Acknowledgment.—The authors are grateful to members of Spectroscopy Investigations of this Laboratory for many of the infrared spectra, to Dr. Robert Barker and Gordon J. Boudreaux for the nmr spectra, and to Mrs. Ann Alford for the molecular weights.

Application of the Haloalkoxy Reaction to 6-Nitroanthroxanic Acid[1a]

D. R. Eckroth,[1b] T. G. Cochran, and Edward C. Taylor

Department of Chemistry, Princeton University, Princeton, New Jersey

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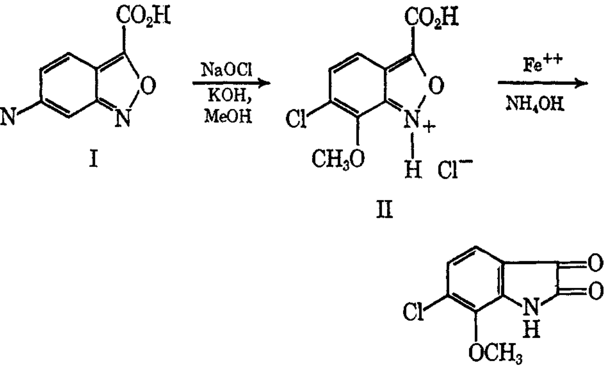
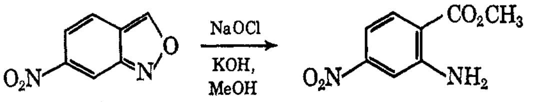
In a series of papers Mallory[2] and co-workers investigated a novel conversion, called the "haloalkoxy substitution reaction," in which the replacement of a nitro group by a chlorine and of an adjacent ring hydrogen by a methoxy group is effected by treatment of certain aromatic nitro compounds with aqueous sodium hypochlorite in alkaline methanol solution. Mallory demonstrated that this reaction takes place with nitro-substituted benzofurazans and their corresponding N-oxides, with 5-nitro-2-phenylbenzotriazole, and with 6-nitro-2,3-diphenylquinoxaline, and he suggested that the reaction may be general for molecules having a nitrogen heterocycle fused to the ring bearing the replaceable nitro group.



I II V



III IV

In support of this suggestion, we have found that 6-nitroanthroxanic acid (I) also undergoes the "haloalkoxy substitution reaction." Compound I is converted under the conditions described by Mallory to 6-chloro-7-methoxyanthroxanic acid hydrochloride (II). The structure of II was confirmed by its nmr spectrum, which exhibited two doublets of an AB system due to the two adjacent ring protons ($J = 9.0$ cps). Attempts to carry out an analogous conversion on 6-nitroanthranil (III) were unsuccessful because III is easily ring opened under the basic reaction conditions to methyl 4-nitroanthranilate (IV).

Since anthroxanic acids are easily converted to isatins by reductive cleavage of the isoxazole ring,[3] the "haloalkoxy substitution reaction" applied to nitro-substituted anthroxanic acids is potentially useful as a means of synthesizing certain isatins with adjacent ring substituents. Illustrative of this synthetic potential is the conversion of II to 6-chloro-7-methoxyisatin (V) with ferrous sulfate and ammonia.

Experimental Section[4]

The preparations of 6-nitroanthroxanic acid and 6-nitroanthranil have been described in a previous paper.[5]

6-Chloro-7-methoxyanthroxanic Acid Hydrochloride (II).—A solution of 0.5 g (0.0024 mole) of 6-nitroanthroxanic acid (I) and 0.8 g of potassium hydroxide (0.014 mole) in 50 ml of methanol was stirred magnetically and heated at reflux during the dropwise addition of 65 ml of aqueous sodium hypochlorite solution.[6] The solution was maintained at 60–65° during the addition, over 15 min, of the hypochlorite solution and for 20 min more, after which time most of the methanol was removed at aspirator pressure on a rotating flash evaporator. The flask was cooled in ice and acidified with 2 *N* hydrochloric acid. The yellow crystals of II were collected by filtration and washed with ice-cold water to give 0.25 g (40%): mp 182°; $\lambda_{\max}^{\mathrm{EtOH}}$ 229 mμ (ε 26,900); $\nu_{\max}$ 3535, 3450, 1690, 1637, 1546, 1520, 1275, 800, and 780 cm^{-1}.

Anal. Calcd for $C_9H_7N_4Cl \cdot HCl$: C, 40.91; H, 2.67; N, 5.31. Found: C, 40.61; H, 2.36; N, 5.11.

6-Chloro-7-methoxyisatin (V).—To a solution containing 5 ml of water and 1.5 ml of concentrated ammonium hydroxide was added 0.15 g of 6-chloro-7-methoxyanthroxanic acid hydrochloride (II) followed by 1.0 g of $FeSO_4 \cdot 7H_2O$. The solution was allowed to stand at room temperature for 30 min, after which time 20 ml of water was added. The mixture was shaken and filtered, and the filtrate was acidified with 15 ml of 2 *N* hydrochloric acid. The orange crystals of V which separated on standing were collected by filtration to give 0.09 g (74%): mp 179°; $\lambda_{\max}^{\mathrm{EtOH}}$ in mμ (ε) 216 (21,600), 248 (17,000), 255 (15,200), 311 (6100); $\nu_{\max}$ 3225, 1770, 1736, 1615, 1325, 1275, 1040, and 760 cm^{-1}.

Anal. Calcd for $C_9H_6NO_3Cl$: C, 51.09; H, 2.86; N, 6.62; Cl, 16.75. Found: C, 50.92; H, 3.00; N, 6.67; Cl, 17.03.

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(1) (a) This work was supported in part by a grant (CA-02551) to Princeton University from the National Cancer Institute, National Institutes of Health, Public Health Service. (b) National Institutes of Health Predoctoral Fellow, 1962–1965.

(2) Part IV: F. B. Mallory, C. S. Wood, and B. M. Hurwitz, *J. Org. Chem.*, **29**, 2605 (1964).

(3) A procedure for reducing anthroxanic acid to isatin was described by A. Reissert, *Ber.*, **41**, 3921 (1908).

(4) All melting points are corrected.

(5) D. R. Eckroth, T. G. Cochran, and E. C. Taylor, in press.

(6) The aqueous sodium hypochlorite solution used in this work was the commercial product Clorox.

Protonolysis of 2-Isopropoxy-2-methyl-1-methylenecyclopropane. A Stable Unsaturated Carbonium Ion

T. C. Shields, B. A. Shoulders, and P. D. Gardner[1]

Department of Chemistry, University of Texas, Austin, Texas

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The study of carbonium ion structures was greatly facilitated by the discovery that nmr data can be obtained quickly and simply for solutions in strong acids.[2] Ions studied in this way are usually produced by protonation of a double bond or by protonolysis of a hy-

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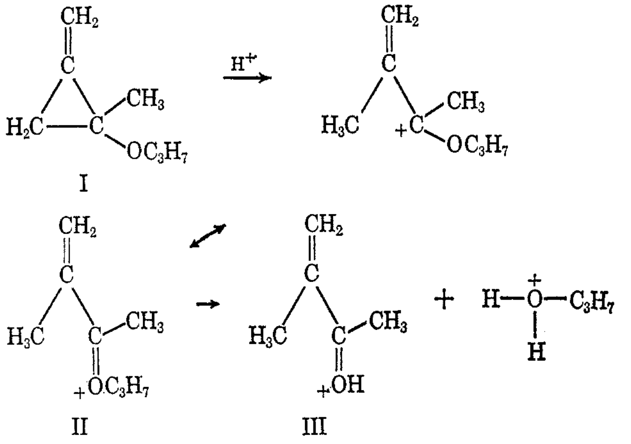
(1) Department of Chemistry, University of Utah, Salt Lake City, Utah.

(2) *Cf.* N. C. Deno, *Chem. Eng. News*, **42**, 88 (1964).

droxyl group.[3] We now report still another approach to stable ions, the protonolysis of appropriately substituted cyclopropanes[4] in 96% sulfuric acid.[2,7]

The nmr spectrum of 2-isopropoxy-2-methyl-1-methylenecyclopropane (I)[8] in 96% sulfuric acid exhibits two slightly broadened singlets at τ 3.22 and 3.49 (two protons, vinyl), a septet centered at τ 4.70 ($J = 6.0$ cps, one proton geminal to oxygen), a sharp singlet at τ 7.43 (methyl group geminal to oxygen), a slightly broadened singlet at τ 8.35 (three protons, allylic methyl), and a doublet centered at τ 8.75 ($J = 6.0$ cps, six protons, isopropyl). As the solution aged (several hours), the spectrum gradually changed. Two singlets emerged at τ 3.08 and 3.35 as the τ 3.22 and 3.49 signals diminished in intensity. Similarly, as the septet at τ 4.70 vanished, another appeared at τ 5.27 ($J = 6.0$ cps) and the singlet at τ 8.35 became replaced by one at τ 8.30. The doublet at τ 8.75 disappeared as a new one grew in at τ 8.94. The methyl signal at τ 7.43 remained unchanged in chemical shift. This transition from one simple spectrum to another equally clean pattern suggested a discrete chemical change as opposed to the indiscriminate destruction of the initially formed ion.



Spectral data first cited are those predicted for ion II, and those obtained from the aged solution are consistent with III and the conjugate acid of isopropyl alcohol in equimolar quantities. These suspicions were confirmed by quenching an aged solution with cold water and extracting the product into carbon tetrachloride. Its nmr spectrum proved to be essentially identical with data reported for 2-methyl-1-buten-3-one.[9] Moreover an equimolar mixture of this substance with isopropyl alcohol gave an nmr spectrum in sulfuric acid which is identical with that of an aged solution of I in sulfuric acid.

It is noteworthy that the spectral changes described occur only slowly and are due primarily to hydrolysis rather than polymerization. The half-life of II is not less than 30 min at 42°. The stability of this ion (II) relative to that of others possessing terminal double bonds[7,10] is perhaps not surprising in view of the extent to which charge is delocalized.

Evidence in hand is insufficient to permit a choice of mechanism for the protonolysis. Reaction could involve a direct attack of proton on the cyclopropane ring or, perhaps more likely, attack on the double bond. The latter would probably not produce a fully developed, rather high energy cyclopropyl ion[11] but would instead involve synchronous rearrangement to II.

The behavior of 2-methoxy-2-methyl-1-methylenecyclopropane in sulfuric acid was examined and found to be similar to that of I. The most notable difference was the diminished half-life of its primary ion.

Experimental Section

Sulfuric Acid Solutions.—Solutions were prepared at concentrations of approximately 10% by volume in reagent grade 96% sulfuric acid. Spectra were obtained with a Varian A-60 nmr spectrometer using standard sample tubes at ambient temperature (~42°). Sodium 3-trimethylsilyl-1-propanesulfonate was used as an internal standard (accepted value τ 9.92).

Acknowledgment.—The authors are indebted to the Robert A. Welch Foundation for the financial support of this study.

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[3] For leading references, see C. U. Pittman, Jr., and G. A. Olah, *J. Am. Chem. Soc.*, **87**, 2998 (1965); N. C. Deno, J. S. Liu, J. O. Turner, D. N. Lincoln, and R. E. Fruit, Jr., *ibid.*, **87**, 3000 (1965).

[4] The acid-catalyzed solvolysis of cyclopropanes has been rather extensively studied[5,6] but not as a means for preparing stable ions.

[5] A. C. Cope and J. K. Hecht, *J. Am. Chem. Soc.*, **85**, 1780 (1963).

[6] R. L. Baird and A. A. Aboderin, *ibid.*, **86**, 252 (1964), and references cited therein.

[7] The use of sulfuric acid is described by N. C. Deno, "Progress in Physical Organic Chemistry," Vol. II, Interscience Publishers, Inc. (John Wiley and Sons, Inc.), New York, N. Y., 1964, p 129; N. C. Deno, H. G. Richey, N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **85**, 2991 (1963).

[8] T. C. Shields, B. A. Shoulders, J. F. Krause, C. L. Osborn, and P. D. Gardner, *ibid.*, **87**, 3026 (1965).

[9] L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2881 (1960); R. A. Raphael, E. C. Taylor, and H. Wynberg, *Advan. Org. Chem.*, **2**, 265 (1960).

[10] T. S. Sorensen, *Can. J. Chem.*, **42**, 2768 (1964).

[11] The mode of addition of hydrogen bromide to methylenecyclopropane [B. C. Anderson, *J. Org. Chem.*, **27**, 2720 (1962)] is suggestive of an intermediate cyclopropyl ion. However, the solvent employed was nonpolar and a four-center transition state could therefore be involved.

Ultraviolet Spectral Studies of Conjugation in Esters of Acylphosphonic Acids[1]

K. DARRELL BERLIN AND DONALD H. BURPO

Department of Chemistry, Oklahoma State University,
Stillwater, Oklahoma 74074

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The ultraviolet absorption spectra of I–VIII (Table I) provide evidence for a moderately strong conjugative interaction between phosphorus of the phosphoryl group and carbon of the adjacent carbonyl group. The $n \rightarrow \pi^*$ band in analogous aliphatic aldehydes and the $^1A \rightarrow {}^1L_a$ band ($\pi \rightarrow \pi^*$) in the related *para*-substituted benzaldehydes were compared with the same bands in the respective compounds I–VIII.

There was recently reported convincing ultraviolet spectral evidence for $d\pi$–$p\pi$ bonding in tri-2-pyrryl-, 2-(1-methylpyrryl)-, 2-thienyl-, 2-furylphosphine oxides, phosphine oxides, and phosphonium salts which possess a number of *para* substituents on aromatic rings.[2] The remarkably low-range frequencies for infrared absorption (10–15 cm^{-1} less than that for the C═O in corresponding aldehydes) of the carbonyl group in acylphosphonates[3,4] suggests that the carbon–

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[1] We gratefully acknowledge support of this work by the Public Health Service (Grant No. GM 10367-04).

[2] C. E. Griffin, R. P. Peller, K. R. Martin, and J. A. Peters, *J. Org. Chem.*, **30**, 97 (1965).

[3] K. D. Berlin and H. A. Taylor, *J. Am. Chem. Soc.*, **86**, 3862 (1964).

[4] B. Ackerman, T. A. Jordan, C. R. Eddy, and D. Swern, *ibid.*, **78**, 4444 (1956).