Convenient Synthesis of Vinylcyclohexane-α-*d*

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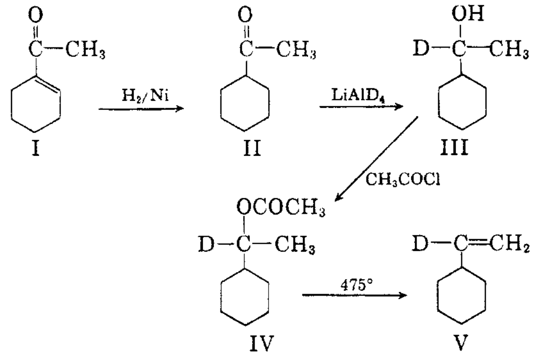
A recent note[3] on the preparation of methyl cyclohexyl ketone has prompted us to report some results we have obtained in the course of preparing the monomer vinylcyclohexane-α-*d* (V).

A convenient laboratory preparation of the deuterated vinylcyclohexane (V) utilized ketone (II) as the starting material.[4] Vinylcyclohexane has previously been reported by Van Derby and Kooyman, prepared by preparation of methyl cyclohexylcarbinol by reaction of cyclohexylmagnesium bromide and acetaldehyde, followed by acetylation and pyrolysis. The ketone (II) had also been prepared by oxidation of 1-cyclohexylethanol[5,6] and more recently by the catalytic reduction of methyl cyclohexen-3-yl ketone.[2]

The ketone (II) was readily accessible from the reduction of methyl cyclohexen-1-yl ketone[6,7] (I). Reduction was carried out in an 86% yield by hydrogenation at room temperature with Raney Nickel W-2[8] as the catalyst. Reduction with lithium aluminum deuteride gave the deuterated alcohol (III) in 91.5% yield which was smoothly acetylated to the deutero acetate (IV) in a 95.3% yield. Pyrolysis of the acetate (IV) gave the desired deuterated monomer (V) after careful fractionation (71%). Fractionations were followed by vapor phase chromatography to insure purity of the monomer. Vinylcyclohexane[4] (V. D = H) was prepared in analogous fashion using lithium aluminum hydride for the reduction of the ketone (II).



EXPERIMENTAL

Methyl cyclohexyl ketone (II). A mixture of methyl cyclohexen-1-yl ketone,[6] 17.5 g. (0.138 mol.), 75 ml. of methanol and 1 g. of W-2 Raney Nickel catalyst[7] in a rocking autoclave pressurized to 500 lbs./in.^{2} was shaken at room temperature for 20–30 min. after which no further hydrogen was absorbed. The catalyst and methanol were removed and distillation of the residual oil furnished 15.2 g. (86%), b.p. 66° (12 mm.), n_D^{26} 1.4491, of methyl cyclohexyl ketone (reported[6] b.p. 182.5–184.5° (676 mm.), $n_D^{25.9}$ 1.44955).

1-Cyclohexylethanol-1-d (III). To a solution of 3.3 g. (6.078 mol.) of lithium aluminum deuteride[9] in 300 ml. of absolute ethyl ether was added dropwise 37.9 g. (0.3 mol.) of II in 100 ml. of absolute ethyl ether. Upon completion of the addition, the mixture was refluxed for 1 hr. and then decomposed with water. The ether was removed and the residual oil was distilled yielding 35.5 g. of carbinol (91.5%), b.p. 65° (3.9 mm.), n_D^{25} 1.4632.

Anal. Calcd. for $C_8H_{15}DO$: C, 74.35; H + D, 13.26. Found: C, 74.31; H + D, 13.23, 0.891 deuterium atom/mol.[10]

1-Cyclohexylethyl-1-d acetate (IV). 1-Cyclohexylethanol-1-*d*, 33.0 g. (0.26 mol.), (III), was added dropwise to 30 g. of acetyl chloride at a rate to maintain reflux and the mixture was refluxed for 2 additional hr. Excess acetyl chloride was removed and the residual oil was distilled to yield 41.6 g. (95.3%), b.p. 67° (4.3 mm.), n_D^{25} 1.4445, of acetate.

Anal. Calcd. for $C_{10}H_{17}DO_2$: C, 70.13; H + D, 11.18. Found: C, 70.29; H + D, 11.28; 0.942 deuterium atom/mol.[9]

Vinylcyclohexane-α-d (V). 1-Cyclohexylethyl-1-*d* acetate, 34.5 g. (0.20 mol.), (IV), was pyrolyzed[11] by dropping the liquid at a rate of 8–12 drops per min. through a 12″ tube packed with Pyrex glass Raschig rings at 475° under a nitrogen atmosphere. The pyrolyzate was washed with aqueous sodium bicarbonate and water and dried over anhydrous sodium sulfate. Distillation in a seventy-five plate concentric tube column yielded 17.8 g. (80%), boiling at 127–129°, n_D^{25} 1.4459, of crude olefin. Careful distillation yielded 12.7 g. (71%), boiling at 127.5–128°, n_D^{25} 1.4441, of vinylcyclohexane-α-*d*. The product was pure as determined by vapor phase chromatography. It absorbed strongly at 11.0 μ in the infrared which indicated that it was a terminal olefin.

Anal. Calcd. for $C_8H_{13}D$: C, 86.40; H + D, 13.60. Found: C, 86.13; H + D, 13.62; 0.889 deuterium atom/mol.[10]

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(3) W. K. Johnson, *J. Org. Chem.*, **24**, 864 (1959).

(4) J. R. Van Derby and E. C. Kooyman, *Rec. trav. Chem.*, **71**, 837 (1952).

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(6) S. van Woerden, *Rec. trav. Chem.*, **45**, 124 (1926).

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(8) R. Mozingo, *Org. Syntheses*, **Coll. Vol. III**, 181 (1955).

(9) Purchased from Metal Hydrides, Inc., Beverly, Mass.

(10) Deuterium analyses were performed by Professor D. B. Denney of Rutgers, the State University of New Jersey, by means of a mass spectrograph.

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Preparation and Properties of 1-Phenyl-4-methyl-2-penten-1-one

Kurt Kulka, Robert J. Eiserle, James A. Rogers, Jr., and Fred W. Richter

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The recent availability of isobutyraldehyde in commercial quantities through the oxo process[1]

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(1) H. J. Hagemeyer and G. C. DeCroes, *The Chemistry of Isobutyraldehyde and its Derivatives*, Tennessee Eastman Co., Kingsport, Tenn., 3 (1953).