TABLE I

	Mercaptan	Ether	Product(s)	Yield,[a] %
1	Thiophenol	Diethylene glycol dimethyl ether	Thioanisole	89
2	Thiophenol	Diethylene glycol diethyl ether	Thiophenetole	26
3	Thiophenol	Ethylene glycol dimethyl ether	Thioanisole	59
4	Thiophenol	Tetrahydrofuran	4-Thiophenoxybutanol	36
5	Thiophenol	2-Methyltetrahydrofuran	5-Thiophenoxypentanol-2	82
			4-Thiophenoxypentanol-1	2
6	*n*-Amyl	Diethylene glycol dimethyl ether	*n*-Amyl methyl sulfide	76[b]
7	Benzyl[c]	Diethylene glycol dimethyl ether	Benzyl methyl sulfide	56
8	Thiophenol	Diethylene glycol diethyl ether and diethylene glycol dimethyl ether (1:1 mole ratio)	Thioanisole	95
			Thiophenetole	0
9	Thiophenol	Anisole and diethylene glycol diethyl ether (1:5 mole ratio)	Thioanisole	6
			Thiophenetole	15
10	Thiophenol	4-*tert*-Butyl cyclohexyl methyl ether and diethylene glycol diethyl ether	Thioanisole	11
			Thiophenetole	7

[a] The reaction of the mercaptan, for example thiophenol, with sodium borohydride gives trithiophenoxyborane and sodium thiophenoxide, the latter being inert in the transfer reaction. The additional diborane generated *in situ* converts the trithiophenoxyborane into the active monothiophenoxyborane. The yields of product are calculated on the basis of the available thiophenoxy groups for transfer. [b] This yield is based on *n*-amyl methyl sulfone isolated after permanganate oxidation of the crude sulfide. [c] Reaction time of 18 hours, the rest being 21 hours.

tion of substituted boranes[6] and certain other intramolecular transfer reactions currently under study.[7]

The mechanism proposed for the above ether cleavage is distinctly different from that proposed for the cleavage of ethers as their boron trichloride complex which proceeds by a carbonium ion mechanism.[8]

Experiments designed to investigate intramolecular alkyl exchange *via* four-centered transition states resembling bicyclo[2.1.1], [3.1.1] and [4.1.1] systems are being carried out.

(6) R. Köster and B. Günther, *Ann.*, **629**, 89 (1960).
(7) D. J. Pasto and J. L. Miesel, manuscript in preparation.
(8) W. Gerrard and M. F. Lappert, *J. Chem. Soc.*, 1486 (1952).

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ACIDITY DEPENDENCE OF THE CARBON-PROTONATION OF PHLOROGLUCINOL AND ITS METHYL ETHERS

Sir:

In a recent paper, Kresge and Chiang[1] reported that equilibrium carbon-protonation of 1,3,5-trimethoxybenzene in aqueous perchloric acid is more closely dependent on the H_R' acidity function[2] than on H_0. Earlier, Deno, Groves and Saines had concluded that the protonation of diarylolefins was dependent on H_R' rather than H_0.[4]

Results bearing on the question of whether protonation on carbon is in general dependent on a different acidity function than protonation on nitrogen or oxygen have been obtained in an ultraviolet spectrophotometric examination of the protonation of phloroglucinol and its methyl ethers in aqueous perchloric acid solutions.[5,6] Values of $[BH^+]/[B]$ were obtained by direct solution of equation 1 at five or six wave lengths in each of several acid percentages. Arbitrary shifting of spectral curves before application of equation 1 (the Hammett "isosbestic method")[7] was unnecessary because medium effects on the spectral bands are relatively small.

$$[BH^+]/[B] = (\epsilon - \epsilon_B)/(\epsilon_{BH^+} - \epsilon) \quad (1)$$

$$pK_{BH^+} = H_0 + \log([BH^+]/[B]) \quad (2)$$

$pK'_{BH^+} = H_R' + \log([BH^+]/[B])$, where

$$H_R' = H_R - \log a_{H_2O} \quad (3)$$

$$[BH^+]/[B] = (A - A_B)/(A_{BH^+} - A) \quad (4)$$

$$K + \epsilon_{BH^+}(h/(\epsilon - \epsilon_B)) - h\epsilon/(\epsilon - \epsilon_B) = 0 \quad (5)$$

The relative constancies with changing perchloric acid of values of pK_{BH^+} (equation 2) and pK'_{BH^+} (equation 3) obtained by the direct method can be compared in Table I. The protonation of phloroglucinol shows somewhat less than an H_0 acidity dependence, $-d\log([BH^+]/[B])/dH_0$ being 0.85, and correlates poorly with H_R'. The protonation of 1-methoxy-3,5-dihydroxybenzene correlates very well with H_0, $-d\log([BH^+]/[B])/dH_0 = 0.98$, and poorly with H_R'. An acidity dependence between H_0 and H_R' is shown for the protonation of 1,3,5-trimethoxybenzene, with $-d\log([BH^+]/[B])/dH_0 = 1.26$ and $-d\log([BH^+]/[B])/dH_R' = 0.78$. Our results on the protonation of 1,3,5-trimethoxybenzene differ in detail from those reported by Kresge and Chiang.[1] However, if one excludes from consideration their calculated $[BH^+]/[B]$ values corresponding to greater than 97% and less that 2% protonation,[8] the disagreement is relatively minor.

(1) A. J. Kresge and Y. Chiang, *Proc. Chem. Soc.*, 81 (1961).
(2) $H_R' = H_R - \log a_{H_2O}$, where H_R is the acidity function for the complex ionization $ROH + H^+ \rightleftarrows R^+ + H_2O$.[3] The function $H_R - \log a_{H_2O}$ was first defined by Deno, Groves and Saines[4] and conveniently labeled H_R' by Kresge.[1]
(3) N. C. Deno, J. J. Jaruzelski and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955); N. C. Deno, H. E. Berkheimer, W. L. Evans and H. J. Peterson, *ibid.*, **81**, 2344 (1959).
(4) N. C. Deno, P. T. Groves and G. Saines, *ibid.*, **82**, 5790 (1959).
(5) This work was begun in 1958 as a necessary adjunct to a study of the kinetics of the hydrolysis of the ethers.
(6) Ultraviolet spectral evidence that protonation of 1,3,5-trimethoxybenzene occurs on carbon rather than on oxygen is given in reference 1. The closely similar spectral changes undergone in strong perchloric acid by phloroglucinol and its mono- and dimethyl ethers leave no doubt that they protonate in the same manner as 1,3,5-trimethoxybenzene. The n.m.r. spectrum of 1,3,5-trimethoxybenzene in 66% perchloric acid (unpublished work, these laboratories) is unequivocally interpretable as being that of the carbon conjugate acid.
(7) L. P. Hammett, C. A. Flexser and A. Dingwall, *J. Am. Chem. Soc.*, **57**, 2103 (1935).
(8) We feel that measurements of such extremes of protonation have little reliability, even when medium effects on spectral bands are small; see, *e.g.*, footnote *g*, Table I.

TABLE I

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

$HClO_4$, %	1,3,5-$C_6H_3(OH)_3$[b] $[BH^+]/[B]$[f,g]	$-pK_{BH^+}$	$-pK'_{BH^+}$	1,3,5-$CH_3OC_6H_3(OH)_2$[c] $[BH^+]/[B]$[h]	$-pK_{BH^+}$	$-pK'_{BH^+}$	1,3,5-$C_6H_3(OCH_3)_3$[d,e] $[BH^+]/[B]$[i]	$-pK_{BH^+}$	$-pK'_{BH^+}$
43.8	.....	..	..	0.136 ± 0.005	3.60	6.89	.....	..	..
44.8	0.135 ± 0.008	2.73	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 method[7] gave: $-pK_{BH^+} = 3.56$–3.62; $-pK'_{BH^+} = 6.82$–7.46. [d] The least squares method[7] 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-$HOC_6H_3(OCH_3)_2$, the least squares method[7] 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 mμ. [g] In 63.5% $HClO_4$, 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 mμ. [i] Average value, for the wave lengths 252, 335, 340, 345, 350 and 355 mμ.

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 mμ 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 diarylolefins[4] 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 $-\mathrm{d}\log([BH^+]/[B])/\mathrm{d}H_0$ 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 $-\mathrm{d}\log[BH^+]/[B]/\mathrm{d}H_0$.

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).

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

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

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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 acetate[1] 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, ϵ = 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 structure[2] (IV).

Assignment of structure IV is based on the evi-

(1) Similar treatment of 3β-acetoxy-5β-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 (5β) 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.