distilled under vacuum. See Table I for boiling points and yields.

Hydrolysis of Diketodioxolanes. Preparation of Triketones.—A solution of 5 ml of ethanol and 3 ml of water was used to dissolve approximately 1 g of the desired diketodioxolane. One drop of concentrated hydrochloric acid was added to this solution. The acidic solution was heated to near reflux temperature for 2 hr. At the end of this time the acidic solution was cooled in an ice bath and scratched occasionally with a stirring rod. The solid triketone precipitated within a few minutes in most cases. A few cases required a greater period of scratching. In a few cases it was necessary to remove some of the solvent at reduced pressure and then repeat the above precedure. The solid, flaky white triketone was filtered and then recrystallized from a small amount of ethanol. The resulting triketones were dried overnight at room temperature at about 0.1–0.2 mm.

Preparation of Copper Chelates.—A small amount of the β-diketodioxolane was dissolved in a small amount of methanol. A saturated solution of cupric acetate was then added two drops at a time. The glass container was scratched with a stirring rod after each addition of cupric acetate. Once the solid chelate was observed the cupric acetate was added more rapidly with continuous stirring. The chelate was filtered and recrystallized from methanol. It was then dried overnight under vacuum at about 0.1–0.2 mm. In the event that the dry blue chelate contained green spots on the surface, it was shaken vigorously with water for several minutes, filtered, and then redried in the vacuum. In only two cases was a solid precipitate formed from a β-diketodioxolane, and then only after a long period of scratching. The others that were attempted gave oils.

The copper chelate of 9-ethylenedioxy-2,4-undecanedione showed the following results.

Anal. Calcd for $C_{26}H_{42}CuO_8$: C, 57.18; H, 7.75 Cu, 11.63. Found: C, 56.99; H, 7.66 Cu, 11.89.

Elemental analysis of the copper chelate of 8-ethylenedioxy-2,4-nonanedione showed the following results.

Anal. Calcd for $C_{22}H_{34}CuO_8$: C, 53.92; H, 6.99; Cu, 12.97. Found: C, 53.71; H, 6.94; Cu, 12.80.

The above procedure was repeated for the triketones which readily formed the copper chelates. See Table IV.

Registry No.—I, 34956-84-8; II (R = Et, X = Br, n = 5), 34956-85-9; II (R = Et, X = Br, n = 4), 34956-86-0; 8-bromo-3-octanone, 2146-62-5; 9-ethylenedioxy-2,4-undecanedione copper chelate, 34952-80-2; 8-ethylenedioxy-2,4-nonanedione copper chelate, 34952-81-3.

Acknowledgment.—The authors wish to thank the Robert A. Welch Foundation and the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Nitration Studies. XVIII. Conversion of Lower Nitroalkanes to Higher Members of the Series

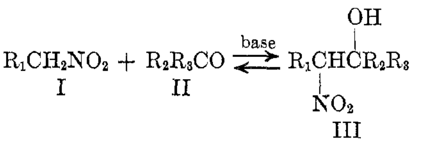
G. BRYANT BACHMAN*[1] AND ROBERT J. MALESKI[2]

Department of Chemistry, Purdue University, Lafayette, Indiana 47907

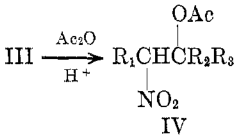
Received January 18, 1972

The lower primary nitroalkanes may be converted to higher nitroalkanes by a one pot synthesis involving successive reactions with aldehydes, acylating agents, and sodium borohydride. Overall conversions are in the 75–80% range. Lower aldehydes also give dialkylated products, *e.g.*, 3-nitropentane from nitromethane and acetaldehyde. With ketones isolation of the intermediate nitro alcohol is desirable. The mechanism of the reduction step in particular is discussed.

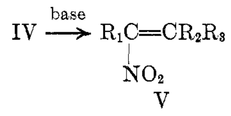
An attractive route for the preparation of higher primary and secondary nitroalkanes involves the condensation of an aldehyde or a ketone with a lower primary nitroalkane followed by acylation, elimination, and reduction of the product (eq 1–4). This process has not proved to be very useful, since published procedures[3] involve isolation of intermediates (III, IV, V), are time consuming (4–5 days) and lead to poor overall yields (14–33%). The low yields result in part from isolation steps and in part from the occurrence of side reactions (eq 5) in the reduction of V leading to 1,3-dinitroalkanes (VII).



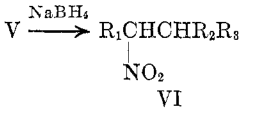
$$\underset{\text{I}}{R_1CH_2NO_2} + \underset{\text{II}}{R_2R_3CO} \xrightleftharpoons{\text{base}} \underset{\text{III}}{R_1\underset{NO_2}{CH}\overset{OH}{C}R_2R_3} \qquad (1)$$



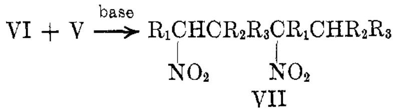
$$\text{III} \xrightarrow[H^+]{Ac_2O} \underset{\text{IV}}{R_1\underset{NO_2}{CH}\overset{OAc}{C}R_2R_3} \qquad (2)$$



$$\text{IV} \xrightarrow{\text{base}} \underset{\text{V}}{R_1\underset{NO_2}{C}{=}CR_2R_3} \qquad (3)$$



$$\text{V} \xrightarrow{NaBH_4} \underset{\text{VI}}{R_1\underset{NO_2}{CH}CHR_2R_3} \qquad (4)$$



$$\text{VI} + \text{V} \xrightarrow{\text{base}} \underset{\text{VII}}{R_1\underset{NO_2}{CH}CR_2R_3\underset{NO_2}{C}R_1CHR_2R_3} \qquad (5)$$

We wish to report an improved procedure for the processes shown in eq 1–4 which involves no isolation of intermediates. The synthesis is generally performed in one reaction vessel over a 24-hr period and provides VI in high yields (*cf.* Table I) based on I or II. In some cases (ketones) much better results are obtained if the intermediate nitro alcohol is isolated.

Various methods[4a] for the preparation of the higher

---

[1] To whom correspondence should be addressed.

[2] NDEA Title IV Predoctoral Fellow, 1966–1969. Commercial Solvents Corporation Research Assistant, 1970.

[3] (a) H. Schechter, D. E. Ley, and E. B. Roberson, *J. Amer. Chem. Soc.*, **78**, 4984 (1956); (b) A. I. Meyers and J. C. Sircar, *J. Org. Chem.*, **32**, 4134 (1967).

[4] (a) N. Kornblum, *Org. React*, **12**, 101 (1962); (b) N. Kornblum, H. O. Larson, R. K. Blackwood, D. D. Mooberry, E. P. Oliveto, and G. E. Graham, *J. Amer. Chem. Soc.*, **78**, 1497 (1956); (c) N. Kornblum and J. W. Powers, *J. Org. Chem.*, **22**, 455 (1957); (d) G. B. Bachman and N. W. Connon, *ibid.*, **34**, 4121 (1969); (e) G. B. Bachman and K. G. Strawn, *ibid.*, **33**, 313 (1968); (f) W. D. Emmons and A. S. Pagano, *J. Amer. Chem. Soc.*, **77**, 4557 (1955); (g) G. B. Bachman and T. F. Biermann, *J. Org. Chem.*, **35**, 4229 (1970).

TABLE I

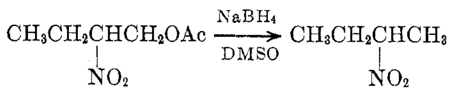
PREPARATION OF HIGHER NITROALKANES FROM LOWER NITROALKANES AND CARBONYL COMPOUNDS

Nitroalkane (mol)	Carbonyl compound (mol)	Ratio[a]	Product	% Convn[b,d]			% Yield[b]		% Convn[c]	
				A	B	C	A	B	B	C
			A. One-Pot Syntheses from Aldehydes							
Nitromethane	Acetaldehyde									
(1)	(1)	0.75	1-Nitropropane	24	24		24	24		
			3-Nitropentane	13	26		13	26		
(2)	(1)	0.75	1-Nitropropane	33	66		44	66		
Nitromethane	Propanal									
(1)	(1)	0.75	1-Nitrobutane	69	69		78	69		
			4-Nitroheptane	1	2		1	2		
(2)	(1)	0.75	1-Nitrobutane	40	80		84	80		
Nitromethane	Pentanal									
(1)	(1)	0.55	1-Nitrohexane	78	78		87	78	63	
(2)	(1)		1-Nitrohexane	43	85		79	85	69	
Nitroethane	Pentanal									
(1)	(1)	0.55	2-Nitroheptane	57	57		63	57		
			2-Nitro-2-heptene	18	18		20	18		
(1)	(1)	0.70[e]	2-Nitroheptane	70	70		75	70	60	
(3)	(2)	0.70	2-Nitroheptane	48	71		68	71	66	
1-Nitropropane	Pentanal									
(1)	(1)	0.70[e]	3-Nitrooctane	70	70		79	70	62	
(2)	(1)	0.70[e]	3-Nitrooctane	34	68		75	68		
Nitromethane	2-Ethylhexanal									
(1)	(1)	0.70[e]	3-Ethyl-1-nitroheptane[f]	66	66		73	66	53	
(2)	(1)	0.70[e]	3-Ethyl-1-nitroheptane[f]	39	78		76	78	71	
			B. Nitroalkanes from Isolated Nitro Alcohols							
Nitromethane	Propanal									
(1)	(1)	0.55	1-Nitrobutane	67	67	86	67	67		78
1-Nitrobutane	Pentanal									
(1)	(1)	0.71	4-Nitrononane[f]	52	52	71	52	52		61
Nitromethane	Acetone									
(1)	(4)	0.75	2-Methyl-1-nitro-Propane	21	5	85	41	5		72
Nitroethane	2-Ethylhexanal									
(1)	(1)	0.81	4-Ethyl-2-nitrooctane[f]	50	50	78	50	50		72
Nitromethane	Cyclohexanone									
(1)	(6)	0.70	Cyclohexylnitromethane	59	9	88	59	49		77
Nitromethane	Benzaldehyde									
(1)	(1)	0.70	2-Phenyl-1-nitroethane	69	69	79	69	69		64
Nitroethane	Benzaldehyde									
(1)	(1)	0.70	1-Phenyl-2-nitropropane	40	43	74	40	43		61

[a] Sodium borohydride–nitroalkyl acetate molar ratio. A 100% conversion to the acetate was assumed. [b] Determined by vpc analysis. [c] Determined by distillation. [d] A, based on starting nitroalkane; B, based on carbonyl compound; C, based on isolated nitroalcohol. [e] Products were contaminated with the aldehyde diacetate and had to be distilled from granular zinc. [f] A new compound. See Experimental Section for physical properties and analytical data.

primary and secondary nitroalkanes have been reported, among which are the reaction of metal nitrites with alkyl halides[4b,c] or nitrates,[4d] the oxidation of amines[4e] and oximes,[4f] and the thermal decomposition of acyl nitrates.[4g] The high conversions observed here along with the simple experimental procedure make this process a valuable addition to these known methods, especially when the starting materials for these other procedures are less readily available.

A key step in the new procedure involves the reduction of nitroalkyl acetates to the corresponding nitroalkane by the action of sodium borohydride in DMSO at 20–25°. Thus addition of 2-nitro-1-butyl acetate (VIII) to sodium borohydride dissolved in DMSO results in an optimum conversion to 2-nitrobutane of 75%. Use of other solvents (ethanol, sulfolane, and DMF) or higher reaction temperatures (40–45°) markedly decreases the conversions.



$$\underset{NO_2}{CH_3CH_2\underset{|}{C}HCH_2OAc} \xrightarrow[DMSO]{NaBH_4} \underset{NO_2}{CH_3CH_2\underset{|}{C}HCH_3} \qquad (6)$$

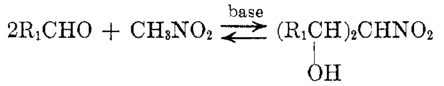
VIII

In order to avoid isolation steps in this synthesis it was first necessary to find one set of conditions adaptable to all three steps. Since the first step required basic conditions, the second step acidic conditions, and the third step a specific solvent (DMSO), a study of various combinations of reactants, catalysts, and solvents was necessary. Eventually it was found that nitroalkanes will condense with aldehydes in the presence of about 5 mol % of powdered sodium hydroxide and in the absence of solvent in high yields. This new process avoids the problem of finding a solvent which will dissolve these reactants but which will not react in the next step with the acylating agent. Other bases, such as potassium hydroxide, calcium hydroxide, or tertiary amines, gave no better and usually considerably poorer results. With ketones the corresponding nitro alcohol had to be made and isolated according to published procedures[5] for best results.

Acylation with acetic anhydride is readily accomplished in the second step after addition of a slight excess of sulfuric acid, and is accompanied by the production of 1 equiv of acetic acid. However, addition of a solution of sodium borohydride and DMSO to the crude nitroalkyl acetate–acetic acid solution provides optimum conversions to the corresponding nitroalkane. The reduction is fast (0.5–1 hr), is accompanied by only moderate gas evolution, and provides product nitroalkane in 66–85% conversion based on starting aldehyde.

In the acylation step any unreacted aldehyde from the first step may be converted to aldehyde diacetate, which remains as an impurity in the final product. In some cases, *e.g.*, in the preparation of 3-nitrooctane and 3-ethyl-1-nitroheptane, this impurity is not readily removed by fractional distillation. When this is the case the addition of a small amount of metallic powdered zinc at the beginning of the distillation has been found to remove the impurity.

Table I lists the nitroalkanes prepared by methods A and B along with the yields and conversions based on the various species involved and also the amount of sodium borohydride necessary for optimum conversions. Use of nitromethane and lower aldehydes (*e.g.*, acetaldehyde, propanal) leads to the formation of significant quantities of symmetric dialkylated nitromethanes, probably as a result of the reduction of the diacetates IX, resulting from bis condensation (eq 7).



$$2R_1CHO + CH_3NO_2 \overset{\text{base}}{\rightleftharpoons} (R_1\underset{\displaystyle OH}{C}H)_2CHNO_2 \qquad (7)$$

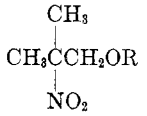
X

$$X \xrightarrow[\text{2. NaBH}_4\text{, DMSO}]{\text{1. H}^+\text{, Ac}_2\text{O}} (R_1CH_2)_2CHNO_2 \qquad (8)$$

Since the condensation step is reversible, conversions and yields of product nitroalkane can often be significantly increased by the use of excess starting nitroalkane. Excess aldehyde, however, must be avoided due to the formation of the aldehyde diacetate impurity mentioned above.

Other derivatives of the alcohol group besides the acetate may be employed with no diminution in overall conversion. Thus the *p*-toluenesulfonate or the *N*-phenylcarbamate may be prepared instead of the acetate and reduced satisfactorily to the nitroalkane, but with no apparent advantage in either conversion or convenience.

Mechanism of the Reduction.—The reduction of nitroalkyl acetates to nitroalkanes with sodium borohydride apparently requires the presence of a proton on the nitro-bearing carbon atom, since all attempts to reduce nitroacetates without this structural feature failed. Thus the acetate (XIa), *N*-phenylcarbamate (XIb), and *p*-toluenesulfonate (XIc) of 2-methyl-2-nitro-1-propanol were recovered unchanged after prolonged treatment with sodium borohydride. This suggests but does not prove that elimination of acetic acid and formation and subsequent reduction of the corresponding nitro olefin is the only mechanistic path for this reduction. It is also conceivable that a direct displacement of the acetate group by hydrogen may occur. Consideration of this possibility is suggested by the fact that reductions of nitro acetates IV give considerably better yields of nitroalkanes than reductions of the corresponding nitroalkenes V under identical conditions. This implies either that the nitroalkene is not an intermediate in the reduction or that its rate of reduction is considerably faster than its rate of conversion to other products (eq 5).



$$CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle NO_2}{C}}CH_2OR$$

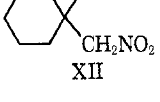
XIa, R = $COCH_3$
b, R = CONHPh
c, R = $SO_2C_6H_4$-*p*-CH_3

We favor the nitro olefin mechanism for three additional reasons.

(1) Inverse addition of the borohydride to the nitro acetate gives poorer yields of nitroalkane than normal addition unless the mixture is buffered with acetic acid. Inverse addition provides higher concentrations of nitronate anion and promotes more Michael addition (eq 5) unless acetic acid is added to buffer the solution.

(2) Nitro olefin intermediates have been isolated from reduction of nitro acetates in which insufficient amounts of sodium borohydride have been used.

(3) The acetate of 1-(nitromethyl)-1-cyclohexanol (XII) is reduced in excellent yield in a short period of time to cyclohexylnitromethane. The acetate group in this case is attached to a tertiary carbon atom and the steric factors involved in the transitions state for an SN2 process replacing this group by hydrogen make such a process highly unlikely. Carbonium ion formation seems equally unlikely due to the adjacent charge rule and it seems most likely that these reductions are proceeding primarily if not entirely by a nitro olefin mechanism.



XII

Experimental Section

General.—Nmr spectra were obtained with a Varian A-60 spectrometer using tetramethylsilane as internal standard. Ir spectra were recorded on a Perkin-Elmer 137 spectrometer.

Many of the conversions and yields reported in this work were calculated from vpc analysis using the common thermal conductivity correction factor method. An F & M Model 720 dual column temperature programmed gas chromatograph was employed. A 6 ft × 0.25 in. column containing 10% diisodecyl phthalate liquid phase on Chromosorb W DMCS A/W was used

---

[5] (a) A. Lambert and A. Lowe, *J. Chem. Soc.*, 1517 (1947); (b) L. M. Kozlov, E. E. Fink, and G. B. Liorber, *Tr. Kazan Khim.-Tekhnol. Inst.*, **23**, 148 (1958).

to analyze 1-nitrobutane and 1-nitropropane product solutions. All other products were analyzed on either as 12 ft or a 6 ft × 0.25 in. column containing 10% FFAP liquid phase on Chromosorb W DMCS A/W.

Materials.—All solvents and reagents were either of reagent grade or were purified by standard procedures.[6] Sodium borohydride was obtained from Metal Hydrides Co., and assayed according to a published procedure.[7] The method of Sprang and Degering[8] was used to prepare 1-nitro-2-butanol in 75% conversion. Crude 1-nitro-2-phenyl-2-ethanol and crude 1-phenyl-2-nitro-2-propanol were prepared in 88 and 58% conversions, respectively, by the method of Hass.[9] The method of Vanderbilt and Hass[10] was used to prepare 4-ethyl-2-nitro-3-octanol in 64% conversion. 2-Methyl-1-nitro-2-propanol was prepared according to the procedure of Lambert and Lowe[5a] in 48% yield, and the method of Kozlov[5b] was employed to prepare 1-(nitromethyl)-1-cyclohexanol in 67% yield. 2-Nitro-1-butene was prepared according to a published procedure.[11]

4-Nitro-5-nonanol.—This new nitro alcohol was prepared by the method of Vanderbilt and Hass[10] in 74% conversion: bp 86–87° (0.3 mm); $n^{20}{}_D$ 1.4472; ir (neat) 2.98 (–OH) and 6.48 μ (–NO_2).

Anal. Calcd for $C_9H_{19}NO_3$: C, 57.10; H, 10.13; N, 7.41. Found: C, 57.23; H, 9.99; N, 7.60.

2-Nitro-1-butyl *p*-toluenesulfonate was prepared by a modification of Riebsomer's procedure.[12] Exactly 11.7 ml (0.1 mol) of 2,6-lutidine was added over 0.5 hr to a solution of 11.91 g (0.1 mol) of 2-nitro-1-butanol (obtained from Commercial Solvents Corp.), 19.0 g (0.1 mol) of *p*-toluenesulfonyl chloride, and 50 ml of diethyl ether cooled to 0–5° by means of an ice bath. The mixture was kept at 0–5° for 3 hr and was allowed to warm to room temperature overnight. The lutidine salt was filtered and washed with ether, and the filtrate was evaporated under reduced pressure to give a yellow solid which was recrystallized three times from isopropyl alcohol to provide 16.02 g (59% conversion) of the tosylate: mp 52–53° (lit.[12] mp 52.5–53°); ir (Nujol) 6.48, 7.38 (–NO_2), 8.39 μ (–SO_3–); nmr (CCl_4) δ 7.50 (m, 4, ArH), 4.30–4.80 (m, 3, –$CHNO_2$ and –CH_2O_3S–), 2.47 (s, 3, ArCH_3), 1.82 (m, 2, $CH_3C\mathbf{H}_2$–), and 0.92 (t, 3, $C\mathbf{H}_3CH_2$–).

Reduction of 2-Nitro-1-butyl *p*-Toluenesulfonate.—Exactly 1.365 g (0.005 mol) of the above tosylate dissolved in 8 ml of acetonitrile was added over 0.5 hr to a solution of 0.60 g (0.152 mol) of sodium borohydride and 20 ml of ethanol cooled to 0–5° by means of an ice bath. The solution was stirred overnight and was poured into 50 ml of ice and water. The resulting mixture was extracted with four 25-ml portions of ether and the ether solution were combined, dried ($MgSO_4$), and analyzed by vpc. A 68.5% conversion to 2-nitrobutane was observed. The product was identified by its vpc retention time and by comparison of its ir spectrum with that of an authentic sample.

Reduction of 2-Nitro-1-butyl Acetate.—Exactly 1.61 g (0.01 mol) of the acetate was added over a 5-min period to a rapidly stirred solution of 0.14 g (0.0035 mol) of sodium borohydride and 20 ml of DMSO. A water bath was used to control the temperature at 20–25° during the addition. Moderate gas evolution was accompanied by a change in the solution from colorless to light yellow. Stirring was continued 1 hr after the addition had been completed and the solution was worked up for vpc analysis exactly as above. A 75% conversion to 2-nitrobutane was observed. The product was identified exactly as above.

Reverse Addition.—The above experimental procedure was repeated except that the sodium borohydride solution was added to the acetate. After 1 hr a 52% conversion to 2-nitrobutane was observed.

Effect of Acetic Acid.—A solution of 3.22 g (0.02 mol) of 2-nitro-1-butyl acetate and 1.2 g (0.02 mol) of acetic acid was added at 20–25° to 0.55 g (0.014 mol, 97%) of sodium borohydride dissolved in 20 ml of DMSO. The temperature was maintained by means of an ice bath. The reaction was stirred for 1 hr and worked up for vpc analysis as above. The conversion to 2-nitrobutane was 76%. The above procedure was repeated except that a reverse addition of borohydride to acetate was employed. A 77% conversion to 2-nitrobutane was observed.

Reduction of 2-Nitro-1-butene.—Exactly 1.01 g (0.01 mol) of 2-nitro-1-butene was added at 20–25° to 0.140 g (0.035 mol, 97%) of sodium borohydride dissolved in 20 ml of DMSO. An ice bath was used to control the temperature. The solution was stirred for 1 hr and worked up for vpc analysis as above. A 10% conversion to 2-nitrobutane was observed. Removal of the ether under reduced pressure left 0.78 g of a heavy, brown oil whose ir spectrum indicated the presence of a nitro group. The nmr ($CDCl_3$) spectrum of the oil was very complex, but again a broad signal at δ 4.48 indicated protons bound to a carbon atom bearing a nitro group. The rest of the spectrum consisted of a broad, unresolved region at δ 3.2–0.9. The oil was probably polymerized nitroolefin.

Preparation and Reduction of 2-Nitro-1-butyl *N*-Phenylcarbamate in DMSO.—Phenyl isocyanate (13.09 g, 0.11 mol) was added over 0.75 hr to 11.90 g (0.1 mol) of 2-nitro-1-butanol and 76 ml of DMSO at 18–20°. A change from colorless to green to amber was observed during the addition. Stirring was continued overnight at room temperature and at the end of 20 hr the solution was divided.

Isolation of the Urethane.—Exactly one-half of the above solution was poured into 300 ml of ice and water. The yellow solid was collected on a filter, washed thoroughly with water, dried in a desiccator, and recrystallized twice from benzene–pentane to give 8.1 g (71% conversion) of the new urethane: mp 73–74°; ir (Nujol) 3.01 (NH), 5.73 (amide I), 6.19 (amide II), 6.43 μ (–NO_2); nmr ($CDCl_3$) δ 7.38 (m, 5, ArH), 7.01 (m, 1, –NH), 4.52 (m, 3, CH_2O_2C– and –$CHNO_2$), 1.80 (m, 2, $CH_3C\mathbf{H}_2$–), and 0.99 (t, 3, $C\mathbf{H}_3CH_2$–).

Anal. Calcd for $C_{11}H_{14}N_2O_4$: C, 55.38; H, 5.92; N, 11.76. Found: C, 55.65; H, 5.93; N, 11.67.

Reduction of the Urethane.—The other half of the solution was used for the reduction. Aliquots containing theoretically 0.01 mol of the urethan were added at 20–25° to the prescribed amount of sodium borohydride dissolved in 20 ml of DMSO. Work-up, vpc analysis, and product identification were all performed as described earlier for 2-nitrobutane. An optimum conversion of about 50% (based on the nitro alcohol) may be realized using a sodium borohydride:urethane ratio of 0.76:1.50 and a duration of reaction of 0.5–24 hr.

Preparation of Higher Nitroalkanes from Lower Nitroalkanes and Aldehydes.—The following general procedure (A) was used. Exactly 0.2 mol of starting nitroalkane and 0.01 mol of catalyst (triethylamine or powdered sodium hydroxide, the latter added slowly and in small portions to the cold nitroalkane) were cooled to 0–5° in an ice bath and 0.2 mole of aldehyde was added with stirring over 0.25 hr at the above temperature. The bath and contents were allowed to warm to room temperature overnight, during which time a change from colorless to light yellow was generally observed. The solution or mixture was cooled again to 0–5° and concentrated sulfuric acid (0.012 mol) was added carefully and in very small portions. The contents of the flask were allowed to warm to room temperature and acylated with 20.4 g (0.2 mol) of acetic anhydride at 30–40°. The temperature was regulated by means of an ice bath. The yellow solution was allowed to stand for 0.5 hr at room temperature and 100 ml of a DMSO solution containing the appropriate amount (see Table I) of sodium borohydride (95–97% purity) was added over 20–30 min at 20–25° with vigorous stirring to control foaming. After 1 hr an aliquot containing theoretically 0.01 mol of product was taken and poured into 75 ml of ice and water. The resulting mixture was extracted with 75 ml of ether and the ether solutions were combined, dried ($MgSO_4$), and analyzed by vpc.

The rest of the solution was poured in small portions into 300 ml of ice and water layered over with 40 ml of ether. The product was extracted with four 40-ml portions of ether and was recovered by distillation after back washing the ether solutions with four 50-ml portions of water and drying ($MgSO_4$).

Physical properties of the nitroalkanes prepared by this method are presented in Table II. Analytical data for the new nitroalkane, 3-ethyl-1-nitrohaptane, will be found in Table III.

Isolation of a Nitroalkene Intermediate.—Use of an insufficient amount of sodium borohydride in the preparation of 2-nitro-

---

[6] D. D. Perrin, W. L. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals," Pergamon Press, New York, N. Y., 1966, pp 54–285.

[7] D. A. Lyttle, E. H. Jensen, and W. A. Struck, *Anal. Chem.*, **24**, 1843 (1952).

[8] A. Sprang and F. Degering, *J. Amer. Chem. Soc.*, **64**, 1063 (1942).

[9] H. B. Hass, M. B. Neher, and R. T. Blickenstaff, *Ind. Eng. Chem.*, **43**, 2875 (1951).

[10] B. M. Vanderbilt and H. B. Hass, *ibid.*, **44**, 1388 (1952).

[11] H. B. Hass, A. G. Susie, and R. L. Heider, *J. Org. Chem.*, **15**, 8 (1950).

[12] J. L. Riebsomer, *J. Org. Chem.*, **11**, 182 (1946).

TABLE II

PHYSICAL PROPERTIES OF NITROALKANES

Nitroalkane[a]	Method	Bp, °C (mm)	n^{20}_D	Lit. bp, °C (mm)	Lit. n^{20}_D	Ref
4-Nitrononane[b]	B	55–57 (0.2)	1.4266			
4-Ethyl-2-nitrooctane[b]	B	62–64 (0.1)	1.4336			
2-Methyl-1-nitropropane	B	63–65 (52)	1.4050	140 (760)	1.4050	*c*
Cyclohexylnitromethane	B	48 (1.5)	1.4632	63–64 (3)	1.4635	*d*
2-Phenyl-1-nitroethane	B	74–75 (0.1)	1.5261	126 (14)	1.5270	*e*
1-Phenyl-2-nitropropane	B	67–69 (0.2)	1.5167	96 (2)	1.5159	*f*
1-Nitrohexane	A	80–81 (14)	1.4212	81 (15)	1.4225	*g*
2-Nitroheptane	A	67–70 (1.5)	1.4236	194 (760)		*h*
3-Nitrooctane	A	64–65 (0.2)	1.4240	101 (20)	1.4253	*i*
3-Ethyl-1-nitroheptane[b]	A	66–67 (0.1)	1.4359			

[a] The ir spectra of all compounds contained strong absorption in the 6.45–6.50 and 7.4–7.5 regions; nmr spectra of all compounds were consistent with their structures. [b] A new nitroalkane. [c] H. B. Hass, E. B. Hodge, and B. M. Vanderbilt, *Ind. Eng. Chem.*, **28**, 341 (1936). [d] R. W. Rimmer, Ph.D. Thesis, Purdue University, 1953. [e] S. Kaneo, *J. Pharm. Soc. Jap.*, **58**, 256 (1938). [f] N. Kornblum, J. E. Ungnade, A. M. White, B. Taub, and S. A. Herbert, *J. Amer. Chem. Soc.*, **77**, 5528 (1951). [g] A. I. Vogel, *J. Chem. Soc.*, 1847 (1948). [h] F. Beilstein, *Ber.*, **13**, 2028 (1880). [i] F. Asinger, G. Geiseler, and M. Hoppe, *ibid.*, **90**, 115 (1954).

TABLE III

ANALYSES OF NEW NITROALKANES

Nitroalkane	Calcd, %			Found, %		
	C	H	N	C	H	N
4-Nitrononane	62.34	11.08	8.09	62.55	11.10	7.95
3-Ethyl-1-nitroheptane	62.34	11.08	8.09	62.29	11.00	8.21
4-Ethyl-2-nitrooctane	64.13	11.30	7.48	64.33	11.34	7.55

heptane led to an 18% conversion to 2-nitro-2-heptene: ir (neat) 6.01 (C=C), 6.59, 7.47 μ ($-NO_2$); nmr ($CDCl_3$) δ 7.19 (t, 1, $-CH{=}CNO_2$), 2.5–2.0 (s and m, 5, $CH_3CNO_2{=}$ and $-CH_2-CH{=}$), 1.40 [m, 4, $-(CH_2)_2-$], and 0.90 (m, 3, CH_3CH_2-).

Isolation of an Aldehyde Diacetate.—In the preparation of 3-nitrooctane, pentanal diacetate was isolated as an impurity from the distilled product: ir (neat) 5.69 (C=O), 8.04 μ (CO); nmr ($CDCl_3$) δ 6.78 [t, 1, $-CH(OAc)_2$], 2.08 (s, 6, CH_3CO-), and 1.8–0.9 (m, 9, aliphatic protons).

Preparation of Nitroalkanes from Isolated Nitro Alcohols.—The following general procedure (B) was used. Exactly 20.4 g (0.2 mol) of acetic anhydride was added to a solution of 0.2 mol of the nitro alcohol and 5 drops of concentrated sulfuric acid contained in a 300-ml Morton flask equipped with an overhead stirrer. The temperature was regulated at 30–40° by means of an ice bath. The solution was allowed to stand for 0.5 hr at room temperature and 100 ml of a DMSO solution containing the appropriate amount of sodium borohydride (95–67% purity) was added over a 0.5-hr period at 20–25° with vigorous stirring. After 1 hr an aliquot containing theoretically 0.01 mol of product was taken and worked up for vpc analysis as in A.

The rest of the solution was worked up and distilled as reported in A. The new nitroalkanes prepared by this procedure are 4-nitrononane and 4-ethyl-2-nitrooctane, and the analytical data for these compounds are to be found in Table III. Physical properties of these compounds are presented in Table II.

Registry No.—3-Ethyl-1-nitroheptane, 34566-10-4; 4-nitrononane, 34566-11-5; 4-ethyl-2-nitrooctane, 34566-12-6; 4-nitro-5-nonanol, 34566-13-7; 2-nitro-1-butyl *N*-phenylcarbamate, 6526-60-9.

The Conformational Effect of the Spiro Linkage between Three- and Six-Membered Rings

JOSEPH B. LAMBERT,*[1a] JACK L. GOSNELL, JR.,[1b] AND DAVID S. BAILEY

Department of Chemistry, Northwestern University, Evanston, Illinois 60201

Received March 9, 1972

The conformational properties of a six-membered ring linked in a spiro fashion to a three-membered ring are examined in spiro[2.5]octane (**1**), dispiro[2.2.2.2]decane (**2**), and 6-methylenespiro[2.5]octane (**3**). In contrast to the *exo*-methylene group, the spirocyclopropyl substituent has little effect on the barrier to ring reversal, and brings about only a slight flattening of the ring. It is concluded that the spiro linkage alters the hybridization of the orbitals of the quaternary carbon in comparison to those in unsubstituted cyclopropane. The free energies of activation to ring reversal were found to be 10.5 kcal/mol for **1**, 10.9 for **2**, and 8.7 for **3**. A complete line-shape analysis for the spectral changes of **2** gave E_a = 12.1 kcal/mol and log A = 13.8. The R values for **2** and **3** were measured to be 2.01 and 1.73, respectively.

Both the static and the dynamic conformational properties of a six-membered ring are considerably altered by the introduction of an *exo*-methylene or oxo grouping. The substituted carbon atom becomes nearly sp^2 hybridized, so that the valence angle within the ring is expanded over that in cyclohexane. A structural alteration of this type gives rise to a flattening distortion in the ring[2] and a diminished barrier to ring reversal.[3] The magnitude of the directly bonded ^{13}C–H coupling constant indicates that the hybridization of orbitals emanating from a cyclopropyl ring is similar to that from an ethylenic source. We therefore wished to investigate the effect of a spiro linkage between a six- and a three-membered ring on the shape

---

[1] (a) This work was supported by the National Science Foundation (Grant GP-22942) and by the Petroleum Research Fund, administered by the American Chemical Society (Grant 2970-AC4,5). (b) NDEA Fellow, 1966–1969; National Science Foundation Trainee, 1969–1970.

[2] J. B. Lambert, *J. Amer. Chem. Soc.*, **89**, 1836 (1967); J. B. Lambert, *Accounts Chem. Res.*, **4**, 87 (1971).

[3] J. T. Gerig and R. A. Rimerman, *J. Amer. Chem. Soc.*, **92**, 1219 (1970); F. R. Jensen and B. H. Beck, *ibid.*, **90**, 1066 (1968).