Anal. Calcd for $C_{16}H_{19}ClN_4O_7$: C, 46.33; H, 4.62; Cl, 8.58; N, 13.51. Found: C, 46.01; H, 4.82; Cl, 8.73; N, 13.27.

Reaction of Adduct 3 with Sodium Methoxide.—Allene **3** (7.41 g, 40.1 mmol) was added to a solution prepared from 1.80 g (78.3 mg-atoms) of sodium in 60 ml of methanol; the mixture was held at reflux 17 hr. The mixture was flooded with water and extracted with ether. The ether extracts were washed with 0.5 *N* sulfuric acid, dried, and evaporated to leave 2.79 g of crude product. Distillation gave 2.48 g (34%) of **7**: bp 78–79° (0.1 mm); uv (heptane) λ_{max} 222 nm (ϵ 5800);[6] uv (5 *M* H_2SO_4) λ_{max} 266 nm (ϵ 3900);[7,10] nmr δ 6.3 and 5.8 (m, pattern analogous to that of 1-*n*-propyl-3-methyl pyrrole[11]), 3.68 (t, J = 6.5 Hz, NCH_2), 3.27 (t, J = 6.5 Hz, OCH_2), 3.22 (s, OCH_3), 2.03 (s, ring CH_3), and 1.8–1.1 ppm (m, $-(CH_2)_3-$); nmr (H_2SO_4) consistent with protonation at the 2 position[7] δ 8.52 (br s, C^5 H), 6.71 (br s, C^4 H), 4.80 (br s, C^2 H_2), 4.35 (t, $J \sim 7$ Hz, $=\overset{+}{N}CH_2$), 4.05 (s, OCH_3), 4.02 (t, $J \sim 7$ Hz, OCH_2), 2.40 (br s, ring CH_3), and 2.35–1.0 ppm (br m, $-(CH_2)_3-$); mass spectrum (70 eV) *m/e* (rel intensity) 181 (85), 166 (60), 95 (100), and 94 (75).[12]

Addition of *N*-Chloropiperidine to 1-Penten-3-yne (2).—Reaction of 14.6 g (0.122 mol) of the crude chloramine and 8.0 g (0.121 mol) of enyne **2** gave, after the usual work-up, 0.32 g of neutral product and 14.0 g of basic product. Distillation of the latter gave several arbitrary fractions, bp 83–110° (0.5 mm), totalling 9.14 g. The first (0.2 g) had spectral properties consistent with adduct **4**: ir 1965 cm^{-1} (C=C=C); nmr δ 5.4 (m, CH=), 2.98 (d, J = 6.5 Hz, NCH_2), 2.4 (m, CH_2NCH_2), 2.08 (d, J = 2.5 Hz, $=CClCH_3$), and 1.5 ppm (m, $-(CH_2)_3-$); the nmr spectrum suggested ~85% purity. The final fraction (4.0 g) had an nmr spectrum consistent with bisamine **5**: δ 3.35 (m, area 1, NCHC≡), 2.24 (m, area 10, NCH_2), 1.82 (d, J = 2 Hz, area 3, $\equiv CCH_3$), and 1.5 ppm (m, area 12, $-(CH_2)_3-$). The nmr spectra of intermediate fractions showed a singlet at δ 2.00 (ir 1740 cm^{-1}, CH_3CO_2, ?), a cluster of bands at δ 1.8 ($\equiv CCH_3$ in a family of similar compounds, ?), and at least two broad multiplets at δ 3.9 and 4.2 ppm (CHXC≡, ?).

A parallel reaction was carried out with 17.9 g (0.15 mol) of the chloramine and 11.2 g (0.17 mol) of **2**. After reaction was complete, piperidine (12.75 g, 0.15 mol) was added with cooling; work-up gave 0.28 g of neutral product and 25.9 g of basic product. Distillation gave, after removal of piperidine at ~20 mm, (1) 1.7 g, bp 58–59° (0.05 mm), (2) 1.5 g, bp 70–95° (0.05 mm), and (3) 14.5 g, bp 95–102° (0.05 mm), $n^{22}D$ 1.5040. The nmr spectrum of 1 showed it to contain ~60% (6% yield) adduct **4** plus several minor components. Treatment of 0.31 g of 1 with picric acid in ethanol gave, after addition of water, 0.42 g of picrate, mp 129–133°; two crystallizations from ethanol–water gave 0.26 g, mp 139–140°.

Anal. Calcd for $C_{16}H_{19}ClN_4O_7$: C, 46.33; H, 4.62; Cl, 8.58; N, 13.51. Found: C, 45.84; H, 4.75; Cl, 9.01; N, 13.39.

The nmr spectrum of **3** showed it to be pure **5**. A very insoluble bispicrate formed in 97% yield and could be crystallized from a large volume of ethanol, mp 200° dec.

Anal. Calcd for $C_{27}H_{32}N_8O_{14}$: C, 46.82; H, 4.66; N, 16.18. Found: C, 46.55; H, 5.05; N, 15.75.

Addition of *N*-Chloropiperidine to Vinylacetylene.—Reaction between 13.7 g (0.11 mol) of the crude chloramine and 6.4 g (0.12 mol) of vinylacetylene, introduced as a gas in a stream of nitrogen into the reaction solution topped by a Dry Ice filled condenser, gave 1.2 g of neutral product and 5.8 g of basic product which quickly became deeply colored. Short-path distillation gave only 0.9 g, bp 68–71° (0.3 mm). The nmr spectrum showed the following reasonable bands for 1-chloro-4-piperidino-1,2-butadiene but they accounted for only 65% of the integrated area: δ 6.2–5.4 (m, CH=C=CHCl), 3.05 (d, d, J = 7 and 2 Hz, NCH_2), 2.4 (m, CH_2NCH_2), and 1.5 ppm (m, $-(CH_2)_3-$). The nmr spectrum of the original basic residue suggested that it was at least 50% this same product, but purification could not be achieved.

Registry No.—**3**, 30344-85-5; **3** picrate, 30344-86-6; **4**, 30344-87-7; **4** picrate, 30344-88-8; **5**, 30344-89-9; **5** picrate, 30344-90-2; **7**, 30344-91-3; 1-chloro-4-piperidino-1,2-butadiene, 30344-92-4; *N*-chloropiperidine, 2156-71-0.

(10) The group shifts in ref 7 predict λ_{max} 263 nm for an α-protonated 1,3-dialkylpyrrole.

(11) F. Y. Perveev, V. Y. Statsevich, and L. P. Gavryuchenkova, *J. Org. Chem. USSR*, **2**, 395 (1966).

(12) See A. M. Duffield, R. Beugelmans, H. Budzikiewicz, D. A. Lightner, D. H. Williams, and C. Djerassi, *J. Amer. Chem. Soc.*, **87**, 805 (1965), for discussion of the analogous *m/e* 81 and 80 in *N*-*n*-alkylpyrroles.

The Conversion of Vicinal Nitro Nitrates to Nitroalkanes with Sodium Borohydride

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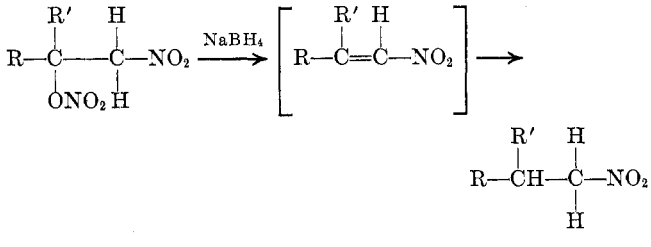
Received January 25, 1971

Available literature procedures for the conversion of 1-alkenes to terminal nitroalkanes[1-3] have certain limitations. The operation consists of first converting the olefin to dinitroalkanes, nitro alcohols, nitro nitrites, or mixtures of these compounds, treating the latter with base to form nitro olefins, and then catalytically hydrogenating the nitro olefins to nitroalkanes. The disadvantages are that (a) two separate steps are involved in converting the substituted nitro compounds to nitroalkanes, (b) nitro olefins often dimerize[4] or polymerize,[5] (c) catalytic reductions are sometimes inconvenient on a laboratory scale, and (d) care must be exercised that the nitro paraffins are not further reduced to amines in the last step.

The sodium borohydride reduction of β-nitro nitrates provides a route to nitroalkanes free from these disadvantages. 1-Nitro-2-alkyl nitrates are readily obtained in high yield from 1-alkenes, nitrogen oxides, and oxygen.[6] The sodium borohydride reduction step requires only simple mixing of reactants in ordinary glassware at room temperature. Sodium borohydride has been employed previously in the preparation of nitroalkanes from α-nitro ketones[7] and β-nitro hydroxy and chloro compounds.[8] The reaction presumably proceeds *via* the nitroalkene intermediate resulting from base-induced nitric acid elimination.



Rapid reduction of the nitroalkene intermediate apparently precludes side reactions such as dimerization and polymerization. By contrast, in the reduction of

(1) G. A. Bonetti, J. J. Gavigan, H. O. Hansen, and R. Rosenthal, U. S. Patent 3,240,823 (March 15, 1966).

(2) C. Michalski and G. A. Bonetti, U. S. Patent 3,297,769, (Jan 10, 1967).

(3) W. K. Seifert and L. L. Ferstandig, U. S. Patent 3,035,101 (May 15, 1962); W. K. Seifert, *J. Org. Chem.*, **28**, 265 (1963).

(4) A. I. Meyers and J. C. Sicar, *ibid.*, **32**, 4134 (1967).

(5) G. D. Buckley and C. W. Scaife, *J. Chem. Soc.*, 1471 (1947).

(6) (a) D. R. Lachowicz and K. L. Kreuz, U. S. Patent 3,282,983 (Nov 1, 1966). (b) D. R. Lachowicz, J. M. Larkin, and K. L. Kreuz, unpublished results; a less suitable procedure is described in the earlier work of N. Levy, C. W. Scaife, and A. E. Wilder-Smith, *J. Chem. Soc.*, 52 (1948).

(7) A. Hassner, J. M. Larkin, and J. E. Dowd, *J. Org. Chem.*, **33**, 1733 (1968).

(8) A. Hassner and C. H. Heathcock, *ibid.*, **29**, 1350 (1964).

nitroalkenes with $NaBH_4$, the maintenance of acidic conditions is necessary to prevent dimerization.[4]

By using the sodium borohydride procedure, the nitro nitrates listed in Table I were converted to the

TABLE I
REACTION OF VICINAL NITRO NITRATES (NN) WITH SODIUM BOROHYDRIDE

Nitro nitrate	Product	Reaction time, hr	Mol of $NaBH_4$/mol of NN	Yield, %
1-Nitro-2-octyl nitrate	1-Nitrooctane (1)	19	3.3	94
4-Methyl-1-nitro-2-pentyl nitrate	1-Nitro-4-methylpentane (2)	24	3.2	72
1-Nitro-2,4,4-trimethyl-2-pentyl nitrate	1-Nitro-2,4,4-trimethylpentane (3)	60	3.6	83
3-Nitro-2,4,4-trimethyl-2-pentyl nitrate	No reaction	41	4.3	0
1-Nitro-2-tetradecyl nitrate	1-Nitrotetradecane (4)	25	3.9	58

corresponding saturated nitro compound. The yields given are based on a single run only, and so are probably not optimal.

The nitroalkanes **1**, **2**, and **4** have ir and nmr spectra like those previously recorded[4] (ir absorption at 6.45 and 7.25 μ; nmr triplets at δ 4.35–4.37). 1-Nitro-2,4,4-trimethylpentane (**3**) gives an ABX pattern at δ 4.21 for the protons adjacent to the nitro group and a complex multiplet at δ 2.38 for the tertiary proton.

Only starting material was obtained from the reaction of 3-nitro-2,4,4-trimethyl-2-pentyl nitrate with sodium borohydride. The steric hindrance of the nitro olefin derived from this internal nitro nitrate may be too great to permit its formation.

Experimental Section

The nitro nitrates were prepared as previously described.[6] Ir spectra were recorded on a Perkin–Elmer Model 137 spectrophotometer and nmr spectra were obtained on a Varian Associates Model V-4311 spectrometer operating at 60 Mc.

1-Nitro-2,4,4-trimethylpentane (3). General Procedure.—Sodium borohydride (1.25 g) was slowly added to a solution of 2.00 g of 1-nitro-2,4,4-trimethyl-2-pentyl nitrate in 50 ml of 95% ethanol. The mixture was stirred briefly at room temperature and allowed to stand for 2.5 days. It was diluted with H_2O (100 ml), acidified with 1.2 *N* HCl, and extracted with ether. The extract was washed (NaCl solution), dried ($MgSO_4$), and evaporated. 1-Nitro-2,4,4-trimethylpentane (**3**) (1.20 g, 83%) remained as a pale yellow liquid. The ir spectrum is nearly identical with that of an analytical sample prepared by chromatography on silica gel using mixtures of methylene chloride and hexane as eluents, $n^{20}D$ 1.4317. *Anal.* Calcd for $C_8H_{17}NO_2$: C, 60.3; H, 10.8; N, 8.8. Found: C, 60.2; H, 10.7; N, 8.8.

Nitroalkanes **1**, **2**, and **4**, all colorless liquids, were prepared similarly using the conditions stated in Table I.

Registry No.—**1**, 629-37-8; **2**, 14424-33-0; **3**, 30344-80-0; **4**, 4609-87-4; sodium borohydride, 16940-66-2.

Acknowledgments.—We wish to thank Mr. Lewis P. Larson and Mr. George A. Taylor for recording the nmr spectra and Mr. Paul J. McMahon for technical assistance.

Photolysis of Penta-*O*-acetyl-*aldehydo*-D-glucose[1]

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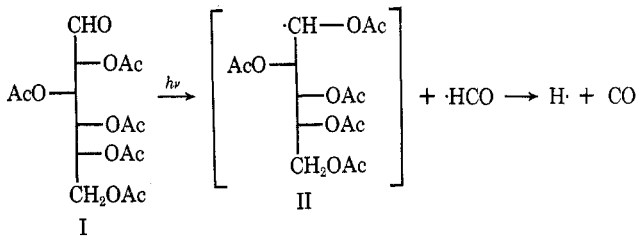
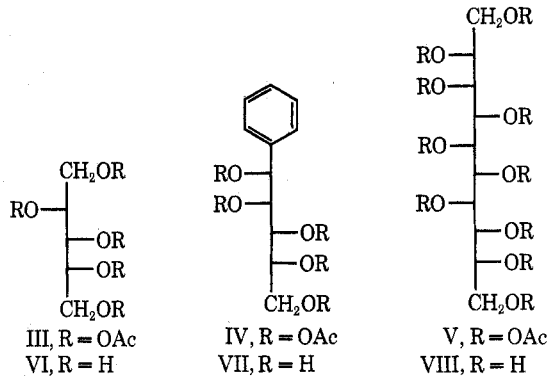
Received February 12, 1971

Although photodecarbonylation of aliphatic aldehydes occurs readily in the vapor phase,[2,3] elimination of carbon monoxide is almost entirely suppressed in solution at 25°. At temperatures above 100°, however, decarbonylation has been observed with quantum efficiency.[4]

It is interesting to observe, therefore, that when a benzene solution of *aldehydo*-D-glucose pentaacetate (I) is irradiated with ultraviolet light at 10–15°, it produces three major crystalline photoproducts, all of which are derived by way of radical II, realized through α-bond cleavage. Compounds III, IV, and V are formed in 16, 2.5, and 1% yield, respectively. At 60° the starting material is consumed in 6 hr as compared to 70 hr at 10–15° and the yields of III, IV, and V increase to 17.5, 6, and 2%, respectively. The small increase in yields might be due to the loss of radical II





through secondary reactions which may also be temperature dependent. The formation of III is, as with aliphatic aldehydes, most prominent and is formed by α-bond fission producing carbon monoxide and a five-carbon radical that combines with a hydrogen atom to produce D-arabinitol pentaacetate, identified by comparison of mixture melting point and ir and nmr spectra with an authentic sample.[5] The nmr spectrum of photoproduct IV gives, in addition to the charac-

(1) This work was presented in part before the 161st Meeting of the American Chemical Society, Los Angeles, Calif., March 1971; Journal Paper No. 4338 of the Purdue Agricultural Experiment Station, Lafayette, Ind. 47907.

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(4) C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1544 (1938).

(5) C. S. Hudson, *J. Amer. Chem. Soc.*, **57**, 1753 (1935).