2,3-dimethoxy-β-nitrostyrene (8 mmol, 1.784 g) in 25 mL of THF and $BH_3{\cdot}THF$ (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; ^1H 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 $BH_3{\cdot}THF$ (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; ^1H 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; ^1H 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.

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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; $BH_3{\cdot}THF$, 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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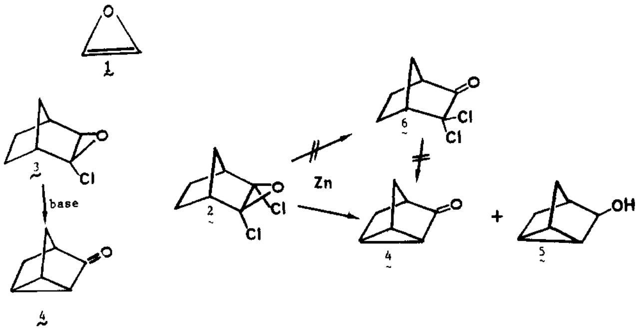
Oxirene (1) and its derivatives are of considerable current interest.[1] There is only one report of the possible preparation[1b] (under matrix-isolation conditions) of oxirenes, and it is unclear if they are actual molecules or only transition states,[2] although it is known that species with the symmetry 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.

[4] McDonald, R. N.; Steppel, R. N.; Cousins, R. C. *J. Org. Chem.* **1975**, *40*, 1694.

[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.

clo[2.2.1]hept-2-ene oxide to **5** by base.[8] The ketone **4** may arise from an oxo carbene that could in turn arise from an oxirene, or the latter could act directly as a carbenoid,[9] by undergoing transannular insertion.

Whatever the actual mechanism of the conversion of **2** to **4**, these results show that, like dehydrohalogenation of halo epoxides,[4] dehalogenation of *vic*-dihalo epoxides leads to the product expected from the generation of an oxo carbene.[10]

Experimental Section

GC was performed on an Antek 461 gas chromatograph equipped with a thermal conductivity detector and fitted with a 1.5 m × 3.2 mm 5% Carbowax 20M on Chromosorb W stainless steel analytical column or a 1 m × 6.4 mm 20% Carbowax 20M on Chromosorb W stainless steel preparative column. The carrier gas was helium at a flow rate of 60 mL/min. IR spectra were taken with a Pye Unicam SP-3-100 spectrometer, and ^{1}H NMR spectra were taken with a JEOL C-60 HL spectrometer in $CDCl_3$ with $(CH_3)_4Si$ as an internal standard. Zinc dust (J. T. Baker) was used without further treatment. Dioxane (B.D.H.) was refluxed overnight over sodium in a nitrogen atmosphere, distilled, and then stored over type 4-A molecular sieves.

2,4-Dichloro-3-oxatricyclo[3.2.1.$0^{2,4}$]octane (2) was prepared by reacting cyclopentadiene with trichloroethylene and dehydrochlorinating the trichlorobicycloheptenes with KOH in PrOH to give 2,3-dichlorobicyclo[2.2.1]hepta-2,5-diene.[11] The diene was reduced with hydrogen and palladium–charcoal in EtOH to 2,3-dichlorobicyclo[2.2.1]hept-2-ene.[12] The dichloroalkene was epoxidized with 3-chloroperoxybenzoic acid in CH_2Cl_2 to give **2**.[3b]

Reaction of 2,4-Dichloro-3-oxatricyclo[3.2.1.$0^{2,4}$]octane (2) with Zn. The epoxide **2** (221 mg, 1.23 mmol) and Zn powder (86 mg, 1.31 mmol) in dioxane (5 mL) were stirred under nitrogen at 22 °C for 12 h. Water (15 mL) was added and the mixture was extracted with two 10-mL portions of ether. The ether extracts were dried with anhydrous $MgSO_4$ and evaporated (rotary evaporator, room temperature) to give 132 mg of an oil, the ^{1}H NMR spectrum of which showed it to consist of nortricyclanone (**4**) and nortricyclanol (**5**) in a molar ratio of 9:1, corresponding to 90% and 10%, respectively. **4** and **5** were separated by preparative GC and identified by direct comparison (GC retention times and IR spectra) with authentic samples.[6a,b]

3,3-Dichlorobicyclo[2.2.1]heptan-2-one (6) was made analogously to the method of Shive et al. for the preparation of dibromocamphor.[6c] Bicyclo[2.2.1]heptan-2-one (2.0 g, 18.2 mmol) was placed in a 100-mL round-bottomed flask equipped with a reflux condenser and a dropping funnel. A 2 M solution of Cl_2 in AcOH (18 mL, 36 mmol) was added over 15 min, and the mixture was then heated on the steambath for several minutes (until the evolution of HCl ceased). A further 18-mL portion of Cl_2 in AcOH was added, and the mixture was heated on the steambath for 24 h. After being cooled to room temperature, the solution was poured over ice and the precipitated product was recrystallized from CH_2Cl_2–hexane and sublimed to give 2.5 g (77%) of **6**, mp 100–103 °C (lit.[7] mp 101.5–102.5 °C). The IR and ^{1}H NMR spectra corresponded with those reported.[7]

Attempted Reaction of 3,3-Dichlorobicyclo[2.2.1]heptan-2-one (6) with Zn. The dichloro ketone **6** (221 mg, 1.24 mmol) and Zn powder (85 mg, 1.3 mmol) in dioxane (5 mL) were stirred under nitrogen at 22 °C for 12 h. Workup as for the reaction of **2** with Zn gave 214 mg of a liquid that was shown by GC and ^{1}H NMR spectroscopy to be only the starting material **6**.

Reaction of 2-Chloro-3-oxatricyclo[3.2.1.$0^{2,4}$]octane (3) with Zn. The chloro epoxide **3**[7] (221 mg, 1.53 mmol) and Zn powder (100 mg, 1.53 mmol) in dioxane (5 mL) were stirred under nitrogen at 22 °C for 12 h. Workup as for the reaction of **2** with Zn gave 160 mg of a liquid that was shown by GC to consist of nortricyclanol (**5**) and the starting epoxide **3** in the molar ratio ca. 47:53. The identities of **5** and **3** were confirmed by collecting them (preparative GC) and comparing them (GC, IR) with authentic samples.

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Registry No. **2**, 50744-55-3; **3**, 16709-75-4; **4**, 695-05-6; **5**, 695-04-5; **6**, 16720-17-5; $Cl_2C{=}CHCl$, 79-01-6; cyclopentadiene, 542-92-7; *exo*-5,5,6-trichlorobicyclo[2.2.1]hept-2-ene, 37580-22-6; *endo*-5,5,6-trichlorobicyclo[2.2.1]hept-2-ene, 37580-23-7; 2,3-dichlorobicyclo[2.2.1]hepta-2,5-diene, 18990-07-3; 2,3-dichlorobicyclo[2,2.1]hept-2-ene, 21604-74-0; 3-chloroperbenzoic acid, 937-14-4; bicyclo[2.2.1]heptan-2-one, 497-38-1.

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[10] Besides β-elimination on halo and dihalo epoxides, only these routes to oxo carbenoids have been reported: (a) Diazo ketone decomposition.[1a] (b) Peroxy acid oxidation of alkynes.[1a] (c) Debromination of α,α-dibromo ketones with zinc.[5] (d) Dehydrobromination of α-bromoketones (Kowalski, C. J.; Fields, K. W. *J. Am. Chem. Soc.* **1982**, 104, 321). (e) Extrusion of CO_2, etc., from vinylene carbonates or their sulfur analogues (Torres, M.; Clement, A.; Strausz, O. P. *J. Org. Chem.* **1975**, *40*, 1694). Only in diazo ketone decomposition and in the photoexcitation of ketenes has the involvement of oxirenes been rigorously proved.[1]

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Reductive Dephosphorylation of (*Z*)-Bis(diethoxyphosphinyl)stilbene to Diphenylacetylene

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Alkynes represent an exceedingly important and useful class of organic compounds, the chemistry and preparation of which has been reviewed.[1] Only a few synthetic methods are available for the direct conversion of a carbonyl derivative to an alkyne. Structural and regioselective limitations of classical alkyne syntheses by alkylation or elimination procedures make new synthetic methods for the construction of alkynes from carbonyl compounds highly desirable. The most notable syntheses of alkynes from carbonyl compound precursors are (1) oxidation [$CuCl/O_2$[2]; NiO_2[3]; $AgOCOCF_3$[4]; HgO[5][of bis hydrazones derived from 1,2-diketones; (2) treatment of 2-substituted [epoxy[6]; OBz[7]; OAc[7,8]; Cl[8]; Br[8]; OMs[8]; SMe[9]] ketones with *p*-toluenesulfonyl hydrazine[6–9] or triphenylphosphine;[10]

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