride in ethyl ether at –40° and below. Reduction of these nitroalkenes to oximes, hydroxylamines and amines is avoided by proper temperature control; competitive processes involving addition of the initial reduction product to the parent nitroalkene giving substituted 1,3-dinitroalkanes do occur, however (eq. 4). The apparent stoichiometry (eq. 5) and mechanics^{9,11,12,16} of reduction and of formation of the polynitroalkanes (eq. 4) are analogous to those involved in reduction of nitroalkenes with sodium trimethoxyborohydride, lithium borohydride and sodium borohydride, respectively.



As with the previous hydrides, the reduction reactions are advantageously accelerated, and the conversions of nitroalkenes to mononitroalkanes are increased by use of excess lithium aluminum hydride.

The previous reductions of 2-nitro-1-phenyl-1-propene^{5a} and of polyfluoroalkyl nitroalkenes^{5b} have been effected by inverse addition of lithium aluminum hydride to the nitroolefins. Since a major competitive process is addition of the initial reduction product to the nitroolefin, it is to be expected that a better procedure for obtaining the initial nitroalkane will involve addition of the unsaturated nitro compound to the hydride (excess). Under comparable conditions it has been found that addition of 2-nitro-1-phenyl-1-propene to lithium aluminum hydride produces 2-nitro-1-phenylpropane in 44% conversion; inverse addition gives only 31% conversion to 2-nitro-1-phenylpropane. Normal addition to ω -nitrostyrene results in 50% conversion to 1-nitro-2-phenylethane; inverse addition gives 47% conversion. Inverse reduction of 5,5,6,6,7,7,7-heptafluoro-3-nitro-3-heptene has been previously reported^{5b} to yield 1,1,1,2,2,3,3-heptafluoro-5-nitroheptane in 69% conversion; in the present study normal addition gives the initial reduction product in 85% conversion. The procedure of normal addition is also much the better method for reducing the readily polymerizable nitroolefin, 2-(2-nitrovinyl)-furan. Considerable difficulty was experienced, however, in reduction of 3,3,3-trifluoro-1-nitropropene to 3,3,3-trifluoro-1-nitropropane, even upon using the best techniques of temperature control and of normal addition of the nitroalkene to large excesses of reducing agent; this system is unsatisfactorily complicated by the ease with which the initial product reacts with 3,3,3-trifluoro-1-nitropropene to give, after acidification, 1,3-dinitro-2,4-bis-(trifluoromethyl)-butane.²²

(21) It has been previously reported^{9d} that ethyl benzoate and ethyl butyrate are reduced only very slowly by sodium trimethoxyborohydride at 100–140°.

(22) The reduction of 3,3,3-trifluoro-2-methyl-1-nitropropene with lithium aluminum hydride (Table I) is also complicated by the marked tendency of the initial reduction product to add to the parent nitroolefin.

Experimental

Reagents.—Sodium trimethoxyborohydride, lithium borohydride, lithium aluminum hydride and sodium borohydride were purchased from Metal Hydrides, Inc., Beverly, Mass. 1-Nitro-1-propene,^{23a} ω -nitrostyrene,^{23b} 2-nitro-1-phenyl-1-propene,^{23c} 2-(2-nitrovinyl)-furan,^{23d} *D-arabo*-tetraacetoxy-1-nitro-1-hexene,^{4d} 1-(nitromethyl)-cyclopentene^{23e} and 2-nitro-1-butyl acetate^{23f} were prepared by literature procedures. 2-Nitro-1-butene,^{23f,24a,5c} 2-nitro-2-butene^{23f,24a,b} and 2-methyl-1-nitro-1-propene^{24d} were obtained in 74, 66 and 76% conversions, respectively, from their acetates by reaction with hot sodium acetate. 3,3,3-Trichloro-1-nitropropene^{25a} was prepared by reaction of 1,1,1-trichloro-3-nitro-2-propyl acetate^{25b} and sodium carbonate. 4,4,5,5,6,6,6-Heptafluoro-2-nitro-2-hexene^{5b} and 5,5,6,6,7,7,7-heptafluoro-3-nitro-3-heptene^{5b} were the gifts of Dr. O. R. Pierce.

4-Nitro-3-heptanol.—4-Nitro-3-heptanol (248.3 g., 1.54 moles, 77% conversion, light yellow) was prepared by reaction of propanal (116.2 g., 2.0 moles), 1-nitrobutane (206.2 g., 2.0 moles) and sodium hydroxide (3.5 *N*, 23 ml.) in ethanol (95%, 200 ml.) at 30–35° for 48 hours; b.p. 71.0–71.5° (0.5 mm.), n_D^{20} 1.4475, d_{20}^{20} 1.0324, *M*R_D (calcd.) 41.79, *M*R_D (found) 41.76, strong infrared absorption for aliphatic mononitro²⁶ (6.4 and 7.2 μ) and hydroxyl (2.9 μ) groups.

Anal. Calcd. for C₇H₁₅NO₃: C, 52.15; H, 9.38; N, 8.69. Found: C, 52.67; H, 9.41; N, 8.49.

3-Acetoxy-4-nitroheptane.—Reaction of acetic anhydride (128.6 g., 1.26 moles) and sulfuric acid (1 ml.) with 4-nitro-3-heptanol (193.4 g., 1.2 moles) at 40–50° for 2.5 hours gave colorless 3-acetoxy-4-nitroheptane (216.9 g., 1.07 moles, 89% conversion), b.p. 69° (0.1 mm.), n_D^{20} 1.4352, d_{20}^{20} 1.0409, *M*R_D (calcd.) 51.12, *M*R_D (found) 50.97, strong infrared absorption for carbonyl (5.7 μ), mononitro²⁶ (6.4 and 7.2 μ) and acetate (8.1 μ) groups.

Anal. Calcd. for C₈H₁₇NO₄: C, 53.19; H, 8.43; N, 6.89. Found: C, 53.26; H, 8.32; N, 6.88.

4-Nitro-3-heptene.—3-Acetoxy-4-nitroheptane (131.5 g., 0.65 mole) and sodium acetate (6.6 g.) were heated at 115° (12 mm.) in a Claisen flask equipped with a Vigreux column, a downward condenser and an ice receiver; the reaction product distilled at 75–80° (12 mm.). The distillate was dissolved in ethyl ether, washed with saturated aqueous sodium bicarbonate, dried over sodium sulfate and distilled to give 4-nitro-3-heptene (67.6 g., 0.473 mole, 72.8% conversion) as a light-green lachrymatory liquid, b.p. 70.0–70.8° (5.2 mm.), n_D^{20} 1.4585, strong infrared absorption for an olefinic mononitro group²⁶ (6.6 μ).

1,1,1-Trifluoro-3-nitro-2-propanol.—Condensation of excess nitromethane^{27a} (92.0 g., 1.5 moles), fluoral hydrate^{27b} (76.0 g. of fluoral hydrate–water azeotrope, 47.0 g. of fluoral, 0.48 mole) and sodium carbonate (4.0 g., 0.029 mole) at 50° for 4 hours and then at 25–30° for 15 hours gave colorless 1,1,1-trifluoro-3-nitro-2-propanol (64.4 g., 0.405 mole) in

(23) (a) E. Schmidt and G. Rutz, *Ber.*, **61**, 2147 (1928); G. D. Buckley and C. W. Scaife, *J. Chem. Soc.*, 1471 (1947); (b) D. E. Worrall, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 413; (c) L. Bouveault and A. Wahl, *Compt. rend.*, **134**, 1145 (1902); *Bull. soc. chim. France*, [3] **29**, 519 (1903); (d) J. Thiele and H. Landers, *Ann.*, **369**, 303 (1909); O. Moldenhauer, W. Irion, D. Mastaglio, R. Pfluger and H. Doser, *ibid.*, **583**, 57 (1953); (e) H. B. Frazer and G. A. R. Kon, *J. Chem. Soc.*, 604 (1934); (f) B. M. Vanderbilt and H. B. Hass, *Ind. Eng. Chem.*, **32**, 34 (1940).

(24) (a) A. Lambert and A. Lowe, *J. Chem. Soc.*, 1517 (1947); (b) H. B. Hass, A. G. Susie and R. L. Heider, *J. Org. Chem.*, **15**, 8 (1950); (c) W. J. Seagers and P. J. Elving, *THIS JOURNAL*, **73**, 947 (1951); (d) N. Levy, C. W. Scaife and A. E. Wilder-Smith, *J. Chem. Soc.*, 52 (1948).

(25) (a) F. Brower and H. Burkett, *THIS JOURNAL*, **75**, 1082 (1953); (b) prepared from 1,1,1-trichloro-3-nitro-2-propanol and warm acetic anhydride; the preparation may be simplified by removing the excess acetic anhydride, adding ethanol, and allowing the product to crystallize at 0°, m.p. 58–60°. ^{25a}

(26) D. C. Smith, C.-Y. Pan and J. R. Nielsen, *J. Chem. Phys.*, **18**, 707 (1950); R. N. Haszeldine, *J. Chem. Soc.*, 2525 (1953).

(27) (a) Improved procedure: previously reported^{5b} in 47% yield from equimolar quantities of fluoral hydrate and nitromethane in the presence of potassium carbonate. (b) D. R. Husted and A. H. Ahlbrecht, *THIS JOURNAL*, **74**, 5422 (1952); D. D. Krehbiel, Ph.D. dissertation, The Ohio State University, Columbus, Ohio, 1954.

84% conversion, b.p. 62–66° (5.5 mm.), n_D^{20} 1.3792; lit.^{6b} b.p. 84° (17 mm.), n_D^{20} 1.3771.

3,3,3-Trifluoro-1-nitropropene.—(a) A mixture of 1,1,1-trifluoro-3-nitro-2-propanol (45.5 g., 0.286 mole) and phthalic anhydride (45.5 g., 0.306 mole) was heated at 140° in a vacuum distillation apparatus. After the mixture became homogeneous, it was heated to 180°, and the product, an oil dispersed in water, was collected. The pressure was lowered gradually during the dehydration until evolution of the volatile product was complete. The distillate was dissolved in ethyl ether, dried and then rectified to give 3,3,3-trifluoro-1-nitropropene (19.2 g., 0.136 mole, yellow-green lachrymator) in 48% conversion, b.p. 89°, n_D^{20} 1.3609, d_{20}^{20} 1.423, marked infrared absorption for a conjugated nitro group at 6.41²⁸ and 7.32 μ .²⁸

Anal. Calcd. for C₃H₂NO₂F₃: C, 25.53; H, 1.42; N, 9.93. Found: C, 26.33; H, 1.71; N, 10.25.

An attempt to dehydrate refluxing 1,1,1-trifluoro-3-nitro-2-propanol with excess tetrachlorophthalic anhydride for 2 hours resulted in 68% recovery of the initial trifluoronitro alcohol. Efforts to convert 1,1,1-trifluoro-3-nitro-2-propanol to 1,1,1-trinitro-3-nitro-2-propyl acetate and then effect conversion of the acetate to 3,3,3-trifluoro-1-nitropropene by reaction with sodium carbonate were unsuccessful because of the difficulty in separating the trifluoronitropropene from its parent ester.

(b) 1,1,1-Trifluoro-3-nitro-2-propanol (50.1 g., 0.315 mole) was added at atmospheric pressure to stirred phosphoric anhydride (50.0 g., 0.35 mole as P₂O₅) at a rate such that the yellow-green product distilled slowly from the reaction mixture. Occasional hand stirring was necessary to prevent excessive foaming of the viscous mixture. After the dehydration was nearly completed, additional product was obtained upon reducing the pressure of the distillation. Rectification of the crude product gave 3,3,3-trifluoro-1-nitropropene (30.2 g., 0.214 mole) in 68% conversion, b.p. 89–90°, n_D^{20} 1.3607, d_{20}^{20} 1.423.

Attempts to dehydrate 1,1,1-trifluoro-3-nitro-2-propanol with excess polyphosphoric acid or with mixtures of phosphoric anhydride and polyphosphoric acid at 160° resulted in low conversions to 3,3,3-trifluoro-1-nitropropene.

1-Nitro-2-trifluoromethyl-2-propanol.—1,1,1-Trifluoroacetone (30.1 g., 0.269 mole) was added dropwise to a stirred mixture of nitromethane (565 g., 9.2 moles) and anhydrous potassium carbonate (4.0 g., 0.029 mole) at 0°. The solution was warmed to 20–30° and stirred for 3 days. The mixture was neutralized, dried with saturated sodium chloride and with sodium sulfate, and then distilled to give colorless 1-nitro-2-trifluoromethyl-2-propanol (29.3 g., 0.169 mole) in 63% conversion, b.p. 42–43° (3 mm.), n_D^{20} 1.3881, d_{20}^{20} 1.2302.

Anal. Calcd. for C₄H₈NO₂F₃: C, 27.75; H, 3.49; N, 8.09. Found: C, 27.96; H, 3.32; N, 8.04.

1-Nitro-2-trifluoromethyl-2-propyl Acetate.—Acetyl chloride (41.6 g., 0.53 mole) was heated with 1-nitro-2-trifluoromethyl-2-propanol (81.0 g., 0.47 mole) for 20 hours at 30°. Distillation gave 1-nitro-2-trifluoromethyl-2-propyl acetate (88.4 g., 0.41 mole) in 87% yield, b.p. 93.5–94.5° (30 mm.), n_D^{20} 1.3905.

Anal. Calcd. for C₈H₈NO₄F₃: C, 33.49; H, 3.75; N, 6.51. Found: C, 33.42; H, 3.73; N, 6.63.

1-Nitro-2-trifluoromethyl-1-propene.—(a) 1-Nitro-2-trifluoromethyl-2-propanol (60.0 g., 0.347 mole) was added dropwise to stirred phosphoric anhydride (60.0 g., 0.423 mole at P₂O₅) at 190–200°. Constant attention and occasional hand stirring were necessary to minimize formation of foam and of large viscous clumps in the reaction vessel. A light-green product was distilled (3 hours) from the reaction mixture at reduced pressure into a receiver at –80°. Redistillation (twice) of the volatile product gave: (1) 1-nitro-2-trifluoromethyl-2-propanol (11.2 g., 0.064 mole, 18% recovery) and (2) 1-nitro-2-trifluoromethyl-1-propene (34.4 g., 0.222 mole, 64% conversion, 79% yield), b.p. 79–82° (200 mm.), n_D^{20} 1.3791, d_{20}^{20} 1.353, a powerful lachrymator of green color, infrared absorption for a conjugated nitro group at 6.42 and 7.42 μ .^{28,29}

(28) The infrared absorption for a nitro group in conjugated nitroolefins usually occurs in the regions of 6.6 and 7.4 μ .¹⁸

(29) It is possible that the 1-nitro-2-trifluoromethyl-1-propene is or becomes contaminated with its unconjugated isomer, 3-nitro-2-trifluoromethyl-1-propene; see ref. 18.

Anal. Calcd. for C₄H₄NO₂F₃: C, 30.98; H, 2.59; N, 9.03. Found: C, 31.13; H, 3.41; N, 9.13.

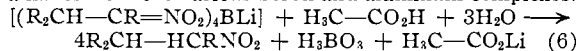
(b) 1-Nitro-2-trifluoromethyl-2-propyl acetate (40.0 g., 0.186 mole) in ethyl ether (100 ml.) was stirred with aqueous sodium bicarbonate (10%) until carbon dioxide was no longer evolved. The ether solution was dried over sodium sulfate and then distilled to give 1-nitro-2-trifluoromethyl-1-propene (6.05 g., 0.039 mole) in 21% yield, b.p. 80.0–80.5° (210 mm.), n_D^{20} 1.3785.

Techniques of Reduction.—Sodium trimethoxyborohydride and lithium borohydride were used (Table I) in suspension in mixtures of ethyl ether (3–4 parts) and tetrahydrofuran (1 part) at –70 to 0°. Tetrahydrofuran may be used to effect homogeneous reductions with sodium trimethoxyborohydride or with lithium borohydride. The single solvent is somewhat unsatisfactory, however, since the reaction mixtures are acidified with aqueous acetic acid-urea; in such systems the reduction products cannot be conveniently ether-extracted. Reductions with sodium trimethoxyborohydride or lithium borohydride may be effected in suspension in ethyl ether. Ethyl ether as a single solvent, however, offers the disadvantages that (1) reductions of the nitroolefins occur slowly because of the limited solubilities of the hydrides, (2) if reduction is insufficiently complete, it is often difficult to control the exothermic activity of the reaction mixture upon allowing it to warm up before being acidified, and (3) consecutive Michael processes involving the reduction product and the initial nitroolefin become of greater importance.

Absolute ethanol at –40 to 0° was employed as the solvent for reductions with sodium borohydride. Conjugated nitroalkenes, even in trace concentrations, catalyze decomposition of sodium borohydride in ethanol. There is an apparent maximum concentration of sodium borohydride in ethanol (~2.84 g., in 50 ml.) at 0° that can be used satisfactorily for reduction; if more concentrated solutions of sodium borohydride are used, decomposition of the hydride occurs very rapidly, often in a few seconds, upon introduction of the nitroalkene. When using more dilute solutions, gases are evolved slowly; the reduction of nitroalkenes usually occurs so rapidly however that competitive destruction of the borohydride is of minor importance in this method. Ethanol does have the disadvantage that it is difficult to separate from low-boiling nitroalkanes. An attempt to effect heterogeneous reduction of 5,5,6,6,7,7,7-heptafluoro-3-nitro-3-heptene in tetrahydrofuran (3 parts)-ethyl ether (7 parts) was unsuccessful.

In all reductions, except those which allowed a special study of the effect, a solution of the nitroolefin was added to a homogeneous hydride solution or to a heterogeneous hydride slurry. It was found (Tables II and III) that the rate of addition of each nitroolefin, the temperature and time permitted for reduction to occur, the ratio of hydride to nitroolefin, and the period allowed for the reaction mixture to warm before being acidified are important experimental variables. The results reported in Table I are usually for satisfactory preparative procedures; no exhaustive efforts were made to determine the optimum conditions for reduction of the various nitroolefins.

The reaction products (Table IV) were hydrolyzed (as in eq. 6) with aqueous acetic acid-urea¹⁰ to free the nitroalkanes from the various boron and aluminum complexes.



The excess acetic acid was removed by extracting an ether solution of the product with aqueous sodium bicarbonate. Caution must be exercised in this separation because electro-negatively-substituted nitro compounds such as 3,3,3-trifluoro-1-nitropropane are sufficiently acidic to react with sodium bicarbonate.

Reaction of 2-Nitro-1-butene and Sodium Trimethoxyborohydride.—2-Nitro-1-butene (15.2 g., 0.15 mole) in ethyl ether (25 ml.) was added in 70 minutes (Tables I and II) to a stirred suspension of sodium trimethoxyborohydride³⁰ (28.8 g., 0.225 mole) in ethyl ether (125 ml.) and

(30) The reduction of nitroolefins may be effected with stoichiometric quantities of metal hydride (Equations 1, 2 and 5); incomplete reduction may occur, however, resulting in formation of mixtures of nitroalkane and nitroalkene. It is more practical usually to use excess reducing agent and drive the reduction to (near) completion. The remaining nitroalkene may then be removed by reaction with aqueous sodium bisulfite; R. L. Heath and H. A. Piggott, *J. Chem. Soc.*, 1481 (1947).

TABLE IV
 PHYSICAL PROPERTIES OF REDUCTION PRODUCTS

Products ^a	°C.	B.p.	Mm.	n_{20}^D	d_{20}^{20}	Analyses, %					
						C	Calcd. H	N	C	Found H	N
$C_2H_5CH_2NO_2^{b,c}$	129		742	1.4023							
$C_2H_5CH(NO_2)CH(CH_3)CH_2NO_2$	86.3		0.8	1.4558	1.1707	40.90	6.87	15.90	41.17	7.00	15.82
$C_2H_5CH(NO_2)CH_2^{c,d}$	138.5		756	1.4044	0.9676						
$C_2H_5CH(NO_2)CH_2C(CH_3)(NO_2)C_2H_5^d$	79-81		0.7	1.4573	1.1125	47.05	7.90	13.70	47.98	7.80	13.50
$C_2H_5C(CH_3)(NO_2)CH(CH_3)CH(NO_2)CH_3$	78-80		0.1	1.4657	1.126	47.05	7.90	13.70	47.09	7.86	13.79
$(CH_3)_2CHCH_2NO_2^{c,e}$	69-70.7		70	1.4090	0.9627						
$C_3H_7CH(NO_2)C_3H_7^{c,f,g}$	70-71		9	1.4224-1.4236	0.9269	57.90	10.41	9.65	58.32	10.53	9.50
$CCl_3CH_2CH_2NO_2$	70.0-71.3		3	1.4899	1.5347	18.72	2.10	7.28	19.10	2.21	7.13
$CCl_3CH_2CH(NO_2)CH(CCl_3)CH_2NO_2$	150-151 ^{h,i}					18.82	1.58	7.32	18.78	1.71	7.28
$CF_3CH_2CH_2NO_2^j$	132		750.6	1.3549-1.3555	1.4203						
$CF_3CH_2CH(NO_2)CH(CF_3)CH_2NO_2$	76.9		0.9	1.3910	1.6181	25.36	2.13	9.86	25.65	2.41	9.77
$CF_3(CH_2)CHCH_2NO_2$	83.5-84		150	1.3643	1.312	30.58	3.85	8.92	31.52	3.92	8.87
$C_3F_7CH_2CH(NO_2)CH_3^k$	77.0-78.8		39-40	1.3407	1.4861						
$C_3F_7CH_2CH(NO_2)C_2H_5^{d,k}$	78.5-79.0		23-25	1.3488	1.4286						
$C_6H_5CH_2CH_2NO_2^{c,d,l}$	73.0-74.5		0.5	1.5270	1.1314	63.56	6.00	9.27	63.52	6.03	9.38
$C_6H_5CH_2CH(NO_2)CH(C_6H_5)CH_2NO_2^d$	120.5-121.0 ^h					63.99	5.37	9.33	63.87	5.18	9.39
$C_6H_5CH_2CH(NO_2)CH_3^m$	81.5-82		0.8	1.5214							
$(C_4H_9O)CH_2CH_2NO_2^{n,o}$	61.5-63.0		2.0	1.4843	1.2052	51.06	5.00	9.93	51.17	5.00	10.10

^a All products reported, as indicated by infrared analyses, are free of initial nitroalkene and give strong absorption for aliphatic mononitro groups except as noted, at 6.4 and 7.2 μ . The molar refractions of all liquids were in satisfactory agreement with that calculated. ^b Lit. b.p. 130.5° (761 mm.), n_{20}^D 1.4013 (A. I. Vogel, *J. Chem. Soc.*, 1833 (1948)). ^c Converted via the Nef reaction to the corresponding 2,4-dinitrophenylhydrazones (45-62% yields), no depression by an authentic sample. ^d See Experimental. ^e Lit. b.p. 140.5°, n_{20}^D 1.4050, d_{20}^{20} 0.9625 (H. B. Hass, E. B. Hodge and B. M. Vanderbilt, *Ind. Eng. Chem.*, **28**, 339 (1936)). Possibly slightly contaminated with 2-methyl-3-nitro-1-propene and 2-methyl-1-nitro-1-propene. ^f Lit. b.p. 10° (25 mm.), n_{20}^D 1.4200, d_{20}^{20} 0.919. ^g Slightly contaminated. ^h M.p. ⁱ Crystallized from methanol and from carbon tetrachloride as a white fibrous solid. ^j Lit. b.p. 134-134.8° (748 mm.), n_{20}^D 1.3558, d_{20}^{20} 1.4220 (H. Shechter and F. Conrad, *This Journal*, **72**, 3371 (1950)); b.p. 135.5°, n_{20}^D 1.3525, d_{20}^{20} 1.4259 (E. T. McBee, H. B. Hass and I. M. Robinson, *ibid.*, **72**, 3579 (1950)). ^k The infrared absorption of the aliphatic mononitro group is shifted to 6.34-6.35 and 7.2 μ ; lit. ^l b.p. 64° (23 mm.), n_{20}^D 1.3412. ^m W. Borsche and F. Sinn, *Ann.*, **533**, 265 (1942). ⁿ Lit. ^o b.p. 103-104° (4 mm.). ^p 2-(2-Nitroethyl)-furan (colorless.) ^q Strong infrared absorption for a mononitro group (6.35 and 7.15 μ) and a furan ring (13.5 μ).

tetrahydrofuran (50 ml.) at -60 to -65°. After the mixture had been stirred for 30 minutes at -60 to -65°, it was acidified in one hour at 0° with aqueous acetic acid-urea¹⁰ and then saturated with sodium chloride. The aqueous layer was separated and extracted with ethyl ether. The ether extract was washed with saturated aqueous sodium bicarbonate and saturated aqueous sodium bisulfite (3 X 150 ml.), dried over sodium sulfate, concentrated and then distilled to yield: (1) 2-nitrobutane (colorless, 6.95 g., 0.0675 mole, 45% conversion), b.p. 60-70° (80 mm.), 137.5° (742.3 mm., capillary method), n_{20}^D 1.4048-1.4050; (2) 3-methyl-3,5-dinitroheptane (5.34 g., 0.026 mole, 35% conversion), b.p. 86-90° (0.5 mm.), n_{20}^D 1.4568-1.4577; and (3) residue (1.3 g., unidentified). Redistillation of fraction 1 gave purified 2-nitrobutane (Table IV) in only slightly lower yield, b.p. 138.5° (756.4 mm.), n_{20}^D 1.4044, d_{20}^{20} 0.9676; lit. b.p. ³¹ 139.6° (760 mm.), n_{20}^D 1.4036, ^{3a} 1.4042, ³¹ d_{20}^{20} 0.968. ³¹

Redistillation of fraction 2 gave purer 3-methyl-3,5-dinitroheptane in slightly lower yield, b.p. 79-81° (0.7 mm.), n_{20}^D 1.4573, d_{20}^{20} 1.1125, MR_D (calcd.) 50.61, MR_D (found) 50.03. The 3-methyl-3,5-dinitroheptane³² was similar in properties to that prepared from 2-nitro-1-butene and 2-nitrobutane. The 3-methyl-3,5-dinitroheptane was converted to 3-methyl-3-nitro-5-heptanone via the Nef reaction¹³ and then to 3-methyl-3-nitro-5-heptanone 2,4-dinitrophenylhydrazones (41% over-all conversion), m.p. 131.5-132.5°, no depression by an authentic sample.

Anal. Calcd. for $C_{14}H_{19}N_3O_6$: C, 47.59; H, 5.42; N, 19.82. Found: C, 47.48; H, 5.29; N, 19.96.

(31) E. B. Hodge, *Ind. Eng. Chem.*, **32**, 748 (1940).

(32) This product may exist in two racemic modifications.

Reaction of 2-Nitro-1-butene and 2-Nitrobutane.—2-Nitro-1-butene (4.45 g., 0.044 mole) was added in 35 minutes to a solution of 2-nitrobutane (4.54 g., 0.044 mole) and potassium hydroxide (2.91 g., 0.052 mole) in ethanol (20 ml.). The mixture was acidified¹⁰ below 0° and then extracted with ethyl ether. Distillation of the dried extract gave colorless 3-methyl-3,5-dinitroheptane (2.64 g., 0.0129 mole, 29% conversion), b.p. 80-85° (1 mm.), n_{20}^D 1.4565, d_{20}^{20} 1.1132. 3-Methyl-3-nitro-5-heptanone 2,4-dinitrophenylhydrazones, m.p. 131.5-132.5°, was prepared in 52% over-all conversion from 3-methyl-3,5-dinitroheptane via the Nef reaction¹³ and subsequent reaction with 2,4-dinitrophenylhydrazine. The derivative is identical with that obtained from 3-methyl-3,5-dinitroheptane derived from reduction of 2-nitro-1-butene with sodium trimethoxyborohydride.

Reaction of 5,5,6,6,7,7,7-Heptafluoro-3-nitro-3-heptene and Lithium Borohydride.—A solution of 5,5,6,6,7,7,7-heptafluoro-3-nitro-3-heptene (15.34 g., 0.057 mole) in ethyl ether (25 ml.) was added in 4 hours (Table I) to a stirred suspension of lithium borohydride (0.62 g., 0.0285 mole) in ethyl ether (125 ml.) and tetrahydrofuran (50 ml.) at -60 ± 2°. The mixture was stirred for 4 hours at -60°, then acidified¹⁰ below 0° in 45 minutes. The product was extracted and dried as described previously. Distillation gave colorless 1,1,1,2,2,3,3-heptafluoro-5-nitroheptane (14.08 g., 0.052 mole, 91% conversion), b.p. 79.0-79.5° (24.5-25.0 mm.), n_{20}^D 1.3493; lit. ^{5b} b.p. 60° (9 mm.), n_{20}^D 1.3493.

Nef Reaction¹³ of 1,1,1,2,2,3,3-Heptafluoro-5-nitroheptane.¹³—A solution of 1,1,1,2,2,3,3-heptafluoro-5-nitroheptane (1.00 g., 0.00369 mole) in methanol (10 ml.) was added to a mixture of sodium hydroxide (0.4 g., 0.01 mole) and water (10 ml.) and kept at 0° for 18 hours. The solution

was dropped into a mixture of concd. sulfuric acid (2.5 ml.) and water (12 ml.) at 0°; 2,4-dinitrophenylhydrazine in sulfuric acid was then added. An oil separated which was crystallized from hot ethanol to yield 5,5,6,6,7,7,7-heptafluoro-3-heptanone 2,4-dinitrophenylhydrazone (0.83 g., 0.00198 mole, 53.5% conversion) as orange needles, m.p. 123–124°.

Anal. Calcd. for $C_{13}H_{11}N_4O_4F_7$: C, 37.15; H, 2.64; N, 13.33. Found: C, 37.62; H, 2.85; N, 13.53.

1-Nitro-1,2-dideoxy-D-arabo-hexitol Tetraacetate (II).—(a) A solution of D-arabo-tetraacetoxy-1-nitro-1-hexene (I, 1.81 g., 0.005 mole) in ethyl ether (10 ml.) and tetrahydrofuran (4 ml.) was added (Table I) in 70 minutes to a stirred suspension of lithium borohydride (0.11 g., 0.005 mole) in ethyl ether (15 ml.) and tetrahydrofuran (5 ml.) at 0°. The mixture was stirred for 2 hours at 0° and then acidified below 0° in 15 minutes with aqueous acetic acid-urea. The mixture was saturated with sodium chloride; the ether layer was separated, extracted with aqueous sodium bicarbonate, and then dried over sodium sulfate. After concentrating the extract, ethyl ether (5 ml.) was added, and the mixture was cooled; crude 1-nitro-1,2-dideoxy-D-arabo-hexitol tetraacetate (II, 1.37 g.) separated, m.p. 63–73°. Recrystallization of the product from ethyl ether did not raise its melting point (the product is possibly contaminated at this stage because of reduction or of hydrolysis of some of the acetyl groups).

Crude II was heated with acetic anhydride (15 ml.) and concd. sulfuric acid (1 drop) for one hour at 85–95°. The acetic acid and acetic anhydride were removed at reduced pressure; ethyl ether was added, and the mixture was cooled. A yellow solid (1.08 g.) separated; two recrystallizations from ethyl ether gave II (0.99 g., 0.00271 mole, 54% conversion) as a white solid, m.p. 90–92°, lit. m.p. 91–92°. ^{4d}

(b) A solution of I (1.00 g., 0.0028 mole) in absolute ethanol (10 ml.) was added in 45 minutes (Table I) to a stirred suspension of sodium borohydride (0.12 g., 0.0032 mole) in absolute ethanol (10 ml.) at 0°. The mixture was stirred for 2 hours at 0° and then acidified in 10 minutes below 0°. The mixture was concentrated at reduced pressure to a volume of approximately 5 ml., then diluted with ethyl ether and dried over sodium sulfate. Removal of solvents yielded crude II (0.65 g., 0.00179 mole, 64% conversion) as a white solid, m.p. 82–84°. One recrystallization from absolute ethyl ether gave pure II³³ in only slightly lower yield, m.p. 91–92°, lit. m.p. 91–92°. ^{4d}

Reaction of ω -Nitrostyrene and Lithium Aluminum Hydride (Reverse Addition).³⁴—A solution of lithium aluminum

hydride (1.90 g., 0.05 mole) in ethyl ether (100 ml.) was added in 2.2 hours to a stirred mixture of ω -nitrostyrene (14.90 g., 0.1 mole), ethyl ether (125 ml.) and tetrahydrofuran (25 ml.) at –40 to –45°. The mixture was stirred at –40 to –45° for 3 hours and then acidified below 0° in 45 minutes. The hydrolysate was worked up as described previously and distilled to give: (1) 1-nitro-2-phenylethane (7.15 g., 0.0473 mole, 47.3% conversion), b.p. 73–74.5° (0.5 mm.), n_D^{20} 1.5275, d_4^{20} 1.1314, M_{R_D} (calcd.) 41.37, M_{R_D} (found) 41.52 (lit. values, Table IV); and (2) residue (viscous, 6.9 g.).

Fraction 2 was crystallized from ethanol to give amorphous products and 1,3-dinitro-2,4-diphenylbutane³² (0.25 g., 0.00083 mole, 1.7% conversion, Table IV), white plates, m.p. 120–121°, strong infrared absorption for an aliphatic mononitro group (6.4 and 7.3 μ) and a mono-substituted benzene ring (14.4 μ). The melting point of this product is not depressed by the 1,3-dinitro-2,4-diphenylbutane³² obtained from reduction of ω -nitrostyrene with sodium trimethoxyborohydride or sodium borohydride.

In reduction of ω -nitrostyrene with sodium trimethoxyborohydride at –40° (Table I), an amorphous white solid (20% conversion), m.p. ca. 255° dec., is obtained along with 1-nitro-2-phenylethane and 1,3-dinitro-2,4-diphenylbutane. At –2° (as in Table I), a similar amorphous product, m.p. 263° dec., is formed in 89% conversion. Reaction of ω -nitrostyrene with sodium borohydride at 0° (as in Table I) yields an unidentified white solid (34% conversion), m.p. ca. 228–232° dec.; at –40° the reduction products are 1-nitro-2-phenylethane (11% conversion), 1,3-dinitro-2,4-diphenylbutane (22% conversion) and the unidentified white solid (19% conversion), m.p. ca. 232–235° dec. The unidentified solids are insoluble in boiling Skellysolves, ethyl ether, benzene, methanol, ethanol, carbon tetrachloride, chloroform, acetone and acetic acid. They dissolve in hot aqueous sodium hydroxide to form dark red solutions; oxidation of an alkaline solution of the product, m.p. ca. 255° dec., by sodium permanganate gave benzoic acid upon acidification. The unidentified products are believed to be polymers of ω -nitrostyrene.³⁵ These products have properties which are similar to that obtained, m.p. ca. 205–210° dec., by anionic polymerization (87% conversion) of ω -nitrostyrene by benzyltrimethylammonium hydroxide in methanol at 25°. Analysis of the product, m.p. ca. 255° dec., is in agreement with that calculated for poly- ω -nitrostyrene.

Anal. Calcd. for $(C_8H_7NO)_x$: C, 64.40; H, 5.73; N, 9.32. Found: C, 64.42; H, 4.73; N, 9.39.

COLUMBUS 10, OHIO

(33) In reduction of nitrocarbohydrate esters of this type, sodium borohydride may be the reagent of choice since it reduces conjugated carbon-carbon double bonds, but does not rapidly reduce carboxylic esters. Sodium borohydride also provides an advantage in that aliphatic nitro derivatives of carbohydrates will often be much more soluble in ethanol than in tetrahydrofuran or ethyl ether.

(34) Reverse addition of lithium aluminum hydride to ω -nitrostyrene at –40 to –50° and subsequent Nef hydrolysis of the products has been reported³⁴ to give phenylacetaldehyde (0–10%). Evidence was obtained³⁴ for the formation of 1-nitro-2-phenylethane; however, it was not isolated.

(35) (a) P. Herrmann and D. Vörländer, *Chem. Zentr.*, **70**, **1**, 730 (1899), report that ω -nitrostyrene is polymerized to a white amorphous solid $(C_8H_7NO)_x$, m.p. ca. 280° dec., by sodium ethoxide and ethyl malonate in ethanol. (b) 2-(2-Nitrovinyl)-furan is also rapidly converted to polymer (95% conversion), m.p. >350°, by benzyltrimethylammonium hydroxide in methanol-ethyl ether. This polymer is insoluble in all usual organic solvents and is similar in properties to that isolated from reaction of sodium trimethoxyborohydride and 2-(2-nitrovinyl)-furan (Table I).