Figure 1.—The 60-MHz aromatic proton spectra of (a) I and (b) II. The 100-MHz ring-proton spectra of (c) I and (d) II. The 60-MHz ring-proton spectra of (e) II. Magnetic field increases left to right. All sweep scales are equal.

reaction of phenylmagnesium bromide with 2,5-dichloro-1,4-dioxane. (These same two compounds can be obtained using styrene oxide as a starting material and anhydrous stannic chloride as catalyst.[2]) They identified the compounds as the two isomeric 2,5-diphenyl-1,4-dioxanes and, on the basis of the melting points, assigned the *cis* structure to I and the *trans* structure to II.

The 60- and 100-MHz proton spectra of I and II as their 10% solutions in $CDCl_3$ are shown in Figure 1. The aromatic region of I at 60 MHz is a broad, complicated multiplet while that of II is much narrower and simpler (Figures 1a and b) indicating the phenyl rings in I may be more hindered that in II, although neither spectrum was temperature dependent. The ring protons of I at 60 MHz form an ABC system which has been analyzed in detail to yield the two vicinal coupling constants of 5.8 and 3.1 Hz and a geminal coupling constant of -11.9 Hz.[3] These values are consistent with the 100-MHz spectrum shown in Figure 1c. The ring protons of II form an ABX system (by comparison of 100- and 60-MHz spectra in Figures 1d and e) with vicinal coupling constants of 10.4 and 2.9 Hz and a geminal coupling constant of -11.5 Hz (the choice of signs being made by analogy to the assignments for I). The values for the vicinal coupling constants obtained from ring-proton spectra of I and II in dimethyl sulfoxide at 30 and 140° are the same.

Making the reasonable assumption of a chair geometry for both I and II[4] and using the fact that for vicinal coupling constants in these kinds of rings $J_{ea} \sim J_{ae} \sim J_{ee} < J_{aa}$,[5] the observed nmr data are consistent with the assignment of *cis* (Ph$_e$, Ph$_a$ $\rightleftarrows$ Ph$_a$, Ph$_e$) to I and *trans* (Ph$_e$, Ph$_e$) to II, so that the vicinal coupling constants are given by $(J_{aa} + J_{ee})/2 = 5.8$ Hz and $(J_{ea} + J_{ae})/2 = 3.1$ Hz in I, and $J_{aa} = 10.4$ Hz and $J_{ea} = 2.9$ Hz in II. The only other way to assign chair conformations to the isomers consistent with the nmr data involves the unreasonable assumption of a rigid *cis* structure and a rapidly interconvering *trans* structure.

(2) R. K. Summerbell and M. J. Kland-English, *J. Amer. Chem. Soc.*, **77**, 5095 (1955).

(3) C. Altona and E. Havinga, *Tetrahedron*, **22**, 2275 (1966).

(4) G. Gatti, A. L. Segre, and C. Morandi, *ibid.*, **23**, 4385 (1967).

(5) See, for example, E. L. Eliel and C. Knoeber, *J. Amer. Chem. Soc.*, **90**, 3444 (1968).

There is little possibility that the bulky phenyl groups cause the *cis* isomer to assume twist-boat conformations[6] in which both phenyls are exclusively in equitorial orientations with respect to the ring. If this were the case, the *cis* isomer would display a large vicinal coupling constant. However, only one vicinal coupling constant greater than 6 Hz is observed so that if a twist-boat conformation is adopted for the *cis* isomer, the *trans* structure must be either in a twist-boat conformation itself or undergoing rapid chair interconversions. Either situation is unlikely. Furthermore, any room-temperature dynamic equilibrium involving substantial amounts of boat and chair forms is unlikely since the spectra of both isomers are unchanged at higher temperatures.

Thus, the original structural assignments given by Summerbell are correct and the *cis*- and *trans*-2,5-diphenyl-1,4-dioxanes are, in fact, an example of the higher melting of two geometrical isomers being the one with the greater molecular symmetry.

(6) R. D. Stolow and M. N. Bonaventura, *ibid.*, **85**, 3636 (1963); E. W Garbisch, Jr., and D. B. Patterson, *ibid.*, **85**, 3228 (1963); H. Booth and E. O. Gidley, *Tetrahedron Lett.*, 1449 (1964). These authors discuss this possibility for cyclohexane derivatives with large *cis* substituents at C-1 and C-4.

Ionization Constants of Squaric Acid[1]

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Squaric acid, $C_4H_2O_4$ (1,2-dihydroxycyclobutenedione), is an unusually strong organic acid, so strong that its first ionization constant cannot be easily measured, and until now there seems not to have been any serious attempt to do so. Its second ionization constant has been variously reported as $pK_2 = 2.2$[3] and as $pK_2 = 3.0$.[4] The availability of a digital-computer program[5] designed for the precise evaluation of the pK values of a dibasic acid from experimental titration data made it feasible to do an accurate determination of the pK values of squaric acid, the results of which are reported in this communication.

Experimental Section

The experimental data (shown in Table I) were obtained by measuring with a Radiometer pH meter (using a type G202B glass electrode and a type K401 calomel reference electrode) the pH of a 0.173 F aqueous solution of squaric acid (squaric acid supplied by Chemische Werke Hüls, A.G., and used after drying for 1 hr at 110°) thermostated to 25.0 $\pm$ 0.1° as successive increments of 2.00 N KOH were added to it from a micrometer syringe buret. The pH meter and electrodes were calibrated

(3) S. Cohen, J. R. Lacher, and J. D. Park, *J. Amer. Chem. Soc.*, **81**, 3480 (1959).

(4) J. D. Park, S. Cohen, and J. R. Lacher, *ibid.*, **84**, 2919 (1962).

(5) A copy of the program, written in FORTRAN II, with a description of how it works, will be sent on request to interested individuals.

pH	Equiv of KOH per mol of squaric acid
1.01	0.000
1.04	0.077
1.09	0.154
1.11	0.232
1.14	0.308
1.20	0.386
1.24	0.463
1.30	0.540
1.38	0.617
1.46	0.695
1.58	0.772
1.70	0.848
1.86	0.925
2.04	1.003
2.25	1.080
2.42	1.158
2.59	1.233
2.73	1.311
2.87	1.389
3.00	1.466
3.12	1.542
3.27	1.620
3.40	1.698
3.59	1.774
3.81	1.851
4.20	1.929

against standard buffer solutions[6] having pH's of 1.68 and 4.01 at 25°. Duplicate titrations done in this manner yielded nearly identical results, from which the following values (and their standard deviations) were calculated: $pK_1 = 1.2 \pm 0.2$ and $pK_2 = 3.48 \pm 0.02$ (at $25.0 \pm 0.1°$ and corrected to zero ionic strength by use of the Davies equation[7] for activity coefficients). The sum of these pK values, *i.e.*, $pK_1 + pK_2$, equals 4.7 ± 0.2.

In principle, a more precise measurement of pK_1 could be obtained by using a larger concentration of squaric acid, but its limited solubility (about 2 wt % or 0.176 F at 20°) makes that approach impracticable.

Discussion

The acidity of squaric acid is similar to that of oxalic acid, a substance which squaric acid resembles structurally. For oxalic acid at 25°, $pK_1 = 1.28$,[8] $pK_2 = 4.27$,[9] and $pK_1 + pK_2 = 5.55$.

For both acids, a part of the free-energy change during ionization reflects an entropy effect caused by the change in symmetry number, *i.e.*, $\sigma = 4$ for the oxalate ion and $\sigma = 8$ for the more symmetrical squarate ion. This rotational entropy effect therefore contributes to the *difference* in $pK_1 + pK_2$ between oxalic acid and squaric acid, an amount $T\Delta S = 298\, R \ln 2 = 0.4$ kcal/mol of free energy, a relatively small but not insignificant quantity.

A larger part of the difference in acidity between squaric acid and oxalic acid depends on the extra delocalization energy possessed by the squarate ion. According to West and Powell,[10] molecular orbital calculations indicate that this delocalization energy amounts to

(6) Prepared as described by R. G. Bates, "Electrometric pH Determinations," John Wiley & Sons, Inc., New York, N. Y., 1954, p 74.

(7) J. N. Butler, "Ionic Equilibrium: A Mathematical Approach," Addison-Wesley, Reading, Mass., 1964, p 437.

(8) L. S. Darken, *J. Amer. Chem. Soc.*, **63**, 1007 (1941).

(9) G. D. Pinching and R. G. Bates, *J. Res. Nat. Bur. Stand.*, *A*, **40**, 405 (1948).

(10) R. West and D. L. Powell, *J. Amer. Chem. Soc.*, **85**, 2577 (1963).

0.240β for each of two π electrons. If it is assumed that β is about 18 kcal/mol, then the delocalization energy of squarate would be about 9 kcal/mol. If delocalization energy were the major energy factor in the ionization of squaric acid, then the difference $[(pK_1 + pK_2)_{\text{squaric}} - (pK_1 + pK_2)_{\text{oxalic}}]$ should equal 6.05. It is remarkable that this difference is actually only 0.85 ± 0.2. This discrepancy can be explained on the basis of a difference in the hydration energy of the two types of dianions. Ionization of oxalic acid is relatively favored by the concentration of negative charge on the oxygen atoms of the oxalate ion, a concentration of negative charge which results in a relatively large hydration energy. In the squarate ion, however, the hydration energy should be relatively smaller, to the extent that the charge delocalization extends over a larger region of space, *i.e.*, over the four-carbon ring in addition to the four oxygen atoms. If this analysis is correct, then the hydration energy for the squarate ion must be less than that for the oxalate ion by about 7.0 kcal/mol.[11]

Registry No.—Squaric acid, 2892-51-5.

(11) NOTE ADDED IN PROOF.—It has recently come to the author's attention that another paper has been published [by D. T. Ireland and H. F. Walton, *J. Phys. Chem.*, **71**, 751 (1967)] containing data in agreement with those described here. The author regrets that his literature search was not thorough enough to permit location of Ireland's and Walton's work prior to the time this Note was submitted for publication.

### Catalyzed Rearrangements of 2-Alloxypyridine and 2-Crotoxypyridine

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The rearrangement of alloxypyridine has been the subject of several recent investigations.[2-4] These reactions, carried out above 240°, were generally characterized by low yields of all possible "Claisen type" rearranged products.

We found that several Lewis acids facilitated rearrangement of 2-alloxypyridine (I) exclusively to 1-allyl-2-pyridone (II) in high conversion at moderate reaction temperatures.
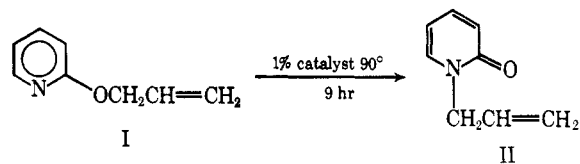
The thermal rearrangements[2,3] of I were classified as ortho-Claisen rearrangements as a result of the nature of the products formed and the experimental

(1) To whom all correspondence should be addressed at the Department of Chemistry, University of Wisconsin, Madison, Wis. 53706.

(2) R. B. Moffett, *J. Org. Chem.*, **28**, 2885 (1963).

(3) F. J. Dinan and H. Tieckelman, *ibid.*, **29**, 892 (1964).

(4) B. S. Thyagarajan, *Advan. Heterocycl. Chem.*, **8**, 143 (1967).