The initial complex probably results from coordination of ferric chloride at each of the carbonyl oxygens.[7] It would be reasonable to expect the complexed carbonyl groups to assume the *anti* conformation with respect to each other. Chlorine transfer in this conformation from the complexed Lewis acids to the neighboring acetylenic carbons would then yield the observed product.

Experimental Section

The diethyl acetylenedicarboxylate used in this study was purchased from Farchan Research Laboratories (Wickliffe, Ohio) and was used without further purification. The sublimed anhydrous ferric chloride powder and the cyclohexane were Matheson Coleman and Bell analytical reagent grade. Gas chromatography was performed on a Barber-Coleman Model 5000 gas chromatograph with 6 ft × 0.25 in. 10% SE30 on 60-80 Chromosorb W columns. The check for volatile products was carried out by programming column temperature from 100-270°, while the quantitative gas chromatography was done isothermally at 125° using hexamethylbenzene as a standard.

Reaction of Diethyl Acetylenedicarboxylate with Ferric Chloride. General Procedure.—To a stirred suspension of 1.6260 g (9.41 mmol) of anhydrous ferric chloride in 10 ml of cyclohexane was added dropwise over 35 min a solution of 0.790 g (4.64 mmol) of diethyl acetylenedicarboxylate in 10 ml of cyclohexane. After stirring for 17 hr, the cyclohexane solution was decanted onto 10 g of ice. The residue in the reaction flask was dissolved in ice water and added to the cyclohexane above. The organic layer was separated and saved and the aqueous layer extracted once with 30 ml of cyclohexane. The combined organic layers were dried over anhydrous magnesium sulfate, the dessicant removed by filtration, and the filtrate concentrated to a volume of *ca.* 10 ml on a rotary evaporater without the application of heat. Hexamethylbenzene (0.1280 g) was added and the composition of the solution was found by quantitative gas chromatography to be 0.086 g of IV (7.7%) and 0.56 g of III. A pure sample of IV was obtained by preparative gas chromatography using a 5 ft × $^3/_8$ in. 5% SE 30 on 60-80 Chromosorb W at 100°. The analytical sample had n^{25}_{D} 1.4672.

Anal. Calcd for $C_8H_{10}Cl_2O_4$: C, 39.84; H, 4.18; Cl, 29.42; mol wt, 241. Found: C, 39.75; 39.85; H, 4.03, 4.14; Cl, 29.25; 29.28; mol wt, 246 (osmometry).

Diethyl Dichloromaleate.—A solution of 5.2 g of dichloromaleic anhydride (0.031 mol) and 0.2 g of *p*-toluensulfonic acid in 300 ml of absolute ethanol and 150 ml of anhydrous benzene was refluxed for 12 days, using a Dean-Stark moisture trap to periodically remove 20-ml portions of the condensate. The product was worked up in the usual manner to give diethyl dichloromaleate as a clear colorless liquid, bp 70-72° (0.1 mm), which was homogeneous to vapor phase chromatography.

Registry No.—Diethyl acetylenedicarboxylate (III), 762-21-0; ferric chloride, 7705-68-0; diethyl dichlorofumarate (IV), 15649-40-8; diethyl dichloromaleate, 15649-41-9.

(7) M. Zackrisson and I. Lindqvist, *J. Inorg. Nucl. Chem.*, **17**, 69 (1961).

Reaction of Nitro Alcohols with Sulfur Tetrafluoride[1]

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Received October 16, 1967

No general method is available for the synthesis of β-halo derivatives of polynitroalkanes. The preparation of 2,2,2-trinitrochloroethane and 2,2-dinitrochloropropane from mixed acetals of the corresponding alcohols and phosphorous pentachloride has been reported.[2] Sulfuryl chloride[3] has been used to convert 2,2-dinitropropanol and 2,2-dinitropropanediol into the chloro derivatives and thionyl chloride[4] was used similarly with these alcohols and with 2,2,2-trinitroethanol. Attempts to prepare 2,2,2-trinitrobromoethane from the alcohol were unsuccessful using a variety of brominating agents.[4] The nitration of 2,3-dibromopropene has been reported to give 1,2-dibromo-1,1-dinitroethane, 1,1-dinitro-2-bromoethane, and 2-nitro-2,3-dibromopropanoic acid.[5] The β-iodo and -fluoro derivatives of polynitro compounds have not been reported.

Hydroxy groups have been replaced with fluorine by the reagent, sulfur tetrafluoride, but the reaction was not used as a preparative method for simple fluoroalkanes.[6] The reactivity of hydroxylic compounds with sulfur tetrafluoride was reported to be a function of the acidity of the hydroxyl groups. Moderate yields of fluorinated products were obtained with acidic hydroxy groups such as in tropolones, but with aliphatic alcohols ethers were major by-products. Nitro groups would, therefore, be expected to enhance the reactivity of alcohols toward sulfur tetrafluoride.

It was found that 2,2,2-trinitroethanol could be converted into 2,2,2-trinitrofluoroethane at ambient temperature in 63% yield in 4 days. 2,2-Dinitropropanol and 2,2-dinitro-1,3-propanediol were less reactive, and were converted into 2,2-dinitrofluoropropane and 2,2-dinitro-1,3-difluoropropane at 85-90°, with a 46% yield after 20 hr of reaction time for the former and a 62% yield after 8 hr for the latter. Attempts to prepare 2-methyl-2-nitrofluoropropane from 2-methyl-2-nitropropanol were unsuccessful. After a reaction period of 8 hr at 110°, only starting material and a trace of material with carbonyl absorption in its infrared spectrum were found.

$$(NO_2)_3CCH_2OH \xrightarrow{SF_4} (NO_2)_3CCH_2F$$

$$CH_3C(NO_2)_2CH_2OH \xrightarrow{SF_4} CH_3C(NO_2)_2CH_2F$$

$$HOCH_2C(NO_2)_2CH_2OH \xrightarrow{SF_4} FCH_2C(NO_2)_2CH_2F$$

The nmr spectra of the latter two products showed long-range H-F coupling of 2-2.5 cps through four bonds. The nmr and ir spectra are described in the Experimental Section.

Experimental Section

2,2,2-Trinitrofluoroethane.—Sulfur tetrafluoride (103 ml at −78°) was condensed into an evacuated 300-ml stainless steel bomb containing 100 g (0.55 mol) of trinitroethanol, and the mixture was allowed to stand at ambient temperature for 4 days. The bomb was then vented through an aqueous alkali trap. The residue was dissolved in 300 ml of methylene chloride, and the solution was washed six times with 50-ml portions of water.

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(1) Supported by the Office of Naval Research.

(2) S. S. Novikov and G. A. Shvekgheimer, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2026 (1960).

(3) L. W. Kissinger, T. M. Benziger, H. E. Ungnade, and R. K. Rohner, *J. Org. Chem.*, **28**, 2491 (1963).

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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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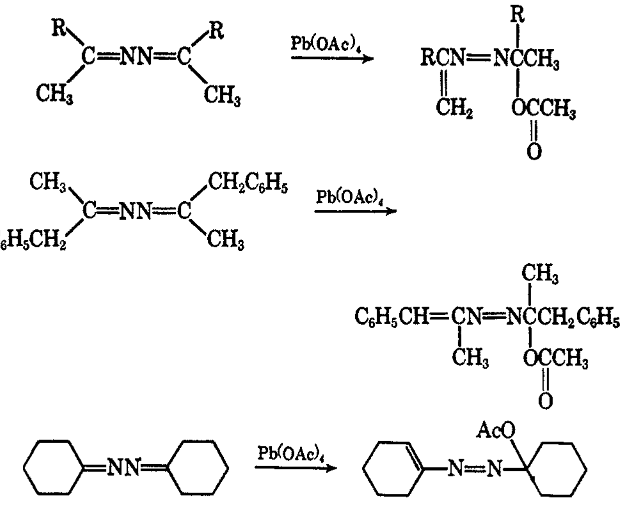
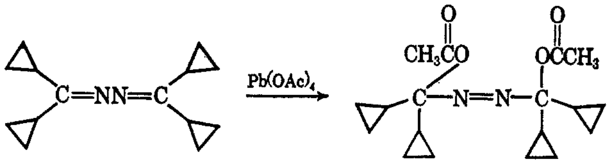
It was reported earlier[2] that the oxidation of ketazines with lead tetraacetate afforded α,β-unsaturated azoacetates in 40–70% yield (Scheme I). It was also noted that these products arose *via* abstraction of one of the active hydrogens on an α-carbon atom followed by conjugate addition of an acetate 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



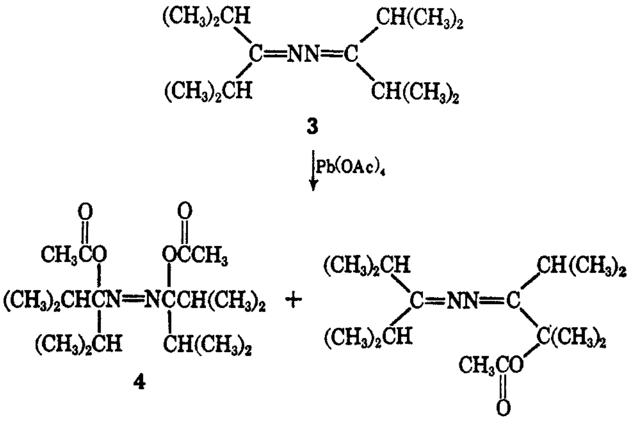
$R = CH_3$ or C_2H_5

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.



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



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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).