

TABLE I
 VALUES OF $[BH^+]/[B]$, pK_{BH^+} AND pK'_{BH^+} ^a

HClO ₄ , %	1,3,5-C ₆ H ₃ (OH) ₃ ^b			1,3,5-CH ₃ OC ₆ H ₃ (OH) ₃ ^c			1,3,5-C ₆ H ₃ (OCH ₃) ₃ ^{d,e}		
	$[BH^+]/[B]$ ^f	$-pK_{BH^+}$	$-pK'_{BH^+}$	$[BH^+]/[B]$ ^f	$-pK_{BH^+}$	$-pK'_{BH^+}$	$[BH^+]/[B]$ ^f	$-pK_{BH^+}$	$-pK'_{BH^+}$
43.8	0.136 ± 0.005	3.60	6.89
44.8	0.135 ± 0.008	3.73	7.10	0.192 ± .006	3.58	6.94	0.085 ± 0.001	3.91	7.26
47.8	.371 ± .013	3.72	7.26	0.486 ± .018	3.60	7.14	.289 ± .002	3.83	7.37
48.1	.673 ± .005	3.81	7.53	0.546 ± .019	3.61	7.17	.349 ± .002	3.78	7.44
50.1	1.05 ± .04	3.62	7.40	.847 ± .008	3.73	7.48
52.2	1.30 ± .03	3.84	7.83	2.26 ± .04	3.59	7.56	2.18 ± .02	3.65	7.64
54.1	2.09 ± .04	3.91	8.07	4.29 ± .25	3.62	7.80	4.41 ± .07	3.62	7.80
55.7	3.48 ± .21	3.96	8.29	7.13 ± .33	3.64	7.99	11.81 ± 1.23	3.43	7.75

^a Spectra of the ethers in the higher acids were taken within 40 sec. of mixing, due to slow ether cleavage. The decline in ϵ_{BH^+} is experimentally negligible in that period of time. ^b The "Area Method" (equation 4) gave: $-pK_{BH^+} = 3.71-3.90$; $-pK'_{BH^+} = 7.10-8.24$. ^c The least squares method⁷ gave: $-pK_{BH^+} = 3.56-3.62$; $-pK'_{BH^+} = 6.82-7.46$. ^d The least squares method⁷ gave: $-pK_{BH^+} = 3.81-3.96$; $-pK'_{BH^+} = 7.22-7.65$. The area method using least squares gave $-pK_{BH^+} = 3.85-3.98$. ^e For 1,3,5-HOC₆H₃(OCH₃)₃, the least squares method⁷ gave $-pK_{BH^+} = 3.61-3.65$; $-pK'_{BH^+} = 7.32-8.29$. ^f Average value, for the wave lengths 242, 335, 340, 345 and 350 m μ . ^g In 63.5% HClO₄, the calculated $[BH^+]/[B]$ ranged from 14.9 to 31.1, illustrating the inaccuracy in determining very large indicator ratios. ^h Average value, for the wave lengths 244, 335, 340, 345 and 350 m μ . ⁱ Average value, for the wave lengths 252, 335, 340, 345, 350 and 355 m μ .

The least squares method of Hammett also was used to calculate pK_{BH^+} and pK'_{BH^+} of phloroglucinol and its methyl ethers. For all four compounds, the pK_{BH^+} values obtained in this manner are fairly constant with changing perchloric acid percentage, whereas pK'_{BH^+} drifts badly. Of course, the linear equation that is applied,⁷ 5, assumes that the particular acidity function used therein is applicable. A new method, in which the areas of the spectra in the region 290-380 m μ were employed, also was used to determine $[BH^+]/[B]$ (equation 4) for phloroglucinol (direct method) and 1,3,5-trimethoxybenzene (least squares method). The Area Method, which requires that the area of the spectral bands change little with medium, is independent of lateral shifts of the bands, but offers no special advantage here. Values of $[BH^+]/[B]$ determined by this method correlate well with H_0 and poorly with H_R' .

The results herein constitute an exception to any belief that carbon-protonation should, in general, be dependent on the H_R' function. The difference in behavior between the carbon-protonation of phloroglucinol and its methyl ethers and that of diarylolefins⁴ may lie in the fact that in the former instance both the free bases and conjugate acids have structures not unlike the free bases and conjugate acids of the indicator bases used to define H_0 in the media used; *i.e.*, solvation of free base and conjugate acid is such as to cause f_B/f_{BH^+} to change with medium in approximately the same way as for the Hammett indicator bases. It is to be noted that the greatest departure from H_0 behavior (toward H_R' behavior) found in this work is for 1,3,5-trimethoxybenzene, the free base or conjugate acid of which has no positive hydrogens bonded to a hetero-atom, and that the value of $-d \log ([BH^+]/[B])/dH_0$ declines as methoxyl substituents are successively replaced by hydroxyl substituents. Hydrogen-bonding solvation of the positive OH hydrogens of the conjugate acid may be a major factor here. Such solvent stabilization of BH^+ relative to B would be expected to decrease with increasing mineral acid percentage (decreasing a_{H_2O}) and hence act to decrease $-d \log [BH^+]/[B]/dH_0$.

The results reported herein may indicate that

neither the H_0 nor the H_R' function is unique in describing protonation equilibria. This would not be surprising, since variations of f_B/f_{BH^+} with medium, while presumably primarily dependent on charge type and on whether protonation is on carbon or a heteroatom,⁴ should also depend on the specific structure and charge distribution in base and conjugate acid (*cf.* refs. 4, 9, 10).

Support of this work by the National Science Foundation is gratefully acknowledged.

(9) L. P. Hammett, *Chem. Rev.*, **16**, 67 (1935).

(10) M. A. Paul and F. A. Long, *ibid.*, **57**, 1 (1957), particularly p. 10.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WASHINGTON
SEATTLE 5, WASHINGTON

W. M. SCHUBERT

RODNEY H. QUACCHIA

RECEIVED MAY 10, 1962

FORMATION OF BICYCLO-OCTANE SYSTEMS BY AN ACID-CATALYZED CONDENSATION OF ENOL ETHERS OF α,β -UNSATURATED KETONES

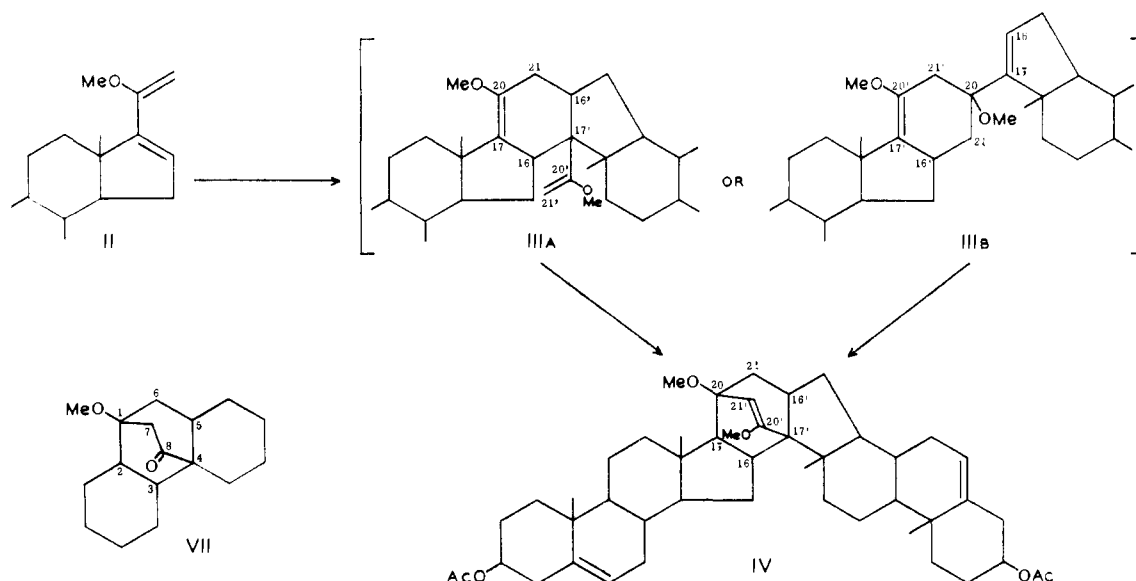
Sir:

When a methanol solution of 16-dehydropregnenolone acetate¹ is treated with trimethyl orthoformate in the presence of an acid catalyst, there precipitates after three minutes at room temperature the corresponding 20-dimethylketal (I). This substance soon redissolves in the reaction mixture, and after fifteen minutes there precipitates a dimeric enol ether (m.p. 301-304°) which was shown to possess the decacyclic structure (IV). The same dimer is obtained by treatment of the monomeric enol ether (II, m.p. 115-120°, λ_{max} 238, $\epsilon = 11,000$, obtained by heating I in xylene) with boron trifluoride in benzene, and appears to arise *via* an intermediate Diels-Alder type adduct (IIIa or IIIb) which undergoes further cyclization to produce the bicyclo[2.2.2]octane structure² (IV).

Assignment of structure IV is based on the evi-

(1) Similar treatment of 3 β -acetoxy-5 β -pregna-16-en-20-one gives rise to a decacyclic enol ether (m.p. 213-217°) and ketone (m.p. 252-253°) which are the tetrahydro (5 β) analogs of IV and V, respectively.

(2) In order to illustrate its derivation, the numbering shown in IV is that of the component steroids. The product, IV, may be precisely designated as 1,8-dimethoxy-3' β -acetoxyandrost-5'-eno[17',16':2,3]-3' β -acetoxyandrost-5'-eno[17',16':4,5]-bicyclo[2.2.2]oct-7-ene, while V is 1-methoxy-3' β -acetoxyandrost-5'-eno[17',16':2,3]-3' β -acetoxyandrost-5'-eno[17',16':4,5]-bicyclo[2.2.2]octan-8-one.



dence of: (1) analysis³ and molecular weight (690); (2) presence of only one new double bond (n.m.r. and perbenzoic acid titration); (3) mild acid hydrolysis of the enol ether group to produce a six membered ring ketone (V, m.p. 312–313°, $\nu_{\text{KBr}}^{\text{C=O}}$ 1705 cm^{-1}) possessing no new double bonds; (4) reaction with perchloryl fluoride to produce an α -fluoroketone (VI, m.p. 291.5–292.5°, $\gamma_{\text{KBr}}^{\text{C=O}}$ 1723 cm^{-1}) possessing one atom of fluorine per two steroid residues with the fluorine located on a carbon atom which also bears a hydrogen substituent but which is adjacent to carbon atoms with no hydrogen substituents (n.m.r.); and (5) studies of the model compound 1-methoxy-2,3,4,5-bis-butanobicyclo[2.2.2]octan-8-one (VII) obtained by hydrolysis of the dimeric enol ether arising from the analogous reaction of 1-acetylcyclohexene with trimethyl orthoformate in the presence of acid.

The model dimeric ketone (VII) was found to consist of a 3 to 1 mixture of two diastereoisomers (the minor one crystalline, m.p. 79–79.5°) which were separated by vapor phase chromatography and each shown to possess structure VII by n.m.r. and infrared spectra ($\nu_{\text{KBr}}^{\text{C=O}}$ 1701 cm^{-1} , $\nu_{\text{liq.}}^{\text{C=O}}$ 1705 cm^{-1}) and by selenium dehydrogenation to yield phenanthrene and 9-methylphenanthrene. Selenium dioxide oxidation of the unresolved ketone mixture gave no unsaturated ketone but rather a diketone, which reacted with *o*-phenylenediamine to form a quinoxaline (m.p. 186.5–187°) and was readily cleaved by alkaline hydrogen peroxide to yield a diacid (m.p. 236–240° dec.).

Although the same decacyclic structure (IV) can arise from either IIIa or IIIb, the more probable intermediate is IIIa, since its formation by an acid-catalyzed Diels–Alder reaction and its further cyclization both can take place by reaction sequences in which an electrophilic species interacts with the strongly nucleophilic center in an enol ether group. Compound IV and the ketone (V) derived from it appear to consist predominantly

(3) All novel compounds here described gave satisfactory analyses.

of one stereochemical modification, the nature of which will be discussed in a subsequent paper.

The formation of a bicyclooctane system by further cyclization of a Diels–Alder type adduct bears a formal relation to the Woodward–Katz rearrangement⁴ of the Diels–Alder adducts of cyclopentadiene derivatives, a process which recently has been shown to be strongly catalyzed by acid.⁵ The carbon–carbon bond formed in the final step of the present reaction corresponds to the new bond produced in the Woodward–Katz rearrangement. In the cyclopentadiene case, formation of this bond is accompanied by cleavage of one of the original carbon–carbon bonds of the Diels–Alder adduct, whereas, in the present reaction, both original carbon–carbon bonds are retained, and a carbon–hydrogen bond is broken instead.

(4) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959). The authors are indebted to Prof. Woodward for his helpful comments.

(5) P. Yates and P. Eaton, *Tetrahedron Letters*, no. 11, 5 (1960); R. C. Cookson, J. Hudec and R. O. Williams, *ibid.*, no. 22, 29 (1960).

BEN MAY LABORATORY
UNIVERSITY OF CHICAGO
CHICAGO 37, ILLINOIS
THE UPJOHN COMPANY
KALAMAZOO, MICHIGAN

KEN-ICHI MORITA
GEORGE SLOMP, JR.
ELWOOD V. JENSEN

RECEIVED AUGUST 6, 1962

THE HEPTAPHENYL TROPYLIUM (HEPTAPHENYLCYCLOHEPTATRIENYL) RADICAL IN SOLUTION¹

Sir:

On the basis of some simple molecular orbital treatments the odd electron of the tropylium radical is predicted to be in an anti-bonding orbital which is, furthermore, doubly degenerate and subject to Jahn–Teller distortions.² In apparent accord with this predicted instability, no simple derivative of the seven- π -electron tropylium radical has been prepared previously or observed unambiguously in

(1) Polyarylcycloheptatrienes, III; previous papers in this series (a) Part II, M. A. Battiste, *J. Am. Chem. Soc.*, **83**, 4101 (1961); (b) Part I, M. A. Battiste, *Chem. and Ind.*, 550 (1961).

(2) Cf. A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 260 and 279.