0.16 mol) with a solution of sodium dichromate dihydrate (30 g) in glacial acetic acid (60 g) gave starting material **1f** (2.03 g, 0.019 mol) and ketone **2f** (0.27 g, 0.002 mol): yield 1%; bp 72° (15 mm); mp 76–77° (lit.[4] mp 76–78°); NMR 2.69 [3 H, s,.-(C=O)CH_3], 8.60 and 8.71 (2 H, 2 d, ArH), 9.22 ppm (1 H, s, ArH); mass spectrum *m/e* 43, 122 (molecular ion), 80, 79, 52, 53.

Acknowledgment. I wish to express my appreciation to Dr. W. I. Taylor for his interest in this work. I also wish to thank Mr. M. Jacobs for the NMR analyses, Ms. A. Sanderson for the mass spectral analyses, and Mr. H. Bondarovich for the high-resolution mass spectral analyses.

Registry No.—**1a,** 15707-23-0; **1b,** 15707-24-1; **1c,** 27043-05-6; **1d,** 13360-65-1; **1e,** 13360-64-0; **1f,** 13925-00-3; **2a,** 23787-80-6; **2b,** 32974-92-8; **2c,** 54300-08-2; **2d,** 54300-09-3; **2e,** 22047-27-4; **2f,** 22047-25-2; sodium dichromate dihydrate, 7789-12-0.

References and Notes

(1) B. D. Mookherjee and E. M. Klaiber, *J. Org. Chem.*, **37,** 511 (1972).
(2) Mariot and Pulland, C. R. *Acad. Sci.*, **248,** 252–254 (1959).
(3) Yields are based on consumed starting material.
(4) S. Kushner, H. Dalalian, J. L. Sanjurjo, F. L. Bach, Jr., S. R. Safir, V. K. Smith, Jr., and J. H. Williams, *J. Am. Chem. Soc.*, **74,** 3617 (1952).

Sulfonation of Unsaturated Compounds. II. Isolation and Characterization of a Carbyl Sulfate

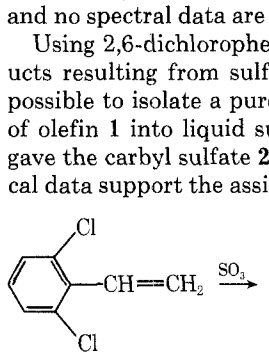
John C. Sheehan* and Uri Zoller

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

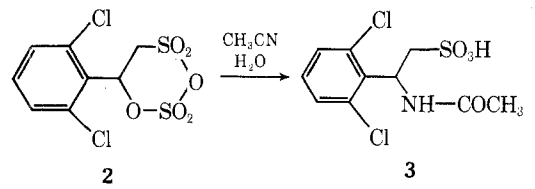
Received June 6, 1973

Cyclic sulfonate–sulfate anhydrides **2** (carbyl sulfates) have been proposed as intermediates in some sulfonations of olefins[1] with sulfur trioxide. Evidence for these intermediates comes from the identification of isolated products, usually after alkaline hydrolysis of the sulfonation mixture. In some cases, the carbyl sulfate has been isolated as a crystalline product[2] from a sulfonation mixture. However, these carbyl sulfates have not been characterized directly and no spectral data are available for them.

Using 2,6-dichlorophenylethylene (**1**) to avoid side products resulting from sulfonation into the phenyl ring, it is possible to isolate a pure carbyl sulfate. Dropwise addition of olefin **1** into liquid sulfur dioxide in 1,2-dichloroethane gave the carbyl sulfate **2** in 96% yield. Spectral and analytical data support the assignment of structure **2.**



1



2 **3**

The carbyl sulfate can also be obtained from the sulfur trioxide–dioxane adduct as sulfonating agent, but in lower yields.

Carbyl sulfate **2** reacted readily with wet acetonitrile to give the β-aminosulfonic acid **3** through a Ritter-type reaction.[3] Treatment of **2** with aqueous alkali, pyridine, and piperidine gave mixtures of sulfate and sulfonate salts.

Experimental Section

1-(2,6-Dichlorophenyl)-1-sulfate-2-sulfonate Anhydride (Carbyl Sulfate, 2). Method A. Freshly distilled sulfur trioxide (Sulfan, Allied Chemicals), 2.6 g (0.032 mol), was added to 25 ml of dry 1,2-dichloroethane at 0°. To this solution 2,6-dichlorostyrene (5.5 g, 0.032 mol) in 12.5 ml of 1,2-dichloroethane was added dropwise over 25 min at 2–6° with stirring. A precipitate of **2** started to appear immediately. After 12 min of stirring 50 ml of pentane was added and the solution was filtered. The product was washed with pentane–1,2-dichloroethane (1:1) and pentane to yield 5.2 g of the thermally unstable carbyl sulfate **2:** 96%; mp 81.5–83.5°; ir (KBr) 3020, 1580, 1447, 1422, 1380, 1250, 1231, 1215, 1190, 957, 913, 749 cm^{-1}; NMR (DMSO-d_6) δ 7.35 (m, 3 H), 6.35 (m, 1 H), 3.55 (m, 2 H); mass spectrum *m/e* 174, 172 (M − $2SO_3$), 139, 137 (M − $2SO_3$ − Cl), 80 (SO_3), 64 (SO_2); neut equiv, calcd 333.17; found (tritration with 0.05 *N* NaOH in xylene–isopropyl alcohol, 1:1), 335.

Anal. Calcd for $C_8H_6Cl_2O_6S_2$: C, 28.84; H, 1.82; Cl, 21.29; S, 19.25. Found: C, 29.18; H, 2.12; Cl, 21.62; S, 19.55.

Method B. The dioxane–sulfur trioxide complex[4] was prepared from 2.30 g (0.0288 mol) of sulfur trioxide and 2.53 g (0.0288 mol) of dioxane in dry 1,2-dichloroethane (27.5 ml). A solution of 5.5 g (0.032 mol) of **1** in 12.5 ml of 1,2-dichloroethane was added dropwise over 25 min with stirring at 2–4°. After 15 min of stirring, petane (45 ml) was added and the mixture was allowed to stand in the cold overnight. Filtration and washing as described gave 3.05 g (63.7%) of **2.**

2-(2,6-Dichlorophenyl)-2-(*N*-acetamido)ethanesulfonic Acid (3). A solution of 0.6 g (0.002 mol) of **2** in 15 ml of wet acetonitrile was refluxed for 2 hr. Cooling and filtration gave 0.121 g of **3:** 21.6%; ir (KBr) 3255, 3095, 1670, 1560, 1450, 1250, 1205, 1007, 722 cm^{-1}; NMR (D_2O) δ 7.38 (m, 3 H), 6.27 (m, 1 H), 3.61 (m, 2 H), 2.07 ppm (s, 3 H); mass spectrum *m/e* 174, 172 (M − $CH_3CONHSO_3H$), 139, 137 ($C_6H_3Cl_2CHCH_2$ − Cl), 102 ($C_6H_3Cl_2CHCH_2$ − 2Cl), 101, 64; neut equiv, calcd, 312.18; found (tritration), 308.

Anal. Calcd for $C_{10}H_{11}Cl_2NO_4S$: C, 38.54; H, 3.55; N, 4.51; S, 10.27. Found: C, 38.64; H, 3.44; N, 4.55; S, 10.27.

Acknowledgment. This work was supported by the Sloan Basic Research Fund. One of us (U.Z.) thanks the Iad Avi Hayishuv Foundation, Israel, and the Hebrew Technical Institute, New York, N.Y., for financial support.

Registry No.—**1,** 28469-92-3; **2,** 54276-72-1; **3,** 54276-73-2; SO_3, 7446-11-9; acetonitrile, 75-05-8; 1,2-dichloroethane, 107-06-2.

References and Notes

(1) (a) F. G. Bordwell and C. S. Rondestvedt, Jr., *J. Am. Chem. Soc.*, **70,** 2429 (1948); (b) W. E. Truce and P. F. Gunberg, *ibid.*, **72,** 2401 (1950); (c) F. G. Bordwell and M. L. Peterson, *ibid.*, **76,** 3952 (1954); (d) H. Pepponse, *Bull. Soc. Chim. Belg.*, **34,** 133 (1925).
(2) (a) V. Regnault, *Justus Liebigs Ann. Chem.*, **25,** 32 (1838); (b) A. Michael and N. Wiener, *J. Am. Chem. Soc.*, **58,** 294 (1936); (c) D. C. England, M. A. Dietrich, and R. V. Lindsey, Jr., *ibid.*, **82,** 6181 (1960); (d) C. M. Suter and F. G. Bordwell, *ibid.*, **65,** 507 (1943); (e) D. S. Breslow and R. R. Hough, *ibid.*, **79,** 5000 (1957).
(3) J. J. Ritter and J. Kalish, *J. Am. Chem. Soc.*, **70,** 4048 (1948); F. R. Benson and J. J. Ritter, *ibid.*, **71,** 4128 (1949).
(4) C. M. Suter, P. B. Evans, and J. M. Kiefer, *J. Am. Chem. Soc.*, **60,** 538 (1938).

Ionization Constants and Volumes of Highly Hindered Pyridines in Methanol[1]

W. J. le Noble and T. Asano

Department of Chemistry, State University of New York, Stony Brook, New York, 11794

Received December 16, 1974

Although the pK_a's of several 2,6-dialkylpyridinium hydrochlorides have been reported, there is no single com-

plete set of data for the series hydrogen, methyl, ethyl, isopropyl, and *tert*-butyl in a single solvent. In the course of another study,[2] we prepared this series of pyridines and measured both the ionization constants and the ionization volumes in methanol at 25°. We present the data here, and note that the latter data permit some insight into the trend in the former.

Experimental Section

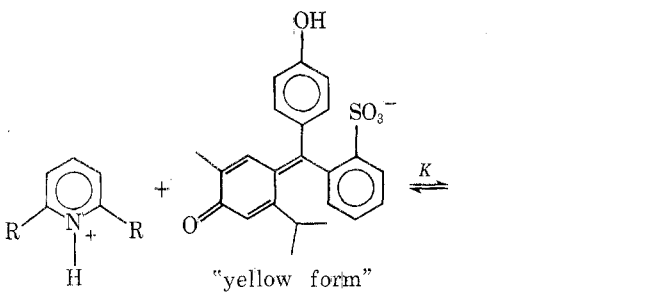
The pyridines were obtained as described.[2]

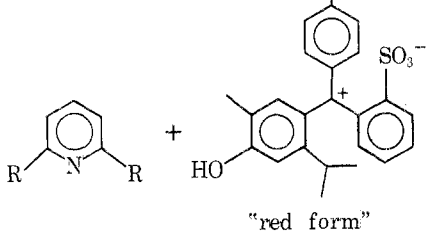
Thymol Blue was obtained from J. T. Baker, and used without purification. For the pK_a measurements, the spectra of the red and yellow forms of Thymol Blue, of the pyridines, and of their hydrochlorides were measured in methanol solution at 25.00 ± 0.05° by means of a Cary 14, with special attention to the wavelength regions of 250–275 and 545–555 nm. Five-milliliter samples of methanolic solutions of Thymol Blue and of the pyridine of accurately known strength (about 10^{-3} to 10^{-4} *M*) were pipetted into a 25-ml volumetric flask. A hydrochloric acid solution in methanol was added to give the appropriate color (by eye). The flask was thermostated at 25.00° and filled to the mark.

The optical densities in the long wavelength region were used to calculate the ratio of the indicator species;[3] the actual concentrations were also calculated and used in turn to furnish the ratio of free to protonated base. These calculations were repeated for several wavelengths; reproducibility was generally about 1% for the indicator and somewhat less than that for the pyridine. The pK_a is then calculated as shown below. The error in pK_a due to ionic strength effects is less than 0.05,[4] hence less than that in the pK_a reported for Thymol Blue. The density measurements were carried out as before;[2] the hydrochloride solutions were obtained by mixing equivalent quantities of base and hydrochloric acid solutions by means of a microburette.

Results and Discussion

The pK_a values are based on the competition for protons between a given pyridine and the indicator Thymol Blue.[5]





For this equilibrium

$$K = \frac{[B][InH]}{[BH^+][In^-]} = K_{a(BH^+)}/K_{a(InH)}$$

The pK_a of the indicator is known[4] to be 4.7, so that we may write

$$pK_a = 4.7 - \log K$$

The advantage of the indicator method is that it can be carried out spectrophotometrically with very low concentrations at an ionic strength of 10^{-4} or less with good accuracy, provided that K is not too greatly different from unity. The difference in pK_a between the pyridines can then be determined to better than 0.1 unit. Our observations with 2,6-diisopropylpyridine may serve as an example. Twelve measurements were made in which the $[In^-]/[InH]$ ratio was varied over an eightfold range, giving a value of K_{av} of 0.0123 ± 0.0006, so that $pK_a = 4.7 + (1.91 \pm 0.02)$. The final results are shown in Table I.

In one case a direct comparison can be made: when R = H, our result is in excellent agreement with the one reported.[6] The general trend is also in agreement with results obtained by others. We subscribe to the interpretation that protonation is facilitated by α-carbon substitution because of inductive electron donation, and that it can be hindered in some way by increasing substitution and crowding. When R = *t*-Bu, there is no longer any possibility of rotating the hindering methyl groups out of the way, and the change in pK_a is then especially severe.[7] The detailed nature of the hindrance—whether to solvation, H bonding, or bonding—is touched on further below.

Basically, two methods are available for the measurement of ionization volumes. In one of these, use is made of the effect of pressure on the pK_a via the relation

$$\Delta V_i = 2.303RT\,\partial pK_a/\partial p$$

Thus, one could measure the spectra of mixtures of a given pyridine and Thymol Blue under pressure; however, the pressure dependence of $pK_a(InH^+)$ in methanol is not known for Thymol Blue or any other suitable indicator. A disadvantage of the method is, furthermore, that only a difference in volume is obtained and information whether any trends are due to changes in volume of the free base or conjugate acid remains hidden. We furthermore noted that mercury (required to keep the solution of interest separated from hydraulic fluid) is rapidly attacked by methanolic hydrogen chloride to give a species absorbing at 238 nm (neither basic methanol solutions nor those acidic with perchloric acid behave this way), and hence we abandoned this approach. In the other method, one determines ΔV_i as the net sum of several partial molar volumes at infinite dilution, such that the species add up to the ionization reaction under consideration. Errors due to dissociation of the conjugate acids become appreciable at very low concentration, and hence the pycnometric technique was used. The measurements are summarized in Figure 1, and the results are shown in Table II.

The ionization volumes given are calculated on the assumption that $\phi v°$ for hydrochloric acid in methanol is −5.3 cm^3/mol,[10] and by making use of the known $\phi v°$ values of the pyridines in methanol.[2] All of them are positive, presumably a reflection of the fact that the charge in the pyridinium ions must to some degree be delocalized; we have reviewed the evidence bearing on this point elsewhere.[11] They are also remarkably independent on interference by 2,6-alkyl groups except for *tert*-butyl; $\Delta V_i°$ for 2,6-di-*tert*-butylpyridinium hydrochloride is by all odds the largest known volume change for proton transfer.[12] Obviously a large fraction of this change can be attributed to the apparent difficulty of the neutral base to be hydrogen bonded in that case.[2]

Finally, a further comment on the pK_a's of these compounds is in order. The declines in pK_a, absent or small at first but then steep at *tert*-butyl, may be caused by steric hindrance to solvation or to steric compression of the conjugate acid itself.[13] The former explanation has been favored by Wepster,[14] and by McDaniel;[8] the latter author found that the changes in pK_a became more pronounced if the solvent is systematically varied from water to aqueous alcohol, or from methanol to 2-propanol. On the other hand, Brown[7] has favored the idea of sterically compressed

Table I
pK_a Values of 2,6-Dialkylpyridinium Hydrochlorides in Several Solvents at 25°

Substituent	Methanol	50% Aqueous Ethanol	Water	Registry no.
H	5.37,[a] 5.4[b]	4.38[c]	5.22[e]	628-13-7
Me	6.86[a]	5.77[c]	6.72[e]	15439-85-7
Et	6.9[b]			54384-36-0
i-Pr	6.6[b]	5.34[c]		54384-37-1
t-Bu	4.2[b]	3.65,[d] 3.58[c]		54384-38-2

[a] Reference 6. [b] This work. [c] Reference 7. [d] Reference 8. [e] Reference 9.

Table II
Partial Molal Volumes of the Pyridinium Hydrochlorides at Infinite Dilution, and the Ionization Volumes in cm^3/mol in Methanol at 25.00°

Substituent	Φ_V°	ΔV_I°
H	63.69 ± 0.22	+9.8
Me	97.72 ± 0.19	+8.1
Et	128.39 ± 0.29	+10.0
i-Pr	164.36 ± 0.31	+10.8
t-Bu	196.02 ± 0.17	+22.0

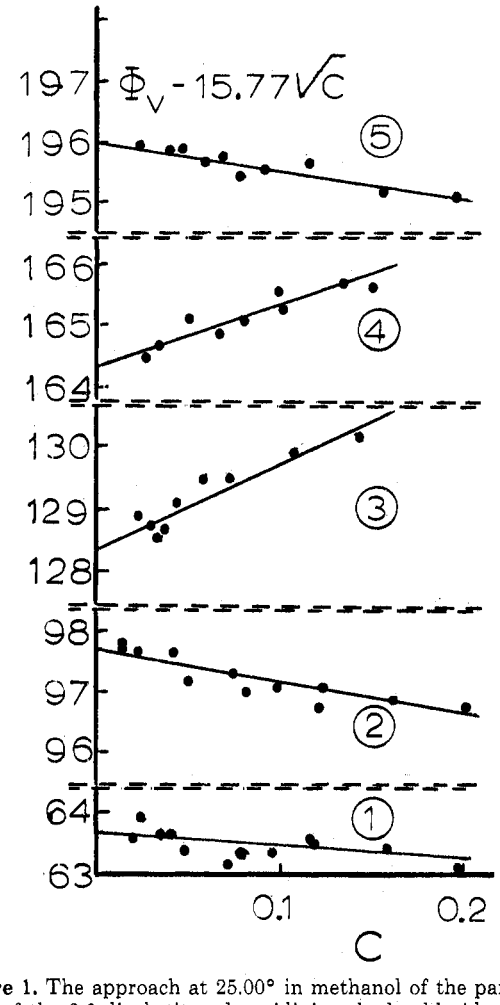


Figure 1. The approach at 25.00° in methanol of the partial volumes of the 2,6-disubstituted pyridinium hydrochlorides to their limiting values: (1) R = H; (2) R = Me; (3) R = Et; (4) R = *i*-Pr; (5) R = *t*-Bu.

pyridinium ions primarily on the grounds that the change at *tert*-butyl is so much more dramatic than with the other alkyl groups. He includes a stressed NH–SOH hydrogen bond as a possibility in his point of view. Our volume data do not allow a clear choice to be made between Brown's two possibilities; however, they do cast doubt on the hindered solvation. Solvation of ions is normally accompanied by a large volume decrease, and if this electrostriction were absent or greatly diminished in the *tert*-butyl cation, this should surely be reflected in an ionization volume much less than that of the lower homologs. What is observed is a volume change much *larger*, and even if allowance is made for the inability of the solvent to form hydrogen bonds with the neutral base, one would still have to conclude that there is no evidence for a conspicuous lack or absence of electrostriction around the cation.

Acknowledgment. This work was generously supported by the National Science Foundation.

References and Notes

(1) Paper XXXI in the series Kinetics of Reactions in Solutions under Pressure.
(2) W. J. le Noble and T. Asano, *J. Am. Chem. Soc.*, **97**, 0000 (1975).
(3) L. A. Flexser, L. P. Hammett, and I. A. Dingwall, *J. Am. Chem. Soc.*, **57**, 2103 (1935).
(4) I. M. Kolthoff and L. S. Guss, *Trans. Faraday Soc.*, **50**, 918 (1954).
(5) This general method has been discussed in detail by M. T. Rogers, T. W. Campbell, and R. W. Maatman, *J. Am. Chem. Soc.*, **73**, 5122 (1951).
(6) C. H. Rochester, *J. Chem. Soc. B*, 33 (1967).
(7) H. C. Brown and B. Kanner, *J. Am. Chem. Soc.*, **88**, 986 (1966).
(8) D. H. McDaniel and M. Özcan, *J. Org. Chem.*, **33**, 1922 (1968).
(9) R. J. L. Andon, J. D. Cox, and E. F. G. Herington, *Trans. Faraday Soc.*, **50**, 918 (1954).
(10) F. J. Millero, *J. Phys. Chem.*, **73**, 2417 (1969).
(11) W. J. le Noble, B. L. Yates, and A. W. Scaplehorn, *J. Am. Chem. Soc.*, **89**, 3751 (1967); see also W. Kauzmann, A. Bodanszky, and J. Raspar, Ibid., **84**, 1777 (1962).
(12) E. Whalley, *Adv. Phys. Org. Chem.*, **2**, 93 (1964).
(13) P. D. Bartlett, M. Roha, and R. M. Stiles, *J. Am. Chem. Soc.*, **76**, 2349 (1954).
(14) B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, **76**, 335 (1957).

Blocking and Deblocking of α-Methylene-γ-butyrolactones[1]

Paul A. Grieco*[2] and Masaaki Miyashita

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

Received November 25, 1974

Recent reports in the literature have been concerned with the use of protecting groups which prevent Michael-type additions of nucleophilic reagents to the reactive sites of α-methylene lactones. These include dimethylamine,[3] thiols (1-propanethiol,[4] cysteine[5]), and phenylselenium anion.[6] We wish to report that sodium thiophenoxide can be employed in a high-yield reaction as a reagent for blocking α-methylene lactones. In addition, the removal of the β-phenylthio blocking group for regeneration of the α-methylene unit can be readily accomplished in high yield (see Table I) employing an alternate method from that previously utilized for β-thio adducts. Previously deblocking of a β-thio adduct required conversion to its corresponding