drying (K_2CO_3), the hydroxy ester is distilled: ^1H NMR (CCl_4) 1.1 (t, J = 7 Hz, 3 H, CH_3), 2.5 (d, J = 7 Hz, 2 H, CH_2CO), 3.95 (q, J = 7 Hz, 2 H, $COOCH_2$), 4.7–3.2 (m, 1 H, $CHOH$), 3.35 (s, 1 H, OH), 7.1–7.3 (m, 5 H, C_6H_5).

Ethyl 1-Hydroxycyclohexylacetate (6),[1] Procedure B. Cyclohexanone (2 g, 0.02 mol) is rapidly added at room temperature to the suspension of activated zinc. After the mixture is heated to reflux, the heating is stopped, and pure ethyl bromoacetate (4 g, 0.024 mol) is slowly added at such a rate that ether gently refluxes (20 min). After being heated to reflux for 1 h, the mixture is cooled and poured into iced 12 M ammonia (100 mL). The aqueous phase is extracted with ether (2 × 50 mL), the combined phases are dried (K_2CO_3) and the hydroxy ester is distilled: ^1H NMR (CCl_4) 1.1–1.8 (m, 13 H, $(CH_2)_5/CH_3$), 2.3 (s, 2 H, CH_2CO), 3.2 (s, 1 H, OH), 4.0 (q, J = 7 Hz, 2 H, $COOCH_2$).

Ethyl 1-Hydroxycyclopentylacetate (5),[7,10] Procedure C. After the suspension of activated zinc is heated to reflux, the heating is stopped, and pure ethyl bromoacetate (4 g, 0.024 mol) is added at such a rate that ether gently boils (20 min). After being heated to reflux for 1 h, the mixture is stirred for 1 h at room temperature. (The solution thus obtained can be decanted off the excess zinc: the mass of the residual zinc shows that the reaction of the bromo ester is practically quantitative.) A solution of cyclopentanone (1.7 g, 0.02 mol) in ether (5 mL) is added while the temperature of the mixture is maintained at 18–20 °C by intermittent cooling (when an aldehyde is used, the mixture should be cooled at −10 °C). After being stirred for 1 h at room temperature, the mixture is poured into iced 12 M ammonia (100 mL). Treatment as above gives the hydroxy ester: ^1H NMR (CCl_4) 1.1–2.0 (m, 11 H, $(CH_2)_4/CH_3$), 2.5 (s, 2 H, CH_2CO), 3.2 (s, 1 H, OH), 4.0 (q, J = 7 Hz, 2 H, $COOCH_2$).

Ethyl 4-Pentenoate (8).[14c] The zinc derivative prepared (procedure C) from zinc (4.4 g, 0.067 mol), trimethylchlorosilane (0.55 mL, 0.0043 mol), ethyl bromoacetate (8.4 g, 0.05 mol), and ether (60 mL) is decanted off the excess zinc. After addition of copper(II) acetylacetonate (0.3 g, 0.0012 mol), a solution of 3-bromo-1-propene (3.6 g, 0.03 mol) in ether (5 mL) is added within 10 min while the mixture is maintained at 25 °C (intermittent external cooling). When the addition is over, fresh catalyst (0.3 g, 0.0012 mol) is added, and the mixture is stirred at room temperature for 1 h. After being poured into an iced saturated ammonium chloride solution (100 mL) and extracted with ether (3 × 50 mL), the combined organic phases are washed with a 5% $NaHCO_3$ solution (2 × 50 mL), dried (K_2CO_3), and distilled: bp (°C/mmHg) 59–60/53; ^1H NMR (CCl_4) 1.2 (t, J = 7 Hz, 3 H, CH_3), 2.0–2.5 (m, 4 H, CH_2CH_2), 4.0 (q, J = 7 Hz, 2 H, $COOCH_2$), 4.7–5.2 (m, 2 H, $=CH_2$), 5.3–6.1 (m, 1 H, $=CH$).

Ethyl (Trimethylsilyl)acetate (9).[18,19] The zinc derivative of ethyl bromoacetate is prepared exactly as described in the preparation of ethyl 4-pentenoate. The excess zinc is decanted off and, after adding copper(I) chloride (0.7 g, 0.0067 mol), trimethylchlorosilane (3.3 g, 0.03 mol) is added (5 min) to the mixture heated to reflux. Reflux is next maintained for 2 h. After being cooled, the mixture is poured into iced 2 M hydrochloric acid (100 mL). After extraction with ether (3 × 50 mL) washing of the organic phases with a 5% $NaHCO_3$ solution (3 × 50 mL), and drying (K_2CO_3), the ester is distilled: bp (°C/mmHg) 86–87/92; ^1H NMR (CCl_4) 0.12 (s, 9 H, $Si(CH_3)_3$), 1.2 (t, J = 7 Hz, 3 H, CH_3), 1.8 (s, 2 H, CH_2CO), 3.95 (q, J = 7 Hz, 2 H, $COOCH_2$).

1-Hydroxycyclohexylacetic Acid (10). The zinc derivative prepared (procedure C) from zinc (4.4 g, 0.067 mol), trimethylchlorosilane (0.55 mL, 0.0043 mol), trimethylsilyl bromoacetate[21] (10.5 g, 0.05 mol), and ether (60 mL) is decanted off the excess zinc. The mass of the residual zinc shows that the reaction of the bromo ester is practically quantitative. To the green solution thus obtained is added a solution of cyclohexanone (4.1 g, 0.042 mol) in ether (5 mL), while the temperature is maintained at 18–20 °C. After being stirred for 1 h at room temperature, the mixture is added to iced 2 M hydrochloric acid (80 mL). After extraction with ether (50 mL), the organic phase is treated with 2 M sodium hydroxide (55 mL). After being washed with ether (2 × 30 mL), the aqueous phase is mixed with 2 M hydrochloric acid (70 mL) and extracted with ether (2 × 50 mL). The organic phase is washed with water (10 mL), dried ($MgSO_4$), and evaporated, leaving a yellow solid: mp 59 °C; ^1H NMR (CCl_4) 1.1–1.8 (m, 10 H, $(CH_2)_5$), 2.4 (s, 2 H, CH_2), 7.2–7.6 (m, 2 H, OH, COOH).

Registry No. 1, 2305-25-1; 2, 40309-42-0; 3, 5764-85-2; 4, 80256-55-9; 5, 3197-76-0; 6, 5326-50-1; 7, 110027-23-1; 8, 1968-40-7; 9, 4071-88-9; 10, 14399-63-4; CuC, 7758-89-6; ethyl bromoacetate, 105-36-2; butyraldehyde, 123-72-8; 2-methylpropionaldehyde, 78-84-2; benzaldehyde, 100-52-7; 5-nonanone, 502-56-7; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; octyl bromoacetate, 38674-98-5; copper(II) acetylacetonate, 13395-16-9; 3-bromo-1-pentene, 106-95-6; trimethylsilyl bromoacetate, 18291-80-0.

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(21) Okada, T.; Okawara, R. *J. Organomet. Chem.* **1972**, *42*, 117.

(22) **Note added in proof**: for a review dealing with use of activation methods for organozinc reagents, see: Erdik, E. *Tetrahedron* **1987**, *43*, 2203.

A Comparison of the Hammett Acidity Function Method for Determination of pK_a Values with the Bunnett-Olsen and Excess Acidity Function Methods

C. David Johnson* and Belinda Stratton

School of Chemical Sciences, University of East Anglia, Norwich, NR4 7TJ, U.K.

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In a previous paper,[1] we noted that estimates of pK_a values derived by the Hammett acidity function method (HAFM) differed, in many cases by considerable amounts, from those derived by the Marziano–Cox–Yates excess acidity function method (EAM). This was particularly true for strong conjugate acids whose experimentally observable ionization region was in concentrated aqueous acid. We posed the question of which method gave the more accurate estimate of the real thermodynamic quantity and suggested that an appraisal could be based on the proposal: do the pK_a values obtained by any given procedure correlate in the "expected"[2] manner with other physicochemical properties of the substrates not dependent on acidity function theory in any way for their definition? By comparing HAFM and EAM in a manner conforming to this suggestion, the tentative conclusion was drawn that, at the present stage of development, HAFM performs as well as, and in some cases better than, EAM.

No comparison with the Bunnett–Olsen method (BOM)[3] was described because a close correspondence between EAM and BOM had been noted.[4] The relationship between these two approaches can be seen by comparing eq 1, for BOM, with eq 2, for EAM.

$$\log\,[BH^+]/[B] - \log\,[H^+] = (\phi_e - 1)(H_0 + \log[H^+]) + pK_a \quad (1)$$

$$\log\,[BH^+]/[B] - \log\,[H^+] = m^*X + pK_a \quad (2)$$

Correspondence between $-(H_0 + \log\,[H^+])$ and X, and therefore between $(1 - \phi_e)$ and m^*, apparently makes the

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[1] Johnson, C. D.; Stratton, B. *J. Org. Chem.* **1986**, *51*, 4100.

[2] The quotes arise from the fact that the manner in which pK_a values might correlate in the way described, although established to a reasonable extent by precedent, may also involve subjective expectations arising from individual experience and thus opinion.

[3] Bunnett, J. F.; Olsen, F. P. *Can. J. Chem.* **1966**, *44*, 1899. It is interesting to note that these workers elaborated, in this paper, sources of errors in both the HAFM and BOM that are echoed by the views of R. Cox given in ref 1. We thank Professor Bunnett for discussion of this and other relevant points.

[4] Lucchini, V.; Modena, G.; Scorrano, G.; Cox, R. A.; Yates, K. *J. Am. Chem. Soc.* **1982**, *104*, 1958.

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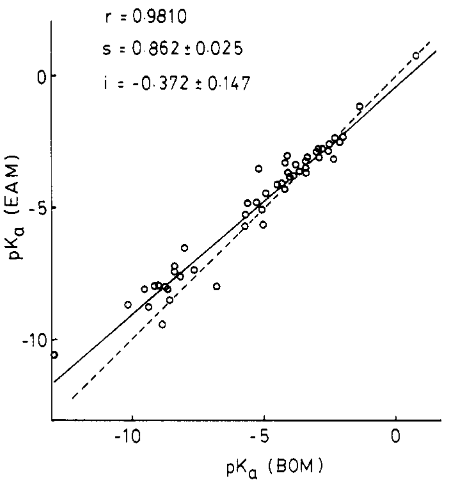

Figure 1. Comparison of pK_a values derived from both the EAM and BOM. The solid line represents the least-squares regression while the broken line is of unit slope through the origin.

two approaches coincident;[4] however, we have found that, in practice, evaluation of pK_a values via eq 1 and 2 often leads to estimates differing quite considerably in magnitude. This is illustrated in Figure 1, which shows a comparison of 50 pK_a values, used in the correlations (Table I), calculated by the two methods. (Numbers in brackets are correlation coefficients.) In consequence, the BOM and EAM performed rather differently in the correlations previously reported,[1] and this we now detail.[5]

The consequences of the comparisons made in this paper may be summarized as follows, provided one accepts that the method of comparison is realistic.

First, the BOM is sometimes more satisfactory, judged solely by the arbitrary criterion we have selected, than the EAM and is often comparable to the HAFM. If this comparison is legitimate, the reason must be that the H_0 acidity function on which it is based is a well-behaved accurate function obtained from experimentally reliable data on acids that conform in a closely consistent manner.[9]

Any such correlation that shows a smooth transition from the pH region, where the pK_a's have been measured under standard-state conditions, to the acidity function region must be of particular importance, as it indicates that not only are the relative pK_a changes correct but that the values themselves represent true thermodynamic quantities. This is significant in the light of Wojcik's study[10,11] of indeterminant constants in pK_a values derived from acidity function methods. An example of such a correlation was described previously,[1] by using pK_a values for anilinium ions plotted against $\Delta H°_{25}$ values. The HAFM (using H_0) performs particularly well, exhibiting a smooth transition as described above, with no apparent manifestation of the increasingly large uncertainties detailed by Wojcik. Unfortunately, the correlation is difficult to check with the BOM, since the anilinium data (H_0 scale) is used as the standard acidity scale for the method. By the same token, however, it does again emphasize the reliability of the H_0 acidity function.

Table I. Comparison of the HAFM, BOM, and EAM for Determination of pK_a Values

pK_a Values of Ethyl ThiobenzoatesH$^+$ and ThiobenzamidesH$^+$:[6] Correlation with σ		
HAFM (H_T, thiobenzamides)		$\rho = -1.29 \pm 0.07$ (0.9937)
BOM (thiobenzamides)		$\rho = -1.04 \pm 0.24$ (0.9174)
EAM (thiobenzamides)		$\rho = -1.53 \pm 0.20$ (0.9658)
HAFM (H_T, thiobenzoates)		$\rho = -2.68 \pm 0.10$ (0.9949)
BOM (thiobenzoates)		$\rho = -2.15 \pm 0.24$ (0.9659)
EAM (thiobenzoates)		$\rho = -1.00 \pm 0.23$ (0.8750)
pK_a Values of 1,1-Diarylethyl Cations:[6] Correlation with $\Sigma\sigma^+$		
HAFM (H_R)		$\rho = -3.21 \pm 0.27$ (0.9930)
BOM		$\rho = -1.30 \pm 0.92$ (0.7056)
EAM		$\rho = -0.48 \pm 1.00$ (0.3203)
pK_{R^+} Values of Triarylmethanols:[6] Correlation with $\Sigma\sigma^+$		
HAFM (H_R)		$\rho = -3.78 \pm 0.12$ (0.9960)
BOM		$\rho = -2.79 \pm 0.29$ (0.9602)
EAM		$\rho = -2.40 \pm 0.34$ (0.9281)
Omitting the 4,4′,4″-Trimethoxy and -Trichloro Derivatives		
HAFM (H_R)		$\rho = -3.97 \pm 0.11$ (0.9976)
BOM		$\rho = -2.70 \pm 0.35$ (0.9524)
EAM		$\rho = -2.25 \pm 0.32$ (0.9444)
pK_a Values of AcetophenonesH$^+$:[6] Correlation with σ^+		
HAFM		$\rho = -1.45 \pm 0.10$ (0.9848)
BOM		$\rho = -1.47 \pm 0.09$ (0.9873)
EAM		$\rho = -1.50 \pm 0.28$ (0.8984)
Correlation with ν_{CO}[9]		
HAFM		p$K_a = -0.124\ (\pm 0.01)\nu_{CO} + 205.80\ (\pm 20.21)$ (0.9733)
BOM		p$K_a = -0.127\ (\pm 0.01)\nu_{CO} + 210.48\ (\pm 15.88)$ (0.9840)
EAM		p$K_a = -0.131\ (\pm 0.02)\nu_{CO} + 217.35\ (\pm 32.76)$ (0.9400)
pK_a Values of BenzophenonesH$^+$:[8] Correlation with $\Sigma\sigma$ and $\Sigma\sigma^+$		
HAFM	σ	$\rho = -2.01 \pm 0.17$ (0.9787)
	σ^+	$\rho = -1.05 \pm 0.10$ (0.9724)
BOM	σ	$\rho = -1.70 \pm 0.43$ (0.8482)
	σ^+	$\rho = -0.87 \pm 0.25$ (0.8186)
EAM	σ	$\rho = -1.07 \pm 0.39$ (0.7437)
	σ^+	$\rho = -0.53 \pm 0.22$ (0.6930)
pK_a Values of Aryl Methyl SulfoxidesH$^+$:[8] Correlations with σ and σ^+		
HAFM (H_A)	σ	$\rho = -0.92 \pm 0.10$ (0.9775)
	σ^+	$\rho = -0.67 \pm 0.04$ (0.9912)
BOM	σ	$\rho = -0.80 \pm 0.06$ (0.9902)
	σ^+	$\rho = -0.55 \pm 0.08$ (0.9561)
EAM	σ	$\rho = -0.69 \pm 0.11$ (0.9515)
	σ^+	$\rho = -0.46 \pm 0.12$ (0.8941)
Correlation with Half-Neutralization Potentials[8]		
HAFM (H_A)		p$K_a = -0.54\ (\pm 0.05)\mathrm{HNP} \times 10^{-2} + 0.29\ (\pm 0.31)$ (0.9810)
BOM		p$K_a = -0.47\ (\pm 0.03)\mathrm{HNP} \times 10^{-2} + 0.36\ (\pm 0.15)$ (0.9941)
EAM		p$K_a = -0.40\ (\pm 0.06)\mathrm{HNP} \times 10^{-2} + 0.23\ (\pm 0.35)$ (0.9579)

We therefore deduce that the EAM may have a weakness in the manner of selection of the data used for evaluation of X. Possibly, rather than using all available data,[12] a more selective and critical choice could be based on series that perform particularly systematically in the correlations discussed above. This modification of the Cox–Yates method appears worthy of investigation, particularly as the inherent theoretical and practical advantages of the more general EAM, which although possibly flawed in some cases, probably offers the best chance of

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[5] It should be noted that in certain cases, *very* small differences exist between the reported data here and those of ref 1. These arise from the use of various sources for the different σ values in the latter case, which often produced small discrepancies between values for a given substituent. For the results reported here, a recent comprehensive compilation has been used: Jones, R. A. Y. *Physical and Mechanistic Organic Chemistry*, 2nd ed.; Cambridge University: New York, 1984. At the same time, a few errors that arose in calculating the standard deviation of the intercept for some correlations have also been corrected.

[6] See ref 1, and references therein, for the sources of ionization ratio data used in the calculation of pK_a estimates for these correlations.

[7] Binev, I. G.; Kolev, T. M.; Juchnovski, I. N. *Can. J. Chem.* **1985**, *63*, 3149.

[8] Andersen, K. K.; Edmonds, W. H.; Biasotti, J. B.; Strecker, R. A. *J. Org. Chem.* **1966**, *31*, 2859 and references therein.

[9] Yates, K.; Shapiro, S. A. *Can. J. Chem.* **1972**, *50*, 581.

[10] Wojcik, J. F. *J. Phys. Chem.* **1982**, *86*, 145.

[11] Wojcik, J. F. *J. Phys. Chem.* **1985**, *89*, 1748.

[12] Cox, R. A.; Yates, K. *J. Am. Chem. Soc.* **1978**, *100*, 3861.

Table II. A Selection of pK_a Values Showing the Effect of Using Different log [H$^+$] Values for EAM, BOM and BSMOM Calculations

		EAM		BOM		BSOM	
	HAFM[a]	pK_a[b]	pK_a[c]	pK_a[b,d]	pK_a[c,d]	pK_a[b,e]	pK_a[c,e]
phenyl methyl sulfoxideH$^+$[f]	−2.72	−2.32 ± 0.06	−2.47 ± 0.06	−2.29 ± 0.06	−2.37 ± 0.06	−2.40 ± 0.06	−2.55 ± 0.06
3-chlorophenyl methyl sulfoxideH$^+$[f]	−2.99	−2.79 ± 0.20	−2.94 ± 0.21	−2.55 ± 0.15	−2.63 ± 0.14	−2.86 ± 0.21	−3.02 ± 0.21
4-nitrophenyl methyl sulfoxideH$^+$[f]	−3.37	−2.76 ± 0.13	−2.91 ± 0.13	−2.78 ± 0.11	−2.87 ± 0.11	−2.82 ± 0.14	−2.98 ± 0.14
reserpiline[g]	−7.26	−6.09 ± 0.14	−6.23 ± 0.15	−6.07 ± 0.09	−6.05 ± 0.09	−6.28 ± 0.20	−6.45 ± 0.16
yohimbine[g]	−8.30	−6.22 ± 0.16	−6.38 ± 0.16	−6.68 ± 0.08	−6.67 ± 0.08	−6.33 ± 0.15	−6.49 ± 0.16
ajmalicine[g]	−8.31	−6.70 ± 0.12	−6.85 ± 0.12	−7.19 ± 0.11	−7.17 ± 0.11	−6.81 ± 0.12	−6.97 ± 0.13
3-methyl-2,4,6-trinitroanilineH$^+$[h]	−8.33	−6.95 ± 0.06	−7.99 ± 0.14	−8.30 ± 0.07	−8.30 ± 0.06	−7.88 ± 0.27	−9.07 ± 0.45
2,4,6-trinitroanilineH$^+$[h]	−10.03	−7.16 ± 0.18	−10.18 ± 0.14	−9.51 ± 0.09	−9.68 ± 0.06	−10.35 ± 0.19	−15.38 ± 0.35
3-bromo-2,4,6-trinitroanilineH$^+$[h]	−9.34	−8.14 ± 0.31	−10.47 ± 0.17	−10.48 ± 0.27	−10.15 ± 0.21	−11.02 ± 0.30	−14.42 ± 0.29

[a] References 13–15. [b] Calculated by using log [H$^+$] = log $M_{H_2SO_4}$; ref 16. [c] Calculated by using [H$^+$] from ref 12. [d] Calculated by using H_0 from ref 15. [e] Calculated by using X function from ref 17. [f] Calculated from UV data measured in aqueous H_2SO_4: values may differ from averaged values quoted elsewhere. Unpublished ionization ratio data supplied by Professor G. Scorrano. [g] Calculated from unpublished ionization ratio data supplied by Professor M. Balon. [h] Calculated from ionization ratio data of ref 15: values may differ from averaged values quoted elsewhere.

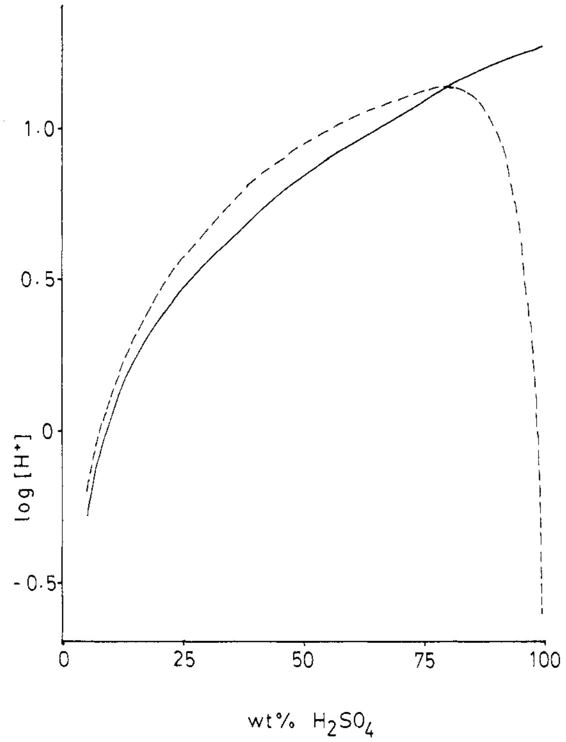

Figure 2. Comparison of operational log [H$^+$][12] (broken line) and log $M_{H_2SO_4}$[16] (solid line).

an ultimate quantitative solution to these problems.

Second, no completely systematic algorithm for calculation of pK_a values can replace the process involved in the HAFM where an arbitrary decision is made on what range of slope parameters constitutes obedience to a given acidity function, to what extent these deviations represent real differences, and to what extent are the experimental errors. Therefore, for the EAM to function optimally, it is necessary that the log I values employed in eq 2 are measured to the greatest possible accuracy.

Note Added in Proof. A referee has pointed out that, while the HAFM does not make an explicit reference to log [H$^+$], the EAM and BOM do. Moreover, Cox and Yates use [H$^+$] = [H$_3$O$^+$], which they describe as operational [H$^+$] values,[12] while Bunnett and Olsen refer to [H$^+$] as the sulfuric acid molarity.[3] The difference between these two definitions is greatest at high acidities, as shown in Figure 2. We have found that, in practice, the choice of log [H$^+$] values has generally only a small effect on the pK_a values calculated by any one method, usually well within experimental error, at the lower acidities. This is demonstrated in Table II, where the same data are treated, using the two definitions of log [H$^+$], by the EAM and BOM and the X function method recently published by Bagno, Scorrano, and More O'Ferrall (BSMOM).[17] For data measured in low to medium acid concentrations, the pK_a values calculated by one method using the different log [H$^+$] values are generally within 1 standard deviation of each other. This is also true for the BOM at high acidities, but not for the X function methods (EAM, BSMOM). This is another factor, therefore, which at the present time makes use of these extrapolative methods somewhat uncertain.

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(17) Bagno, A.; Scorrano, G.; More O'Ferrall, R. A. *Rev. Chem. Intermed.* **1987**, *7*, 313. This X function was derived from the data used by Cox and Yates[12] and a new set of log [H$^+$] values designed to incorporate all species capable of protonating the organic base. It is useful to note that these log [H$^+$] values are numerically almost identical with the log of the sulfuric acid molarity used for the BOM.[16]

Formation of Chiral Alkoxy Dienes in Wittig/Michael Reactions of 2,3,5-Tri-*O*-benzyl-D-arabinose

Allen B. Reitz,* Alfonzo D. Jordan, Jr., and
Bruce E. Maryanoff

*Chemical Research Department, McNeil Pharmaceutical,
Spring House, Pennsylvania 19477-0776*

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In the course of our program[1] to develop new antidiabetic drugs based on carbohydrates, we prepared *C*-arabinofuranosides **1a** and **1b** by treatment of 2,3,5-tri-*O*-benzyl-D-arabinose (**2**) with (cyanomethylene)triphenylphosphorane[2] (86% yield as a 76:24 mixture of **1a** and **1b**, see Scheme I).[1c] Cyclization of the intermediate olefin **3** had occurred spontaneously under the reaction condi-

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