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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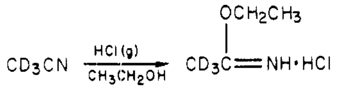
The synthesis of 3-halo-3-methyldiazirines by oxidation of acetamidine precursors has become the standard procedure since Graham's original report.[1] In the study of reactions of hydrogen atoms with 3-chloro-3-methyldiazirine it was crucial to an understanding of the mechanism to prepare the trideuterio 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.

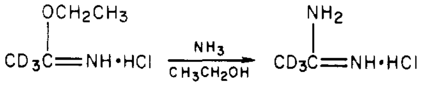
The deuterated methyl group is derived from acetonitrile-d_3 (1) which was converted to the acetimino ethyl ether (2) with hydrogen chloride in ethanol. Reaction of



$$CD_3CN \xrightarrow[CH_3CH_2OH]{HCl(g)} CD_3C(OCH_2CH_3){=}NH\cdot HCl$$

1 2

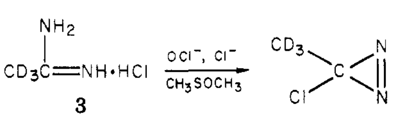
2 with anhydrous ammonia produced acetamidine hydrochloride (3). As this is hygroscopic it should be kept in



$$CD_3C(OCH_2CH_3){=}NH\cdot HCl \xrightarrow[CH_3CH_2OH]{NH_3} CD_3C(NH_2){=}NH\cdot HCl$$

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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[2] C. D. Burkholder, W. E. Jones, J. S. Wasson, and M. T. H. Liu, *J. Am. Chem. Soc.*, **102**, 2847 (1980).

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Pyrrole Studies. 22.[1a] [$4\pi + 2\pi$] 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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[1] (a) Presented in part at the 4th Lakeland Heterocyclic Chemistry Symposium, Grasmere, England, May 1979. Part 21: R. S. Budhram, R. A. Jones, R. O. Jones, and B. C. Uff, *Org. Magn. Reson.* **13**, 89 (1980). (b) On leave from the Department of Pharmacy, University of Valencia, Spain.

[2] R. J. Sundberg, "The Chemistry of Indoles", Academic Press, New York, 1970.

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