

REDUCTION OF HYDROXYMETHYLENE DERIVATIVES OF CAMPHOR

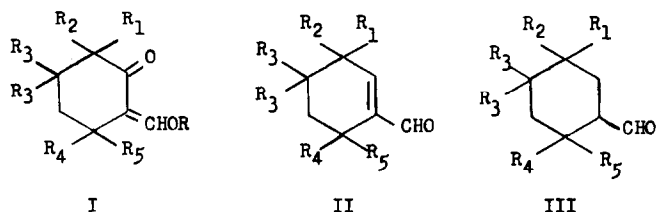
WITH COMPLEX HYDRIDES*

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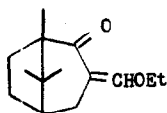
The reduction of the enol ethers of 2-hydroxymethylene cyclohexanone (I) by lithium aluminum hydride have been reported^{1,2} to yield α,β -unsaturated aldehydes (II) by means of a hydride addition to the carbonyl group according to the scheme a (see flow sheet I). Saturated carbonyl compounds suspected of being the aldehydes III_d and III_e have been isolated in the reduction of the ethers I_d and I_e.



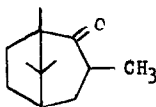
	R ₁	R ₂	R ₃	R ₄	R ₅
a	H	H	H	H	H
b	CH ₃	H	H	H	H
c	CH ₃	CH ₃	H	H	H
d	H	H	CH ₃	CH ₃	H
e	H	H	Cl ₃	CH ₃	CH ₃

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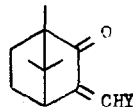
It was shown recently³ that the reduction of the ethyl ether (IV) derived from 3-formylhomocamphor does not lead to any aldehydic material. Only 3-methylhomocamphor (V) could be isolated from the reaction mixture. This result was



IV



V



VI

VIa Y = N(CH₃)
 VIb Y = SBU
 VIc Y = OBU
 VI d Y = H

explained by a reduction involving two successive 1,4-additions of hydride to the cisoid⁴ system formed by the carbonyl group and the exocyclic double bond (reduction scheme c in flow sheet I)

In order to evaluate the factors influencing these types of reactions, the derivatives (VI) were reduced with lithium aluminum hydride and with sodium borohydride. The results are reported in table I.

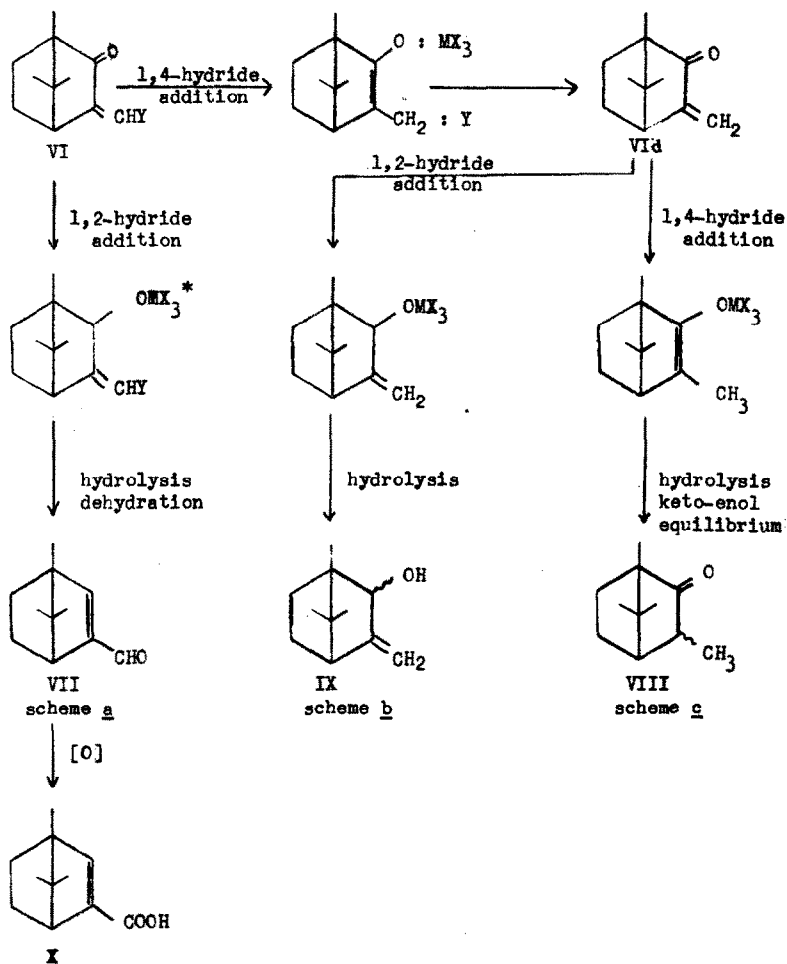
TABLE I

RESULTS OF THE VARIOUS HYDRIDE REDUCTIONS

Reducing agent	Derivatives	Percentage of products		
		VII	VIII	IX
LiAlH ₄	VIa	0-5%	60-65%	30-35%
	VIb	35-40%	0-10%	50-55%
	VIc	5-10%	60-65%	30-35%
	VI d	-	60-65%	35-40%
NaBH ₄	VIa	25%	10%	65%
	VI d	-	15%	85%

FLOW SHEET I

MECHANISTIC SCHEMES FOR THE REDUCTIONS



* In these mechanistic schemes, $-\text{MX}_3$ stands for undetermined alkoxyaluminum hydrides or alkoxyborohydrides.

The presence of 3-methylcamphor (VIII) in the reduction mixtures is demonstrated by peak superposition in the vapor phase chromatography with a sample prepared by an unambiguous method⁵ and by the formation of the corresponding semicarbazone m.p. 230° (lit.⁵ 229.5-230°). 3-Methyleneborneol (IX) whose presence in the reaction mixtures is indicated by peaks at 5.00 p.p.m.* (olefinic protons) and 3.58 p.p.m. (carbinolic proton) is characterized by the 3,5-dinitrobenzoate, m.p. 86°**.

The aldehyde (VII) presenting peaks at 9.50 p.p.m. (aldehydic proton) and 6.58 p.p.m. (olefinic proton) is characterized by the 2,4-dinitrophenylhydrazone m.p. 226° and by conversion to the known acid X m.p. 109-110° (lit.^{7,8} 112°) and $[\alpha]_D^{25} + 136.5^\circ$ (lit.^{7,8} + 140°).

The results obtained for the reduction of the compounds (VIa, VIb and VIc) can be explained by the mechanistic schemes proposed in the flow sheet, I.

The hypothesis that 3-methylenecamphor (VIc) is a common intermediate in the reduction paths b and c (flow sheet I) is confirmed by the fact that for a given reducing agent the ratio of 3-methylcamphor (VIII)/3-methyleneborneol (IX) present in the reduction mixtures is the same whether the derivatives (VIa and VIc) or 3-methylenecamphor (VIc) are reduced.

* All n.m.r. measurements were carried out at 60Mc/sec. for CCl₄ solutions. Chemical shifts (δ) are expressed in p.p.m. scale⁴ relative to internal tetramethylsilane

** Correct analysis were obtained for all the new compounds described in this paper.

