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Eaton Laboratories
Division of the Norwich Pharmacal Co.
Norwich, N. Y.

An O^{18} Tracer Study of the Acid-Catalyzed Formation of Enol Ethers

Kenneth B. Wiberg and Klaus A. Saegebarth

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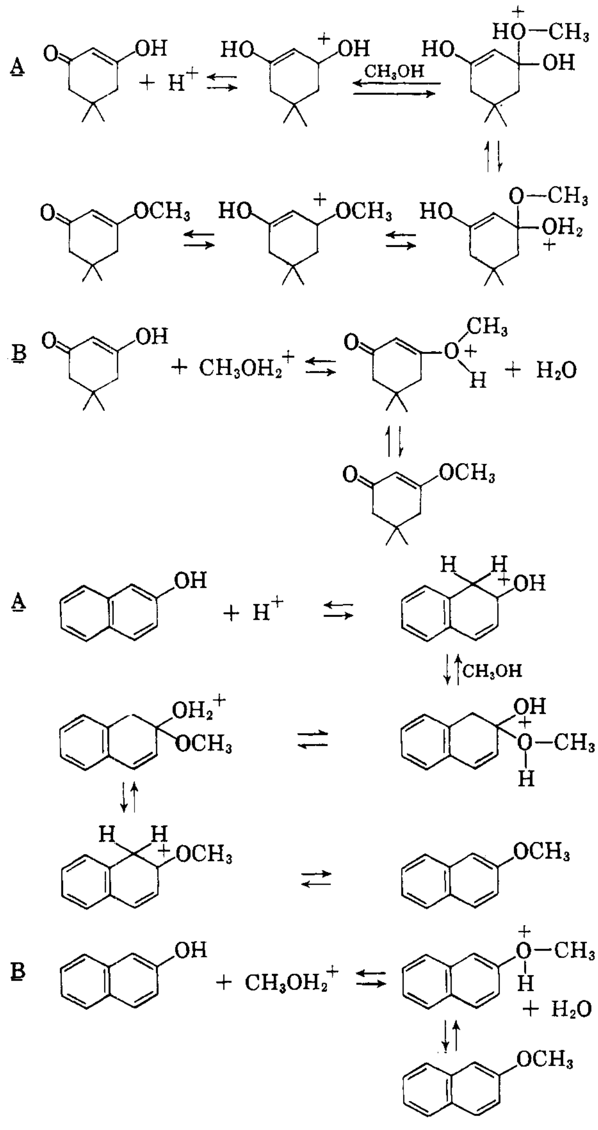
The conversion of enols, such as dimethyldihydroresorcinol,[1] and of some reactive phenols, such as β-naphthol[2] to the corresponding ethers may be effected by the acid-catalyzed reaction with the corresponding alcohol. In either case, there are two possible mechanisms:



The type A mechanism is, *a priori*, the more reasonable considering the facile formation of these ethers, and the small likelihood that the phenols are much more effective nucleophiles than is water. Further evidence for this mechanism may be found in the observation that resorcinol,[3] but not phenol, catechol, or hydroquinone, will form a monomethyl ether in this reaction, and that a dimethyl ether is not formed. Similarly, phloroglucinol reacts readily to form a dimethyl ether, but not a trimethyl ether.[4]

The two mechanisms are easily differentiated by using oxygen-18–labeled methanol, since mechanism A predicts incorporation of the label into the product ether, whereas mechanism B predicts that the ether will be devoid of isotope oxygen. The experiments were performed in the usual fashion and the results of the oxygen-18 analyses are given in Table I. It is readily apparent that nearly quantitative transfer of the label occurred, indicating the addition-elimination mechanism to be correct. The results also suggest that oxygen-18–labeling of these compounds should be easily effected by heating in acidified oxygen-18–enriched water, and that the ethers should be easily cleaved by acid-catalyzed hydrolysis.

TABLE I

Oxygen-18 Analytical Data

Compound	% O^{18} in CO_2	% excess O^{18}
Methanol	0.742	1.08
	0.749	1.09
2-Methoxynaphthalene	0.726	1.04
	0.726	1.04
5,5-Dimethyl-3-methoxy-cyclohexene-2-one	0.448	0.972
	0.448	0.972

EXPERIMENTAL

Reaction of dimethyldihydrolrescrcinol. To 5 g. (36 mmoles) of dimethyldihydroresorcinol was added 50 ml. of benzene, 3.0 ml. of methanol-O^{18} (100% excess, containing 1.09 excess O^{18}), and 0.2 g. of *p*-toluenesulfonic acid. The solution was heated at reflux for 24 hr. in an apparatus in which the distilled solvent containing water was passed through potassium carbonate before being returned to the solution. Distillation gave 4.5 g. (81%) of the enol ether having b.p. 145–146° at 35 mm. Oxygen-18 analysis indicated the presence of 0.972 excess O^{18}.[5]

Reaction of β-naphthol. A solution of 1 g. of β-naphthol and 50 mg. of *p*-toluenesulfonic acid in 2.5 ml. of methanol was sealed in a tube and heated at 100° for 40 hr. The tube was opened and the contents were mixed with 10% potassium hydroxide solution and washed with same after filter-

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ing. The product was allowed to dry after being washed with water several times. Recrystallization from ethanol-water gave 0.75 g. (70%), m.p. 70–71°.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WASHINGTON
SEATTLE 5, WASH.

Benkeser Reduction of Norbornadiene and Norbornene[1]

JAMES G. TRAYNHAM

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The question of occurrence and extent of conjugation effects in norbornadiene has been of interest in recent years. Although conjugation effects are not manifested in heat of hydrogenation experiments[2] and in free radical addition reactions,[3] the products obtained in ionic addition reactions are well accounted for in terms of a bridged-ion intermediate with homoconjugative character.[4] The exclusive formation in aqueous solution of a 1:1 norbornadiene-silver ion complex suggested conjugation effects (orbital overlap)[5] and the abnormal ultraviolet spectrum[6] of the diene is strong evidence for such conjugation effects in the excited state.

Recently Benkeser has shown that lithium in ethylamine is a powerful and selective reducing reagent toward aromatic rings.[7] The aromatic systems are rapidly reduced to monoolefins which are themselves far more slowly reduced.[7,8] Implicit in the tentative mechanism proposed[7] is the facile reduction of nonaromatic conjugated systems, specifically 1,3-dienes. It seemed of interest then to use the Benkeser reagent with norbornadiene to provide a different system for evaluating conjugation effects in that compound. Since isolated double bonds are reduced with difficulty,[7,8] it was expected that if the compound were reduced readily, nortricyclene would be formed by homoconjugative 1,5-addition.

When reduction of norbornadiene with lithium in ethylamine was tried, rapid color changes, similar to those described for the reduction of aromatic systems,[7] took place and nortricyclene was indeed present in the product mixture. It constituted a surprisingly small portion (13%) of that mixture however. The principal reduction product (64%) was that formed by simple 1,2- addition, norbornene. An appreciable amount of norbornane was also formed; with a 50% excess of lithium it became the major product (55%).

Since the equilibrium mixture of norbornene and nortricyclene contains 77% nortricyclene,[9] it seems very unlikely that the small amount of nortricyclene comes from a rearrangement of initially-formed norbornene precursor. Instead it is most probably a primary product itself, formed by some 1,5- addition to the homoconjugative system. Were isomerization a probable path, one might well expect that far more of the thermodynamically-favored isomer would be formed.[10,11] Homoconjugative addition of lithium to norbornadiene then seems possible but is a minor path in the over-all reaction.

The appearance of norbornane in the product mixture suggested that norbornene should be reduced by the Benkeser reagent also. When the experiment was tried, the color changes were again rapid, reduction proceeded, and norbornane was the only product isolated. In view of the slow reductions of other monoolefins,[7,8] the rapid reaction of norbornene is unexpected and is another example of unusual properties of these strained bridgehead compounds.

Although homoconjugative reduction of norbornadiene occurs only to a minor extent, two observations indicate that reduction (principally 1,2- addition) of the diene is nonetheless a faster process than reduction of norbornene (also 1,2-addition). Both norbornadiene and norbornene were reduced rapidly, but the color changes accompanying the reductions seemed to take place more rapidly with the diene. Secondly, with a small

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(1) This research was supported in part by a grant from The Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund.

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(10) This assumes of course that the rate of isomerization is sufficiently rapid to allow equilibrium to be approached during the time of experiment. Some support for this assumption comes from the reaction between chilled norbornadiene and *p*-thiocresol;[3] within thirty minutes, a product mixture is formed which consists of 60% substituted nortricyclene and 40% substituted norbornene. The nortricyclene derivative was shown to be formed by rearrangement of the substituted norbornene precursor.

(11) One can envision a process whereby norbornene might be formed other than by simple 1,2- addition. Half-protonation of the nortricyclene 2,6-dianion would give an anion that could be pictured as a hybrid of nortricyclenyl-2 anion and norbornenyl-5 anion; final protonation to product could conceivably be rate-controlled so that norbornene was formed predominantly rather than nortricyclene, even through the initial reduction was actually a 1,5- addition. It is difficult to see, however, why the kinetic factor should so strongly favor formation of the thermodynamically-unfavored isomer from a hybrid anion whose canonical structures are essentially equivalent in geometry and steric requirements.