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CONVERSION OF 7-SUBSTITUTED NORBORNADIENES TO TROPYL DERIVATIVES: A NOVEL ANION-INDUCED REARRANGEMENT.

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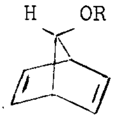
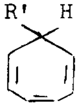
The isomerization of norbornadiene to cycloheptatriene takes place under relatively severe thermal conditions (425°);[3] however 7-alkoxy or 7-phenyl substituted norbornadienes undergo a more facile (170°) thermal rearrangement to the corresponding tropyl derivative.[4] A similar reaction involving conversion of a norbornadiene system into a cycloheptatriene, occurring under milder conditions, was observed in the reduction of 7-acetoxynorbornadiene (I) with lithium aluminum hydride in tetrahydrofuran.[5] The product obtained in this case using lithium aluminum deuteride was 1-deuteriocycloheptatriene (II).



I, R = $COCH_3$

III, R = H



II, R' = D

IV, R' = OCH_3

V, R' = OH

Story[6] reported that attempted preparations of 7-norbornadienol (III) by the hydrolysis of the corresponding ester (I) were unsuccessful, leading instead to complicated product mixtures. Acid-catalyzed hydrolysis of I would be expected to give 7-norbornadienol (III)[7a] (formation of the carbonium ion in a weak acid medium would not be likely[7b]); more noteworthy was the failure to obtain the simple hydrolysis product (III) from the base-catalyzed reaction. We have reinvestigated the saponification of 7-acetoxynorbornadiene and have observed transformations to tropyl derivatives induced by methylate or hydroxide ions. These reactions are related to the hydride reduction of I and represent novel anion-induced rearrangement of the norbornadiene skeleton.

When 7-acetoxynorbornadiene was treated with sodium methoxide in methanol at ambient temperature, the major product was identified as methyl tropyl ether (IV[8]). The same product was obtained in 32% yield when I was treated with a methanol-water solution of sodium hydroxide.

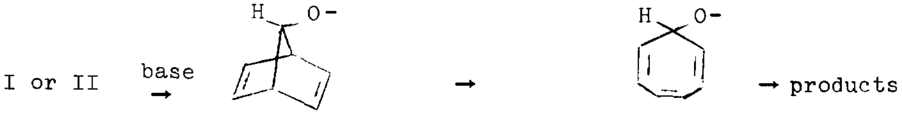
The possibility of a mechanistic pathway involving proton abstraction (as would be expected were carbenoid moieties to be reaction intermediates) was excluded by an experiment utilizing sodium deuteroxide with 1-deuteriomethanol and deuterium oxide as solvent. No deuterium was incorporated in the product IV (obtained in 37% yield).

Reaction of 7-norbornadienol (III) with methanol-water containing catalytic quantities of sodium hydroxide gave a 57% yield of methyl tropyl ether, a remarkable result in that two alcohols (III and methanol) were converted to an ether by alkaline catalysis.

That this type of reaction was not limited to ether formation was clear from observing the interaction of 7-acetoxynorbornadiene with sodium deuteroxide in acetone-d_6/ deuterium oxide mixture. The product detected was the unstable tropyl alcohol (V) which could be converted to tropylium ion in the presence of acid[9].

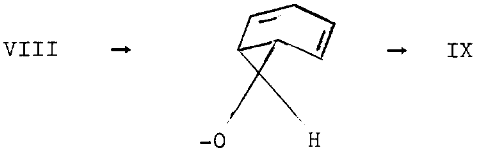
Mechanisms for transformations leading to methyl tropyl ether involving cleavage of the carbon-oxygen bond of methanol under the conditions of these experiments would be unprecedented and highly unlikely from a thermodynamic point of view. In addition, a carbonium ion mechanism can be eliminated since a 0.02 M stock solution of I in methanol gave no evidence of reaction after six months' storage. Postulating an initial nucleophilic attack of alkoxide or hydroxide ion on the pi-bonds of the norbornadienyl system (syn or anti with respect to the acetate or hydroxyl groups) could be more reasonable. Such an attack might or might not be concerted with elimination of acetate or hydroxide ion; but in any case, such hypothetical pathways suffer from the necessity of eliminating hydroxyl in the case of 7-norbornadienol reacting to form methyl tropyl ether.

An attractive pathway would involve the intermediacy of the alkoxide VIII, which could readily be generated from the 7-acetate or 7-hydroxy compound under the alkaline conditions of these reactions. The function of the base catalyst would be to bring about the formation of VIII. Support for this possibility comes from the failure of either 7-t-butoxynorbornadiene or 7-methoxynorbornadiene to undergo reaction in alkaline methanol. Neither of these ethers would be expected to form VIII.



VIII IX

One possible mechanism for the conversion of VIII to IX involves a concerted, symmetry-allowed 1,3-sigmatropic shift of C_7 (with inversion at C_7) to give a norcaradienyl intermediate (X) which can open by a symmetry-allowed process to produce the tropyl derivative (IX).[10] In the transition state, C_7 is sp^2 hybridized and may possess carbonium ion character, resulting in a stabilizing effect relative to the ground state from substituents such as alkoxyl or phenyl, and an even greater stabilizing effect should be exerted by $-O^-$.[11]



X

The above mechanism implies that IX, the conjugate base of the unstable tropyl alcohol, is the precursor to methyl tropyl ether, and that tropyl alcohol is the species which is unusually prone to facile etherification. Were this to be the case, it would be of interest to know whether such an etherification was S_n1 or S_n2 in nature. Experiments are under way to determine the course of reaction of 7-d-7-norbornadienol so as to test these possibilities. Also in progress are experiments designed to extend the reaction to other nucleophiles and to examine the potentiality for rearrangement with leaving groups other than hydroxyl or acetyl.

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