methyl)tetrahydropyran, 18420-41-2; cyclohexenyl trifluoroethyl ether, 85355-26-6; hex-5-yn-1-yl tetrahydropyranyl ether, 1720-37-2; hex-4-yn-1-yl trifluoroethyl ether, 85355-27-7; 5-chloro-1-pentanol, 5259-98-3; 5-chloropentyl acetate, 20395-28-2; 5-chloropentyl tetrahydropyranyl ether, 13129-60-7; dihydropyran, 110-87-2; hept-1-yn-1-ol, 63478-76-2; sodium acetylide, 2881-62-1; cycloheptanone, 502-42-1; hept-6-yn-1-yl trifluoroethyl ether, 85355-28-8; cycloheptenyl trifluoroethyl ether, 85355-29-9; 1,2-dibromo-5-hexene, 4285-48-7; hex-4-yn-1-yl tetrahydropyranyl ether, 85355-30-2; hex-4-yn-1-ol, 928-93-8; 2-methylcyclohexenyl trimethylsilyl ether, 19980-35-9.

1-Benzyl-1,4-dihydronicotinamide as a Reagent for Replacing Aliphatic Nitro Groups by Hydrogen. An Electron-Transfer Chain Reaction[1]

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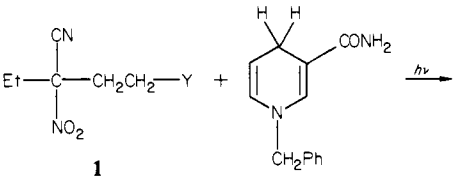
Abstract: The reaction of α-nitro nitriles, α-nitro esters, and α-nitro ketones with 1-benzyl-1,4-dihydronicotinamide (BNAH) can occur with selective replacement of the nitro group by hydrogen without affecting other functional groups. Evidence is presented to support the claim that the reaction proceeds via an electron-transfer chain mechanism in which radical anions and free radicals are intermediates.

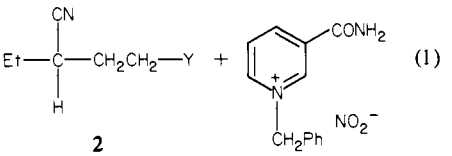
1-Benzyl-1,4-dihydronicotinamide (BNAH) is of interest as a model of the biochemistry important reduced nicotinamide–adenine dinucleotide phosphate [NAD(P)H] and, also, because it has been shown to reduce a very wide variety of organic compounds.[2] Most of these reductions are believed to proceed by a direct hydride-transfer mechanism,[3] but recently some reductions have been proposed which proceed via electron-transfer mechanism[4] (transfer of an electron and a hydrogen, or transfer of two electrons and a proton in three steps). We now present a new reaction of BNAH: the replacement of an aliphatic nitro group by hydrogen, which proceeds as an electron-transfer chain reaction. Reduction of organic nitro compounds with BNAH was first reported in 1962 by Dittmer and Kolyer.[5] Since then there have been no reports concerning the reduction of nitro compounds by 1,4-dihydropyridines. Recent interest in the electron-transfer reaction of nitro compounds[6] and in the mechanism of the reduction by 1,4-dihydropyridines led us to study the reaction of aliphatic nitro compounds with BNAH.[1]

Results and Discussion

Simple nitroalkanes such as *tert*-nitrobutane or 2-nitropropane cannot be reduced by BNAH as reported previously.[5] However, nitro compounds substituted with a cyano, carboalkoxy, or keto group at the α position were reduced by BNAH to the corresponding denitrated compounds. For example, the reaction of 3-cyano-3-nitroheptan-6-one (**1a**) with BNAH proceeded smoothly under irradiation of a 150-W tungsten lamp to give 3-cyanoheptan-2-one (**2a**) in 60% isolated yield; the pyridinium salt was isolated in 58% yield. In the dark, the starting material (**1a**) was recovered completely unchanged. Results of the conversion of α-nitro nitriles (**1**) to the denitrated compounds (**2**) are summarized in Table III of the Experimental Section.



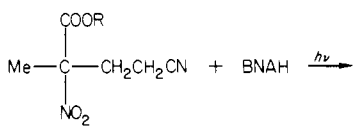
1



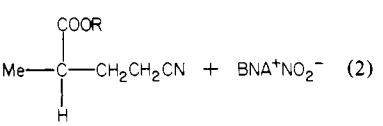
2 (1)

Y = C(=O)Me, COOMe, CN

In the same way, the nitro group of α-nitro esters (**3**) was replaced by hydrogen under irradiation of a 150-W tungsten lamp (eq 2). The methyl ester (**3**) was reduced readily in benzene to



3



4 (2)

R = Me, Et, Me_2CH

(1) Abstracted from the Ph.D. dissertation of R. T. Kyoto, 1980. Preliminary communication: N. Ono, R. Tamura, and A. Kaji, *J. Am. Chem. Soc.*, **102**, 2851 (1980).

(2) Various unsaturated compounds such as C=O, C=S, or $C=N^+$ are reduced by BNAH or related compounds, which is well documented in D. M. Stout and A. T. Meyers, *Chem. Rev.*, **82**, 223 (1982).

(3) (a) H. Sund in "Biological Oxidation", T. P. Singer, Ed., Wiley-Interscience, New York, 1968, pp 621–624; (b) D. J. Creigton and D. S. Sigman, *J. Am. Chem. Soc.*, **93**, 6314 (1971); (c) D S Sigman, J. Hadiu, and D. J. Creigton, *Bioorg. Chem.*, **4**, 385 (1978); (d) I. MacInnes, D. C. Nonhebel, S. T. Orszulik, and C. J. Sukling, *J. Chem. Soc., Chem. Commun.*, 121 (1982); (e) J. W. Bunting and S. Sindhuatmadia, *J. Org. Chem.*, **46**, 4211 (1981); J. M. Bunting, V. S. F. *Chew*, and G. Chu, *ibid.* **47**, 2303 (1982).

(4) (a) A. Ohno and N. Kito, *Chem. Lett.*, 369 (1972); (b) T. Okamoto, A. Ohno, and S. Oka, *J. Chem. Soc., Chem. Commun.*, 300 (1978); (c) A. Ohno, H. Yamamoto, and S. Oka, *J. Am. Chem. Soc.*, **103**, 2041 (1981); (d) A. Ohno, T. Shio, H. Yamamoto, and S. Oka, *ibid.* **103**, 2045 (1981); (e) S. Sinkai, T. Tsuno, and O. Manabe, *J. Chem. Soc., Chem. Commun.* 592 (1982); (f) T. Endo and M. Okawara, *J. Org. Chem.*, **45**, 2663 (1980); (g) R. J. Kill and D. A. Widdowson, *Bioorg. Chem.*, **4**, 239 (1978). Considerable confusion still exists in the reduction mechanism by 1,4-dihydropyridine derivatives. For example, the reduction of isoquinolinium cations is claimed to proceed via one-step hydride transfer mechanism;[3e] on the other hand, the reduction of *N*-methylacridinum cation is claimed to proceed via an electron–proton–electron transfer mechanism[4d] Both conclusions are derived from the same experiments: kinetic isotope effect and substituent effect.

(5) D. C. Dittmer and J. M. Kolyer, *J. Org. Chem.*, **27**, 56 (1962).

(6) (a) N. Kornblum, *Angew. Chem., Int. Ed. Engl.*, **14**, 734 (1975); (b) N. Kornblum, S. D. Boyd, and F. W. Stuchal, *J. Am. Chem. Soc.*, **92**, 5783 (1980); (c) N. Kornblum and A. S. Erickson, *J. Org. Chem.*, **46**, 1037 (1981); (d) G. A. Russel, B. Mudryk, H. Jawdosiuk, and Z. wrobal, *ibid.*, **47**, 1879 (1982); (e) N. Ono, R. Tamura, T. Nakatsuka, J. Hayami, and A. Kaji, *Bull. Chem. Soc. Jpn.*, **53**, 3295 (1980); (f) R. K. Norris and R. J. Symth-King, *Tetrahedron*, 1051 (1982).

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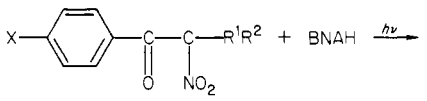
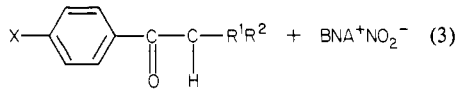
give **4** in 71% yield, but the ethyl and isopropyl esters were not so readily reduced in benzene. However, they were reduced in HMPA to give **4** in 60% yields. Results are summarized in Table IV of the Experimental Section.

The reaction of a series of α-nitro ketones (**5**) with BNAH also proceed smoothly with replacement of the nitro group in 45–91% yields (eq 3). Results are summarized in Table V of the Experimental Section. The general order of reactivity based on yields of the denitrated compounds (**6**) is tertiary nitro > secondary nitro > primary nitro compounds; for the parasubstituents in the aromatic ring, Cl > H, Me, MeO. However, the *p*-nitro group inhibited the reaction as will be discussed later.



5

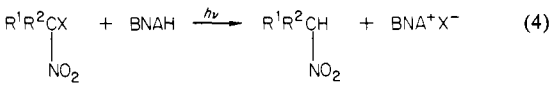


(3)

6

X = H, Cl, Me, MeO, NO_2; R^1,R^2 = Me or H

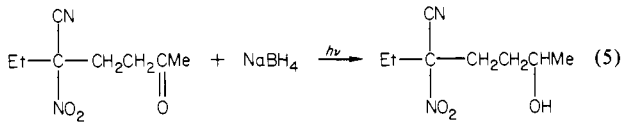
When bromo or sulfonyl groups are substituted at the α position to the nitro group, the reduction by BNAH takes a different course to give the debrominated or the desulfonated products rather than replacing the nitro group by hydrogen (eq 4).[7,8]



(4)

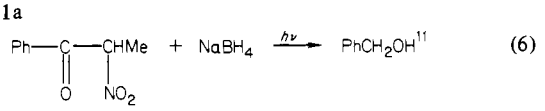
X = Br, $ArSO_2$; R^1,R^2 = alkyl groups or hydrogen

Although 1,4-dihydronicotinamide can reduce various organic compounds,[1-4] most of them are reduced more conveniently by metal hydrides such as sodium borohydride. However, compounds **1**, **3**, and **5** were not converted to **2**, **4**, and **6**, respectively, by sodium borohydride. Instead, the reduction of **1a** by sodium borohydride gave the alcohol as in eq 5. α-Nitro ketones are generally reduced to the corresponding β-nitro alcohols by sodium borohydride in protic solvents.[9] Reduction of **5c** by sodium borohydride was carried out under the same conditions as the reduction by BNAH to give benzyl alcohol (eq 6). Thus, BNAH selectively replaces the nitro group by hydrogen without affecting other functions, while it selectively reduces the borohydride reducible group (e.g., keto) without affecting the nitro group. This is not the first example of the superiority of 1,4-dihydropyridine derivatives over metal hydrides. Recently, BNAH has been demonstrated to be a more useful reagent for the reduction of α-nitro sulfones,[8] RHgX and RTlX.[10]



(5)

1a



(6)

5c

(7) R. J. Kill and D. A. Widdowson, *J. Chem. Soc., Chem. Commun.*, 755 (1976).

(8) (a) N. Ono, R. Tamura, R. Tanikaga, and A. Kaji, *J. Chem. Soc., Chem. Commun.*, 71 (1981); (b) P. A. Wade, H. R. Hinney, N. V. Amin, P. O. Vail, S. D. Morrow, S. A. Hardinger, and M. S. Saft, *J. Org. Chem.*, **46**, 765 (1981).

(9) P. Dampawan and W. W. Zajac, Jr., *Tetrahedron Lett.*, 135 (1982) and references therein.

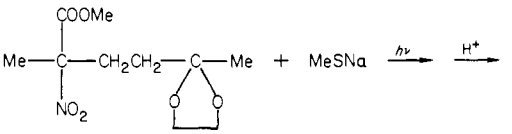
(10) (a) H. Kurosawa, H. Okada, and M. Yasuda, *Tetrahedron Lett.*, 959 (1980); (b) H. Kurosawa, H. Okada, and M. Yasuda, *ibid.*, 4495 (1981).

Table I. Effect of *m*-Dinitrobenzene and Di-*tert*-butyl Nitroxide on Reactions 1 and 3

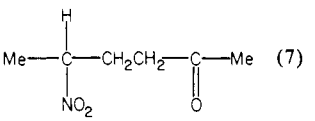
compd	inhibitor (mol %)	time, h	product: yield, %[a]
1a	none	6	2a, 85
1a	m-DNB (10)	6	2a, 0
1a	DTBN (20)	6	2a, 0
1a	none	17	2a, 90
1a	m-DNB (10)	17	2a, 13
1a	DTBN (20)	17	2a, 81
5a	none	14	6a, 57
5a	m-DNB (10)	14	6a, 0
5a	DTBN (20)	14	6a, 29

[a] Yields were determined by GLC with an internal standard.

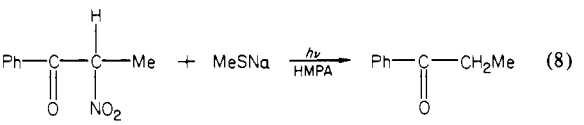
Three other methods for replacing a nitro group by hydrogen have recently been described: the use of the sodium salt of methyl mercaptan at 25 °C,[12] treatment with KOH in ethylene glycol at 120–140 °C,[13] and the use of tributyltin hydride in the presence of free-radical initiators.[14] Although the present reaction requires the presence of a cyano, carboalkoxy, or keto group on the carbon undergoing substitution, it appears that in some cases it may prove to be of special value as discussed below. Attempts to replace the nitro group of **1a** by hydrogen using MeSNa yielded no product.[15] When compound **7**, where the carbonyl group is protected as an acetal to prevent a retro-Michael reaction, was treated with MeSNa, the result was clean demethoxycarbonylation in 75% yield and no replacement of the nitro group by hydrogen (eq 7). The reduction of **5c** by MeSNa gave **6c** in only poor yield (eq 8) and 80% of the starting **5c** was recovered.[16]



7



(7)



(8)

5c **6c**, 16%

The use of KOH is thought to be unsuitable for the reduction of **5**, for α-nitro ketones are generally labile to basic conditions to cause the cleavage of the carbon–carbon bonds.[17] In fact, treatment of **5a** with KOH in ethylene glycol at 120 °C did not give **6c** at all, but gave benzoic acid in good yield. Tributyltin hydride can replace the nitro group of compounds **1**, **3**, and **5** by hydrogen,[14b] but BNAH is a rather more selective reagent. For

(11) β-Nitro alcohol was not obtained in this reaction. Benzyl alcohol may be obtained by the similar reaction as reduction of benzoyl chloride with sodium borohydride; namely, nitroethane serves as a leaving group here.

(12) N. Kornblum, S. C. Carlson, and R. G. Smith, *J. Am. Chem. Soc.*, **101**, 647 (1979).

(13) A. L. Krasuska, H. Piotrowska, and T. Urbanski, *Tetrahedron Lett.*, 1243 (1979).

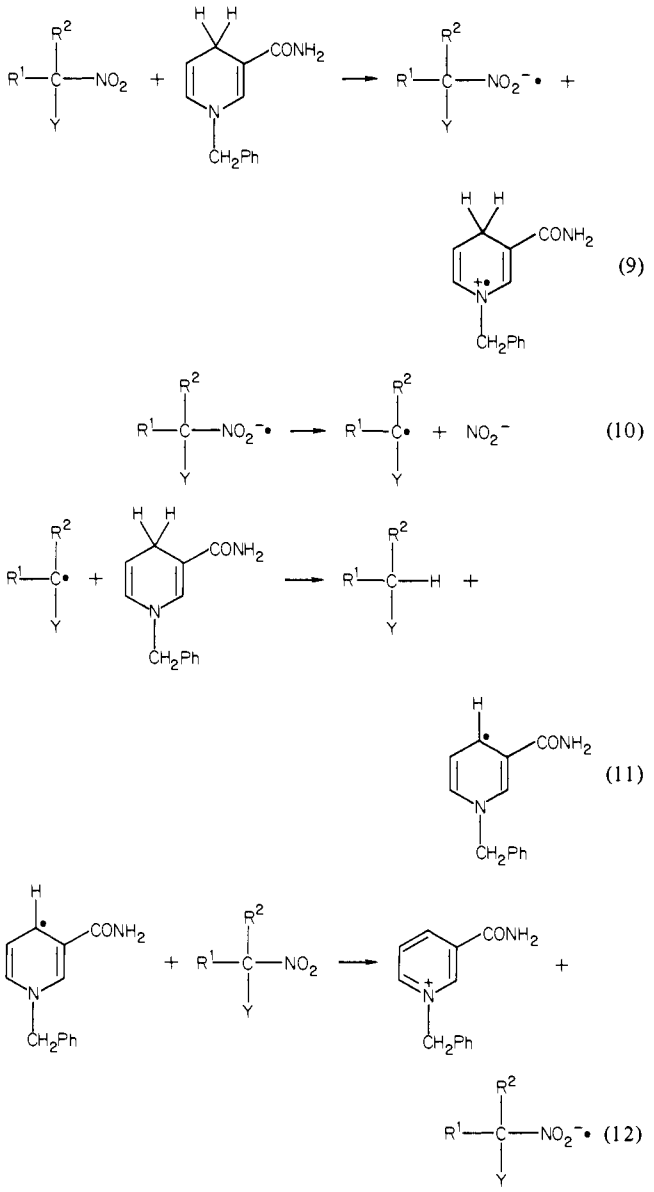
(14) (a) D. D. Tanner, E. V. Blackburn, adn G. E. Diaz, *J. Am. Chem. Soc.*, **103**, 1557 (1981); (b) N. Ono, H. Miyake, R. Tamura, and A. Kaji, *Tetrahedron Lett.*, 1705 (1981).

(15) This may be a consequence of a reverse Michael reaction.

(16) One of referee points out that low reactivity of **5c** to CH_3SNa may be due to the existence of an acidic hydrogen. Therefore, the reaction of **5a**, which had no acidic hydrogens, with CH_3SNa was carried out in HMPA, but again **6c** was formed in low yield and methyl thiobenzoate was obtained mainly. This difference in reactivity of **5a** and **5c** is unclear, but the anion of nitroethane may be acylated by methyl thiobenzoate to give **5c**, and acylation of 2-nitropropane with methyl thiobenzoate may be difficult.

(17) R. H. Fischer and H. M. Weitz, *Synthesis*, 261 (1980).

Scheme I



example, tributyltin hydride reduces readily alkyl halides, while most alkyl halides are inert to BNAH.

Reduction Mechanism. The matter of mechanism is of special interest. Previous discussions of reductions by BNAH have focused on the ability of BNAH to act as a hydride-transfer agent.[3] We proposed here that BNAH replaces the nitro group by hydrogen via an electron-transfer chain mechanism (Scheme I) and present evidence in support of this novel mechanistic assignment.

To begin with, these reactions exhibit a strong light effect. They do not occur in the dark, but no exposure to a 150-W tungsten lamp they proceed readily at room temperature as shown in Tables III–V. Furthermore, these reactions are inhibited by di-*tert*-butyl nitroxide (DTBN) and *m*-dinitrobenzene (m-DNB). Table I summarizes the results of a set of experiments, where the reactions of eq 1 and 3 were allowed to proceed in the presence of various inhibitors.

The reaction of **1** with BNAH is completely inhibited for 6 h by the presence of 10 mol % of *m*-DNB; at the end of this time the reaction proceeds very slowly. In the absence of *m*-DNB the reaction is 85% completed in 6 h. In the same way, the presence of 20 mol % of DTBN completely stops the reaction for 6 h, after which time the reaction proceeds at the usual rate. Analogous results using 10 mol % of m-DNB and 20 mol % of DTBN were obtained for the reaction of **5a** with BNAH. Di-*tert*-butyl nitroxide is a free-radical inhibitor[6] and *m*-dinitrobenzene is generally

Table II. Effect of Initiations on the Reaction of 1a with BNAH[a]

BNAH, mol %	additive (mol %)	temp, °C	time, h	2a: yield, %[b]
300	none	25	24	0
0	$Na_2S_2O_4$ (300)	25	24	0
300	$Na_2S_2O_4$ (300)	25	24	65 (40)[c]
300	DTPO (8)	25	24	61 (40)[c]
300	none	80	3	10
300	AIBN (10)	80	3	50

[a] The reaction was carried out in the dark. [b] Yields were determined by GLC. [c] Isolated yields.

regarded as a scavenger for radical anions.[6] These facts strongly support our contention that the present reduction by BNAH is an electron-transfer chain process. Apropos of the inhibition by *m*-dinitrobenzene, failure of the reaction of **5g** (Table V) may reflect analogous inhibition associated with the presence of a *p*-nitro group.

In accord with the proposed mechanism the transformation of **1a** to **2a** (eq 1) is induced by electron donors and by free radicals. Thus, although there is no detectable reaction in DMF in the dark at room temperature after 24 h, in the presence of $Na_2S_2O_4$ (3 equiv) none of the nitro compound (**1a**) remains after 24 h in the dark at room temperature and a 40% yield of the pure product (**2a**) is isolated.[18] Furthermore, in the presence of 8 mol % of di-*tert*-butyl peroxyoxalate (DTPO),[19] the reaction of **1a** with BNAH proceeds in the dark at room temperature and a 40% yield of pure **2a** is isolated. Azobisisobutyronitrile (AIBN) also induces the reaction of **1a** with BNAH at 80 °C in the dark. Results are summarized in Table II. The use of free radidals to induce an electron-transfer chain process is especially noteworthy and should prove of wide applicability. Conceivably, the hydrogen which replaces the nitro group comes from a source other than BNAH. But this is ruled out by the following facts. The reaction of **1a** with BNAH in deuterated acetonitrile gave **2a**, in which deuterium was not incorporated. Furthermore, the reaction of **1a** with 1-benzyl-1,4-dihydronicotinamide-*4,4-d*$_2$ (D content is about 85%) gave **2a** whose D content is about 60%. Thre can then be little doubt that the hydrogen comes from BNAH.

It appears that reduction by 1,4-dihydropyridine derivatives via a one-electron-transfer mechanism such as is given by Scheme I may be of some generality.[20] A similar mechanism has been proposed for the reduction of α-bromo nitro compounds,[7] α-nitro sulfones,[8] sulfonium salts,[21] alkylmercury compounds,[10] or disulfides[22] by BNAH. Indeed, it is conceivable that substances which undergo the $S_{RN}1$ reaction may be reduced by 1,4-dihydropyridine derivatives via the chain mechanism proposed here.

Experimental Section

NMR spectra were recorded on JEOL PS-100 spectrometers; chemical shifts are expressed in part per million relative to Me_4Si. IR spectra were recorded on a Hitachi 215 spectrophotometer, and GLC analyses were performed on a Varian Aerograph 920 using a column containing silicon DC-500. GLC yields were determined by the internal standard method. GC–mass was measured on a Hitachi M-52 (22 eV). Elementary analyses were performed by the Kyoto University Microanalytical Laboratories.

(18) Sodium dithionite is known to be a one-electron transfer agent; for example, P. L. Kolker, and W. A. Waters, *J. Chem. Soc.*, 1136. (1964). It is not clear how much of added $Na_2S_2O_4$ is used to induce the reaction, for $Na_2S_2O_4$ is only slightly soluble in DMF. However, **1a** is not converted into **2a** on treatment with $Na_2S_2O_4$ in the absence of BNAH (see Table II).

(19) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Am. Chem. Soc.*, **82**, 1762 (1960).

(20) Analogous electron-transfer reactivity of aminocarboxy-substituted free radicals has been proposed in some cases; i.e., (a) M. Mohammed and E. M. Kosower, *J. Am. Chem. Soc.*, **93**, 2713 (1971); (b) B. H. J. Bielski and C. P. Chan, *ibid.*, **102**, 1713 (1980); (c) K. A. Reich, L. E. Marshall, D. R. Graham, and D. S. Sigman, *ibid.*, **102**, 1713 (1980); (d) J. M. Burns, D. L. Wharry, and T. H. Koch, *ibid.*, **103**, 849 (1981).

(21) T. J. van Bergen, D. M. Hedstrand, W. H. Kruizinga, and R. M. Kellog, *J. Org. Chem.*, **44**, 4953 (1979).

(22) S. Oae, T. Nagata, T. Yoshimura, and K. Fujimori, *Tetrahedron Lett.*, 3189 (1982).

Table III. Reduction of α-Nitro Nitriles (1) by BNAH

1	Y	solvent	time, h	light	product: yield, %[a]
1a	C(=O)Me	DMF	24	150 W-T[b]	2a, 93
1a	C(=O)Me	DMF	24	20 W-F[c]	2a, 51
1a	C(=O)Me	DMF	24	dark	2a, 0
1a	C(=O)Me	CH_3CN	24	150 W-T	2a, 92
1a	C(=O)Me	EtOH	24	150 W-T	2a, 90
1a	C(=O)Me	benzene	24	150 W-T	2a, 97 (60)[d]
1b	COOMe	benzene	24	150 W-T	2b, 90 (67)[d]
1c	CN	benzene	24	150 W-T	2c, 91 (61)[d]

[a] Yields were determined by GLC using an internal standard. [b] Tungsten lamp. [c] Fluorescent lamp. [d] Isolated yield.

Table IV. Reduction of α-Nitro Esters (3) by BNAH

3	R	solvent	time, h	light	product: yield, %[a]
3a	Me	benzene	24	150 W-T	4a, 96 (71)[b]
3a	Me	HMPA	12	150 W-T	4a, 86 (61)[b]
3a	Me	HMPA	12	dark	4a, 0
3b	Et	benzene	24	150 W-T	4b, 25
3b	Et	HMPA	12	150 W-T	4b, 80 (61)[b]
3c	Me_2CH	benzene	24	150 W-T	4c, 23
3c	Me_2CH	HMPA	12	150 W-T	4c, 90 (62)[b]

[a] Yields were determined by GLC. [b] Isolated yields.

Materials. Reagent grade solvents were purified by distillation and kept over drying agent (molecular sieves 3A and 4A). 1-Benzyl-1,4-dihydronicotinamide (BNAH)[23] and BNAH-*4,4-d*$_2$[24] were prepared according to literature procedures.

α-Nitro nitriles (**1**) were prepared by the Michael addition of 2-nitrobutyronitrile[25] to methyl vinyl ketones, methyl acrylate, or acrylonitrile; **1a**, **1b**, or **1c** were obtained, respectively. A typical procedure, preparation of **1a**, follows. A solution of 2-nitrobutyronitrile (11.4 g, 0.1 mol) and methyl vinyl ketone (8.5 g, 0.12 mol) in THF (100 mL) was cooled to 0 °C and triethylamine (1.0 g) was added to this solution. The resulting solution was stirred at 0 °C for 1 h and then allowed to stand for 24 h at room temperature. The reaction mixture was poured into water and extracted with ether. The ether layer was dried over anhydrous magnesium sulfate. Removal of the solvent followed by distillation gave **1a**, 13.8 g (75% yield), bp 144.5–148 °C (7 mm Hg): IR (neat) 1720, 1560, 1360 cm^{-1}; NMR (CCl_4) δ 1.14 (t, 3 H), 2.18 (s, 3 H), 2.25–2.93 (m, 6 H). Anal. Calcd for $C_8H_{12}N_2O_3$: C, 52.16; H, 6.57; N, 15.21. Found: C, 52.40; H, 6.68; N, 15.37.

1b: 72% yield; bp 109 °C (0.9 mmHg); IR (neat) 1740, 1560, 1360 cm^{-1}; NMR (CCl_4) δ 1.16 (t, 3 H), 2.0–2.7 (m, 6 H), 3.63 (s, 3 H).

1c: 68% yield; bp 110 °C (0.8 mmHg); IR (neat) 2250, 1560, 1340 cm^{-1}; NMR (CCl_4) δ 1.15 (t, 3 H), 2.2–2.7 (m, 6 H).

4-Carboalkoxy-4-nitropentanenitrile (**3**) was prepared by the Michael reaction of methyl 2-nitropropionate, ethyl 2-nitropropionate, and isopropyl 2-nitropropionate with acrylonitrile; thus, **3a**, **3b**, and **3c** were obtained, respectively. A typical procedure, preparation of **3a**, follows. Tetramethylguanidine (1.0 g) was added to a cooled solution of methyl 2-nitropropionate (27.1 g, 0.2 mol) and acrylonitrile (15.9 g, 0.3 mol) in THF (100 mL) at 0 °C. The resulting solution was stirred at room temperature for 24 h and worked up in the same way of the preparation of **1a**. Distillation gave **3a**, 31.6 g (85% yield), bp 118 °C (1 mmHg): IR (neat) 2250, 1750, 1550, 1350 cm^{-1}; NMR (CCl_4) δ 1.83 (s, 3 H), 2.48 (m, 4 H), 3.81 (s, 3 H). Anal. Calcd for $C_7H_{10}N_2O_4$: C, 45.16; H, 5.41; N, 15.05. Found; C, 45.45; H, 5.22, N, 14.97.

3b: 88% yield; bp 120 °C (1 mmHg); IR (neat) 2250, 1750, 1550, 1350 cm^{-1}; NMR (CCl_4) δ 1.32 (t, 3 H), 1.80 (s, 3 H), 2.47 (7, 4 H), 4.22 (q, 2 H). Anal. Calcd for $C_8H_{12}N_2O_4$: C, 48.00; H, 6.04; 13.99. Found: C, 48.26; H, 6.05; N, 13.93.

3c: 87% yield; bp 124 °C (1 mmHg); IR (neat) 2250, 1740, 1550, 1360 cm^{-1}; NMR (CCl_4) δ 1.28 (d, 6 H), 1.79 (s, 3 H), 2.5 (m, 4 H), 5.06 (m, 1 H). Anal. Calcd. for $C_9H_{14}N_2O_4$: C, 50.46; H, 6.59; N, 13.08. Found: C, 50.28; H, 6.68; N, 13.22.

α-Nitro ketones (**5**) were prepared by the oxidation of the corresponding β-nitro alcohols with sodium dichromate.[26] A typical procedure, preparation of **5a**, follows. Concentrated sulfuric acid (5.1 mL) was added to a stirred mixture of 1-phenyl-2-methyl-2-nitropropanol (10.1 g, 0.052 mol) and sodium dichromate (15.4 g, 0.052 mol) in water (10 mL) at 0 °C. The resulting mixture was stirred at room temperature for 24 h, poured into water, and then extracted with benzene. The benzene layer was dried over anhydrous magnesium sulfate. Removal of the solvent followed by distillation gave α-nitroisobutyrophenone (**5a**), 5.6 g (60% yield), bp 160 °C (20 mmHg): IR (neat) 1700, 1550, 1365 cm^{-1}; NMR ($CDCl_3$) δ 1.86 (s, 6 H), 7.3 (m, 3 H), 7.6 (m, 3 H). Anal. Calcd for $C_{10}H_{11}NO_3$: C, 62.67; H, 5.86; N, 7.23. Found: C, 62.47; H, 5.74: N, 7.25. The following compounds were prepared by the same procedure. The structure of **5** is given in Table V.

5b: 65% yield; bp 106 °C (0.4 mmHg), mp 30 °C; IR (Nujol) 1690, 1540, 1365 cm^{-1}; NMR ($CDCl_3$) δ 1.90 (s, 6 H), 7.43 (d, 2 H), 7.72 (d, 2 H). Anal. Calcd for $C_{10}H_{10}NO_3Cl$: C, 52.76; H, 4.43; N, 6.15. Found: C, 53.05; H, 4.34; N, 6.36.

5c: 68% yield; bp 119–120 °C (1 mmHg) [lit.[27] 124 °C]; NMR ($CDCl_3$) δ 1.78 (d, 3 H), 5.98 (q, 1 H), 7.4 (m, 3 H), 7.7 (m, 2 H).

5d: 70% yield; mp 76–77 °C; IR (Nujol) 1690, 1560 cm^{-1}; NMR ($CDCl_3$) δ 1.82 (d, 3 H), 6.05 (q, 1 H, 7.4 (d, 2 H), 7.8 (d, 2 H). Anal. Calcd for $C_9H_8NO_3Cl$: C, 50.60; H, 3.77; N, 6.55. Found: C, 50.88; H, 3.75; N, 6.34.

5e: 73% yield; mp 42.5–43 °C; IR (Nujol) 1680, 1555 cm^{-1}; NMR ($CDCl_3$) δ 1.81 (d, 3 H), 2.43 (s, 3 H), 6.10 (q, 1 H), 7.3 (d, 2 H), 7.7 (d, 2 H). Anal. Calcd for $C_{10}H_{11}NO_3$: C, 62.17; H, 5.74; N, 7.25. Found: C, 62.45; H, 5.71; N, 7.23.

5f: bp 141 °C (0.5 mmHg); IR (neat) 1695, 1550 cm^{-1}; NMR ($CDCl_3$) δ 1.73 (d, 3 H), 3.81 (s, 3 H), 5.96 (q, 1 H), 6.84 (d, 2 H), 7.74 (d, 2 H). Anal. Calcd for $C_{10}H_{11}NO_4$: C, 57.41; H, 5.30; N, 6.70. Found: C, 57.72; H, 5.53; N, 6.54.

5g: 55% yield; mp 74.5–75.5 °C; IR (Nujol) 1693, 1560 cm^{-1}; NMR ($CDCl_3$) δ 1.88 (d, 3 H), 6.16 (q, 1 H), 8.07 (d, 2 H), 8.29 (d, 2 H). Anal. Calcd for $C_9H_8N_2O_5$: C, 48.22; H, 3.60; N, 12.50. Found: C, 48.13; H, 3.68; N, 12.24.

Reduction of α-Nitro Nitriles (1) by BNAH. Results are summarized in Table III. The reaction proceeds in various solvents and benzene is the most convenient for the preparative experiment, for the workup is very simple.

Reduction of 5-Cyano-5-nitro-2-heptanone (1a) by BNAH. A mixture of **1a** (1.84 g, 10 mmol) and BNAH (6.42 g, 30 mmol) in benzene (150 mL) was stirred at room temperature under nitrogen with exposure to a 150-W tungsten lamp for 24 h. The resulting mixture was washed with 2 N aqueous HCl and then with water. The benzene layer was dried over anhydrous magnesium sulfate. Removal of the solvent followed by distillation gave 5-cyano-2-heptanone (**2a**), 0.82 g (60% yield), bp 96 °C (2.8 mmHg): IR (neat) 2230, 1715 cm^{-1}; NMR (CCl_4) δ 1.09 (t, 3 H, J = 7.5 Hz), 1.44–1.94 (m, 4 H), 2.13 (s, 3 H), 2.60 (t, 2 H, J = 7.5 Hz), 2.5 (m, 1 H). Anal. Calcd for $C_8H_{13}NO$: C, 69.03; H, 9.41; N, 10.06. Found: C, 69.32; H, 9.71; N, 9.83.

The above aqueous solution was concentrated under reduced pressure to dryness and the residue was recrystallized from water–ethanol to give the pyridinium salt, $BNA^+NO_2^-$ (1.5 g, 58% yield): NMR (D_2O) δ 5.78 (s, 2 H), 7.40 (m, 5 H), 8.14 (t, 1 H), 8.90 (d, 1 H), 8.89 (d, 1 H). The spectrum was in good agreement with that of an authentic sample of BNA^+ Cl^-.

The reaction of **1a** with BNAH was also carried out under the following conditions: (A) **1a** (0.184 g, 1 mmol) and BNAH (0.642 g, 3 mmol) in DMF (10 mL) are stirred for 24 h at room temperature under nitrogen with exposure to a 150-W tungsten lamp. (B) This was duplicate of A except that a 20-W fluorescent lamp was used instead of a 150-W tungsten lamp. (C) This was duplicate of A except that the reaction was carried out in the dark. (D) The experiment differed from A in that acetonitrile was used as the solvent. (E) The experiment differed from A in that ethanol was used as the solvent. GLC analyses revealed that **2a** was formed in 93, 51, 0, 92, and 90% yields from the reaction of A, B, C, D, and E, respectively.

Reduction of Methyl 4-Cyano-4-nitrohexanoate (1b) by BNAH. The procedure used for the reduction of **1a** was employed. **1b** (2.0 g, 10 mmol) and BNAH (6.42 g, 30 mmol) in benzene (150 mL) gave methyl 4-cyanohexanoate (**2b**), 0.94 g (67% yield), bp 66–67 °C (0.28 mmHg): IR (neat) 2250, 1745 cm^{-1}; NMR (CCl_4) δ 1.11 (t, 3 H, J = 7.5 Hz), 1.47–1.98 (m, 4 H), 2.48 (t, 2 H, J = 7.5 Hz), 2.5 (m, 1 H), 3.62 (s, 3 H); m/e 155 (M^+, 1), 140 (6), 124 (100), 96 (47).

Reduction of 4-Cyano-4-nitrohexanenitrile (1c) by BNAH. The same procedure used to reduce **1a** was employed. **1c** (1.7 g, 10 mmol) and

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Table V. Reduction of α-Nitro Ketones (5) with BNAH

5	X	R^1	R^2	solvent	time, h	light	product: yield, %[a]
5a	H	Me	Me	HMPA	24	150 W-T	6a, 91 (61)[b]
5a	H	Me	Me	HMPA	24	dark	6a, 0
5a	H	Me	Me	DMF	24	150 W-T	6a, 50
5a	H	Me	Me	benzene	24	150 W-T	6a, 10
5b	Cl	Me	Me	DMF	24	150 W-T	6b, (91)[b]
5c	H	Me	H	HMPA	48	150 W-T	6c, 97 (58)[b]
5d	Cl	Me	H	HMPA	48	150 W-T	6d, 95 (62)[b]
5e	Me	Me	H	HMPA	48	150 W-T	6e, 80 (45)[b]
5f	MeO	Me	H	HMPA	48	150 W-T	6f, 99 (52)[b]
5g	NO_2	Me	H	HMPA	48	150 W-T	6g, 0[c]
5h	H	H	H	HMPA	48	150 W-T	6h, 0[d]

[a] Yields were determined by GLC. [b] Isolated yields. [c] Starting material (5g) was recovered quantitatively. [d] Acetophenone (6h) was not detected by GLC, but some unidentified products were formed.

BNAH (6.42 g, 30 mmol) in benzene (150 mL) gave 4-cyanohexanenitrile (**2c**), 0.74 g (61% yield), bp 86–87 °C (0.5 mmHg): IR (neat) 2250 cm^{-1}; NMR (CCl_4) δ 1.10 (t, 3 H, J = 7.5 Hz), 1.50–1.85 (m, 2 H), 1.95 (q, 2 H, J = 7.5 Hz), 2.52 (t, 2 H, J = 7.5 Hz), 2.5 (m, 1 H); m/e 122 (M^+, 1), 96 (20), 82 (100).

Reduction of α-Nitro Esters (3) by BNAH. Results are summarized in Table IV.

Reduction of 4-Nitro-4-carbomethoxypentanenitrile (3a) by BNAH. A mixture of **3a** (1.9 g, 10 mmol) and BNAH (6.4 g, 30 mmol) in benzene (150 mL) was stirred for 24 h at room temperature under nitrogen with exposure to a 150-W tungsten lamp. The resulting mixture was washed with 2 N aqueous HCl and then with water. The benzene layer was dried over anhydrous magnesium sulfate. Removal of the solvent followed by distillation gave 4-carbomethoxypentanenitrile (**4a**), 1.0 g (71% yield), bp 72 °C (0.2 mmHg): IR (neat) 2250, 1730 cm^{-1}; NMR (CCl_4) δ 1.21 (d, 3 H, J = 7.5 Hz), 1.66–2.05 (m, 2 H), 2.36 (t, 2 H, J = 7.5 Hz), 2.5 (m, 1 H), 3.64 (s, 3 H). Anal. Calcd for $C_7H_{11}NO_2$: C, 59.56; H, 7.88; N, 9.92. Found: C, 59.29; H, 8.13; N, 9.74.

The reaction of **3a** (10 mmol) with BNAH (30 mmol) in HMPA (40 mL) was carried out in the same way as the reaction in benzene. The reaction mixture was poured into water after 12 h and extracted with diethyl ether. The ethyl layer was washed with 2 N aqueous HCl and water, and then dried over anhydrous magnesium sulfate. Removal of the solvent followed by distillation gave **4a**, 0.86 g (61% yield). The reaction of **3a** (1 mmol) with BNAH (3 mmol) in HMPA (4 mL) was also carried out in the dark. After 12 h, GLC analyses revealed that no reaction had occurred.

Reduction of 4-Carboethoxy-4-nitropentanenitrile (3b) by BNAH. A mixture of **3b** (2.0 g, 10 mmol) and BNAH (6.4 g, 30 mmol) in HMPa (40 mL) was treated in the same way as the reaction of **3a** for 12 h. Distillation of the crude product gave 4-carboethoxypentanenitrile (**4b**), 0.63 g (60% yield), bp 61 °C (0.35 mmHg): IR (neat) 2250, 1725 cm^{-1}; NMR (CCl_4) δ 1.08–1.41 (m, 6 H), 1.58–2.20 (m, 2 H), 2.35 (t, 2 H, J = 7.5 Hz), 2.5 (m, 1 H), 4.07 (t, 2 H, J = 7.5 Hz).

Anal. Calcd for $C_8H_{13}NO_2$: C, 61.92; H, 8.44; N, 9.03. Found: C, 61.74; H, 8.36; N, 9.12.

The reaction of **3b** (10 mmol) with BNAH (30 mmol) in benzene (150 mL) was carried out in the same way as above. After 24 h, GLC analyses revealed that **4b** was produced in 25% yield, and 60% of **3b** was recovered.

Reduction of 4-Carboisopropoxy-4-nitropentanenitrile (3c) by BNAH. A mixture of **3c** (2.1 g, 10 mmol) and BNAH (6.4 g, 30 mmol) in HMPA (40 mL) was treated in the same way as the reaction of **3a** for 12 h. Column chromatography (silica gel/benzene) of the crude product gave 4-carboisopropoxypentanenitrile (**4c**), 1.0 g (62% yield): IR (neat) 2250, 1725 cm^{-1}; NMR (CCl_4) δ 1.12–1.21 (m, 9 H), 1.67–2.17 (m, 2 H), 2.37 (t, 2 H, J = 7.5 Hz), 2.5 (m, 1 H), 4.9 (m, 1 H). Anal. Calcd for $C_9H_{14}NO_2$: C, 64.26; H, 8.39; N, 8.33. Found: C, 63.98; H, 8.67; N, 8.10. The reaction of **3c** (10 mmol) with BNAH (30 mmol) in benzene (150 mL) was carried out in the same way as above. After 24 h, GLC analyses revealed that **4c** was produced in 23% yield, and 63% of **3c** was recovered.

Reduction of α-Nitro Ketones (5) by BNAH. Results are summarized in Table V.

Reduction of α-Nitroisobutyrophenone (5a) by BNAH. A mixture of **5a** (1.9 g, 10 mmol) and BNAH (6.4 g, 30 mmol) in HMPA (40 mL) was stirred for 24 h at room temperature under nitrogen mixture was exposed to a 150-W tungsten lamp. The reaction mixture was poured into water and extracted with diethyl ether. The ether layer was washed with 2 N aqueous HCl, and water, and then dried over anhydrous magnesium sulfate. Removal of the solvent followed by column chromatography (silicagel/benzene) gave isobutyrophenone (**6a**), 0.89 g (61% yield): IR (neat) 1680 cm^{-1}; NMR (CCl_4) δ 1.20 (d, 6 H, J = 7.5 Hz), 3.45 (m, 1 H), 7.4 (m, 3 H), 7.9 (m, 2 H). Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.88; H, 8.42.

When the reaction of **5a** (1 mmol) with BNAH (3 mmol) in HMPA (4 mL) was carried out in the dark, GLC analyses revealed that no **6a** had formed after 24 h. When the reaction of **5a** (1 mmol) with BNAH (3 mmol) in DMF (4 mL) or benzene (15 mL) was carried out with exposure to a 150-W tungsten lamp for 24 h, GLC analyses revealed that **6a** was formed in 50 and 10% yields, respectively.

Reduction of α-Nitro-*p*-chloroisobutyrophenone (5b) by BNAH. A mixture of **5b** (1.1 g, 5 mmol) and BNAH (3.2 g, 15 mmol) in DMF (20 mL) was stirred under the same conditions of the reduction of **5a** for 24 h. Column chromatography of the crude product gave the pure *p*-chloroisobutyrophenone (**6b**), 0.83 g (91% yield): IR (neat) 1685 cm^{-1}; NMR (CCl_4) δ 1.18 (d, 6 H, J = 6.9 Hz), 3.45 (m, 1 H), 7.42 (d, 2 H), 7.89 (d, 2 H). Anal. Calcd for $C_{10}H_{11}OCl$: C, 65.76; H, 6.07. Found: C, 65.49; H, 6.22.

Reduction of α-Nitropropiophenone (5c) by BNAH. A mixture of **5c** (0.90 g, 5 mmol) and BNAH (3.2 g, 15 mmol) in HMPA (20 mL) was stirred for 48 h under the same conditions used for the reduction of **5a**. Propiophenone (**6c**) was obtained by distillation, 0.39 g (58% yield), bp 105 °C (19 mmHg): IR (neat) 1685 cm^{-1}; NMR (CCl_4) δ 1.18 (t, 3 H, J = 7.5 Hz), 2.91 (q, 2 H, J 7.5 Hz), 7.3 (m, 3 H), 7.8 (m, 2 H). Anal. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.38; H, 7.53.

The following compounds were also prepared by the procedure employed for the reduction of **5a**.

***p*-Chloropropiophenone (6d)**: 62% yield; mp 33–34 °C (lit.[28] 34–35 °C); NMR (CCl_4) δ 1.17 (t, 3 H, J = 7.5 Hz), 2.89 (g, 2 H, J = 7.5 Hz), 7.3 (d, 2 H), 7.8 (d, 2 H).

***p*-Methylpropiophenone (6e)**: 45% yield; bp 70.5 °C (0.4 mmHg) [lit.[29] 90 °C (3 mmHg)]; NMR (CCl_4) δ 1.16 (t, 3 H, J = 7.5 Hz), 2.36 (s, 3 H), 2.86 (q, 2 H, J = 7.5 Hz), 7.1 (d, 2 H), 7.8 (d, 2 H).

***p*-Methoxypropiophenone (6f)**: 52% yield; bp 105 °C (0.9 mmHg) [lit.[29] 106 °C (8 mmHg)]; NMR (CCl_4) δ 1.12 (t, 3 H, J = 7.5 Hz), 2.81 (q, 2 H, J = 7.5 Hz), 3.76 (s, 3 H), 6.80 (d, 2 H), 7.80 (d, 2 H).

Attempted Reduction of α,*p*-Dinitropropiophenone (5g) by BNAH. A mixture of **5g** (1.12 g, 5 mmol) and BNAH (3.2 g, 15 mmol) in HMPA (20 mL) was stirred for 48 h under the same conditions as employed in the reduction of **5a**. *p*-Nitropropiophenone (**6g**) was not detected in the reaction mixture by GLC, and 1.0 g (90%) of **5g** was recovered.

Reduction of 1a by $NaBH_4$. A mixture of **1a** (1.8 g, 10 mmol) and $NaBH_4$ (1.1 g, 30 mmol) was stirred for 24 h at room temperature under nitrogen with exposure to a 150-W tungsten lamp. The resulting mixture was poured into water and acidified with 2 H aqueous HCl. After extraction with diethyl ether, washing the ether layer with water, drying, and evaporating the solvent, column chromatography (silica gel/benzene) gave 5-cyano-5-nitro-2-heptanol in 62% yield (1.2 g): IR (neat) 3100–3700, 1555, 1360 cm^{-1}; NMR (CCl_4) δ 1.05–1.32 (m, 6 H), 2.08–2.09 (m, 6 H), 2.69–2.98 (broad 1 H), 3.8 (m, 1 H). Anal. Calcd for $C_8H_{14}N_2O_3$: C, 51.60; H, 7.58; N, 15.04. Found: C, 51.31; H, 7.73; N, 14.88.

Reduction of 5c by $NaBH_4$. A mixture of **5c** (0.9 g, 5 mmol) and $NaBH_4$ (0.55 g, 15 mmol) in HMPA (20 mL) was stirred for 24 h at room temperature under nitrogen with exposure to a 150-W tungsten lamp. The resulting mixture was poured into water and acidified with 2 N aqueous HCl. After extraction with ether, washing the ether layer with water, drying, and evaporating the solvent, column chromatography (silica gel/methylene chloride) gave benzyl alcohol in 60% yield (0.7 g). The spectral data of IR and NMR are identified with those of authentic benzyl alcohol.

Reduction of 1a with CH_3SNa. A mixture of **1a** (1.8 g, 10 mmol) and CH_3SNa (2.1 g, 30 mmol) in HMPA (40 mL) was stirred for 24 h at room temperature under nitrogen with exposure to a 150-W tungsten lamp. The resulting mixture was poured into water and acidified with 2 N aqueous HCl. After extraction with ether, washing the ether layer with water, drying, and evaporating the solvent, small amount of volatile products was obtained in which **1a** and **2a** were not detected by GLC analyses.

Reaction of 2-Nitro-2-carbomethoxyhexan-5-one Ethylene Acetal (7) with CH_3SNa. A mixture of **7** (0.25 g, 1 mmol) and CH_3SNa (0.21 g, 3 mmole in HMPA (10 mL) was stirred for 24 h at room temperature under nitrogen with exposure to a 150-W tungsten lamp. The reaction mixture was poured into 2 N aqueous HCl and extracted with ether. The ether layer was washed with water and dried over anhydrous magnesium

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sulfate. Removal of the solvent followed by column chromatography (silica gel/benzene) gave 2-nitrohexan-5-one, 0.11 g (75% yield): IR (neat) 1720, 1545 cm^{-1}; NMR (CCl_4) δ 1.53 (d, 3 H), 2.09 (s, 3 H), 2.22-2.64 (m, 4 H), 4.2-4.6 (m, 1 H). Anal. Calcd for $C_6H_{11}NO_3$: C, 49.65; H, 7.64; N, 9.65. Found: C, 49.46; H, 7.92; N, 9.38.

Reaction of 5a with CH_3SNa. A mixture of **5a** (0.19 g, 1 mmol) and CH_3SNa (0.21 g, 3 mmol) in HMPA (10 mL) was stirred for 4 h at room temperature under nitrogen with exposure to a 150-W tungten lamp. GLC analyses revealed that no **5a** was left but **6c** was formed in 1% yield. The reaction mixture was worked up in the same way as the reaction of **1a** with CH_3SNa to give methyl thiobenzoate (0.11 g, 65% yield).

Reaction of 5c with CH_3SNa. A mixture of **5c** (0.18 g, 1 mmol) and CH_3SNa (0.21 g, 3 mmol) in HMPA (10 mL) was stirred for 72 h at room temperature under nitrogen with exposure to a 150-W tungsten lamp. GLC analyses revealed that **6c** was formed in 16% yield. After the same workup as employed in the reaction of **1a** with CH_3SNa, 0.14 g of **5c** was recovered.

Reaction of 5a with KOH in Ethylene Glycol. A mixture of **5a** (0.19 g, 1 mmol) and KOH (0.06 g, 1 mmol) in ethylene glycol (10 mL) was stirred for 4 h at 120 °C. The reaction mixture was poured into water and acidified with concentrates HCl to give benzoic acid (0.11 g, 89% yield).

Mechanistic Studies. Inhibition Experiments. The solutions containing **1a** (0.18 g, 1 mmol) and BNAH (0.64 g, 3 mmol) in DMF (10 mL) were prepared, into which a stream of nitrogen was passed. The first solution, the control, was irradiated by a 150-W tungsten lamp. The second solution also contained m-DNB (0.017 g, 0.1 mmol), and the third solution contained DTBN (0.02 g, 0.2 mmol); they were irradiated by a 150-W tungsten lamp. The amount of **2a** formed was measured by GLC after 6 or 17 h. Similar inhibition studies were also carried out using **5a** (1 mmol), BNAH (3 mmol), m-DNB (0.1 mmol), and DTBN (0.2 mmol). Results are summarized in Table IV.

Reduction of 1a by BNAH in the Presence of Sodium Dithionite. A mixture of **1a** (1.84 g, 10 mmol), BNAH (6.42 g, 30 mmol), and $Na_2S_2O_4$ (5.2 g, 30 mmol) in DMF (100 mL) was stirred for 2j h at room temperature under nitrogen in the dark. After the usual workup, column chromatography (silica gel/benzene) gave **2a** (0.42 g, 40% yield). The yield of **2a** was also determined by GLC.

Reaction of 1a with Sodium Dithionite. A mixture of **1a** (0.18 g, 1 mmol) and $Na_2S_2O_4$ (0.52 g, 3 mmol) in DMF (10 mL) was stirred for 24 h at room temperature. After the usual workup, the crude product was analyzed by GLC; no **2a** was detected.

Reduction of 1a by BNAH in the Presence of Di-*tert*-butyl Peroxyoxalate (DTPO). A mixture of **1a** (0.92 g, 5 mmol), BNAH (3.2 g, 15 mmol), and DTPO (0.94 g, 0.4 mmol), BNAH (3.2 g, 15 mmol), and DTPO (0.94 g, 0.4 mmol) in DMF (20 mL) was stirred for 24 h at room temperature under nitrogen in the dark. After the usual workup, column chromatography (silica gel/benzene) gave **2a** (0.82 g, 40% yield); GLC yield was 60%. At the same time a reaction carried out in the absence of DTPO gave no **2a**.

Reduction of 1a by BNAH in the Presence of AIBN. A mixture of **1a** (0.1, g, 1 mmol), BNAH (0.64 g, 3 mmol), and AIBN (0.016 g, 0.1 mmol) in DMF (10 mL) was heated at 80 °C for 3 h in the dark. The control did not contain AIBN. On workup the products were analyzed by GLC. Results are summarized in Table II.

Reduction of 1a by BNAH in CD_3CN. A mixture of **1a** (0.18 g, 1 mmol) and BNAH (0.64 g, 3 mmol) in CD_3CN (10 mL) was stirred for 24 h at room temperature under nitrogen with a exposure to a 150-W tungsten lamp. After the usual workup, column chromatography (silica gel/benzene) gave pure **2a** (0.07 g, 50% yield), in which deuterium was not contained. The content of deuterium was determined by NMR.

Reduction of 1a by 1-Benzyl-1,4-dihydronicotinamide-*4,4-d*$_2$. A mixture of **1a** (0.18 g, 1 mmole and 1-benzyl-**1,4**-dihydronicotinamide-**4,4-*d*$_2$** (D content is 85%, 0.65 g, 3 mmol) in CH_3CN (10 mL) was stirred for 24 h at room temperature under nitrogen with exposure to a 150-W tungsten lamp. After the usual workup, column chromatography (silica gel/benzene) gave the deuterated **2a**, whose D content was determined by NMR to be 65%.

Registry No. 1a, 74261-40-8; **1b**, 74261-41-9; **1c**, 74261-42-0; **2a**, 18397-63-2; **2b**, 74261-48-6; **2c**, 74261-49-7; **3a**, 74261-43-1; **3b**, 85422-78-2; **3c**, 85422-79-3; **4a**, 34927-40-7; **4b**, 10444-16-3; **4c**, 85422-80-6; **5a**, 29329-26-8; **5b**, 74261-44-2; **5c**, 14897-67-7; **5d**, 74261-45-3; **5e**, 74261-47-5; **5f**, 65662-59-1; **5g**, 74261-46-4; **6a**, 611-70-1; **6b**, 18713-58-1; **6c**, 93-55-0; **6d**, 6285-05-8; **6e**, 5337-93-9; **6f**, 121-97-1; **7**, 85422-81-7; CH_3SNa, 5188-07-8; $BNA^+NO_2^-$, 85422-82-8; BNAH, 952-92-1; 5-cyano-5-nitro-2-heptanol, 85422-83-9; 2-nitrohexan-5-one, 35223-72-4; 1-phenyl-2-methyl-2-nitropropanol, 33687-74-0; methyl 2-nitropropionate, 6118-50-9; acrylonitrile, 107-13-1; 2-nitrobutyronitrile, 85422-84-0; methyl vinyl ketone, 78-94-4.

Concerted Fragmentation of *N*-Chloro-α-amino Acid Anions

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Abstract: The decomposition of anions of *N*-chloro-α-amino acids in neutral aqueous solution gives chloride ion, imines (which hydrolyze rapidly to amine and carbonyl products), and carbon dioxide. The reactions are first order in the concentration of the *N*-chloro-α-amino acid anions and are independent of acidity between pH 5 and 9. The rate constants, which range from 4.2×10^{-6} s^{-1} to 9.0×10^{-2} s^{-1} at 25.0 °C, are highly dependent on the amino acid structure and values increase in the order: glycine < sarcosine < threonine < alanine < proline < α-aminoisobutyric acid < 1-amino-1-carboxycyclohexane. The factor of 21 000 in relative reactivity for this sequence, the large positive values found for $\Delta S^{\ddagger}$ (30-61 J K^{-1} mol^{-1}), and the products formed suggest that the reactions proceed by a concerted fragmentation mechanism.

N-Chloro-α-amino acids form rapidly in aqueous solution from the reaction of amino acids with chlorinating agents such as hypochlorous acid,[1-3] chlorine,[3] and monochloramine.[4,5] These reactions often occur when potable or waste waters are chlorinated for disinfection.[1,5] The *N*-chloro-α-amino acids are not stable and decompose to ammonia, chloride ion, carbon dioxide, and carbonyls.[2] The rate of decomposition of *N*-chloroalanine in water is first order in the chloroamino acid anion with a rate constant of 2.7×10^{-4} s^{-1} at 25.0 °C, independent of pH from 5 to 9.[6] The rate-determining step given in eq 1 is followed by the rapid hydrolysis of ethylimine (eq 2). Similar products have been reported when amino acids are brominated.[7]

$$ClNHCH(CH_3)CO_2^- \rightarrow Cl^- + HN{=}CHCH_3 + CO_2 \quad (1)$$

$$HN{=}CHCH_3 + H_2O \rightarrow NH_3 + O{=}CHCH_3 \quad (2)$$

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