of residue. Redistillation gave 19.0 g. of colorless liquid boiling at 140–50° (6 mm.), $n^{22}\mathrm{D}$ 1.4978.[11,12]

1-Carboxybicyclo[4.3.1]dec-3-en-10-one (Ib).—1-Carbethoxybicyclo[4.3.1]dec-3-en-10-one (25 g.) was refluxed with 10% hydrochloric acid. The hydrolysis mixture was extracted with ether, and the ether extract was washed with sodium bicarbonate solution. Acidification of the sodium bicarbonate solution gave a solid which was recrystallized from toluene to give 3 g. of a pure white solid melting at 146–147°. The ester from the *cis* and that from the *trans* dichloride both gave the same acid (mixture melting point). The 2,4-dinitrophenylhydrazone had m.p. 236–238°. The n.m.r. spectrum indicated the structure to be Ib, not IIb.[13]

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.04; H, 7.21. Found: C, 68.12; H, 7.24.

1-Carboxybicyclo[4.3.1]decan-10-one (III). A.—1-Carbethoxybicyclo[4.3.1]dec-3-en-10-one[14] (15 g.) was dissolved in 160 ml. of 95% ethanol containing 1.4 g. of 5% palladium on barium sulfate (Engelhard Industries, Inc.) and agitated at room temperature in the low-pressure hydrogenator under a hydrogen pressure of 32.5 lb./in.² for 23 hr. Filtration of the catalyst and reduced pressure evaporation of the alcohol gave a residue that was refluxed with a solution of 10 g. of sodium hydroxide in 75 ml. of water for 4 hr. The reaction mixture was treated with decolorizing carbon and filtered. The cooled filtrate was washed with ether and then acidified. The resulting oil was taken up in ether, washed with water, and dried over anhydrous magnesium sulfate. The 9 g. of residue from evaporation of the ether was taken up in a bicarbonate solution which was then washed with ether. Acidification gave an oil which was taken up in ether and dried. The solid obtained by evaporation of the ether was recrystallized from methylcyclohexane to give pure white III, melting at 102–103°. The 2,4-dinitrophenylhydrazone had m.p. 189°.

Anal. Calcd. for $C_{11}H_{16}O_3$: C, 67.35; H, 8.16. Found: C, 67.36; H, 8.29.

B.—2-Carbethoxycycloheptanone (0.15 mole) was treated with acrolein at −70° according to the method of Cope and Synerholm[7] to give 18.3 g. of crude β-(1-carbethoxy-2-ketocycloheptyl)propionaldehyde (IV), boiling at 165–185° (7 mm.), $n^{21}\mathrm{D}$ 1.4774. The 18.3 g. of aldehyde gave 3 g. of crude solid (V) after ring closure and hydrolysis. The 2,4-dinitrophenylhydrazone had m.p. 230° dec.

Anal. Calcd. for $C_{17}H_{18}N_4O_6$: C, 54.54; H, 4.81. Found: C, 54.50; H, 4.88.

When the solid was reduced as above and then recrystallized from methylcyclohexane, a pure white solid melting at 102–103° was formed. There was no depression of melting point when mixed with the acid from A.

Bicyclo[4.3.1]dec-3-en-10-one (Ic).—1-Carboxybicyclo[4.3.1]dec-3-en-10-one (1.25 g.) was refluxed with 10 ml. of quinoline for 1 hr. The mixture was cooled and treated with ether. The ether solution was washed with water, sodium bicarbonate solution, water, dilute hydrochloric acid, and again with water. The ether solution was dried and evaporated to give 1 g. of brown residue. Distillation of 3.6 g. of the residue isolated 1 g. of white solid from the quinoline still present, b.p. 85° (4 mm.), m.p. 72–73°. The 2,4-dinitrophenylhydrazone had m.p. 175–176°.

Anal. Calcd. for $C_{16}H_{18}N_4O_4$: C, 58.18; H, 5.45. Found: C, 58.11; H, 5.48.

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[12] There were differences in the boiling points and refractive indices of the distillates from the *cis* and *trans* dihalides only because the distillates contained all the same impurities (alcohol, cyclohexanone, 3,4-dichloro-1-butene, *cis*- and *trans*-1,4-dichloro-2-butene, and carbethoxycyclohexanone) in slightly varying amounts.

[13] Carried out and interpreted by Varian Associates, Palo Alto, Calif.

[14] The ester prepared from *trans*-1,4-dichloro-2-butene was used.

The Reaction of Carbyl Sulfate with Pyridine

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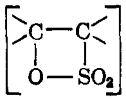
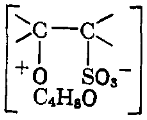
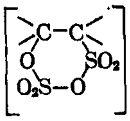
Received February 21, 1964

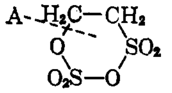
Bordwell and co-workers studied the mechanism of sulfonation of olefins and concluded that β-sultones (I), or their dioxane-solvated oxonium ions (II), and cyclic sulfonate–sulfates (III) are important intermediates when 1 mole of olefin is treated with 1 or 2 moles of sulfur trioxide–dioxane, respectively.[1] The existence of these intermediates, which were isolated in some instances,[2] was supported, for example, by the formation of 2-(1-proto-1-pyridyl)-1-hexanesulfonate[3a] on sequential treatment of 1-hexene with 1 mole of sulfur trioxide–dioxane and excess pyridine, and by the formation of the aniline salt of 2-hydrosulfato-1-hexanesulfonanilide on sequential treatment of 1-hexene with 2 moles of sulfur trioxide–dioxane and aniline.[3b] The reaction of intermediates of type III with tertiary amines was not reported.


I


II


III

The purpose of our investigation was to conduct a limited study of the reactivity of pure carbyl sulfate (IV) with pyridine. We expected that, if reaction occurred, the most probable reaction would be C–O cleavage at bond A with resultant formation of a betaine salt.[4] Such a reaction would suggest that the structures of the products formed on sequential treatment of olefins with sulfur trioxide and amines may not clearly differentiate between reaction paths which involve intermediates of structures I, II, and III.



IV

The reaction of IV and pyridine was carried out in ethylene chloride solvent so that the reactive species was IV and not a decomposition product.[5] At room temperature, IV reacted rapidly with pyridine to afford an oily precipitate which gave a crystalline solid in relatively good yield on crystallization from N,N-dimethylformamide. The crystalline product was characterized as the betaine salt, 2-(1-proto-1-pyridyl)-1-ethanesulfonate (V),[3a] by elemental, infrared, and p.m.r. analyses, and by examination of its chemical properties. The product had a high melting point and was soluble in polar solvents. Aqueous solutions of the product were neutral, gave negative tests for

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[1] For a summary of the literature on the mechanism of reaction of sulfur trioxide with olefins, see E. E. Gilbert, *Chem. Rev.*, **62**, 549 (1962).

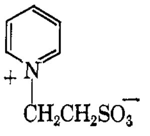
[2] See ref. 1, p. 564.

[3] (a) This nomenclature has been used previously by Professor Bordwell and co-workers. See, for example, F. G. Bordwell, M. L. Peterson, and C. S. Rondestvedt, Jr., *J. Am. Chem. Soc.*, **76**, 3945 (1954). Reference 7 of this paper is reproduced here: "This nomenclature has been suggested by Dr. F. Y. Wiselogle to fill the need for a suitable prefix to designate a substituent which bears a positive charge. "Proto" signifies the addition of a proton; $C_5H_5N\,^+H$ is then protopyridine and $C_5H_5N\,^+–$ is the 1-proto-1-pyridyl group. According to this nomenclature a dipolar ion, such as sulfanilic acid, can be given the systematic name *p*-protoaminobenzenesulfonate, rather than *p*-aminobenzenesulfonic acid, which misrepresents the structure." (b) F. G. Bordwell and M. L. Peterson, *ibid.*, **76**, 3952 (1954).

[4] Betaine-type compounds are defined in this paper as internal salts containing the anion of the sulfonic acid group and a quaternary fully alkylated nitrogen atom.

[5] Infrared analyses of ethylene chloride solutions of IV indicated that decomposition is nil when IV is carefully dissolved in the solvent. Ethylene chloride is a suitable recrystallization solvent for IV.

sulfate anion even after boiling with hydrochloric acid, and liberated pyridine on treatment with warm base. Neutralization equivalent and bromine number determinations carried out according to the method of Bordwell and Peterson[3b] gave the expected values for



V

the betaine salt structure.[6] The infrared spectrum exhibited the two absorption bands which are characteristic of the C=C and C=N vibrations of the N-alkylated pyridine ring.[7] The p.m.r. spectrum exhibited the expected chemical shifts for the two pairs of methylenic protons of V. All of the physical and chemical evidence collected in this investigation supported the betaine salt structure (V) for the reaction product of IV and pyridine.

In other experiments, treatment of IV with equimolar or less than equimolar amounts of pyridine gave V in reduced yields. Attempts to utilize alcohols and water as crystallization solvents for the initial oily precipitate failed. However, V was recrystallizable from methanol after crystallization had been effected from N,N-dimethylformamide. Presumably, the oily precipitate formed initially on treatment of IV with pyridine contains the $-SO_2OSO_3^-$ group which is converted to $-SO_3^-$ by removal of sulfur trioxide to yield V. N,N-Dimethylformamide apparently coordinates with sulfur trioxide to form sulfur trioxide–N,N-dimethylformamide and V.

Thus, our investigation shows that carbyl sulfate (IV) undergoes cleavage at bond A on treatment with pyridine under mild conditions. Cyclic sulfonate–sulfate intermediates (III) will probably react in a similar manner with pyridine or other tertiary heterocyclic amines to yield betaine salts identical with the products formed on treatment of intermediates I or II with the same amine.

Experimental[8]

2-(1-Proto-1-pyridyl)-1-ethanesulfonate.—Carbyl sulfate, 10.0 g. (0.0531 mole), prepared according to the method of Breslow and Hough and recrystallized twice from ethylene chloride,[9] was dissolved in 200 ml. of ethylene chloride by gentle warming on the steam bath. The resulting solution was treated with 19.6 g. (0.25 mole) of pyridine in 80 ml. of ethylene chloride. During the addition, the reaction mixture was maintained at room temperature by external cooling with an ice bath. The exothermic reaction produced an oily precipitate which was separated from unreacted pyridine and solvent by decantation of the supernatant liquid and successive washing of the precipitate with two 100-ml. portions of fresh ethylene chloride and two 100-ml. portions of petroleum ether (b.p. 30–60°). The precipitate was crystallized once from boiling N,N-dimethylformamide to yield 3.5 g. (35.3%) of 2-(1-proto-1-pyridyl)-1-ethanesulfonate as white granular crystals, m.p. 250–255° with sintering at 90°. Evaporation of the mother liquor gave an additional 2.5 g. (25.2%) of product melting at 240°. This product was identical with the first crop of crystals by infrared analysis. Elemental analysis of the first crop gave the results indicated below. The salt was soluble in water and methanol, and insoluble in acetone, ether, petroleum ether, and ethylene chloride.

Anal. Calcd. for $C_7H_9NO_3S$ (mol. wt. 187.21): C, 44.91; H, 4.85; N, 7.48; S, 17.13. Found: C, 44.97; H, 5.03; N, 7.62; S, 17.10.

Aqueous solutions of the salt were neutral and gave negative tests for sulfate anion after boiling with hydrochloric acid for 5 min. Free pyridine was detected by odor on treatment of an aqueous solution of the salt with 1.0 *N* sodium hydroxide solution and warming on the steam bath for a few minutes. The neutralization equivalent was determined by the method of Bordwell and Peterson.[3b] An aqueous solution of the salt was warmed for 30 min. on the steam bath with excess standard sodium hydroxide solution. Back-titration with standard hydrochloric acid solution gave a neutralization equivalent of 177 (calcd. neut. equiv. 187). Determination of the bromine number with an aliquot of the neutralized solution by the bromide–bromate technique gave a value of 86.4 (calcd. 85.3). Another aliquot of the neutralized solution gave a positive test for sulfate anion after sequential treatment with acidic potassium permanganate solution, a few drops of 30% hydrogen peroxide solution to remove manganese dioxide, and barium chloride solution.[10]

The instrument used to record the infrared spectra was a Perkin-Elmer Model 21 recording spectrophotometer. The spectrum of a potassium bromide pellet of 2-(1-proto-1-pyridyl)-1-ethanesulfonate exhibited sharp peaks at 6.1 (strong) and 6.3 μ (weak) in addition to a considerable amount of fine structure beyond 6.5 μ.[7]

The p.m.r. spectrum was measured in deuterium oxide at 60 Mc./sec. and room temperature with a Varian Associates A-60 spectrometer with an internal standard of Tier's salt.[11] The spectrum showed two triplets with relative intensities of 1:1. The triplet at 5.0 p.p.m. was attributed to the methylenic protons β to the sulfonate group, and the triplet at 4.6 p.p.m. was attributed to the methylenic protons α to the sulfonate group.

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(6) This type of neutralization equivalent determination is based upon the quantitative reaction of the betaine salt with sodium hydroxide to afford an aqueous solution of pyridine and sodium vinylsulfonate. The bromine number determination, which is carried out with this aqueous solution, is based upon the reaction of bromine with sodium vinylsulfonate, but the numerical value is calculated as grams of molecular bromine consumed/100 g. of original betaine salt.

(7) Infrared spectra have been measured for several betaine sulfonate and sulfate salts. All spectra exhibit the characteristic absorption bands described in the Experimental section. This work will be published shortly.

(8) Melting points are uncorrected. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Ill. Neutralization equivalent and bromine number determinations were performed by the Analytical Research and Services Division of The Pure Oil Co., Crystal Lake, Ill.

(9) D. S. Breslow and R. R. Hough, *J. Am. Chem. Soc.*, **79**, 5000 (1957).

(10) Characteristic of α,β-unsaturated sulfonates.

(11) The p.m.r. determination was kindly carried out by Mr. Stuart Armstrong of Varian Associates. Assignments of the chemical shifts were made after examination of several betaine sulfonate and sulfate salts. The results of this examination will be published in a future paper.

Base-Catalyzed Preparation of Methyl and Ethyl Esters of Carboxylic Acids

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Received April 24, 1964

Recently[2] the author described a method of making phenacyl esters of carboxylic acids in which dicyclohexylethylamine (DICE) was used as the proton acceptor. Subsequent work has shown that dimethyl sulfate in the presence of this amine rapidly converts carboxylic acids to methyl esters in high yield. The method is simple and rapid, and is useful when the preparation of diazomethane is not feasible or when strongly acidic conditions must be avoided.

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(1) A laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) F. H. Stodola, *Microchem. J.*, **9**, 389 (1963).