Hofmann Elimination in the Reaction of 1-Methylcycloalkyl Chlorides with Bulky Alkoxides. A Convenient Procedure for the Conversion of 1-Methylcycloalkenes into Methylenecycloalkanes *via* Hydrochlorination–Elimination. Synthesis of β-Cedrene

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THE marked preference exhibited by potassium triethylmethoxide in directing elimination in simple aliphatic halides towards the Hofmann direction[1,2] has now been observed to be relatively general in cycloalkyl derivatives. Consequently, hydrochlorination of 1-methylcycloalkenes in the automatic hydrochlorinator[3] followed by elimination by potassium triethylmethoxide or potassium tricyclopentylmethoxide[4] provides a highly convenient shift of the double bond to yield the methylene derivatives. Typical applications are shown in reactions (1)—(3).

It was our need for β-cedrene which led us to develop this procedure. α-Cedrene is readily available from natural sources. However, β-cedrene has been available hitherto only with considerable difficulty.[5] Attempts to isomerize α- to β-cedrene by recognised procedures[6,7] failed. The present method provides a highly convenient route from α- to β-cedrene (reaction 3) and appears to be generally applicable for the movement of a tertiary double bond from the preferred endocyclic to the less stable exocyclic position.

The recommended procedure involves saturation of the olefin in ether at −70° with hydrogen chloride to form the tertiary chloride,[3] which, after removal of ether at 0°, is not purified but is immediately treated with potassium triethylmethoxide in excess at 60°. The elimination requires *ca.* 12 hr.

Four different procedures were studied.

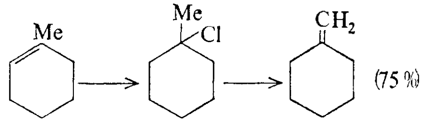
(A) Potassium (100 mmole) was dissolved in triethylmethanol (28 ml) (140°, 2·5 hr) to form a 3·0 M solution. This remains as a thick red solution at 60° but solidifies at room temperature.

(B and C) 2·0 M-Solutions of potassium triethylmethoxide in xylene or undecane were prepared from 120 mmoles of the alcohol and 100 mmoles of potassium in 45 ml. of xylene or undecane, (160°, 6 hr.). Both these reagents remained as clear red liquids at room temperature.

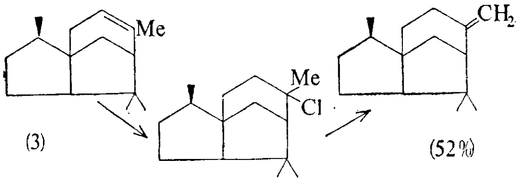
(D) 2·0 M-Solution of potassium tricyclopentylmethoxide was prepared from 25 mmoles of tricyclopentylmethanol and 20 mmoles of potassium in 6 ml. of undecane. This remains in solution at 70°, but solidifies at room temperature.

(1) $Me_2C=CMe_2 \rightarrow Me_2HC-CMe_2Cl \rightarrow Me_2HC-CMe=CH_2$ (97%)

(2)



(3)



TABLE

Results of the hydrochlorination–elimination procedure

Olefin	Time, hr.	Procedure A Yield,[a] %	Procedure A Methylene derivative %	Procedure B Yield,[a] %	Procedure B Methylene derivative %	Procedure C Yield,[a] %	Procedure C Methylene derivative %	Procedure D Yield,[a] %	Procedure D Methylene derivative %
2,3-Dimethylbut-2-ene	12	100	95	33	88	80	97	85	97
	24			64	95	97	96	100	97
1-Methylcyclopentene	12	96 84[c]	40[b]	100	39[b]	94	38[b]	80[e]	47
1-Methylcyclohexene	12	100 84[c]	62 61[b]	99	57 61[b]	100	60 64[b]	100	75 77[b]
1-Methylcycloheptene	12	80[c]	75[b]	100	53 54[b]	89	73	92	76
α-Cedrene	12	85[d]	52[b]						

[a] Analysis by g.l.c. for total olefins. All analyses by Golay squalene column g.l.c. unless otherwise indicated. [b] Isomer distribution by ^1H n.m.r. [c] Isolated yield on 10 mmole scale using 2M solution in triethyl methanol. [d] Isolated yield on 5 mmole scale using 2M solution in triethylmethanol. [e] Isolated yield after 6 hr. on a 10 mmole scale.

To 2 mmoles of hydrochloride containing *ca.* 1 mmole of n-octane as an internal standard, 6 mmoles of the above reagents were added individually under nitrogen, and heated (oil bath) in a stoppered tube for 12 hr. at 60°. The products were isolated by distillation at room temperature under vacuum using a spiral dry-ice trap. The results are summarized in the Table.

The marked preference exhibited by potassium triethylmethoxide in the 2-halogenoalkanes for elimination at the terminal position was said to be due to steric effects.[1] It was argued that the bulky alkoxide group would find it easier to attack a less hindered primary hydrogen atom on the terminal methyl group rather than a more hindered secondary or tertiary hydrogen atom within the chain. Although this interpretation has been questioned,[8] the present results show that the marked preference of potassium triethylmethoxide for Hofmann elimination is general.

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