1.0 Hz, 1 H, H-5), 6.87 (dd, $J_{3,4}$ = 1.6 Hz, $J_{3,5}$ = 1.0 Hz, 1 H, H-3); ^{13}C NMR (C_6D_6) δ 220.0 (C=O), 136.2 (C-2), 130.2 (C-5),[20] 121.7 (C-3),[20] 108.2 (C-4), 37.4 (NCH_3), -1.4 ($Si(CH_3)_3$). Anal. Calcd for $C_9H_{15}NOSi$: C, 59.61; H, 8.35. Found: C, 59.30; H, 8.30.

General Procedure for the Reaction of the Heteroacylsilanes 1a-c with Electrophiles. A dry, nitrogen-purged flask is charged with CsF (0.055 mmol) (dried for 3 h at 150 °C under high vacuum) and THF (1 mL). Equimolar amounts (0.55 mmol) of the acylsilane and of the electrophile dissolved in THF (1 mL) are then added, and the mixture is stirred and eventually refluxed. Reaction progress is monitored by GC, and the obtained mixtures are analyzed by GC/MS analysis.

Reaction of 2-Thenoyltrimethylsilane (1b) with Benzaldehyde. To a stirred suspension of CsF (0.008 g, 0.055 mmol) in 1 mL of anhydrous THF is added dropwise a solution of **1b** (0.10 g, 0.55 mmol) and benzaldehyde (0.058 g, 0.55 mmol) in 1 mL of THF. The mixture is stirred for 6 h at room temperature, then taken up in ether, and washed 3 times with water, and the organic layer is dried over Na_2SO_4. Evaporation of the solvent affords a gummy solid, which when washed with cold ether (1 mL) gives **11a** (0.08 g, 68%); IR (KBr) 3440, 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.40 (d, $^3J_{CH-OH}$ = 5 Hz, 1 H, OH), 5.75 (d, $^3J_{CH-OH}$ = 5 Hz, 1 H, CH), 6.97-7.72 (m, 8 H, aromatic and heterocyclic H).

Registry No. **1a**, 80671-28-9; **1b**, 88372-95-6; **1c**, 93303-99-2; **4a**, 492-94-4; **4b**, 7333-07-5; **5**, 100-52-7; **6**, 123-72-8; **7**, 52844-25-4; **8**, 70-11-1; **9**, 100-39-0; **10**, 59625-54-6; **11a**, 36715-43-2; **11b**, 36715-42-1; **11c**, 93304-00-8; **12a**, 20894-97-7; **13a**, 93304-01-9; **13b**, 93304-02-0; **14a**, 5910-23-6; **14b**, 10471-74-6; **15a**, 86607-65-0; **15b**, 13196-28-6; **15c**, 93304-03-1; **16a**, 93304-04-2; DMI, 80-73-9; $PhCOSi(CH_3)_3$, 5908-41-8; $PhCOCH_2Si(CH_3)_3$, 13735-78-9; $((\pi\text{-allyl})PdCl)_2$, 12012-95-2; hexamethyldisilane, 1450-14-2; 2-furoyl chloride, 527-69-5; 2-thenoyl chloride, 5271-67-0; *N*-methylpyrrole-2-carbonyl chloride, 26214-68-6.

Reduction of α,β-Unsaturated Nitro Compounds with Boron Hydrides: A New Route to N-Substituted Hydroxylamines

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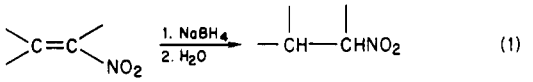
Received April 11, 1984

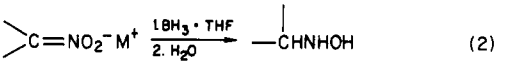
In connection with our ongoing program directed toward the synthesis of radiolabeled amphetamine derivatives,[1] we required a convenient method for the preparation of hydroxylamines. A survey of the literature indicated that the most convenient syntheses of N-substituted hydroxylamines involved the reduction of conjugated nitroalkenes.[2,3] Other methods include the reduction of oximes[4] and nitro salts[5] or the oxidation of amines.[6] The latter methods are involved and are not readily amenable to the synthesis of the desired target molecules.

Since catalytic hydrogenation of conjugated nitroalkenes is reported to be a complex reaction,[2] we investigated the reduction of conjugated nitroalkenes utilizing lithium aluminum hydride.[3] Unfortunately, in our hands, mixtures were obtained under a variety of conditions. We then investigated the reduction of conjugated nitroalkenes with boron hydrides. It had been reported that the sodium borohyride reduction of α,β-unsaturated nitroalkenes produces the corresponding nitroalkanes (eq 1).[7] In a later



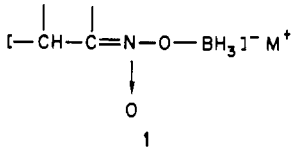
(1)

study, Feuer reported[5] that nitro salts (nitronates) are readily reduced to hydroxylamines by borane complexes, eq 2 (i.e., the nitro compounds are unreactive). These



(2)

reactions presumably occur through a common intermediate 1, which can then be hydrolyzed directly to nitroalkane or reduced with a borane complex to yield hydroxylamine after hydrolysis. It occurred to us that these reactions could be utilized to prepare the desired hydroxylamine directly from the conjugated nitroalkenes.



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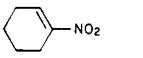
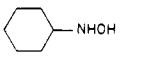
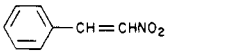
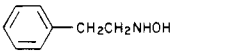
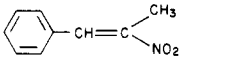
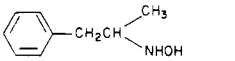
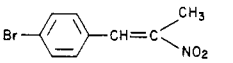
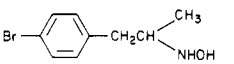
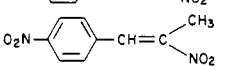
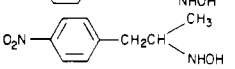
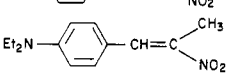
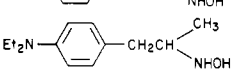
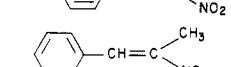
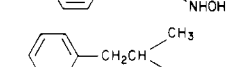
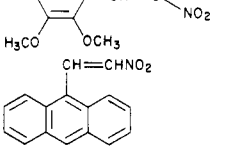
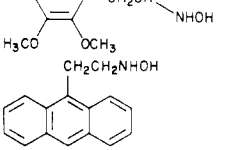
We have found that sodium borohydride catalyzes the reaction of borane complexes with α,β-unsaturated nitro compounds. The reaction is straightforward. A catalytic amount of sodium borohydride is added to a normally unreactive mixture of the α,β-unsaturated nitro compound and the borane complex at room temperature. The pure

Table I. Reduction of α,β-Unsaturated Nitro Compounds with BH_3•THF and Sodium Borohydride (Catalytic Amount)

starting material	product	time, h	yield,[a] %
		0.5	85
		1	80
		2	74
		1	78
		1.5	77
		3	85
		1	70
		1	74

[a] Isolated yield.

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Table II. ^1H and ^{13}C NMR Data for β-Methyl-β-nitrostyrene Derivatives [$RC_6H_4CH{=}C(CH_3)NO_2$]

	chemical shift, δ						
	^1H				^{13}C		
compd (R)	olefinic (1 H)	aromatic	allylic (3 H)	others	CH_3 (allylic)	aromatic and olefinic carbons	others
H	8.04	7.42 (5 H)	2.42		13.94	128.86, 129.92, 132.00, 133.44, 147.00	
p-Br	7.99	7.25–7.64 (4 H)	2.42		14.07	124.42, 131.38, 132.22, 132.30, 148.15	
p-NO_2	8.12	7.6–8.4 (4 H)	2.48		14.01	124.01, 130.59, 130.81, 138.88, 148.09, 150.26	
p-$(C_2H_5)_2N$	8.09	6.64–7.45 (4 H)	2.50	1.22 (t, J = 7 Hz, 6 H, CH_3) 3.43 (q, J = 7 Hz, 4 H, CH_2)	14.42	111.33, 118.67, 133.09, 135.22, 141.92, 149.28	12.58 (CH_3) 44.54 (CH_2)
2,3-$(OCH_3)_2$	8.22	6.8–7.3 (3 H)	2.37	3.86 (s, 3 H, OCH_3) 3.89 (s, 3 H, OCH_3)	14.23	114.12, 121.46, 124.15, 126.86, 129.51, 148.37, 148.45, 152.91	55.94 (OCH_3) 61.33 (OCH_3)

hydroxylamines are readily isolated in high yields (eq 3). Our results are summarized in Table I.

$$-\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}-NO_2 \xrightarrow[\text{catalytic } NaBH_4]{BH_3} \xrightarrow{H_2O} -\overset{|}{\underset{|}{C}}HCHNHOH \qquad (3)$$

Experimental Section

Melting points are uncorrected. NMR spectra were recorded on a JEOL-FX90Q spectrometer and referenced to Me_4Si. Elemental analyses were carried out by Galbraith laboratories, Knoxville, Tenn.

All glassware was thoroughly dried in an oven and cooled under dry nitrogen just before using. THF was dried and distilled over CaH_2 and $LiAlH_4$ and kept under dry nitrogen. the BH_3·THF solution was prepared and standardized according to the published procedure.[8]

Commercially available samples (Aldrich) of 1-nitro-1-cyclohexene, β-nitrostyrene, and 9-(ω-nitrovinyl)anthracene were used as received. Other nitro compounds were prepared via published procedures,[9-11] and the spectral data are summarized in Table II.

Synthesis of N-Substituted Hydroxylamines. General Procedure. The synthesis of *N*-hydroxy-2-phenylethanamine is representative of the procedure employed. A flame-dried, nitrogen-flushed, 250-mL flask, equipped with a septum inlet, magnetic stirring bar, and reflux condenser was cooled to 0 °C. A BH_3·THF solution (10 mmol, 4.0 mL of a 2.5 M) was injected into the reaction flask via a syringe, followed by the slow addition of a solution of β-nitrostyrene in THF (10 mmol, 1.5 g in 20 mL of THF). After the addition, the ice bath was removed and a catalytic amount (~30 mg) of $NaBH_4$ was added to the stirred reaction mixture by means of a spatula. A moderately exothermic reaction ensued. The reaction was allowed to proceed until the yellow color of the starting material disappeared (1 h). Ice–water (100 mL) was added to reaction mixture that was then acidified with 10% HCl (~20 mL). The mixture was stirred, heated at 60–65 °C for 2 h, and then cooled to room temperature. The acidic layer was washed with ether (3 × 50 mL) and then the hydroxylamine liberated via the addition of sodium hydroxide (aqueous). Solid NaCl was added and the product extracted into ether. The combined ethereal extracts were dried over anhydrous $MgSO_4$ and the solvent removed under reduced pressure to yield 1.1 g (80%) of *N*-hydroxy-2-phenylethanamine: mp 85–86 °C (lit.[5] 83–84 °C,[6b] 84–85 °C); melting point of the oxalate salt 171–173 °C (lit.[6b] 170–175 °C dec); ^{13}C NMR ($CDCl_3$) δ 33.22 ($ArCH_2$), 54.83 (CH_2N), 126.37, 128.62, 128.86, 139.21 (Ar carbons).

***N*-Cyclohexylhydroxylamine.** 1-Nitro-1-cyclohexene (2 mmol, 0.254 g) dissolved in 6 mL of THF and BH_3·THF (2 mmol, 0.8 mL of a 2.5 M solution) were mixed, and a catalytic amount of $NaBH_4$ was added as described in the general procedure to yield (30 min) 0.216 g (85%) of *N*-cyclohexylhydroxylamine: mp 137–138 °C (lit.[4b] 138–139 °C); melting point of the hydrochloride 137–142 °C dec (lit.[12] 142 °C); ^{13}C NMR ($CDCl_3$) δ 24.70, 26.17, 30.45 (alkane carbons), 60.65 (CHN).

***N*-Hydroxyamphetamine.** β-Methyl-β-nitrostyrene (4 mmol, 0.652 g) dissolved in 14 mL of THF and BH_3·THF (4 mmol, 1.6 mL of a 2.5 M solution) were mixed, and a catalytic amount of $NaBH_4$ was added to yield (2 h) 0.447 g (74%) of *N*-hydroxyamphetamine: mp 61–62 °C (lit.[6b] 60.5–62 °C); melting point of the oxalate salt 172–173 °C (lit.[6b] 167–169 °C); ^{13}C NMR ($CDCl_3$) δ 17.50 (CH_3), 39.93 (CH_2), 58.44 (CH), 126.32, 128.46, 129.35, 138.64 (Ar carbons).

***N*-Hydroxy-*p*-bromoamphetamine.** *p*-Bromo-β-methyl-β-nitrostyrene (3 mmol, 0.726 g in 10 mL of THF) and BH_3·THF (3 mmol, 1.2 mL of a 2.5 M solution) were mixed, and a catalytic amount of $NaBH_4$ was added to yield (1 h) 0.540 g (78%) of *N*-hydroxy-*p*-bromoamphetamine: mp 60–61 °C; melting point of the oxalate 169–174 °C dec; ^1H NMR ($CDCl_3$) δ 1.07 (d, 3 H, J = 6.1 Hz, CH_3), 2.70 (m, 2 H, CH_2), 3.14 (m, 1 H, CH), 6.03 (br s, 2 H, NHOH), 7.18 ($A_2'B_2'$, 4 H, J = 8.3 Hz, Ar); ^{13}C NMR ($CDCl_3$) δ 17.43 (CH_3), 39.34 (CH_2), 58.33 (CH), 120.28, 131.14, 131.63, 137.64 (Ar carbons). Anal. Calcd for $C_{20}H_{26}Br_2N_2O_6$ (oxalate): C, 43.64; H, 4.73; N, 5.09. Found: C, 43.44; H, 4.69; N, 4.95.

***N*-Hydroxy-*p*-nitroamphetamine.** A mixture of *p*-nitro-β-nitro-β-methylstyrene (5 mmol, 1.04 g) in 25 mL of THF and BH_3·THF (5 mmol, 2.0 mL of a 2.5 M solution) was treated with catalytic amount of $NaBH_4$ to yield (1.5 h) 0.750 g (77%) of *N*-hydroxy-*p*-nitroamphetamine: mp 71–72 °C; melting point of the oxalate 185–186 °C; ^1H NMR ($CDCl_3$) δ 1.08 (d, 3 H, J = 6.1 Hz, CH_3), 2.80 (m, 2 H, CH_2), 3.25 (m, 1 H, CH), 5.75 (br s, 2 H, NHOH), 7.76 ($A_2'B_2'$, 4 H, J = 8.3 Hz, Ar); ^{13}C NMR ($CDCl_3$) δ 17.34 (CH_3), 39.82 (CH_2), 58.27 (CH), 123.74, 130.24, 146.74 (Ar carbons). Anal. Calcd for $C_9H_{12}N_2O_3$: C, 55.10; H, 6.12; N, 14.29. Found: C, 55.04; H, 6.38; N, 14.23.

***N*-Hydroxy-*p*-(diethylamino)amphetamine.** A mixture of *p*-(diethylamino)-β-methyl-β-nitrostyrene (1 mmol, 0.234 g) in 6 mL of THF and BH_3·THF (1 mmol, 0.4 mL of a 2.5 M solution) was treated with a catalytic amount of $NaBH_4$ to yield (3 h) 0.19 g (85%) of *N*-hydroxy-*p*-(diethylamino)amphetamine: melting point of the oxalate 125–126 °C; ^1H NMR ($CDCl_3$) δ 1.13 (m, 9 H, methyls), 2.61 (m, 2 H, $ArCH_2$), 3.1 (m, 1 H, CH), 3.31 (q, 4 H, J = 7 Hz, CH_2N), 6.14 (br s, 2 H, NHOH), 6.82 ($A_2'B_2'$, 4 H, J = 8.5 Hz, Ar); ^{13}C NMR ($CDCl_3$) δ 12.58 (CH_3CH_2), 17.64 (CH_3CH), 38.85 ($ArCH_2$), 44.35 (CH_2N), 58.57 (CHN), 112.18, 125.12, 130.11, 146.41 (Ar carbons). Anal. Calcd for $C_{28}H_{46}N_4O_6$ (oxalate): C, 62.92; H, 8.62; N, 10.49. Found: C, 62.82; H, 9.11; N, 10.46.

***N*-Hydroxy-2,3-dimethoxyamphetamine.** A mixture of

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2,3-dimethoxy-β-nitrostyrene (8 mmol, 1.784 g) in 25 mL of THF and BH_3·THF (8 mmol, 3.2 mL of a 2.5 M solution) was treated with a catalytic amount of $NaBH_4$ to yield (1 h) 1.182 g (70%) of *N*-hydroxy-2,3-dimethoxyamphetamine: mp 66–67 °C; melting point of the oxalate 132–133 °C; ^{1}H NMR ($CDCl_3$) δ 1.11 (d, 3 H, *J* = 6.1 Hz, CH_3CH), 2.75 (m, 2 H, CH_2), 3.25 (m, 1 H, CH), 3.81, 3.84 (2s, 6 H, OCH_3), 5.85 (br s, 2 H, NHOH), 6.5–7.2 (m, 3 H, Ar); ^{13}C NMR ($CDCl_3$) δ 17.86 (CH_3CH), 34.03 ($ArCH_2$), 55.67 (OCH_3), 57.84 (CH), 60.6 (OCH_3), 110.76, 122.87, 123.85, 132.60, 147.58, 152.80 (Ar carbons). Anal. Calcd for $C_{24}H_{36}N_2O_{10}$ (oxalate): C, 56.25; H, 7.03; N, 5.47; Found: C, 56.55; H, 7.25; N, 5.35.

***N*-Hydroxyanthracene-9-ethanamine.** A mixture of 9-(ω-nitrovinyl)anthracene (10 mmol, 2.5 g) in 20 mL of THF and BH_3·THF (10 mmol, 4.0 mL of a 2.5 M solution) was treated with a catalytic amount of $NaBH_4$ (1 h). When an ether extraction of the acidic aqueous layer was attempted, a pale yellow precipitate appeared that was filtered, washed with H_2O and dried to yield 1.532 g (56%) of the hydrochloride of *N*-hydroxyanthracene-9-ethanamine: mp 178–184 °C dec; ^{1}H NMR [$(CD_3)_2SO$] δ 3.40 (m, 2 H, $ArCH_2$), 4.15 (m, 2 H, CH_2N), 7.30–8.70 (m, 9 H, Ar); ^{13}C NMR [$(CD_3)_2SO$] δ 21.84 ($ArCH_2$), 50.06 (CH_2N), 123.87, 125.28, 126.58, 126.88, 128.48, 129.21, 129.56, 131.13 (Ar carbons).

The aqueous filtrate was neutralized with aqueous NaOH and a precipitate was obtained which was filtered, washed with H_2O, and dried to yield an additional 0.43 g (18%) of *N*-hydroxyanthracene-9-ethanamine: mp 126–128 °C dec; ^{1}H NMR [$(CD_3)_2SO$] δ 3.2 (m, 2 H, $ArCH_2$), 3.85 (m, 2 H, CH_2N), 5.36 (br s, 2 H, NHOH), 7.1–8.6 (m, 9 H, Ar); ^{13}C NMR [$(CD_3)_2SO$] δ 25.84 ($ArCH_2$), 54.61 (CH_2N), 124.25, 124.77, 125.50, 125.90, 128.80, 129.48, 131.08, 132.40 (Ar carbons). Anal. Calcd for $C_{16}H_{15}NO$: C, 81.01; H, 6.33; N, 5.91. Found: C, 80.91; H, 6.37; N, 5.77.

Acknowledgment. We wish to thank the Department of Energy for support of this research and Dr. Fred M. Schell for helpful discussions. M.S.M. wishes to thank Al-Baath University, Syria, for the financial support and sabbatical leave.

Registry No. $PhCH{=}CHNO_2$, 2562-37-0; $PhCH{=}C(NO_2)CH_3$, 102-96-5; p-$BrC_6H_4CH{=}C(NO_2)CH_3$, 21892-60-4; p-$NO_2C_6H_4CH{=}C(NO_2)CH_3$, 4231-16-7; p-$Et_2NC_6H_4CH{=}C(NO_2)CH_3$, 18982-49-5; 2,3-$Et_2NC_6H_4CH{=}C(NO_2)CH_3$, 719-89-1; $Ph(CH_2)_2NHOH$, 3217-93-4; $Ph(CH_2)_2NHOH{\cdot}^1/_2HO_2CCO_2H$, 57204-76-9; $PhCH_2CH(CH_3)NHOH$, 63-90-1; $PhCH_2CH(CH_3)NHOH{\cdot}^1/_2HO_2CCO_2H$, 3705-97-3; p-$BrC_6H_4CH_2CH(CH_3)NHOH$, 13235-83-1; p-$BrC_6H_4CH_2CH(CH_3)NHOH{\cdot}^1/_2HO_2CCO_2H$, 93564-57-9; p-$NO_2C_6H_4CH_2CH(CH_3)NHOH$, 93530-63-3; p-$NO_2C_6H_4CH_2CH(CH_3)NHOH{\cdot}^1/_2HO_2CCO_2H$, 93530-67-7; p-$Et_2NC_6H_4CH_2CH(CH_3)NHOH$, 93530-64-4; p-$Et_2NC_6H_4CH_2CH(CH_3)NHOH{\cdot}^1/_2HO_2CCO_2H$, 93530-68-8; 2,3-$(MeO)_2C_6H_3CH_2CH(CH_3)NHOH$, 93530-65-5; 2,3-$(MeO)_2C_6H_3CH_2CH(CH_3)NHOH{\cdot}^1/_2HO_2CCO_2H$, 93530-69-9; BH_3·THF, 14044-65-6; $NaBH_4$, 16940-66-2; 1-nitro-1-cyclohexene, 2562-37-0; 9-(2-nitroethenyl)anthracene, 58349-77-2; *N*-hydroxycyclohexanamine, 2211-64-5; *N*-hydroxycyclohexanamine hydrochloride, 25100-12-3; *N*-hydroxyanthracene-9-ethanamine, 93530-66-6; *N*-hydroxyanthracene-9-ethanamine hydrochloride, 93530-70-2.

Dehalogenation of a *vic*-Dichloro Epoxide To Give a Product Expected from Formation of an Oxo Carbene ("Ketocarbene")

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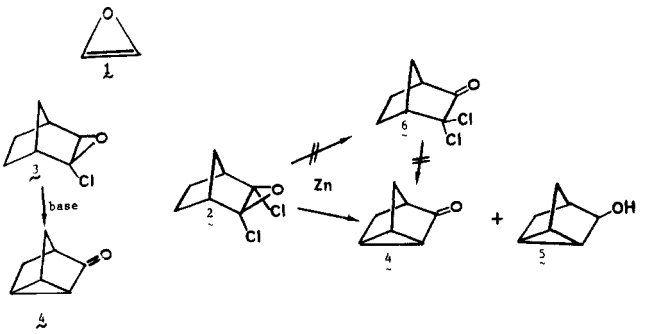
Received June 4, 1984

Oxirene (1) and its derivatives are of considerable current interest.[1] There is only one report of the possible preparation[1b] (under matrix-isolation conditions) of oxirenes, and it is unclear if they are actual molecules or only transition states,[2] although it is known that species with the symmetry of oxirenes are involved in the interconversion of oxo carbenes.[1a] Because the dehalogenation of *vic*-dihalo epoxides is a potential route to oxirenes, and because very little has been published on the reactions of this class of epoxides,[3] we report the results of our investigations of the zinc dechlorination of 2,4-dichloro-3-oxatricyclo[3.2.1.0^{2,4}]octane (2,3-dichlorobicyclo [2.2.1]hept-2-ene oxide, **2**) and compare them with those reported[4] for the dehydrochlorination of 2-chloro-3-oxatricyclo-[3.2.1.0^{2,4}]octane (2-chlorobicyclo[2.2.1]hept-2-ene oxide, **3**).



The chlorooxirane **3** has been shown[4] to lose the elements of hydrogen chloride on treatment with base, giving mainly the carbenoid insertion product **4**, but it is not known if an oxirene is the precursor of, or equilibrates with, the carbenoid. Some years ago, Griesbaum and co-workers[3a] reported the symthesis of some *vic*-dichlorooxiranes with the express intention of investigating their potential utility for the generation of oxirenes. We now report that the dichloro epoxide **2** can be dechlorinated in a reaction that shows characteristic carbene behavior.

When **2** was treated with zinc in dioxane, the product consisted of nortricyclanone (**4**) and nortricyclanol (**5**) in yields of ca. 90% and 10%, respectively. That **2** did not react by first isomerizing to the α,α-dichloro ketone **6** (cf. ref 3) followed by dechlorination (cf. ref 5) was shown by the fact that under the same conditions **6** did not form **4** (or **5**) but was largely recovered.[6]

Nortricyclanol (**5**) appears to be formed by the reduction of **2** to the monochloro epoxide **3** by zinc, the initial anion being protonated by hydrogen chloride arising from some thermal decomposition of **2**;[3b] under the same conditions authentic **3**[7] gave **5** (40%) as the sole product. The reduction of **3** to **5** is analogous to the conversion of bicy-

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(2) See ref 1a and the discussion in Maier, G.; Reisenauer, H. P.; Sayrac, T. *Chem. Ber.* **1982**, *115*, 2192.

(3) (a) Griesbaum, K.; Kibar, R.; Pfeffer, P. *Liebigs Ann. Chem.* **1975**, 214. (b) Griesbaum, K.; Nagendrappa, G. *Che. Ind. (London)* **1973**, *18*, 902.

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(5) Carbenoid formation from a dibromo analogue of **6**: Scott, L. T.; Cotton, W. D. *J. Am. Chem. Soc.* **1973**, *95*, 2708, 5416.

(6) Authentic samples: (a) Nortricyclanone: Meinwald, J.; Crandall, J. K.; Hymans, W. E. "Organic Synthesis"; Wiley: New York, 1973; Collect. Vol. 5, p 866. (b) Nortricyclanol: Crandall, J. K. *J. Org. Chem.* **1964**, *29*, 2831. (c) Dichloro ketone **6** was made by treating the bicycloheptanone with chlorine, cf. dibromocamphor: Shive, B.; Crouch, W. W.; Lochte, H. L. *J. Am. Chem. Soc.* **1941**, *63*, 2979. **6** has also been made by thermal rearrangement of **2**[3b] and by oxidation of the corresponding alcohol.[7]

(7) McDonald, R. N.; Tabor, T. E. *J. Org. Chem.* **1968**, *33*, 2934.

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