The solvent was removed by distillation, and the residue was sublimed onto a −78° cold finger condenser at 0.1 mm to give 64 g (63% yield) of 2,2,2-trinitrofluoroethane, mp 34–35°.

Anal. Calcd for $C_2H_2N_3O_6F$: C, 13.10; H, 1.10; N, 22.95; F, 10.38. Found: C, 13.12; H, 1.11; N, 23.22; F, 10.39.

The infrared spectrum in carbon tetrachloride consisted of the following peaks: 3.38 (w), 3.43 (w), 3.52 (w), 6.30 (s), 7.0 (w), 7.79 (s), 7.93 (m), 9.20 (m), 9.8 (m), 10.15 (m), 11.40 (w), and 11.75 μ (w).

2,2-Dinitrofluoropropane.—Sulfur tetrafluoride (20 ml at −78°) was condensed into an evacuated 75-ml stainless steel bomb containing 15 g (0.10 mol) of 2,2-dinitropropanol. The bomb was heated remotely for 20 hr at 85–90° and was then cooled to room temperature. The above procedure resulted in the isolation of 7.0 g (46% yield), mp 62–63°, with a crystalline phase change at 50°.

Anal. Calcd for $C_3H_5N_2O_4F$: C, 23.68; H, 3.29; N, 18.43; F, 12.50. Found: C, 23.67; H, 3.29; N, 18.43; F, 11.80.

The infrared spectrum of a carbon tetrachloride solution consisted of peaks at 3.50 (w), 6.40 (s), 6.90 (m), 6.96 (m), 7.18 (m), 7.30 (w), 7.40 (w), 7.60 (s), 7.90 (w), 8.10 (w), 8.65 (w), 8.90 (w), 9.49 (s), 11.5–11.65 (doublet, m), and 11.85 μ (m).

The proton nmr spectrum consisted of a methylene doublet at δ 5.12 (J = 46 cps) and a methyl doublet at 2.25 (J = 2 cps). The only[19] nmr signal was a triplet at φ 230.3 (J = 45 cps).

2,2-Dinitro-1,3-difluoropropane.—Sulfur tetrafluoride (20 ml at −78°) and 2,2-dinitro-1,3-propanediol (10 g, 0.060 mol) were allowed to react 8 hr at 85–90° by the above procedure to give 6.3 g (62% yield) of 2,2-dinitro-1,3-difluoropropane, mp 54°.

Anal. Calcd for $C_3H_4N_2O_4F_2$: C, 21.17; H, 2.35; N, 16.47; F, 22.35. Found: C, 21.07; H, 2.07; N, 16.19; F, 22.24.

The infrared spectrum of a solution in carbon tetrachloride contained peaks at 3.40 (w), 3.50 (e), 6.39 (s), 6.90 (m), 7.44 (m), 7.65 (s), 7.95 (w), 8.30 (w), 9.25 (m), 9.50 (s), 9.60 (s), 11.45 (w), and 11.84 μ (m).

The proton nmr spectrum consisted of a doublet of doublets at δ 5.32 (J = 46 and 2.5 cps) and the fluorine nmr spectrum consisted of a triplet at φ 235.0 (J = 45 cps).

Registry No.—2,2,2-Trinitrofluoroethane, 15892-91-8; 2,2-dinitrofluoropropane, 15892-92-9; 2,2-dinitro-1,3-difluoropropane, 15892-93-0; sulfur tetrafluoride, 7783-60-0.

Acknowledgment.—The author is indebted to Mr. K. Inouye for elemental analysis and to Mr. L. A. Maucieri for the nmr spectral determinations.

The Oxidation of Azines with Lead Tetraacetate. II[1]

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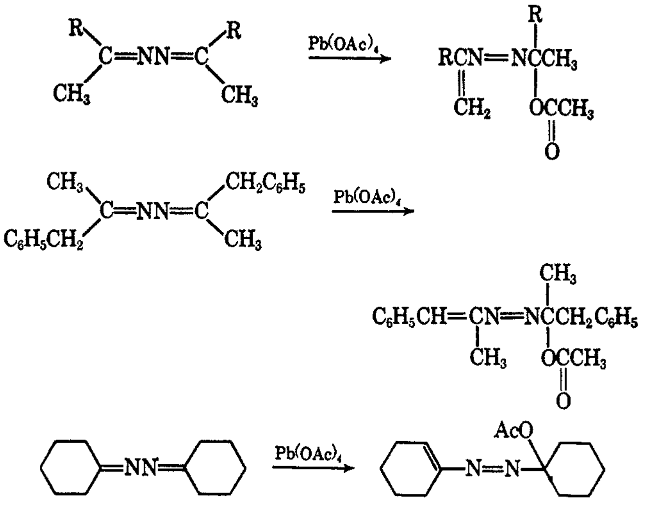
Received November 2, 1967

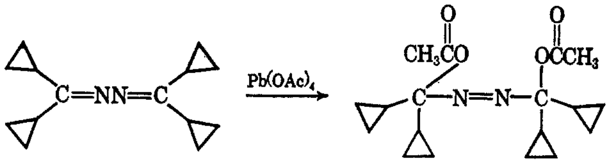
It was reported earlier[2] that the oxidation of ketazines with lead tetraacetate afforded α,β-unsaturated azoacetates in 40–70% yield (Scheme I). It was also noted that these products arose *via* abstraction of one of the active hydrogens on an α-carbon atom followed by conjugate addition of an acetate moiety. It was therefore of interest to investigate the oxidation of ketazines which possessed only less active hydrogens on the α-carbon atom in an attempt to form α,α′-diacetoxyazo compounds. Such compounds would resemble the α,α′-dichloroazo compounds prepared by Goldschmidt and Acksteiner.[3]

Scheme I



R = CH_3 or C_2H_5

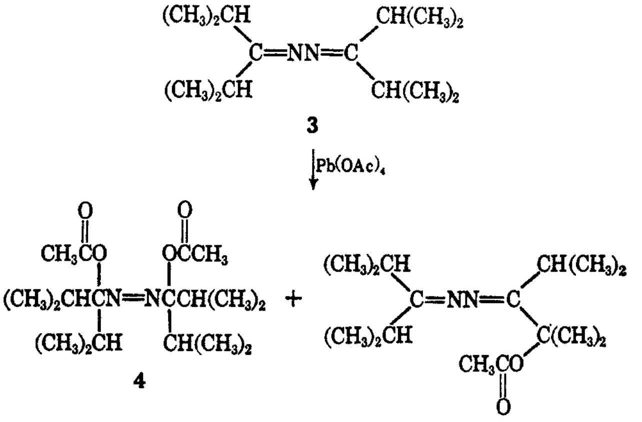
The first case to be investigated was that of dicyclopropylketazine (1). It was found that oxidation of this azine with lead tetraacetate in refluxing benzene afforded the bisacetoxyazo compound (2) in 42% yield. The structure of 2 was clearly defined by its infrared, ultraviolet, and nmr spectra and by its elemental analysis.



1 2

The oxidation of diisopropylketazine with lead tetraacetate was then studied. In this case it was found that oxidation gave rise to a mixture of products: the bisacetoxyazo compound (4) in 36% yield and the α-acetoxyazine (5) in 16% yield (Scheme II). Again the structures of 4 and 5 were established by infrared, ultraviolet, and nmr spectroscopy and microanalysis.

Scheme II



3

4

5

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[1] This investigation was supported by Public Health Service Research Grant AI-02923 from the National Institute of Allergy and Infectious Diseases.

[2] B. T. Gillis and M. P. LaMontagne, *J. Org. Chem.*, **32**, 3318 (1967).

[3] S. Goldschmidt and B. Acksteiner, *Ann.*, **618**, 173 (1958).

Benzophenone azine was found not to react with lead tetraacetate under the conditions used in the previous cases. Starting material was quantitatively recovered in all attempted oxidations even though all the lead tetraacetate had been consumed. It is believed that at 80° the lead tetraacetate would form radicals which could decompose if they did not react with the azine. No obvious reason suggests itself for the lack of reaction of benzophenone azine with lead tetraacetate other than the disruption of the conjugated system.

It is believed that the oxidation of azines **1** and **3** with lead tetraacetate proceed *via* a free-radical mechanism. First, no reaction occurs with either azine **1** or **3** at room temperature but the reaction does proceed nicely at 80°; secondly, the formation of the α-acetoxyazine **5** is consistent with a free-radical mechanism since abstraction of the tertiary hydrogen atom would give rise to a rather stable free radical. Such a type reaction would not likely occur in the case of dicyclopropylketazine. It should also be noted that no allylic acetate was isolated in the oxidation of azine **1**. It was also noted that the oxidations of these azines required somewhat more than 1 equiv of lead tetraacetate indicating that some decomposition of the oxidant probably occurs during the course of the reaction.

Experimental Section[4]

Oxidation of Dicyclopropylketazine (1) with Lead Tetraacetate.—To a solution of 20.0 g (0.092 mol) of dicyclopropylketazine[5] in 300 ml of reagent grade benzene was added 85 g (0.163 mol) of lead tetraacetate (85% active). The reaction mixture was heated to reflux for 24 hr. The lead diacetate was then filtered and the excess lead tetraacetate was destroyed by addition of water. The solution was washed several times with water and saturated sodium bicarbonate solution. The benzene solution was then dried over anhydrous sodium sulfate and the solvent was removed with the aid of an aspirator. The residual oil was allowed to sit in the refrigerator overnight. The crystals which formed were washed with cold ethanol to give 12.0 g (42%) of **2**, mp 83–84°. An analytical sample of **2** was prepared by recrystallization from a minimal amount of hot 95% ethanol. The ultraviolet spectrum of **2** had $\lambda_{\max}^{\mathrm{EtOH}}$ 360 mμ (ε 34).[6] The infrared spectrum of **2** had strong acetate peaks at 1750 and 1250 cm^{-1} but no azine band at 1610 cm^{-1}. The nmr spectrum of **2** had a sharp singlet at 2.0 ppm, a multiplet of peaks at 1.65–1.20 ppm, and a multiplet at 0.9–0.3 ppm. The relative intensities were 6:4:16, respectively.

Anal. Calcd for $C_{18}H_{26}N_2O_4$: C, 64.65; H, 7.84; N, 8.38. Found: C, 64.47; H, 7.82; N, 8.46.

Oxidation of Diisopropylketazine (3) with Lead Tetraacetate.—To a solution of 20.0 g (0.09 mol) of diisopropylketazine[7] in 300 ml of reagent grade benzene was added 84 g (0.16 mol) of lead tetraacetate (85% active). The solution was heated to reflux for 24 hr. Work-up similar to that previously described afforded a residual liquid which upon cooling in the refrigerator overnight gave 11.0 g (36%) of the bisacetoxyazo compound (**4**), mp 100–101.5°. An analytical sample of **4** was obtained by recrystallization from hot 95% ethanol. The ultraviolet spectrum of **4** had $\lambda_{\max}^{\mathrm{EtOH}}$ 355 mμ (ε 21).[6] Its infrared spectrum had strong acetate peaks at 1750 and 1240 cm^{-1} and no azine peak at 1625 cm^{-1}. The nmr spectrum had a septet at 3.1–2.4 ppm, a singlet at 2.05 ppm, and two distorted doublets at 1.3–0.8 ppm. The relative intensities were 4:6:24, respectively.

Anal. Calcd for $C_{18}H_{34}N_2O_4$: C, 63.13; H, 10.01; N, 8.18. Found: C, 63.26; H, 10.14; N, 8.36.

Distillation of the mother liquor obtained in the filtration of **4** afforded 4.1 g (16%) of a yellow liquid (**5**), bp 82–84° (0.25 mm). The infrared spectrum of α-acetoxydiisopropylketazine (**5**) had strong acetate peaks at 1750 and 1245 cm^{-1} in addition to an azine band at 1625 cm^{-1}. The nmr spectrum showed two septets at 3.5–2.4 ppm (due to the two conformations of the azine), an acetate singlet at 2.0 ppm, and a multiplet of peaks at 1.6–0.9 ppm. The relative intensities were 4:3:24, respectively.

Anal. Calcd for $C_{16}H_{30}N_2O_2$: C, 68.04; H, 10.71; N, 9.92. Found: C, 68.19; H, 10.90; N, 10.13.

Oxidation of Benzophenone Azine with Lead Tetraacetate.—To a solution of 10.0 g (0.028 mol) of benzophenone azine in 250 ml of reagent grade benzene was added 14.6 g (0.028 mol) of lead tetraacetate (85% active). The reaction mixture was heated to reflux for 24 hr. A test for lead tetraacetate was weakly positive. Work-up similar to that previously described afforded 9.8 g (98%) of a yellow solid whose infrared spectrum and melting point were identical with that of benzophenone azine.

Registry No.—Lead tetraacetate, 546-67-8; **1**, 15813-18-0; **2**, 15813-21-5; **3**, 15813-19-1; **4**, 15813-20-4; 5, 15856-54-9.

Acknowledgment.—The authors wish to acknowledge the assistance of the National Science Foundation in providing for departmental use a Cary 14 spectrophotometer, upon which the ultraviolet spectra contained herein were obtained.

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[4] Boiling points and melting points are uncorrected. Microanalyses were performed by A. Bernhardt, Mülheim, Germany, and H. Galbraith, Knoxville, Tenn. The spectra were measured on a Cary Model 14 ultraviolet-visible spectrophotometer and a Perkin-Elmer Model 137 double-beam infrared spectrophotometer. The nmr spectra were measured on a Varian Model A-60 spectrophotometer at 60 MHz with tetramethylsilane as an internal standard.

[5] H. Hart and O. E. Curtis, Jr., *J. Amer. Chem. Soc.*, **78**, 112 (1956).

[6] D. C. Iffland, L. Salisbury, and W. R. Schafer, *ibid.*, **83**, 747 (1961).

[7] A. Maihle, *Bull. Soc. Chim. Fr.*, **27**, 541 (1920).

The Hydrolysis of Some Sodium N-Substituted Sulfamates in Aqueous Perchloric Acid[1]

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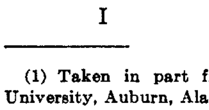
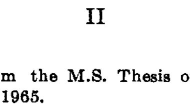
Recently, Kice *et al*,[2] reported that sodium S-alkyl and S-aryl thiosulfates (I) hydrolyze at similar rates in aqueous acid. In contrast, sodium aryl sulfates (II) hydrolyze much faster than sodium alkyl sulfates.[3] This difference has been attributed to increased delocalization of electrons on oxygen into the aryl π system in the transition state for hydrolysis of II compared to its ground state.[4] This effect is presumably absent in hydrolysis of compounds of type I. We wish to report kinetic results that we have obtained on the hydrolysis of the corresponding nitrogen system, the sodium N-substituted sulfamates (III).



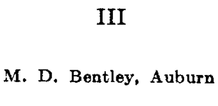
$\mathrm{Ar(R)S{-}\underset{O}{\overset{O}{S}}{-}\overset{-}{O}\overset{+}{N}a}$

I



$\mathrm{Ar(R)O{-}\underset{D}{\overset{O}{S}}{-}\overset{-}{O}\overset{+}{N}a}$

II



$\mathrm{Ar(R)\overset{H}{N}{-}\underset{O}{\overset{O}{S}}{-}\overset{-}{O}\overset{+}{N}a}$

III

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[1] Taken in part from the M.S. Thesis of M. D. Bentley, Auburn University, Auburn, Ala., 1965.

[2] J. L. Kice, J. M. Anderson, and N. E. Pawlowski, *J. Amer. Chem. Soc.*, **88**, 5245 (1966).

[3] S. Burnstein and S. Liberman, *ibid.*, **80**, 5235 (1958).

[4] J. L. Kice and J. M. Anderson, *ibid.*, **88**, 5242 (1966).