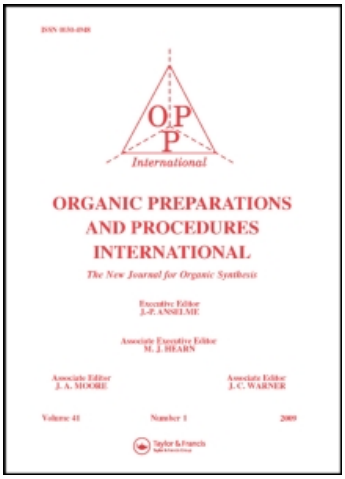

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CONVENIENT ROUTES FOR THE PREPARATION OF 2-ISOPROPYL-5-METHYL CYCLOPENTANONE

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CONVENIENT ROUTES FOR THE PREPARATION OF 2-ISOPROPYL-5-METHYL CYCLOPENTANONE

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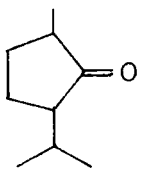
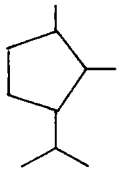
2-Isopropyl-5-methylcyclopentanone (I) has been obtained as a transformation product of several terpenes.[1-4] It has been used for preparing the different stereoisomers of nepetane (iridane)[5] (II) and the sesquiterpenes, oplopanone,[6] acorenone B[7] and 4-epiacorenone B.[8] It is usually prepared from diethyl adipate,[6] diethyl 2-methyladipate[5] or 2-methylcyclopentanone.[7] Two convenient routes for the preparation of I starting from methylheptenone III are presented in this communication.



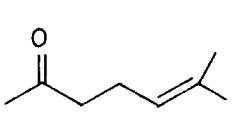
I



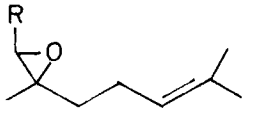
II

Reaction of methylheptenone III with dimethyloxosulfonium methylide furnished the oxirane (IVa)[9] which was readily transformed to the ketone I when treated for a short time with boron trifluoride etherate in benzene solution. It is suggested that in the presence of the Lewis acid, boron trifluoride, the oxirane IVa rearranges to the

aldehyde V which is then transformed to I according to the reaction mechanism shown. Work on the second route to I described below was taken up as a logical sequence of the suggested reaction mechanism for the conversion of IVa to I.

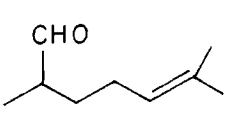


III

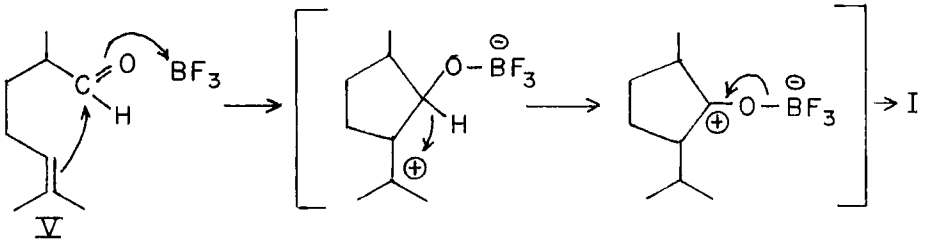


IVa R = H

IVb R = $CO_2C(CH_3)_3$



V



V

2,6-Dimethylhept-5-enal (V) was prepared from methyl heptenone (III) according to the general method of Blanchard and Buchi[10] by pyrolysing the ester IVb obtained by reacting III with t-butylchloroacetate in the presence of potassium tertiary butoxide. Aldehyde V was readily transformed to ketone I on treatment with boron trifluoride etherate.

EXPERIMENTAL

Melting points and boiling points are uncorrected. NMR spectra were taken at 60 MHz with TMS as internal reference.

2-Methyl-2-(4-methyl-3-pentenyl)-oxirane (IVa). - To a mixture of sodium hydride (1.20 g, 0.05 mol) and finely

powdered trimethyloxosulfonium iodide (11.0 g, 0.05 mol) under nitrogen was added dropwise dry dimethylsulfoxide (65 ml) with stirring. After 20 minutes, methylheptenone III (5.04 g, 0.04 mol) dissolved in dimethylsulfoxide (15 ml) was added dropwise. After the addition was complete the reaction mixture was stirred at room temperature for 2 hr at 50° for 1 hr, cooled to 0° and diluted with ice water. The product was extracted with ether. The ethereal extract was washed with water and dried (Na_2SO_4). After the evaporation of solvent, the residue was distilled to furnish the oxirane IVa; yield: 3.90 g (70%); bp. 110-115° (60 mm) lit.[9] bp. 81° (45 mm).

Anal. Calcd. for $C_9H_{16}O$: C, 77.09; H, 11.50;
Found: C, 77.11; H, 11.39.

^1H - NMR (CCl_4): δ 1.27(s, 3 H, CH_3-C(O)-C -), 1.63 (3 H, CH_3-C=C), 1.70 (3 H, CH_3-C=C), 2.43 (s, 2 H, oxirane), 5.10 (m,1H, vinyl).

2-Isopropyl-5-methylcyclopentanone (I) Method a. - Freshly distilled boron trifluoride etherate (2.5 ml) was added dropwise to a solution of the oxirane (IVa) (0.98 g; 0.007 mol) in dry benzene (25 ml). The reaction mixture was kept at room temperature for 1 hr, diluted with ether (50 ml) and washed successively with aqueous sodium carbonate solution (2%; 200 ml) and water (100 ml x 3). The organic layer was dried (Na_2SO_4) and the solvent was evaporated. Distillation of residue furnished I as a mixture of cis-and trans-isomers;

yield: 0.75 g (77%); bp. 180°/710 mm; lit.[6] bp. 185°/760 mm. The NMR spectrum was identical with that of an authentic sample. Ketone I was also characterized as 2,4-dinitrophenylhydrazone, mp. 168°, lit,[3] mp. 170-171°; semicarbazone mp. 196°, lit.[2] mp. 198°-200°.

Method b. - Ketone I was also prepared (yield = 60%) from the aldehyde V on treatment with boron trifluoride etherate following the procedure given above.

t-Butyl β-methyl-β-(4-methyl-3-pentenyl) glycidate (IVb).- A solution of potassium t-butoxide prepared by dissolving potassium (2.73 g; 0.07 mol) in t-butanol (75 ml) was added, with stirring, over a period of 1 hr to a mixture of methylheptenone (III) (8.82 g; 0.07 mol) and t-butyl chloroacetate (10.54 g; 0.07 mol) under nitrogen atmosphere at 10-15°. The reaction mixture was stirred at 10° for 1 hr and t-butanol was removed by vacuum distillation. The residual material was diluted with water and extracted with ether. The ether extract was washed with water, dried (Na_2SO_4) and the solvent was evaporated. Distillation of the residue yielded 2.0 g of (III); bp. 100° (60 mm) and 8.13 g (48%) of (IVb) as a diastereoisomeric mixture; bp. 100-05° (1.0 mm); NMR (CCl_4) δ 3.02 and 3.06 (singlets, oxirane hydrogen).

Anal. Calcd. for $C_{14}H_{24}O_3$: C, 69.96; H, 10.07;
Found: C, 70.16; H, 10.27.

2,6-Dimethyl-hept-5-en-1-al (V). - Glycidic ester IVb (0.96 g, 0.004 mol) was placed in a distillation apparatus and heated with a sand bath. When the temperature of the

ester reached 280°, there was vigorous evolution of gas and the pyrolysis product started distilling. The distilling flask was heated at 290° till distillation was complete. The pyrolysis product was redistilled to furnish V; yield: 0.42 g (75%); bp. 70-75° (15 mm). Aldehyde V thus prepared was identical (IR, NMR) with an authentic sample prepared according to literature method.[11]

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