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Sodium Arenetellurolate-Catalyzed Reduction of Nitroalkanes to Oximes

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ABSTRACT

Treatment of aliphatic nitro compounds with $NaBH_4$ in alkaline ethanol in the presence of a catalytic amount of diaryl ditelluride at 25°C for 5–20 h produces the corresponding oximes, generally as a mixture of E/Z *isomers, in fair to good yields. Arenetellurolate anion ($ArTe^-$) generated in situ is suggested to be the active species for the reduction.*

RESULTS AND DISCUSSION

It was recently reported that treatment of nitroaromatics with $NaBH_4$ in alkaline ethanol in the presence of a catalytic amount of diaryl ditelluride produces the corresponding azoxy and azo compounds in good yields, in situ generated sodium arenetellurolate (ArTeNa) being the active species to reduce nitroaromatics first to aromatic nitroso compounds [1]. We now disclose that the application of this reduction system to aliphatic nitrocompounds results in the formation of the corresponding oximes in fair to good yields.

Nitrocyclohexane (**1**) (2 mmol) was treated with a catalytic amount of sodium benzenetellurolate (PhTeNa), generated in situ from diphenyl ditelluride ($(PhTe)_2$, 0.1 mmol) and $NaBH_4$ (5–10 mmol) in ethanol (15 mL) containing aqueous 5 M NaOH (2.5 mL) at 25°C for 5 h under a nitrogen atmosphere. After neutralization with dilute HCl (actually to slightly acidic), extraction with chloroform afforded a mixture of cyclohexanone oxime (**2**) (42% based on **1**), cyclohexanone (43%), and cyclohexanol (4%) together with recovered **1** (5%). Even without $(PhTe)_2$ the oxime **2** was produced, but in much lower yield (19%), showing that the tellurium compound functions as a catalyst for the formation of **2**. Elongation of the reaction time to 20 h in the presence of $(PhTe)_2$ resulted in a slight decrease of the yield of **2** (33%) without an appreciable change of the yield of the other products. On the contrary, none of **1**, **2**, and cyclohexanone were extracted from the alkaline mixture without neutralization. Here, the absence of **2** in the extract suggests that, in the alkaline mixture, it is doubtful that the reduced species of **1** is simply the resonance hybrid (**A**↔**B**) of Scheme 1 [2]. We confirmed separately that **2** itself can be extracted in over 70% yield from a similar alkaline mixture consisting of **2**, cat. $(PhTe)_2$, $NaBH_4$, aq 5 M NaOH, and EtOH. On the other hand, the absence of cyclohexanone as well as **1** in the extract means that **1** exists as the sodium salt of its aci form (**C**) in the alkaline mixture. By neutralization with dilute HCl this aci form can be converted to cyclohexanone by the so-called Nef reaction [3]. Hoping to avoid ketone formation, we carried out the $(PhTe)_2$-catalyzed reduction without aqueous NaOH, but the reaction was slow and the selectivity for **2** was lower. The oxime formation was not improved by use of other organyltellurolates such as sodium 4-methoxybenzenetellurolate and sodium 2-naphthalenetellurolate.

The reduction using a cat. $(PhTe)_2/NaBH_4$/aqueous NaOH system was then applied to various other aliphatic nitro compounds for 5–20 h. The reductions of 1-nitrodecane (**3**), 6-nitroundecane (**4**), and 1-(nitromethyl)cyclohexene (**5**) were slow and the yields of expected oximes were not high, while 2-arylnitroethanes (**6**) were converted to the corresponding oximes **10** as a mixture of *E*- and *Z*-isomers in good yields. The catalytic effect of $(PhTe)_2$

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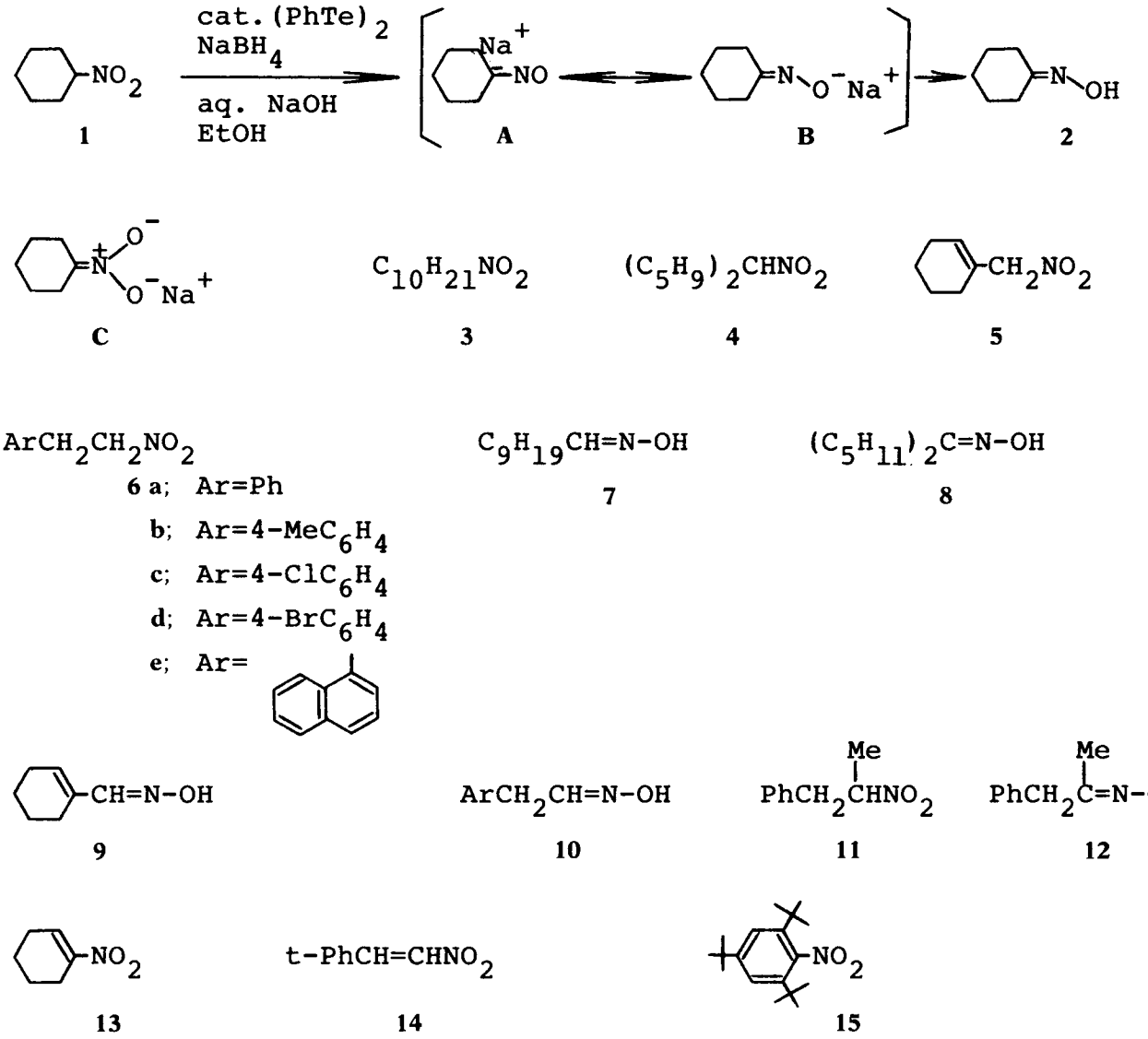


SCHEME 1

appeared much more remarkable in the reduction of 2-phenylnitroethane (**6a**) than in the reduction of **1**; thus, the yield of the produced oxime **10a** was 56% and 4% for 5 h in the presence and absence of $(PhTe)_2$, respectively. The yields of oximes as well as their *E*/*Z* ratios for typical experiments are shown in Table 1. The ratio of *E*- and *Z*-isomers was determined by ^1H NMR spectra in which signals due to the methine proton in the oxime moiety in the *Z*-isomer showed a lower field shift compared with those of the *E*-isomer. The reduction of 1-nitroalkenes such as 1-nitrocyclohexene (**13**) and trans-β-nitrostyrene (**14**) afforded the same oximes as those obtained from the corresponding saturated nitro compounds, **1** and **6a**, respectively, though in a slightly lower yield. Almost the same *E*/*Z* ratio of the produced oxime **10a** from both **14** and **6a** suggests a prior hydrogenation of nitroalkenes to nitroalkanes [4].

As in the reduction of nitroaromatics by a similar system where aromatic nitroso compounds have been proposed as the intermediates for azoxy compounds [1], nitroalkanes seem to be reduced by an arenetellurolate anion ($ArTe^-$) first to nitrosoalkanes, which then tautomerize to the corresponding oximes as shown in Scheme 2. A liberated sodium arenetellurenate (ArTeONa) regenerates ArTeNa by reduction with $NaBH_4$ to complete the catalytic cycle.

The results presented here disclosed another catalytic use of organotellurium compounds in organic synthesis, though of a limited synthetic utility in this case [5]. This also supported the assumption of the intermediacy of aromatic nitroso compounds

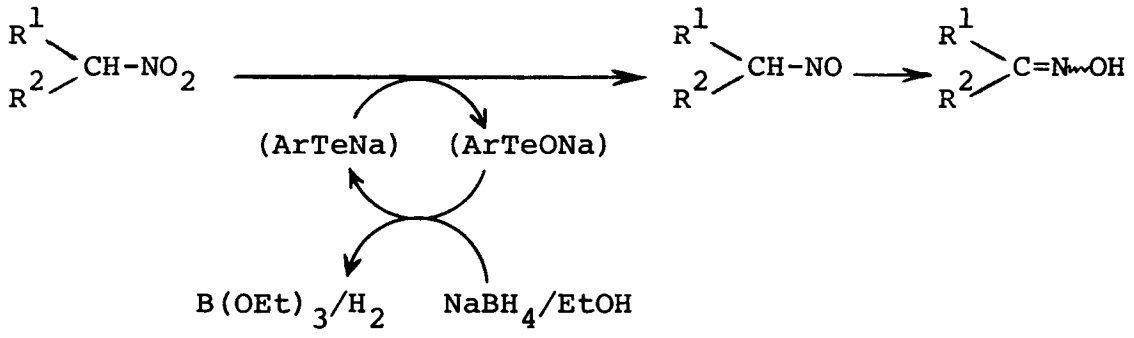
TABLE 1 Sodium Benzenetellurolate (PhTeNa)-Catalyzed Reduction of Nitroalkanes and Nitroalkenes to Oximes[a]

Nitro Compounds	*Reaction Time (h)*	*Conversion (%) of Nitro Compounds*[b]	*Oximes Yield (%)*[c] *and [E/Z]*[d]	
1	5	95	**2**	42[b,e]
1	5[f]	89	**2**	19[b,e]
1	20	86	**2**	33[b,e] (21)[c]
3	20	34	**7**	24 [79/21]
4	20	43	**8**	15
5[g]	20	60	**9**	16 [100/0]
13	20	100	**2**	22[b,e]
6a	5	84	**10a**	56[h]
6a	5[f]	80	**10a**	4[h]
6a	20	100	**10a**	80 [59/41]
14	5	91	**10a**	<20[h]
14	20	100	**10a**	49 [58/42]
11	20	97	**12**	44 [28/72][i]
6b	20	100	**10b**	81 [100/0]
6c	20	100	**10c**	73 [55/45]
6d	20	100	**10d**	77 [100/0]
6e	20	100	**10e**	87 [82/18]

[a] Nitro compounds (2 mmol), $NaBH_4$ (10 mmol), aq 5 M NaOH (2.5 mL), EtOH (15 mL), $(PhTe)_2$ (0.1 mmol) at 25°C for 5–20 h under N_2.
[b] Determined by GLC or isolation.
[c] Isolated yield based on nitro compounds charged. Other products such as ketones and alcohols were not determined accurately except in the case of **1**, **13**, and **11**.
[d] Determined by ^1H NMR.
[e] Other products were cyclohexanone (36–46%) and cyclohexanol (1–4%).
[f] Without $(PhTe)_2$.
[g] Reaction temp. 70°C.
[h] *E/Z* ratio not determined.
[i] Other product was phenylacetone (26%).

in the reduction of nitroaromatics to azoxy compounds by the same reduction system.

Finally, we added new evidence for the mechanism of the reduction of a nitro group to a nitroso group. When 2,4,6-tri-*t*-butylnitrobenzene (**15**) was treated under the present reaction conditions for 10–20 h, none of the corresponding nitroso compound [6] was produced and almost all of **15** was recovered. On the other hand, it is known that compound **15** can be easily reduced to the corresponding amine and its derivatives by reaction with various alkylmagnesium bromides where a radical anion intermediate is involved possibly via a one-electron transfer scheme [7]. Therefore, our result of almost complete recovery of **15** supports our previous proposal [1] that a nucleophilic attack of $ArTe^-$ ion upon NO_2 nitrogen is involved in our reduction system, the large steric hindrance of two *t*-butyl groups preventing the attack of $ArTe^-$ ion upon the nitrogen of **15**. The pathway of one-electron transfer can also be excluded from the fact that $(PhSe)_2$ is not effective at all as a catalyst for the reduction of



SCHEME 2

nitroaromatics [1], because it has been shown that areneselenolate anion ($ArSe^-$) works as a one-electron transfer reagent in several reactions [8].

EXPERIMENTAL

^1H NMR spectra were recorded on a Varian VXR-200 (200 MHz) spectrometer in solution in $CDCl_3$. Chemical shifts are reported in δ units downfield from the internal reference Me_4Si. IR spectra were recorded on a Jasco IR-810 infrared spectrophotometer as KBr pellets (for solids) or thin films (for liquids). GLC analyses (1 m × 0.5 cm column packed with 5% Silicone DC QF-1 and 25% PEG 6000 on Chromosorb W 60-80 mesh) were performed on a Yanaco G 2800 instrument with flame-ionization detectors and N_2 as carrier gas. Mass spectra were measured on a JEOL JMS-DX 303 mass spectrometer. Melting points were determined on a Yanaco MP-S3 micro melting point apparatus and are uncorrected. All column chromatographic separations on SiO_2 were performed with Wakogel C-200 (100-200 mesh).

Diphenyl ditelluride [9], bis(4-methoxyphenyl) ditelluride [10], and di(2-naphthyl) ditelluride [11] were prepared by the reported methods. All aliphatic nitro compounds, except for **1**, **13**, and **14**, which are commercial products, were prepared by literature procedures [12]. Commercially available **2**, cyclohexanone, cyclohexanol, and phenylacetone were used as authentic samples for GLC analysis.

General Procedure for Reduction of Nitroalkanes and Nitroalkenes

To a mixture of diphenyl ditelluride (0.1 mmol) and $NaBH_4$ (10 mmol) in a 50-mL flask were added ethanol (10 mL) and aqueous 5 M NaOH (2.5 mL) successively at room temperature under N_2. An ethanol (5 mL) solution of the nitroalkane (2.0 mmol) was then added to the colorless, homogeneous solution and the mixture was stirred at room temperature for 20 h, during which time the yellow color turned to orange. The mixture was poured into ice-water, which was neutralized to slightly acidic with hydrochloric acid, and extracted with $CHCl_3$ (3 × 50 mL). The extract was dried over $MgSO_4$. The products were determined by GLC using an internal standard, or separated either by column chromatography on silica gel using hexane-ethyl acetate (10:1) as eluant or by washing with hexane. All oximes are known compounds.

Hydroxyiminocyclohexane (**2**). A white solid of mp 91°C was isolated by column chromatography and identified by GLC with an authentic sample, 0.047 g (0.42 mmol, 21% yield); δ_H (200 MHz) 1.48–1.75 (6H, m), 2.20 (2H, t, J 6.0 Hz), 2.49 (2H, t, J 6.0 Hz), 8.4–9.2 (1H, s, br).

1-Hydroxyiminodecane (**7**). A white solid was isolated by column chromatography, 0.082 g (0.48 mmol, 24% yield (E/Z = 79/21)); mp 54–55°C (lit. [13] 67.8°C; E/Z ratio unknown); δ_H (200 MHz) 0.86 (t, J 6.0 Hz, CH_3), 1.12–1.58 (m, CH_2), 2.18 (dt, J 6.2 and 6.6 Hz, Z-CH_2C=N), 2.36 (dt, J 5.4 and 7.0 Hz, E-CH_2C=N), 6.70 (t, J 5.4 Hz, E-CH=N), 7.41 (t, J 6.2 Hz, Z-CH=N), 8.27–8.43 (br s, Z-OH), 8.66–8.92 (br s, E-OH). Anal. Calcd. for $C_{10}H_{21}NO$: C, 70.1; H, 12.2; N, 8.1%. Found: C, 70.0; H, 12.4; N, 7.9.

6-Hydroxyiminoundecane (**8**) [*14*]. A white colorless liquid was isolated by column chromatography: 0.056 g (0.30 mmol, 15% yield); δ_H (200 MHz) 0.875 (3H, t, J 7.2 Hz), 0.883 (3H, t, J 7.2 Hz), 1.20–1.40 (8H, m), 1.40–1.60 (4H, m), 2.15 (2H, t, J 7.6 Hz), 2.32 (2H, t, J 7.8 Hz), 8.31–8.72 (1H, br s); IR (neat) 3250 vs, 3120, 2960, 2870, 1660, 1470, 950 cm^{-1}. Anal. Calcd. for $C_{11}H_{23}NO$: C, 71.3; H, 12.5; N, 7.6%. Found: C, 71.1; H, 12.7; N, 7.4.

(E)-*1-(Hydroxyiminomethyl)cyclohexene* (**9**). A white solid was isolated by column chromatography: 0.040 g (0.32 mmol, 16% yield (E/Z = 100/0)); mp 97–98°C (recryst. from hexane) (lit. [15] mp 98–99°C), δ_H (200 MHz) 1.62–1.66 (4H, m), 2.16–2.21 (4H, m), 5.97–6.06 (1H, m, C=CH), 7.68 (1H, s, CH=N), 8.25 (1H, br s, OH). Anal. Calcd. for $C_7H_{11}NO$: M^+, 125.0841. Found: M^+, 125.0844.

1-Hydroxyimino-2-phenylethane (**10a**). A white solid was isolated by column chromatography: 0.216 g (1.59 mmol, 80% yield (E/Z = 59/41)); mp 93–95°C (recryst. from hexane) (E/Z = 98/2) (lit. [16] mp 96.5–98°C); δ_H (200 MHz) 3.54 (d, J 6.4 Hz, Z-$PhCH_2$), 3.75 (d, J 5.4 Hz, E-$PhCH_2$), 6.91 (t, J 5.4 Hz, E-CH=N), 7.20–7.38 (m, arom H), 7.55 (t, J 6.4 Hz, Z-CH=N), 8.20–8.60 (br s, E-OH), 8.70–9.10 (br s, Z-OH). Anal. Calcd. for C_8H_9NO: C, 71.1; H, 6.7; N, 10.4%. Found: C, 70.7; H, 6.7; N, 10.1.

2-Hydroxyimino-1-phenylpropane (**12**) [*17*]. A pale yellow liquid was isolated by column chromatography: 0.132 g (0.89 mmol, 44% yield (E/Z = 28/72)), δ_H (200 MHz) 1.81 (d, J 0.6 Hz, Z-CH_3), 1.83 (d, J 0.6 Hz, E-CH_3), 3.51 (s, Z-$PhCH_2$), 3.76 (s, E-$PhCH_2$), 7.16–7.40 (m, arom H), 8.80–9.35 (br s, OH). Anal. Calcd. for $C_9H_{11}NO$: M^+, 149.0840. Found: M^+, 149.0846.

(E)-*1-Hydroxyimino-2-(4-methylphenyl)ethane* (**10b**). A white solid was isolated by column chromatography: 0.24 g (1.61 mmol, 81% yield (E/Z = 100/0)); mp 120–122°C (lit. [18] mp 126–126.5°C); δ_H (200 MHz) 2.34 (3H, s), 3.71 (2H, d, J 5.4 Hz), 6.89 (1H, t, J 5.4 Hz), 7.13 (4H, s), 8.80–9.15 (1H, br s). Anal. Calcd. for $C_9H_{11}NO$: C, 72.5; H, 7.4; N, 9.4%. Found: C, 72.45; H, 7.45; N, 9.35.

2-(4-Chlorophenyl)-1-hydroxyiminoethane (**10c**). Evaporation of the solvent from the extract afforded an orange residue, which was washed with hexane to give compound **10c** as a white solid: 0.249 g (1.47 mmol, 73% yield (*E*/*Z* = 55/45)); mp 132°C (recryst. from EtOH) (*E*/*Z* = 100/0) (lit. [19] mp 121–122°C; *E*/*Z* ratio unknown); δ_H (200 MHz) 3.50 (d, *J* 6.2 Hz, *Z*-$ArCH_2$), 3.70 (d, *J* 5.4 Hz, *E*-$ArCH_2$), 6.86 (t, *J* 5.4 Hz, *E*-CH=N), 7.10–7.30 (m, arom H), 7.51 (t, *J* 6.2 Hz, *Z*-CH=N), 7.80–8.10 (br s, *E*-OH), 8.30–8.60 (br s, *Z*-OH). Anal. Calcd. for C_8H_8NOCl: C, 56.65; H, 4.75; N, 8.3%. Found: C, 56.4; H, 4.8; N, 8.0.

(E)-*2-(4-Bromophenyl)-1-hydroxyiminoethane* (**10d**). Evaporation of the solvent from the extract afforded an orange residue, which was washed with hexane to give compound **10d** as a pale brown solid: 0.330 g (1.54 mmol, 77% yield (*E*/*Z* = 100/0)); mp 133–134°C (recryst. from EtOH) (*E*/*Z* = 100/0) (lit. [19] mp 133–134°C; *E*/*Z* ratio unknown; δ_H (200 MHz in DMSO-d_6) 3.55 (2H, d, *J* 5.3 Hz), 6.71 (1H, t, *J* 5.3 Hz), 7.13 (2H, d, *J* 8.4 Hz), 7.40 (2H, d, *J* 8.4 Hz). Anal. Calcd. for C_8H_8NOBr: M^+, 212.9790, 214.9768. Found: M^+, 212.9795, 214.9761.

1-Hydroxyimino-2-(1-naphthyl)ethane (**10e**). Evaporation of the solvent from the extract afforded an orange residue, which was washed with hexane to give compound **10e** as a pale brown solid: 0.320 g (1.73 mmol, 87% yield (*E*/*Z* = 82/18)); mp 118–120°C (recryst. from EtOH) (*E*/*Z* = 99/1) (lit. [20] mp 118°C; *E*/*Z* ratio unknown); δ_H (200 MHz) 4.01 (d, *J* 6.2 Hz, *Z*-$ArCH_2$), 4.19 (d, *J* 5.4 Hz, *E*-$ArCH_2$), 6.93 (t, *J* 5.4 Hz, *E*-CH=N), 7.39–7.59 (m, arom H), 7.65 (t, *J* 6.2 Hz, *Z*-CH=N), 7.78–8.00 (m, arom H), 8.04–8.22 (br s, E-OH). Anal. Calcd. for $C_{12}H_{11}NO$: C, 77.8; H, 6.0; N, 7.6%. Found: C, 77.1; H, 5.95; N, 7.3.

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REFERENCES

[1] K. Ohe, S. Uemura, N. Sugita, H. Masuda, T. Taga, *J. Org. Chem., 54,* 1989, 4169.
[2] For example: J. H. Boyer: Methods of Formation of the Nitroso Group and Its Reactions, in H. Feuer (ed): *The Chemistry of the Nitro and Nitroso Groups,* Part 1, Interscience, New York, p. 256 (1969).
[3] W. E. Noland, *Chem. Rev., 55,* 1955, 137; J. March: *Advanced Organic Chemistry,* 3rd ed., Wiley, New York, pp. 786–787 (1985).
[4] H. Shechter, D. E. Ley, E. B. Robertson, Jr., *J. Am. Chem. Soc., 78,* 1956, 4984.
[5] For recent procedures for the reduction of aliphatic nitro compounds to oximes see, for example: D. H. R. Barton, I. Fernandez, C. S. Richard, S. Z. Zard, *Tetrahedron, 43,* 1987, 551; G. W. Kabalka, N. M. Goudgen, *Synth. Commun., 18,* 1988, 693; H. Takechi, M. Machida, *Synthesis,* 1989, 206.
[6] R. Okazaki, T. Hosogai, E. Iwadare, M. Hashimoto, N. Inamoto, *Bull. Chem. Soc. Jpn., 42,* 1969, 3611.
[7] Y. Inagaki, R. Okazaki, N. Inamoto, *Bull. Chem. Soc. Jpn., 48,* 1975, 3727.
[8] For example: K. Fujimori, H. Yoshimoto, S. Oae, *Tetrahedron Lett.,* 1979, 4397; S. M. Palacios, R. A. Alonso, R. A. Rossi, *Tetrahedron, 41,* 1985, 4147.
[9] N. Petragnani, L. Torres, K. J. Wynne, *J. Organometal. Chem., 92,* 1975, 185.
[10] N. Petragnani, *Tetrahedron, 12,* 1961, 219.
[11] J. Bergman, L. Engman, *Tetrahedron, 36,* 1980, 1275.
[12] G. M. Bachaman, R. J. Maleski, *J. Org. Chem., 37,* 1972, 2810; E. Müller (ed): *Houben-Weyl, Methoden der Organischen Chemie, Vol. X, Part I,* 4th ed., Georg Thieme Verlag, Stuttgart, pp. 336–338 (1971); A. I. Meyers, J. C. Sircar, *J. Org. Chem., 32,* 1967, 4134.
[13] Y. Yukawa, M. Sakai, S. Suzuki, *Bull. Chem. Soc. Jpn., 39,* 1966, 2266.
[14] J. V. Braun, H. Kroper, *Chem. Ber., 62,* 1929, 2880.
[15] E. M. Acton, M. A. Leaffer, S. M. Oliver, H. Stone, *J. Agric. Food Chem., 18,* 1970, 1061.
[16] H. A. Smith, E. L. McDaniel, *J. Am. Chem. Soc., 77,* 1955, 533.
[17] (*E*)-Form of mp 69–71°C; A. C. Huitric, D. B. Roll, J. R. Deboer, *J. Org. Chem., 32,* 1967, 1661.
[18] V. M. Naidan, G. D. Naidan, *Zh. Org. Khim., 14,* 1978, 278; V. M. Naidan, G. D. Naidan, *Chem. Abstr., 88,* 1978, 190309v.
[19] V. M. Naidan, N. V. Dzumedzei, A. V. Dombrovskii, *Zh. Org. Khim., 1,* 1965, 1377; V. M. Naidan, N. V. Dzumedzei, A. V. Dombrovskii, *Chem. Abstr., 64,* 1966, 721e.
[20] K. A. Jensen, E. Dynesen, *Acta Chem. Scand., 4,* 1950, 692.