was stirred under nitrogen for 48 h. The layers were separated, and the bottom layer was extracted with pentane. The extracts were combined with the top layer and this solution was washed with sodium bicarbonate solution and then with water. The solution was dried ($MgSO_4$) and the product was distilled in a semimicro Hickman still (bath 150 °C, 5×10^{-5} torr) to give 2.44 g (93%). An analytical sample was collected by GLC; NMR (CCl_4) δ 0.14 (s, 9 H), 1.20–2.02 (br m, 9 H), 2.20 (m, 2 H), 2.54 (m, 2 H), 4.99 (m, 4 H), 5.75 (m, 2 H). Anal. Calcd for $C_{15}H_{28}OSi$: C, 71.34; H, 11.18. Found: C, 71.19; H, 11.03.

1-[(Trimethylsilyl)oxy]bicyclo[6.4.0]dodec-2- (and -6-) enes (6 and 7). A sample, 0.90 g (3.6 m mol), of 1,2-diallyl-1-[(trimethylsilyl)oxy]cyclohexane in 30 mL of methylcyclohexane was pyrolyzed as described for 1,8-bis[(trimethylsilyl)oxy]bicyclo-[6.4.0]dodec-2-ene at 290 °C for 76 h. After removal of the solvent, 0.76 g (84%) of product was recovered. GLC analysis (2% SE-30 at 115 °C) found two products in a 9:1 ratio, and pure samples of each were obtained by preparative GLC. The major product has NMR (CCl_4) δ 0.06 (s, 9 H), 1.2–1.96 (br m, 14 H), 2.15 (m, 3 H), 5.28 and 5.57 (AB part of Y_2ABX, $J_{AB} = 11$, $J_{AY} = 7.3$, $J_{AX} = J_{BY} = 0$, $J_{BX} = 8$ Hz); minor product, NMR (CCl_4) δ 0.30 (s, 9 H), 1.35–1.95 (br m, 14 H), 2.29 (m, 2 H), 2.87 (m, 1 H), 5.85 (m, 2 H).

6-Bicyclo[6.4.0]dodecen-1-ol. The major product above, 0.10 g, was heated for 12 h under reflux in 35 mL of 0.1 N sodium methoxide in methanol. The solution was neutralized and the methanol was removed in vacuo. The organic product was taken up on ether, and the ether solution was washed with water and then dried ($MgSO_4$). The product was isolated by GLC (2% SE-30 at 120 °C; NMR (CCl_4) δ 1.2–1.9 (br m, 14 H), 2.20 (m, 3 H), 5.34 and 5.62 (AB part of Y_2ABX, $J_{AB} = 11$, $J_{AY} = 7.8$, $J_{AX} = J_{BY} = 0$, $J_{BX} = 8.2$ Hz). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.00; H, 11.22.

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Registry No. *cis*-1 (Y = OH), 74930-46-4; *trans*-1 (Y = OH), 74930-47-5; *cis*-1 (Y = $OSiMe_3$), 74930-48-6; *trans*-1 (Y = $OSiMe_3$), 74930-49-7; *cis*-2 (Y = $OSiMe_3$), 74930-50-0; *trans*-2 (Y = $OSiMe_3$), 74930-51-1; *cis*-2 (Y = OH), 74930-52-2; *trans*-2 (Y = OH), 74930-53-3; 4, 74930-54-4; 4 DNP derivative, 74930-55-5; dihydro-4, 73223-35-5; dihydro-4 DNP derivative, 1050-65-3; *cis*-5 (Y = OH), 74930-56-6; *trans*-5 (Y = OH), 74930-57-7; *cis*-5 (Y = $OSiMe_3$), 74930-58-8; *trans*-5 (Y = $OSiMe_3$), 74930-59-9; *cis*-6, 74930-60-2; *trans*-6, 74930-61-3; *cis*-7, 74947-54-9; *trans*-7, 74930-62-4; 2-allyl-2-hydroxycyclohexanone, 60277-96-5; allyl bromide, 106-95-6; 1,2-cyclohexanedione, 765-87-7; 2-allylcyclohexanone, 94-66-6; *cis*-6-bicyclo[6.4.0]dodecen-1-ol, 74930-63-5; *trans*-6-bicyclo[6.4.0]dodecen-1-ol, 74930-64-6.

Stereochemistry of Molybdenum Peroxide Oxidation of Organoboranes

M. Mark Midland*[1] and Scott B. Preston[2]

Department of Chemistry, University of California, Riverside, California 92521

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Evans[3] has recently reported that organoboranes are efficiently oxidized to alcohols with the molybdenum peroxide reagent MoO_5·py·HMPA (MoOPH). The MoOPH reagent is reported to be an anhydrous reagent capable of oxidizing organoboranes under mild (ambient temperature) conditions. We recently required such a reagent for the oxidation of optically active allylborane derivatives which are prone to undergo protonation and allylic rearrangement.[4] We have noted that the stereochemistry of oxidation of organoboranes with MoOPH has not been reported. Free-radical intermediates have been suggested in the oxidation of Grignard reagents by molybdenum peroxide reagents.[5] If radicals are also involved in organoborane oxidations, then the MoOPH oxidations could lead to a serious loss of stereochemistry.[6] We herein report that oxidation of organoboranes with MoOPH proceeds with complete retention of configuration.

The hydroboration–oxidation of 1-methylcyclohexene was chosen for the study (eq 1). Conventional oxidation

(1)

with basic hydrogen peroxide produces >99% isomerically pure *trans*-2-methylcyclohexanol.[7] Oxidation with MoOPH likewise gave >99% of the trans isomer. None of the cis isomer (prepared by K-Selectride reduction of 2-methylcyclohexanone[8]) could be detected by VPC or NMR. The MoOPH oxidation of organoboranes thus presumably does not occur by a free-radical process since such a process should lead to an epimeric mixture of alcohols. The reagent is thus a mild alternative to trialkylamine *N*-oxides which often require elevated temperature or prolonged reaction times for oxidation of organoboranes under anhydrous conditions.[9] Unfortunately, with the oxidation conditions employed for alkylboranes, the MoOPH reagent failed to oxidize allylboranes to allylic alcohols in high yield.

Experimental Section

All reactions were run in dry glassware under nitrogen by using syringe and double-ended-needle techniques.[10] 1-Methylcyclohexene (Aldrich) was distilled from a small quantity of lithium aluminum hydride. The MoOPH was prepared by the method of Vedejs.[11] The NMR spectra were recorded on a Varian EM390 instrument.

Hydroboration–Oxidation of 1-Methylcyclohexene. A 50-mL flask equipped with a septum-capped inlet, magnetic stirring bar, and a reflux condenser attached to a nitrogen bubbler was charged with 6 mL of tetrahydrofuran and 6 mmol of 1-methylcyclohexene. Then 3 mmol of borane–methyl sulfide was added and the solution stirred at 0 °C for 1 h followed by warming to room temperature for 2 h. Methanol (3 mmol) was added and the solution stirred for 30 min to produce the methoxyborane. The solution was then cooled to 0 °C. A separate round-bottomed flask was charged with 4.4 g of MoOPH (10 mmol) and flushed with nitrogen. The side arm of the flask was attached via a Tygon tube to the side arm of the flask containing the organoborane. The MoOPH was then added to the organoborane over a 5-min period. The mixture was stirred at 0 °C for 30 min and then warmed to room temperature. After 1 h, 5 mL of 3 M sodium hydroxide was added. Hexadecane was added as an internal standard and the mixture analyzed by VPC (10% DC710). There was found 5.65 mmol (94%) of *trans*-2-methylcyclohexanol. The mixture was extracted with ether, washed with water and then 1 N hydrochloric acid, and dried (potassium carbonate). The ether

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(2) University of California Reagents Fellow, 1979–1981.
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solution was concentrated and distilled in a Kugelrohr apparatus (100 °C pot temperature, 30 mm) to provide 0.342 g (50%) of 2-methylcyclohexanol. Analysis by VPC (10% TCEP, 6 ft × $^1/_8$ in., 110 °C) revealed no observable amounts of the cis isomer. The cis and trans isomers may also be distinguished by the NMR signal of the proton on the carbon adjacent to the oxygen. The cis isomer exhibits a multiplet at 3.7 ppm while the trans isomer exhibits a multiplet at 2.9 ppm. Again, none of the cis isomer could be detected.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. 1-Methylcyclohexene, 591-49-1; *trans*-2-methylcyclohexanol, 7443-52-9.

Synthesis of 3-Chloro-3-methyl-d_3-diazirine

M. T. H. Liu* and N. H. Chishti

Deparment of Chemistry, University of Prince Edward Island, Charlottetown, Prince Edward Island, C1A 4P3 Canada

C. D. Burkholder, W. E. Jones,* and J. S. Wasson

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, B3H 4J3 Canada

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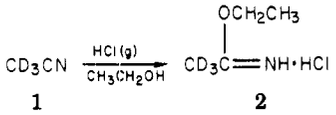
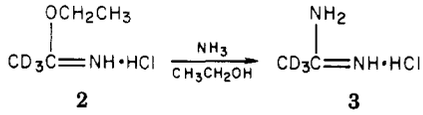
The synthesis of 3-halo-3-methyldiazirines by oxidation of acetamidine precursors has become the standard procedure since Graham's original report.[1] In the study of reactions of hydrogen atoms with 3-chloro-3-methyldiazirine it was crucial to an understanding of the mechanism to prepare the trideuterio compound.[2] This compound is known[3] but no synthetic procedure has been reported. We now report the procedure for the synthesis of the title compound. During preparation, care must be taken to prevent exchange of hydrogen for deuterium.

The deuterated methyl group is derived from acetonitrile-d_3 (1) which was converted to the acetimino ethyl ether (2) with hydrogen chloride in ethanol. Reaction of



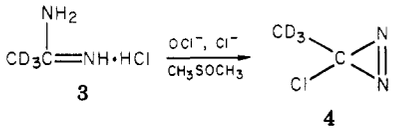
1 2

2 with anhydrous ammonia produced acetamidine hydrochloride (3). As this is hygroscopic it should be kept in



2 3

a desiccator to prevent exchange. 3 was then oxidized to 3-chloro-3-methyl-d_3-diazirine (4) with aqueous sodium hypochlorite. Complete deuteration of 3 was inferred from the proton NMR spectrum and complete deuteration of 4 was found in its mass spectrum.



3 4

Experimental Section

Acetamidine-d_3 Hydrochloride. Anhydrous hydrogen chloride gas was bubbled for 1.5 h at 0 °C into a solution of acetonitrile-d_3 (99 atom % D, 4.4 g, 0.10 mol) in dry ethanol (6 mL, 0.1 mol) in a three-neck flask equipped with drying tubes. The flask was then stoppered and stored for 4 days at 0 °C. Dry diethyl ether (60 mL) was added and the mixture became milky. The solvents were distilled. Acetimine ethyl ether hydrochloride 2 was obtained as a white solid and dried over silica gel in a vacuum desiccator (yield 10.7 g, 85%). Anhydrous ammonia was bubbled for 1 h through dry ethanol (30 mL) at 0 °C in a three-neck flask equipped with a dropping funnel and drying tube. A suspension of 2 (10.7 g) in dry ethanol (50 mL) was added slowly to the stirred ammonia/ethanol solution. The reaction mixture was stirred for 1 h at 0 °C. The precipitated ammonia chloride was filtered out and the solvent evaporated to give acetamidine-d_3 hydrochloride as a white crystalline solid: yield 6.5 g (67%); mp 142–142.5 °C (hygroscopic); IR, (Nujol mull) ν 2380, 2265, 1667, 1441, 1370, 1145, 1081, 1041 cm^{-1}.

3-Chloro-3-methyl-d_3-diazirine (4). Acetamidine-d_3 hydrochloride (3, 2.0 g) was dissolved in 120 mL of dimethyl sulfoxide containing 10 g of lithium chloride in a 500-mL three-neck flask. Aqueous sodium hypochlorite (commercial Javex, 0.78 M, 150 mL) was combined with 150 mL of water containing 50 g of sodium chloride and the resulting solution was added rapidly to the stirred solution of 3. The temperature rose to 55 °C and the gaseous product escaping from solution was dried by passage over 20 g of potassium hydroxide in a U-tube. 3-Chloro-3-methyl-d_3-diazirine (4) was trapped as a liquid at −78 °C. A liquid nitrogen trap was not used because of the hazard of explosion,[4] even though a lower yield results. The liquid diazirine was degassed at −78 °C and expanded into a bulb to give colorless 3-chloro-3-methyl-d_3-diazirine gas (4): yield (P = 120 mm, t = 18 °C, v = 390 cm^3) 2.6 mmol (12%); mass spectrum (70 eV), m/e 65, 58, 30, 28 (100%); mass spectrum (20 eV), m/e 65 (100%), 58, 30; IR (P = 80 mm, t = 22 °C, l = 10 cm) 2975, 1602, 980 cm^{-1}; UV (P = 10 mm, t = 19 °C, l = 9.6 cm) 353 nm (ϵ 130), 348 (40), 344 (69), 342 (54), 366 (90), 333 (41), 328 (42), 325 (34), 320 (34).

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Pyrrole Studies. 22.[1a] [4π + 2π] Cycloaddition Reactions with Vinylpyrroles

R. Alan Jones,* Michael T. P. Marriott, W. Philip Rosenthal, and Jose Sepulveda Arques[1b]

School of Chemical Sciences, University of East Anglia, Norwich, Norfolk NR4 7TJ, England

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The majority of procedures available for the synthesis of indoles involve ring closure to form the five-membered ring,[2] and relatively few methods start from the pyrrole ring system.[3] Although pyrroles generally react with

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