As indicated in Table I the predicted configuration of a number of alcohols is in complete agreement with the experimental results.

It has been shown that hydroboration of a racemic olefin mixture with a deficient amount of diisopinocampheylborane yields optically active olefins.[5] However, in this case the enantiomer with the better steric fit reacts preferentially with the reagent, leaving behind an excess of the other enantiomer (Table I).

The hydroboration of *trans* olefins and slow reacting *cis*-olefins follows a different reaction path. Consequently, the rules outlined above do not apply to these olefins.[6]

Acknowledgment.—We wish to acknowledge the assistance provided by the National Science Foundation (G 19878).

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[5] H. C. Brown, N. R. Ayyangar and G. Zweifel, *J. Am. Chem. Soc.*, **84**, 4341 (1962).

[6] The results obtained will be discussed in a forthcoming paper.

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THE PROTONATION OF PHLOROGLUCINOL AND ITS ETHERS: AN EXCEPTION TO THE ACIDITY FUNCTION CONCEPT[1]

Sir:

For many years after Hammett introduced the acidity function, H_0,[2] this concept of a unique extension of the pH scale to concentrated acids remained a useful and satisfactory way of treating strongly acidic systems.[3] Recently, however, evidence has been accumulating which shows that a single scale does not exist even for indicator bases of the same charge type: large deviations from H_0 have been found.[4] These deviations appear to be uniform within a class of structurally similar bases, and the discrepancies have been handled by defining new acidity functions for each of the new classes of indicator base.[4a,b,d,f] This proliferation of acidity functions did not seriously impair the original concept. We wish, however, to report a phenomenon which may: we have discovered wide variations in the behavior of a group of structurally very similar bases.[5]

Phloroglucinol and its alkyl ethers are weakly basic: they protonate in 35 to 65% $HClO_4$. Three lines of evidence indicate that proton addition occurs on aromatic carbon. (1) The proton n.m.r spectrum of phloroglucinol in 70% $HClO_4$ consists of two lines of equal area at 3.88 and 5.85τ. These can be attributed to ring hydrogens and methylene hydrogens, respectively, in the phenonium ion

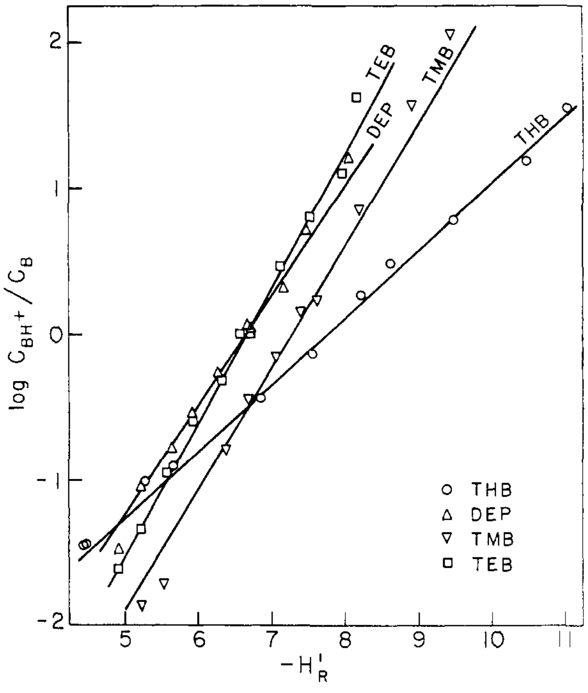
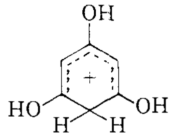


Fig. 1.—Indicator data for phloroglucinol (THB), 3,5-diethoxyphenol (DEP), 1,3,5-trimethoxybenzene (TMB), and 1,3,5-triethoxybenzene (TEB) in aqueous perchloric acid at 25°.



Similar lines are present in the spectra of 1,3,5-trimethoxybenzene and 1,3,5-triethoxybenzene. These lines disappear gradually in D_2SO_4. For phloroglucinol in perchloric acid less concentrated than 70%, the lines broaden, and an estimate of the rate of exchange based on this broadening is consistent with exchange rates determined by a tracer method in dilute acid.[6] (2) The ultraviolet spectra of phloroglucinol and its ethers in concentrated acids consists of two strong bands in the regions 2500 and 3650 Å. both with molar extinction coefficients of the order of 10^4. These spectra are very different from those of phenol and its ethers in concentrated acids (λ_{max} = 2650 Å., $\epsilon \sim 1.5 \times 10^3$) which are known to protonate on oxygen,[7] and they are consistent with predicted[8] and observed[9] spectra for carbon-protonated phenonium ions. (3) Phloroglucinol and its ethers are stronger bases

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[1] Work supported in part by the Atomic Energy Commission under USAEC Contract AT(11-1)-1025.

[2] L. P. Hammett and A. J. Deyrup, *J. Am. Chem. Soc.*, **54**, 2721 (1932).

[3] M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957).

[4] (a) N. C. Deno, J. Jaruzelski and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955); N. C. Deno, P. Groves and G. Saines, *ibid.*, **81**, 5790 (1959); N. C. Deno, P. Groves, J. Jaruzelski and M. Lugasch, *ibid.*, **82**, 4719 (1960); N. C. Deno, unpublished work. (b) R. L. Hinman and J. Lang, *Tetrahedron Letters*, **21**, 12 (1960); A.C.S. Meeting Abstracts, Sept., 1961, p. 58Q; unpublished work. (c) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **82**, 2965 (1960). (d) A. J. Kresge and Y. Chiang, *Proc. Chem. Soc.*, 81 (1961). (e) F. A. Long and J. Schulze, *J. Am. Chem. Soc.*, **83**, 3340 (1961); F. A. Long, unpublished work. (f) Y. Chiang and E. B. Whipple, unpublished work on pyrroles. (g) N. C. Deno and C. H. Spink, unpublished work on benzoic acid.

[5] Similar exceptional behavior for some of the same bases as well as several related substances was discovered simultaneously by W. M. Schubert and R. M. Quacchia (*J. Am. Chem. Soc.*, **84**, 3778 (1962)).

[6] A. J. Kresge, to be published.

[7] E. M. Arnett and C. Y. Wu, *J. Am. Chem. Soc.*, **82**, 5660 (1960); C. Y. Wu, Ph.D. Thesis, University of Pittsburg, 1961.

[8] A. A. Verrijn Stuart and E. L. Mackor, *J. Chem. Phys.*, **27**, 826 (1957); G. Dallinga, E. L. Mackor and A. A. Verrijn Stuart, *Mol. Phys.*, **1**, 123 (1958).

[9] C. Reid, *J. Am. Chem. Soc.*, **76**, 3264 (1954); H. Köhler and G. Scheibe, *Z. anorg. allgem. Chem.*, **285**, 221 (1956); M. Kilpatrick and H. H. Hyman, *J. Am. Chem. Soc.*, **80**, 77 (1958).

TABLE I

EQUILIBRIUM PROTONATION OF PHLOROGLUCINOL AND SOME OF ITS ETHERS IN AQUEOUS PERCHLORIC ACID AT 25°

Base	Wave length at which measurement was made, mμ	Range of acid used, wt. %	Value of H_R'[a] for C_{BH^+}/C_B = 1.00	No. of values of C_{BH^+}/C_B	Parameters for fit to: $\log C_{BH^+}/C_B = a + bH_R'$		
					a	b	σ_b[b]
1,3,5-Trimethoxybenzene	342	40–58	−7.27	10	−6.06	−0.834	0.034
1,3,5-Triethoxybenzene	347	38–53	−6.66	11	−6.16	− .925	.039
3,5-Diethoxyphenol	344	38–53	−6.64	10	−5.01	− .754	.029
Phloroglucinol	342	35–64	−7.74	11	−3.55	− .459	.015

[a] H_R' scale constructed from H_R (N. C. Deno, H. E. Berkheimer, W. L. Evans and H. J. Peterson, *J. Am. Chem. Soc.*, 81, 2344 (1959) and a_{H_2O} (J. N. Pearce and A. F. Nelson, *ibid.*, 55, 3075 (1933); R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth's Scientific Publications, London, 1955, p. 504). [b] Standard deviation of mean value of b.

than phenol and its ethers by six powers of ten (H_R' scale); the "pK_A's" for anisole,[7] 1,3-dimethoxybenzene, and 1,3,5-trimethoxybenzene are −13.1, −10.9, and −7.3 (H_R' scale), respectively. The introduction of successive methoxyl groups in such a series would be expected not to affect the basicity of the oxygens very much, but it should increase carbon basicity markedly. All three of these pieces of evidence indicate proton addition to carbon in phloroglucinol and its ethers, and the third indicates further that simultaneous oxygen protonation is most unlikely.

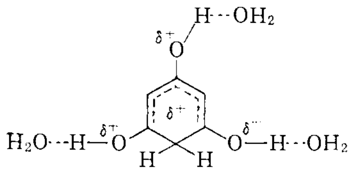
Alkylation of the phenolic groups in phloroglucinol does not affect the basicity of the aromatic ring appreciably (Table I). These substances, therefore, present a particularly useful set of bases with which to test the acidity function concept: comparison of degrees of protonation can be made in acids of the same composition. We accordingly measured indicator ratios for phloroglucinol, its triethyl and trimethyl ethers, and its diethyl ether over the same wide range of acid concentration for each compound. These data, shown in Fig. 1, can be summarized by fitting them to an expression of the type

$$\log C_{BH^+}/C_B = a + bH \qquad (1)$$

where H is some acidity function and a and b are adjustable parameters (Table I). We employed a weighted least squares method of determining a and b which recognizes the fact that the error in $\log C_{BH^+}/C_B$ will be greater when C_{BH^+}/C_B is very large or very small and will be a minimum when this quantity is near unity: the assigned weights were proportional to the reciprocals of the expected variances in $\log C_{BH^+}/C_B$.[10]

The data for this series of bases do not fit any established acidity function, a fact which has been corroborated for two of the substances by independent measurements in another laboratory.[5] Nor do the bases in themselves define a new acidity function: for the two bases with the most different behavior, the parameter b in Equation 1—the usual measure of fit of an indicator base to an acidity function—differs by a factor of two. This is as much as the difference between the two most divergent acidity functions for uncharged bases, H_0 and H_R. This means that over the region where C_{BH^+}/C_B changes from 0.1 to 10, the ratio of activity coefficients, f_{BH^+}/f_B, for phloroglucinol changes with composition of the medium 100 times as rapidly as the same ratio for phloroglucinol triethyl ether.

There is some reason to expect changes in activity coefficient ratios of the type f_{BH^+}/f_B in concentrated acids to be the result largely of changes in f_{BH^+},[4a,c,11] and the difference between phloroglucinol and its ethers can be rationalized on this basis. In protonated phloroglucinol, hydrogen-bonding interaction with the solvent through the hydroxyl groups is possible



This interaction will be stronger than in unprotonated phloroglucinol, and, of course, a similar interaction is not possible with the ethers. The result will be an increase in activity coefficient specific to those bases with hydroxyl groups which can bear positive charge in the protonated form.

We feel that this striking difference in protonation behavior between bases so similar structurally should promote a re-examination of the concept of well-defined acidity functions. We are currently engaged in doing this.

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[10] A. J. Kresge, to be published.

[11] F. A. Long and W. F. McDevit, *Chem. Revs.*, **51**, 119 (1952); N. C. Deno and C. Perizzolo, *J. Am. Chem. Soc.*, **79**, 1345 (1957); N. C. Deno, H. E. Berkheimer, W. L. Evans and H. J. Peterson, *ibid.*, **81**, 2344 (1959).

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CONVENTIONAL ELECTRON PAIR DESCRIPTION OF XENON COMPOUNDS

Sir:

Recent experiments[1] have shown the existence of XeF_4 and XeF_2, thus destroying one of the central postulates of chemical reasoning. It is important to bring to bear any theory available for explaining this phenomenon so that predictions can be made concerning probable compounds and their properties. A description has been given[2] of the quantum mechanical origin of bonding. This theory is based on our present knowledge about the detailed behavior of solutions of Schrödinger's equation.

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[1] C. L. Chernick, *et al.*, *Science*, **138**, 136 (1962); Claassen, Selig and Malm, *J. Am. Chem. Soc.*, **84**, 3593 (1962).

[2] L. C. Allen, *Science*, **138**, 892 (1962).