COMMUNICATIONS TO THE EDITOR

STEREOELECTRONIC EFFECTS ON ORGANIC BASES. III[4]. THE BASICITIES OF SOME SATURATED ETHERS IN AQUEOUS SULFURIC ACID

Sir:

It has been recognized for many years that organic oxygen compounds are bases and various means for estimating their relative basicities have been devised.[1] So far, however, analytical difficulties have prevented placing aliphatic ethers on the pH–H_0 scale which would allow their direct comparison with stronger bases in aqueous solution.

We report here the pK_a values for the conjugate acids of several important simple ethers determined by a combination of the usual Hammett acidity function method[2] with solvent extraction[3] and gas chromatography.

For distribution of the ether between a non-polar, inert, organic solvent and an aqueous acid solvent in which the ether is essentially unprotonated the distribution constant is $K_D = [B]_0/[B]_{aq}$. The observed distribution ratio for the ether between the same organic solvent and an aqueous acid layer in which protonation occurs is $D = [B]_0/([B]_{aq} + [BH^+])$ where $[B]_{aq}$ and $[BH^+]$ are the concentrations of the free ether and its oxonium ion in the aqueous acid layer and $[B]_0$ is the concentration of ether in the organic layer. Combining these expressions with that for the ether protolysis equilibrium,[2] $K_a = h_0[B]_{aq}/[BH^+]$ leads to

$$D = K_D - Dh_0/K_a \qquad (1)$$

or in logarithmic terms

$$H_0 = pK_a + \log\,[D/(K_D - D)] \qquad (2)$$

Because of small activity coefficient effects, K_D is best estimated from equation 1 by a linear plot of D *versus* Dh_0 rather than from the distribution constant for water and organic solvent. As is predicted by equation 2, a plot of $\log\,(D/(K_D - D)]$ *versus* H_0 is linear for all of the compounds listed below and the pK_a is taken from the H_0 where the logarithmic term becomes zero. In addition to this test of the data, a series of control experiments established that the organic and aqueous layers were completely immiscible, that the ether did not react with the acid, that within $0.05H_0$ unit it did not change the H_0 of the acid layer[2] (as measured by indicator), that K_D is essentially constant over an eight-fold range of ether concentration in the organic layer and that the same pK_a may be obtained with different organic solvents even though the value of K_D may vary markedly from one to another.

Extraction was performed by equilibrating a 10-ml. portion of 2% ether in cyclohexane or carbon tetrachloride with an equal volume of aqueous sulfuric acid solution of known H_0 in a specially designed apparatus agitated by a Fisher Vibrostirrer. After separation and filtration drying of the organic layer, a fifty microliter sample was injected into a nonpolar g.l.c. column at appropriate conditions on a Burrell K-2 Kromotog and eluted with helium. The amount of ether in the organic layer was found by comparison of the area of the solvent peak to that of the ether (relative to the original stock solution of ether) and the concentration in the aqueous layer was obtained by difference.

Listed below are the pK_a's (from least squares treatment of equation 2) of several important ethers as estimated by this method at room temperature, and data from two other sources showing the same relative order of basicity.

Ether	pK_a	OD band shift for CH_3OD, cm.$^{-1}$	ΔF_{298} for I_2–ether complex[7] kcal./mole
Dimethyl ether	-3.83 ± 0.19	. . .	. . .
Diethyl ether	$-3.59 \pm .10$	96[5]	1.12
Tetrahydrofuran	$-2.08 \pm .18$	117[5]	1.70
Tetrahydropyran	$-2.79 \pm .15$	115[5]	1.66
1,4-Dioxane	$-2.92 \pm .12$	111[5]	1.3
Anisole[4]	$-6.54 \pm .02$	70[6]	. . .

It is clear from the table that the pK_a's of the ethers in aqueous acid follow the same general order of basicity as would be deduced from their effect on the OD stretching frequency of deuteriomethanol or the stabilities of their iodine complexes. We have found that these compounds and a number of other ethers to be reported later follow the same linear correlation of pK_a *versus* OD shift that has been reported frequently for stronger bases.[5,6] Furthermore, it is found that the pK_a's given above fall in exactly the region of basicity predicted from a plot of all known pK_a's (of weak and strong bases) for which OD shifts have been reported. This lends further support for the general validity of this rough correlation originally suggested by Gordy and Stanford[6] and substantiated recently by other work.[8]

The superior basicity of cyclic ethers has been amply demonstrated in systems using other solvents and other acids[1,7,9] and is powerfully confirmed by our results.

Perhaps the most striking result in the above data and our other results on ether basicities[4,8] is their general failure to correlate with the basicity order of the corresponding amines in aqueous solution and

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[1] W. Gerrard and E. D. Macklen, *Chem. Revs.*, **59**, 1105 (1959).

[2] M. A. Paul and F. A. Long, *ibid.*, **57**, 1 (1957).

[3] (a) C. Golumbic and M. Orchin, THIS JOURNAL, **72**, 4145 (1950); (b) G. H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chemistry," John Wiley and Sons, New York, N. Y., 1957.

[4] For comparison, not done by this method. See: (a) E. M. Arnett and C. Y. Wu, *Chem. and Ind.* 1488 (1959); (b) E. M. Arnett and C. Y. Wu, THIS JOURNAL, **82**, in press (1960).

[5] S. Searles, Jr., and M. Tamres, *ibid.*, **73**, 3704 (1951).

[6] W. Gordy and S. C. Stanford, *J. Chem. Phys.*, **9**, 204 (1941).

[7] M. Brandon, M. Tamres and S. Searles, Jr., THIS JOURNAL, **82**, 2129 (1960).

[8] E. M. Arnett and C. Y. Wu, Paper 97, Division of Organic Chemistry 136th Meeting, American Chemical Society, Atlantic City, N. J., September, 1959.

[9] H. C. Brown and R. M. Adams, *J. Am. Chem. Soc.*, **64**, 2557 (1942).

therefore with Taft's σ^* values.[10] This reflects an entirely different balance of inductive, steric and solvation forces in oxygen bases than in their nitrogen analogues.[4,11] Very likely solvation is the reason for the large disparity between our measurement of the pK_a of dioxane in water and that estimated for the same compound (−4) by Lemaire and Lucas[12] using perchloric acid titration in glacial acetic acid.

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(10) H. K. Hall, Jr., *J. Am. Chem. Soc.*, **79**, 5441 (1957).

(11) P. D. Bartlett and J. D. McCollum, *ibid.*, **78**, 1441 (1956).

(12) H. Lemaire and H. J. Lucas, *ibid.*, **73**, 5198 (1951).

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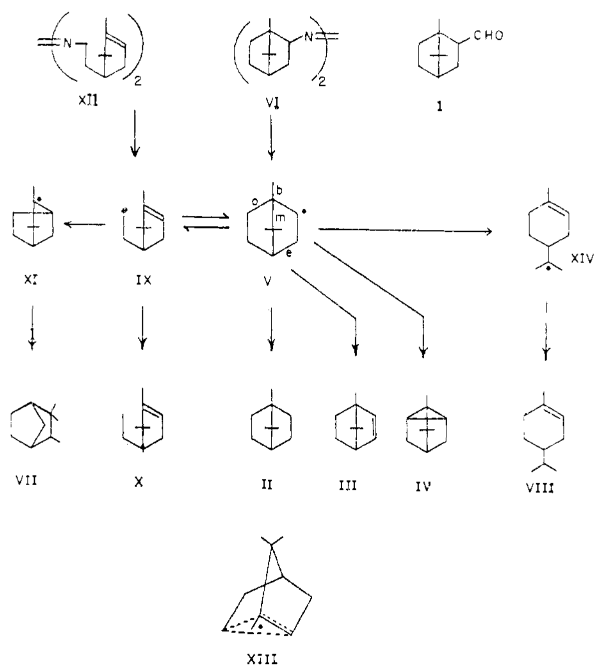
A FREE RADICAL WAGNER-MEERWEIN REARRANGEMENT

Sir:

The failure of alkyl groups to migrate to adjacent free radical centers has been demonstrated repeatedly.[1] In most of the cases investigated,[2] alkyl group rearrangements do not compete observably with such processes as hydrogen abstraction, aryl group migration, dimerization, and disproportionation. We now report a study of a system in which alkyl group migration is observed. The results demonstrate the occurrence of a *formal* free radical analog of the Wagner–Meerwein carbonium ion rearrangement.

Decarbonylation of camphane-2-carboxaldehyde (I) with *t*-butyl peroxide at 140–150° gives mainly the unrearranged product camphane (II). Small amounts of the disproportionation products bornylene (III) and tricyclene (IV) also are observed. Under these conditions, the bornyl radical (V), which is the proximate product of the decarbonylation, does not rearrange. Generation of the radical by decomposition of 2,2′-bis-azocamphane VI at higher temperatures (255–290°), however, gives, among other products, some isocamphane (VII), which is structurally related to II in the Wagner–Meerwein sense.



Among the other products of the decomposition of VI are camphane (II) and *p*-menthene (VIII). The formation of VIII suggests that at high temperatures the bornyl radical V suffers ring-opening by β-elimination; cleavage of bond m would then lead to an unsaturated monocyclic radical (XIV) which would give VIII by hydrogen abstraction. Of the three remaining formally possible β-eliminations of V, the one involving bond b is prohibited by Bredt's rule; the one involving bond e is not thus prohibited, and although we have not yet found the olefin that would result, it presumably is present among the several still unidentified reaction products. Cleavage at bond o would lead to radical IX, which could give olefin X by hydrogen abstraction, radical V by re-cyclization at the original position of attachment of the two-carbon chain, *or radical XI by cyclization in the alternative sense.*

Direct evidence that cyclization of IX to V and XI occurs is provided by the decomposition of the azo compound XII. The latter is prepared by the route α-pinene oxide → (2,2,3-trimethyl-Δ^3-cyclopentenyl)-acetaldehyde (campholenaldehyde)[3] → *campholenaldehyde azine*, b. p. 164–166° (1.5 mm.), $n^{25}\text{D}$ 1.5028, *Anal.* Found: C, 79.69; H, 10.75; N, 9.21) → the corresponding hydrazine → XII, b.p. 150–152° (1.5 mm.), $n^{25}\text{D}$ 1.4858, $\lambda_{\max}$ 360 mμ, log ϵ 1.47, *Anal.* Found: C, 79.37; H, 11.39; N, 9.20. Wolff–Kishner reduction of campholenaldehyde gives *1,5,5-trimethyl-4-ethyl-1-cyclopentene (X)*, b.p. 68–68.5° (43 mm.), $n^{25}\text{D}$ 1.4429, *Anal.* Found: C, 86.68; H, 13.21, which forms two *nitrosochlorides*, m.p. 95–96° and 122.5–123°. *Anal.* Found (for the 123° form): C, 58.85; H, 8.85; N, 6.96. The thermal decomposition of XII gives qualitatively the same products that are obtained from VI, namely, VIII, II, VII, III, IV and X.

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(2) (a) W. H. Urry and N. Nicolaides, THIS JOURNAL, **74**, 5163 (1952); (b) F. H. Seubold, *ibid.*, **76**, 3732 (1954); (c) S. J. Cristol and G. D. Brindell, *ibid.*, **76**, 5699 (1954); (d) G. Dupont, R. Dulou and G. Clement, *Bull. Soc. chim. France*, 1002 (1951); (e) W. von E. Doering, M. Farber, M. Sprecher and K. B. Wiberg, THIS JOURNAL, **74**, 3000 (1952); (f) J. A. Berson and W. M. Jones, *ibid.*, **78**, 6045 (1956); (g) J. W. Wilt and H. Phillip (Hogan), *J. Org. Chem.*, **24**, 441 (1959); (h) J. D. Backhurst, *J. Chem. Soc.*, 3497 (1959); (i) S. Winstein and F. H. Seubold, THIS JOURNAL, **69**, 2916 (1947); (j) D. Y. Curtin and M. J. Hurwitz, *ibid.*, **74**, 5381 (1952); (k) W. H. Urry and M. S. Kharasch, *ibid.*, **66**, 1438 (1944); (l) J. Weinstock and S. N. Lewis, *ibid.*, **79**, 6243 (1957); (m) C. G. Overberger and H. Gainer, *ibid.*, **80**, 4561 (1958).

(3) B. Arbusov, *Ber.*, **68**, 1434 (1935).