TABLE I

TITRATION OF 296 mg OF SQUARIC ACID IN 15.00 ml OF AQUEOUS SOLUTION WITH 2.00 N KOH

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 ± 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 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.

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[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).

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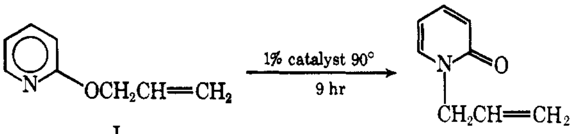
The rearrangement of alloxypyridine has been the subject of several recent investigations.[2-4] These reactions, carried out above 240°, were generally characterized by low yields of all possible "Claisen type" rearranged products.

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.



I

II

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

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

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

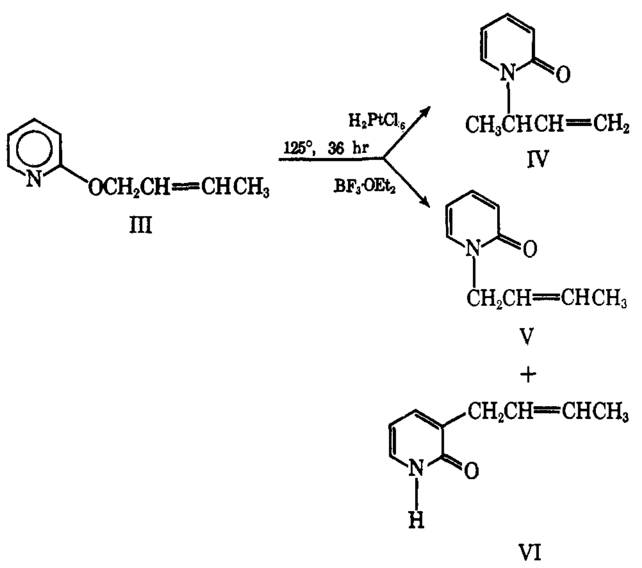
[4] B. S. Thyagarajan, *Advan. Heterocycl. Chem.*, **8**, 143 (1967).

conditions required.[5] Our catalyzed reactions differed in several respects from previously reported results: (1) lower reaction temperatures were permitted for rearrangement, 90 *vs.* 240°; (2) only the N-allyl rearrangement product was formed; (3) a high degree of conversion to the rearranged product was obtained, 90 *vs.* 30–60%; (4) the rearrangement proceeded well, even with impure I, to afford clean reaction mixtures from which the products were easily isolated.

The catalysts which performed best in the neat rearrangement of I to II were soluble Lewis acids. Platinum complexes, boron trifluoride etherate and tin(IV) chloride gave excellent conversions into II during the reaction period. Insoluble species such as aluminum chloride, platinum(0) black, alumina, and nickel(II) chloride (anhydrous) were poor catalysts when used in a similar manner.

The reaction mechanism was investigated by studying the rearrangement of 2-crotoxypyridine (III) (Scheme I). It was established that different products could be obtained from the reaction, depending on the nature of the catalyst used. Reactions catalyzed by chloroplatinic acid provided essentially quantitative conversion to the normal Claisen product, 1-(1-methylallyl)-2-pyridone (IV). The formation of this compound suggests that platinum complexes with III in a manner analogous to 2-allylpyridine and Pt(II),[6] in which the allylpyridine acts as a bidentate ligand. Such a complex could facilitate the intramolecular allyl rearrangement to nitrogen by a pseudo-Claisen cyclic mechanism. Reactions catalyzed by boron trifluoride etherate proceed by an entirely different mechanism, because the two abnormal Claisen products, 1-crotyl-2-pyridone (V) and 3-crotyl-2-pyridone (VI), were obtained in yields of 82 and 18%, respectively. A possible explanation for the formation of these products is that the boron trifluoride coordinates with the ether oxygen of III, providing a pathway for a 1,3-allyl shift, preferably to nitrogen.

SCHEME I



These results suggest that other types of Claisen rearrangements might be catalyzed by metal complexes to afford conversion to fewer isomeric products using moderate reaction conditions.

Experimental Section

2-Alloxypyridine (I) was used as obtained from K & K Laboratories, Inc., Plainview, N. Y. 11803. Glpc analysis[7] of I showed that 2-chloropyridine (5%) was present as an impurity. Its presence did not affect our experimental results.

2-Crotoxypyridine (III) was prepared using the procedure of Dinan and Tieckelman.[3] Its ir and nmr spectra were consistent with the proposed structure, bp 92° (11 mm).

Rearrangement of 2-Alloxypyridine (I) to 1-Allyl-2-pyridone (II).—In a large-scale reaction a mixture of I (340 g, 2.5 mol) and a 4.2% H_2PtCl_6–isopropyl alcohol solution (4.8 g, 4.9×10^{-4} mol) were heated at 90–150° in a nitrogen atm for 9 hr. The reaction was followed by glpc analysis and at the end of this period no I could be detected. Distillation of the reaction mixture through a 30-cm Vigreux column gave II (289 g, 85% of theory) in good yield. The identity of II was confirmed by ir and nmr analysis.[3]

Rearrangement of I to II in Sealed Tubes.—I (2.0 g) was heated at 140° in sealed 6-mm glass tubes with 1% catalyst for 40 hr. The catalysts which gave excellent conversions to II (>85%) were H_2PtCl_6, Na_2PtCl_4, $BF_3 \cdot Et_2O$ and $SnCl_4$; and Pd on C gave 55% II. Less than 15% II was obtained with $AlCl_3$, alumina, $NiCl_2$ and Pt (black). Compound I alone did not rearrange under similar reaction conditions. Analyses of the reactions were obtained by glpc using internal standards. Area percentages were taken as a measure of the degree of conversion.

Rearrangement of 2-Crotoxypyridine (III) with H_2PtCl_6.—III (1.5 g, 0.01 mol) and a 4.2% H_2PtCl_6–isopropyl alcohol solution (0.1 g, 1×10^{-5} mol) were mixed under nitrogen and sealed in a 6-mm glass tube. The cloudy, light yellow solution was heated at 125 ± 1° for 36 hr. A glpc of the clear light orange reaction mixture showed only one peak eluting above 100°. An nmr[8] of this crude sample revealed a large doublet at τ 8.55 ($J = 7.0$ cps) and a smaller upfield doublet at 8.80 ($J = 6.0$ cps). The former is consistent with that found for 1-(1-methylallyl)-2-pyridone (IV).[3] The latter may be due to a complex formed between IV and platinum. The reaction mixture was distilled to dryness with only one pure component being isolated (1.4 g), bp 97° (1.2 mm). The nmr spectra of this material was identical with IV. The ir spectrum was also consistent with this proposed structure.

Rearrangement of 2-Crotoxypyridine (III) with $BF_3 \cdot Et_2O$.—III (1.5 g, 0.01 mol) and freshly distilled $BF_3 \cdot Et_2O$ (0.1 g, 7.0×10^{-4} mol of BF_3) were mixed under nitrogen and sealed in a 6-mm glass tube. This clear solution was heated at 125 ± 1° for 36 hr. A glpc of the crude reaction mixture showed two peaks, both eluting after III or IV, with relative areas of 82–18.[9] (The 82% component was the first to elute.) This solution was distilled to dryness with the main fraction taken at (1.35 g) 105° (0.5 mm). The area ratio of the compounds in the distillate had not changed. The two compounds were separated by preparative glpc and examined by nmr and ir analysis. The data for the larger component were found to be consistent for 1-crotyl-2-pyridone (V)[3] with the methyl protons appearing as distorted quartet (due to independent splitting by two vinylic protons) at τ 8.28 ($J = 3.8, 1.0$ cps). The smaller component was identified as 3-crotyl-2-pyridone (VI),[3] *via* the distorted methyl quartet at τ 8.32 ($J = 3.3, 1.1$ cps), and the absence of the ring three proton doublet at τ 3.40. The ir spectra of both compounds were consistent with these structures.

Registry No.—I, 5831-77-6; III, 17953-65-0; H_2PtCl_6, 16941-12-1; $BF_3 \cdot Et_2O$, 109-63-7.

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(5) For an excellent review of the Claisen rearrangement, see S. J. Rhoads, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, p 655.

(6) R. E. Yingst and B. E. Douglas, *Inorg. Chem.*, **3**, 117 (1964).

(7) All glpc analyses were done using a $^3/_8$ in. × 20 ft 25% Dow Corning DC 200 fluid on 40–60 mesh, Chromosorb W column. The temperature was programmed from 75 to 300° at 15°/min with a helium flow rate of 200 ml/min.

(8) All nmr spectra were obtained using a Varian A-60A spectrometer. Solution samples were made with chloroform or deuteriochloroform using tetramethylsilane as an internal standard.

(9) Other small peaks were detected which represented less than 10% of the total area.