

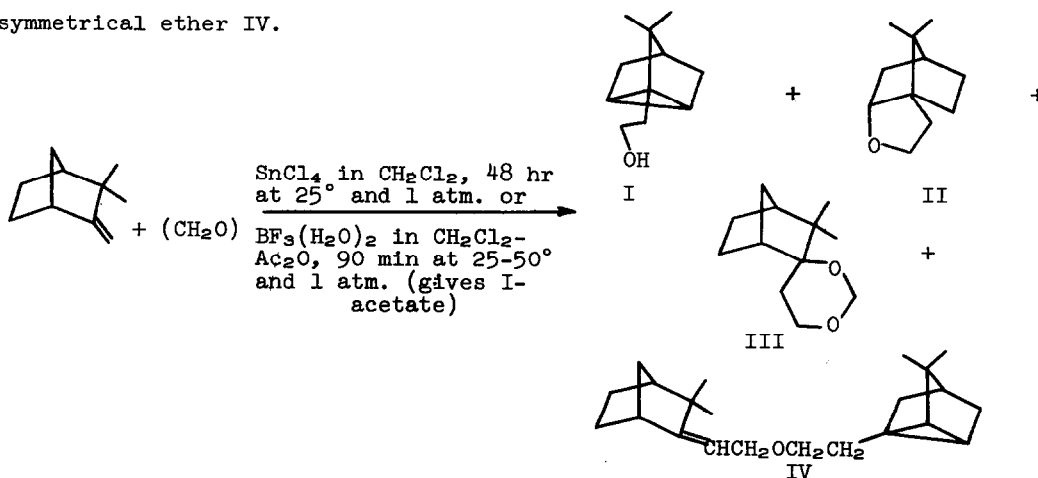
A NOVEL PRODUCT FROM CERTAIN LEWIS ACID-CATALYZED
CAMPHENE-FORMALDEHYDE REACTIONS

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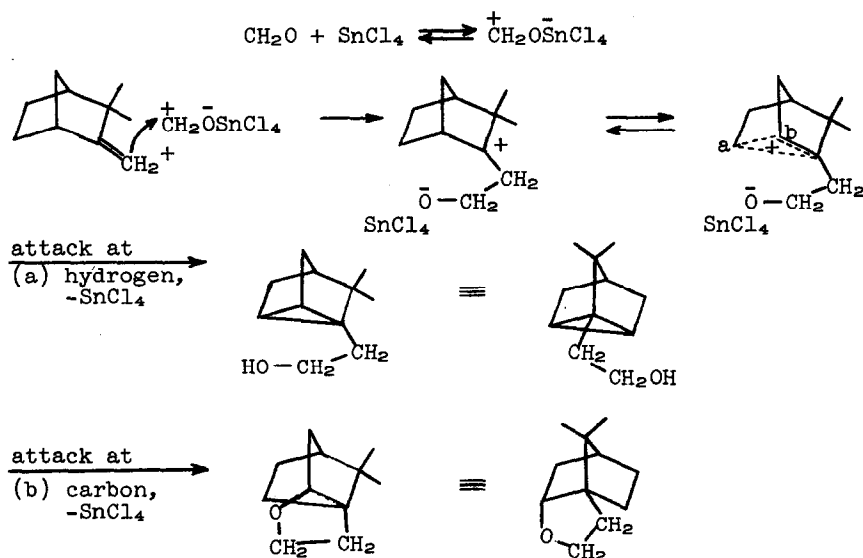
The many examples of Lewis acid-catalyzed isomerization and polymerization of terpenes have, perhaps, discouraged study of terpene-formaldehyde reactions under the aforementioned catalysis.¹⁻⁴ Thus, no reports are to be found on the preparation of primary alcohols via the Lewis acid catalyzed reaction of camphene with paraformaldehyde in organic solvents.

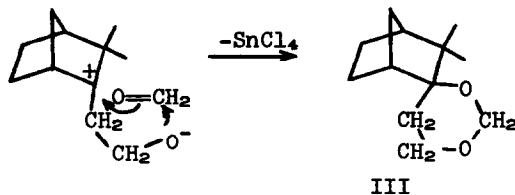
In the course of an extensive examination of camphene-formaldehyde reactions we have observed that under SnCl_4 or $\text{BF}_3(\text{H}_2\text{O})_2$ catalysis camphene and paraformaldehyde react in solvent methylene chloride or methylene chloride-acetic anhydride to give the primary tricyclic alcohol 2-(2'-hydroxyethyl)-3,3-dimethyltricyclo-[2.2.1.0^{2,6}]heptane (I) or its acetate in 49-57% yield (based on formaldehyde). Other products formed are the cyclic ether II, the 1,3-dioxane III, and the unsymmetrical ether IV.



The tricyclo alcohol I, as formed directly by the SnCl_4 -catalyzed reaction, is difficult to purify by distillation; the best fraction (ca. 90% pure) has bp 66-67° (0.20 mm) and n_D^{25} 1.4903. Preparative glpc affords the pure alcohol which gives a positive test with tetranitromethane⁵ in carbon tetrachloride but shows no unsaturation in its infrared and nmr spectrum. Anal. Calcd for $\text{C}_{11}\text{H}_{18}\text{O}$: C, 79.46; H, 10.92; O, 9.63; MW, 166. Found: C, 79.56; H, 10.90; O, 9.54; MW, 168, 170 (benzene). The near infrared spectra of the alcohol I and its acetate show the presence of tertiary cyclopropyl hydrogens, strong absorption at 1.672 μ (in good agreement with values obtained by others for related compounds,⁶⁻⁸ see Table I). Finally, an informed analysis of the alcohol's nmr spectrum shows excellent correlation with the spectra of similarly constructed molecules⁹⁻¹⁰ (see Table II). An important feature of this comparison is the agreement observed for the unsubstituted methylene groups, positions 3 and 5 of the tricycloheptane nucleus. These two pairs of methylene hydrogens give rise to an AB quartet as shown. Structural assignments for the products II, III, and IV are based on elemental analyses and spectral data.

Formation of the alcohol I is considered to arise via the reaction sequence that follows (infra vide); a reaction path similar to the one proposed by Yang¹¹ for the reaction of 2-methyl-2-butene with paraformaldehyde.





A similar mechanism is probably operative in the $\text{BF}_3(\text{H}_2\text{O})_2$ catalyzed camphene-formaldehyde reaction in solvent methylene chloride-acetic anhydride. The higher yield of the acetate of the product I (57%) is probably a consequence of the formation of the acetate in situ that obviates further reactions of the free alcohol.

From the product analysis an interesting result is immediately evident. Other workers¹² have found that carbonium ions generated in aprotic media rearrange less readily than those formed in aqueous solvents. Since aqueous systems stabilize a carbonium ion by solvation, the ion can rearrange to a thermodynamically more stable structure. It is interesting to note that although our experiments were run in methylene chloride, a relatively poor solvent for effective solvation, the products which were observed are predominantly derived from rearranged carbon skeletons.¹³

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TABLE I
Near Infrared Values Associated with Tertiary Cyclopropanyl Hydrogens
in Some Polycyclic Compounds

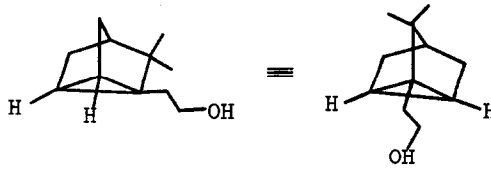

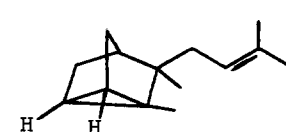
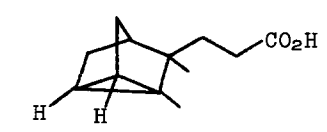
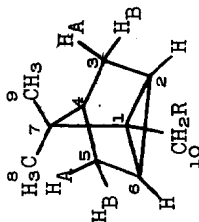
<u>Compound</u>	<u>Absorption, μ</u>
	1.672
 <p>Nortricyclanol^{7,8}</p>	1.663
 <p>α-Santalene⁸</p>	1.675
 <p>Tricycloekasantalic Acid⁸</p>	1.675

TABLE II



Proton NMR Assignments for Derivatives of the Above Structure

Compound	AB Quartet, τ	Bridgehead H(C-4), τ	Cyclopropyl H's, τ	Gem-Dimethyl H's, τ	(C-10) H's, τ
R = OH ⁹	8.22, 8.41, 8.87, ----- ^b	8.63	8.94	9.07	6.36 (7.07 = OH)
R = -O ₂ CC ₆ H ₄ NO ₂ (p)	8.13, 8.32, ----- ^a , ----- ^b	8.53	8.76	9.02	5.52
R = Cl ⁹	8.15, 8.32, 8.81, ----- ^b	8.55	8.76	9.02	6.29
R = H ^c	8.28, 8.46 8.91, 9.09 8.37 9.00 midpoint midpoint	8.64	9.00	9.19	
R = H ¹⁰	8.34 8.97 midpoint midpoint	8.61	8.99	9.18	
R = CH ₂ OH (I)	8.25, 8.39 8.86, 9.02 ^d 8.32 8.94 midpoint midpoint	8.62	9.02	9.14	

^a Value not assignable because cyclopropyl H's superimposed.

^b Value not assignable because gem-dimethyl H's superimposed.

^c Values obtained in this Laboratory.

^d Value estimated from coupling value.

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13. A possible explanation for these anomalous results could lie in the unique character of the carbonium ion generated. In an aprotic solvent such as CH_2Cl_2 and in the presence of a strong Lewis acid such as stannic chloride there is no nucleophile, other than formaldehyde or an intermediate hydroxyethyl compound, capable of carbonium ion capture which would lead to a product stable under the reaction conditions. The presence of geminal methyl groups in the β position as well as the initial generation of a carbonium ion at C_2 prevents direct elimination into the ring, leaving elimination to form an exocyclic allylic alcohol as the only eliminative recourse without rearrangement. We feel that the lack of alternatives could lead to an initial carbonium ion with a sufficient lifetime to yield the observed rearranged products.