Table I

Distribution of the Major Products from the Hydrolysis of Tetrafluoroformamidine

Product	Yield, moles of product per mole of $F_2NCF{=}NF$
CO_2	1.0
HNF_2	0.4
N_2	0.7
NH_4F	0.1
$HONH_3^+F^-$	0.1
HF	3.0

the tetrafluoroformamidine–water reaction to 50 mole %.

Some unexpected products result from the reactions of tetrafluoroformamidine and pentafluoroguanidine with strong acids other than sulfuric acid. Bis(difluoramino)dichloromethane is produced from the relatively rapid reaction between *agua regia* and pentafluoroguanidine. The other products from this reaction include a mixture of nitrogen oxides, hydrofluoric acid, and carbon dioxide. Treatment of the final reaction mixture with an excess of aqueous alkali leaves only bis(difluoramino)dichloromethane and nitrous oxide in the gaseous phase. The nitrous oxide is readily removed by fractional distillation. Although some properties of bis(difluoramino)dichloromethane have been disclosed previously,[4] the reaction described here is the first synthetic approach to this compound to be reported.

With concentrated hydrochloric acid, tetrafluoroformamidine yields chlorodifluoramine, carbon dioxide, hydrofluoric acid, and other products. High yields of chlorodifluoramine result from the combination of pentafluoroguanidine and hydrochloric acid at room temperature. Concentrated nitric acid oxidizes the fluoronitrogen functions of pentafluoroguanidine to a mixture of nitrogen oxides; carbon dioxide and hydrofluoric acid are also produced.

Experimental Section

Materials.—Tetrafluoroformamidine and pentafluoroguanidine were prepared according to the method of Koshar, Husted, and Wright[1] and purified by gas chromatography with the column described previously.[5] The other materials used were reagent grade.

Safety Precautions.—Because tetrafluoroformamidine and pentafluoroguanidine tend to explode upon impact, freezing, or contact with alkali, the safety precautions recommended by Koshar, Husted, and Meiklejohn[6] were closely followed.

Method of Hydrolysis.—The reactions were carried out at 25° in a 10-ml erlenmeyer flask attached to a calibrated vacuum manifold (*ca.* 20 ml) through a glass gas sampling loop (Figure 1). Samples of the fluoronitrogen, usually 0.1 mmole, were measured manometrically and condensed into the previously evacuated reactor containing 1.0 ml of water, acid, or base. The mixtures were allowed to warm to room temperature and were stirred magnetically.

Methods of Analysis.—The progress of the reactions was followed by gas chromatography. A series of 0.2-ml samples of the gaseous phase was analyzed with a modified Fisher gas partitioner equipped with a single 12-ft column of 3M Brand inert fluorochemical FC-43 on an acid-washed Celite support. The relative molar responses of the various gases to detection by thermal conductivity were determined empirically: N_2 (1.00), CO_2 (1.19), $F_2NCF{=}NF$ (1.85), and $(F_2N)_2C{=}NF$ (2.22). At the completion of each reaction, the gaseous phase was also analyzed with the infrared and mass spectrometric equipment described previously.[6] Difluoramine was also determined iodometrically by the method of Lawton and Weber.[7] Hydroxylammonium and ammonium ions were separated from fluoride, sulfate, fluorosilicate, and fluoroborate ions by percolating the diluted, hydrolyzed solution over a bed of Bio-Rad AGIX4 (Cl^-, 100–200 mesh). The resulting chloride salts were identified by their infrared spectra. Hydroxylammonium ion was determined by bromate oxidation, and fluoride ion by the classical thorium nitrate titration.

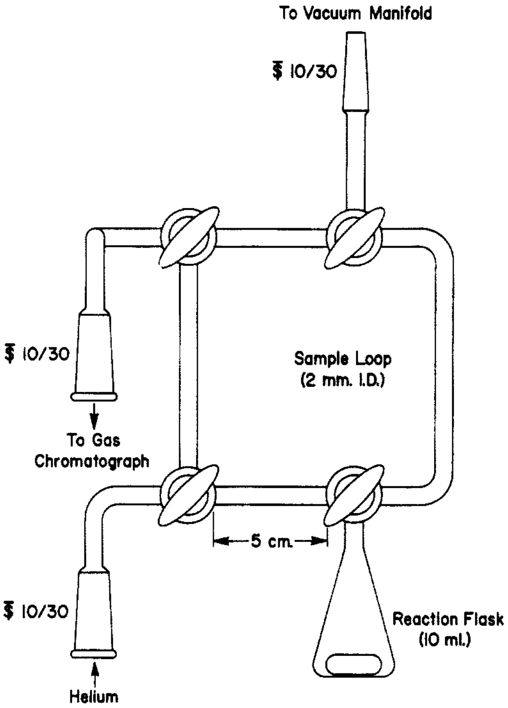

Figure 1.—Reaction vessel and sampling loop.

Acknowledgment.—The authors gratefully acknowledge the suggestions made by G. B. Rathmann, J. G. Erickson, R. J. Koshar, and C. D. Wright. They also thank J. G. Gagnon for technical assistance in carrying out many of the experiments. The work described in this paper was sponsored by the Advanced Research Projects Agency and monitored by the Bureau of Naval Weapons.

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[4] R. L. Rebertus, J. J. McBrady, and J. G. Gagnon, *J. Org. Chem.*, **32**, 1944 (1967).

[5] R. A. Mitsch, *J. Heterocyclic Chem.*, **3**, 245 (1966).

[6] R. J. Koshar, D. R. Husted, and R. A. Meiklejohn, *J. Org. Chem.*, **31**, 4232 (1966).

(7) E. A. Lawton and J. Q. Weber, *J. Am. Chem. Soc.*, **81**, 4755 (1959).

Organic Fluoronitrogens. IX.[1] Oxidation–Reduction Reactions of Tris(difluoramino)fluoromethane, Tetrafluoroformamidine, and Pentafluoroguanidine

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Recently several new organic fluoronitrogens were disclosed.[2-4] The synthetic methods reported lead to

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(1) Previous publication in this series: R. L. Rebertus and B. W. Nippoldt, *J. Org. Chem.*, **32**, 4044 (1967).

(2) R. A. Davis, J. L. Kroon, and D. A. Rausch, *ibid.*, **32**, 1662 (1967).

(3) R. J. Koshar, D. R. Husted, and C. D. Wright, *ibid.*, **32**, 3859 (1967).

(4) R. J. Koshar, D. R. Husted, and R. A. Meiklejohn, *ibid.*, **31**, 4232 (1966).

compounds containing the N,N,N′-trifluoramidino moiety[2,3] and to saturated perfluoramines containing up to three difluoramino groups bonded to the same carbon atom.[3,4] While the chemical reductions of some saturated perfluoramines have been studied,[5-7] no comparable reactions of compounds containing the tris(difluoramino)methyl or the N,N,N′-trifluoramidino group have been reported. In this communication we describe some oxidation–reduction and electrochemical reactions which illustrate the behavior of the saturated perfluoramino and the N,N,N′-trifluoramidino classes of compounds.

Tris(difluoramino)fluoromethane is reduced by iodide ion in acetonitrile and acetonitrile–water mixtures. At room temperature the reaction is complete within a period of about 1 hr. If 3% water or less is present and if the mole ratio of iodide salt to fluoronitrogen is less than 3:1, mainly difluoraminofluorodiazirine[8] and unreacted starting material are found in the gaseous phase. If the water content is increased

$$(F_2N)_3CF \text{ (excess)} + 4KI \xrightarrow[25°]{CH_3CN-H_2O} F_2NCFN_2 + 4KF + 2I_2$$

to 10% and if the relative amount of iodide is also increased, little diazirine is ultimately recovered, although it is observed as an intermediate product. Under these conditions, over-reduction to inorganic materials (nitrogen and the hydrolysis products of cyanate ion) consumes about 7 moles of iodide salt/mole of fluoronitrogen. Tris(difluoramino)fluoromethane does not react with aqueous potassium iodide at room temperature. Neither does it react with aqueous bromide, sulfite, iron(II), or titanium(III), nor with acetonitrile solutions of diphenylamine, hydroquinone, or octylmercaptan.

Tetrafluoroformamidine reacts with a variety of reducing agents to give difluorodiazirine. A relatively rapid reaction occurs with potassium iodide ion in acetonitrile, and the yield is nearly quantitative if the water content of the solvent is 3% or less. Tetra-

$$F_2NCF{=}NF + 2I^- \xrightarrow[25°]{CH_3CN} CF_2N_2 + 2F^- + I_2$$

fluoroformamidine also reacts rapidly with aqueous potassium iodide, but the reduction products are nitrogen and the degradation products of cyanate ion. Difluorodiazirine is again produced when tetrafluoroformamidine reacts with diphenylamine in acetonitrile. However, even in the absence of added water the yield is limited to about 25% because a considerable amount of nitrogen and other reduction products are formed. The diphenylamine is apparently oxidized to its blue quinoidal form. Hydroquinone in acetonitrile reacts very slowly with tetrafluoroformamidine yielding carbon dioxide, nitrogen, and compounds in which the nitrogen exhibits an oxidation number of 3⁻.

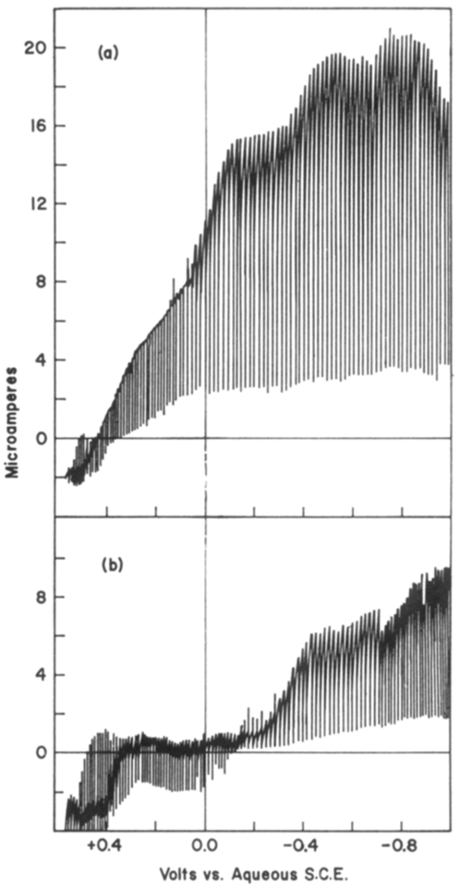

Figure 1.—Current–voltage curve of pentafluoroguanidine in acetonitrile–0.1 *M* sodium perchlorate: (a) *ca.* 2×10^{-3} *M*; (b) after mercury pool cathode electrolysis at 0.2 v for 60 min.

The fluoronitrogens in acetonitrile solution are reduced at the dropping mercury electrode. The current–voltage curve of pentafluoroguanidine is shown in Figure 1a. Controlled potential electrolysis at −0.2 v *vs.* aqueous saturated calomel electrode (sce) resulted in the production of difluoraminofluorodiazirine, and the theoretical *n* value of 2.0 was cal-

$$(F_2N)_2C{=}NF + 2e^- \rightarrow F_2NCFN_2 + 2F^-$$

culated from the coulometric data. The wave remaining after electrolysis (Figure 1b) probably corresponds to the reduction of the difluoraminofluorodiazirine. The current–voltage curve of tetrafluoroformamidine in acetonitrile is ill-defined, with the half-wave potential estimated to be about −0.2 v *vs.* aqueous sce. However, electrolysis at −0.4 v produced difluorodiazirine, and the integrated electrolysis current corresponded to a two-electron reduction.

$$F_2NCF{=}NF + 2e^- \rightarrow CF_2N_2 + 2F^-$$

The current–voltage curve for tris(difluoramino)fluoromethane in acetonitrile is shown in Figure 2. No well-defined diffusion current plateau is observed. The sharp decrease in current with increasing voltage may be the result of film formation which was observed on the mercury drop. The half-wave potential is estimated to be −0.4 ± 0.1 v *vs.* aqueous sce, which is somewhat more cathodic than the values obtained for the N,N,N′-trifluoroamidino compounds. Controlled potential electrolyses at a mercury pool proceeded extremely slowly, and reproducible *n* values were not obtained.

Thus, while tetrafluoroformamidine and pentaflu-

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[5] R. A. Mitsch, *J. Am. Chem. Soc.*, **87**, 328 (1965).

[6] R. A. Mitsch, *J. Heterocyclic Chem.*, **3**, 345 (1966).

[7] R. L. Rebertus, J. J. McBrady, and J. G. Gagnon, *J. Org. Chem.*, **32**, 1944 (1967).

[8] R. A. Mitsch, E. W. Neuvar, R. J. Koshar, and D. H. Dybvig, *J. Heterocyclic Chem.*, **2**, 371 (1965).

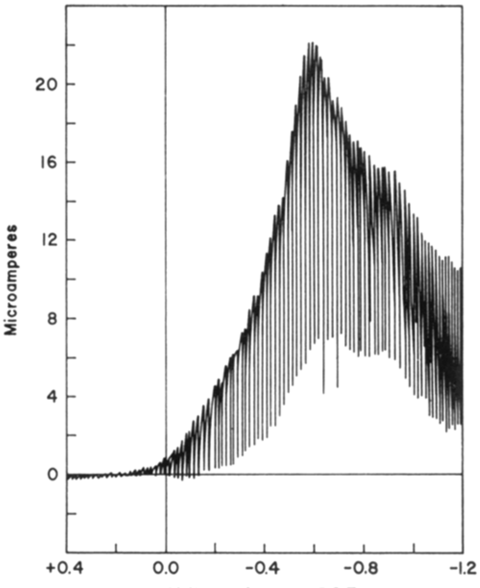
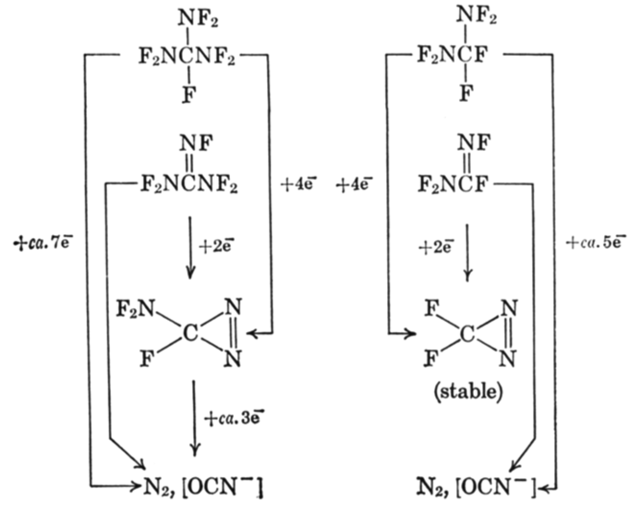


Figure 2.—Current–voltage curve of *ca.* 2×10^{-3} *M* tris(difluoramino)fluoromethane in acetonitrile–0.1 *M* sodium perchlorate.

oroguanidine are possible two-electron reduction products of bis(difluoramino)difluoromethane and tris(difluoramino)fluoromethane, respectively, no experiments to date have given any evidence that the N,N,N′-trifluoramidino compounds are isolable intermediates. Instead, tris(difluoramino)fluoromethane and bis(difluoramino)difluoromethane[7] are reduced in a minimal step of four electrons per molecule to give substituted diazirines. Furthermore, the corresponding N,N,N′-trifluoramidino compounds give the same products by two-electron reductions. The most rigorous reaction conditions did not completely reduce all of the nitrogen in the fluoronitrogens; some nitrogen gas was always found together with compounds in which nitrogen exhibits an oxidation number of 3⁻. The reduction reactions are summarized in Scheme I.

SCHEME I



The N,N,N′-trifluoramidino compounds are susceptible to oxidation by strong acids and by dry metal oxides. Thus, bis(difluoramino)dichloromethane[7] and nitrogen oxides are formed from pentafluoroguanidine and *aqua regia;*[1] chlorodifluoramine is produced from either pentafluoroguanidine or tetrafluoroformamidine and concentrated hydrochloric acid;[1] and degradation to oxides of nitrogen occurs when the N,N,N′-trifluoramidino compounds react with nitric acid.[1] When tetrafluoroformamidine contacts manganese or lead dioxide, rapid gas–solid reactions yield mixtures of *cis-* and *trans-*difluorodiazines. Some difluoraminoperfluoromethane, nitrous oxide, and silicon tetra-

$$F_2NCF{=}NF + MnO_2 \rightarrow N_2F_2 + CO_2 + MnF_2$$
$$F_2NCF{=}NF + PbO_2 \rightarrow N_2F_2 + CO_2 + PbF_2$$

fluoride are also observed as gaseous products. *cis-* and *trans-*difluorodiazines also result from the oxidation of pentafluoroguanidine with manganese dioxide.

No reactions occur between tris(difluoramino)fluoromethane and manganese or lead dioxides at 25°. Pentafluoroguanidine is inert toward solid potassium permanganate and silver vanadate; the latter can be used to remove nitrosyl chloride from the fluoronitrogen.

Experimental Section

Safety Precautions.—The organic fluoronitrogens described in this paper are explosive. Therefore, the safety precautions outlined previously[4] were closely followed.

Materials.—Tris(difluoramino)fluoromethane, tetrafluoroformamidine, and pentafluoroguanidine were prepared and purified by the method of Koshar, Husted, and Wright.[3] Spectrograde acetonitrile was used, and generally the other materials were reagent grade.

Reactions in Sealed Ampoules.—A sample of tris(difluoramino)fluoromethane (0.05 mmole) was condensed into a previously evacuated 3-ml ampoule containing 1 ml of one of the following solutions: 0.1 *M* aqueous potassium bromide, 0.1 *M* aqueous potassium iodide, 0.1 *M* sodium sulfite in 10% aqueous sodium hydroxide, 0.1 *M* aqueous iron(II) sulfate, 0.1 *M* aqueous titanium(III) chloride, 0.1 *M* octyl mercaptan in acetonitrile, 0.1 *M* hydroquinone in acetonitrile, or 0.1 *M* diphenylamine in acetonitrile. The mixture was allowed to warm to room temperature. After a standing time of 24 hr, the gas and liquid phases were analyzed by the methods described below.

Similarly, a sample of tris(difluoramino)fluoromethane, tetrafluoroformamidine, or pentafluoroguanidine (0.03 mmole) was condensed into a 3-ml ampoule containing 0.5 mmole of one of the following solids: manganese dioxide, lead dioxide, potassium permanganate, or silver vanadate. After standing for 2 hr at 25°, the gaseous phase was analyzed by the methods given below.

Reductions in Stirred Reactor.—The reactor and sampling loop described previously[1] were used. A sample of the fluoronitrogen (0.03 mmole) was condensed into the evacuated reactor containing 1.0 or 2.0 ml of one of the following solutions: 0.05 *M* potassium iodide in 99% (v/v) acetonitrile–water, 0.25 *M* potassium iodide in 97% (v/v) acetonitrile–water, 0.50 *M* potassium iodide in 90% (v/v) acetonitrile–water, 1.0 *M* aqueous potassium iodide, 0.1 *M* diphenylamine in acetonitrile, or 0.1 *M* hydroquinone in acetonitrile. The mixture was allowed to warm to 25° and stirred. The progress of the reaction was followed by a series of gas chromatographic analyses, and the final products were analyzed by the methods given below.

Electrochemical Measurements.—A conventional three-electrode operational amplifier instrument was used. The sample cell and gas-circulating system described by Toren[9] was assembled with acetonitrile–0.1 *M* sodium perchlorate and a mercury pool in the electrolysis cell, and a known amount of the sample gas (usually about 0.03 mmole) in the sample bulb. After deaeration of the electrolyte and introduction of the sample bulb into the loop, the pump was operated until gas–liquid equilibrium was established. The pump was then stopped and the current–voltage curve recorded using the dropping mercury electrode (with platinum counter electrode and aqueous saturated calomel reference). The working electrode connection was then changed to the mercury pool, and the desired

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[9] P. E. Toren, *Anal. Chem.*, **35**, 120 (1963).

quantitative electrolysis was carried out with the circulating pump operating. The electrolysis current was integrated electronically. When the electrolysis current had decreased enough to indicate essentially complete reaction, another current–voltage curve at the dropping mercury electrode was recorded to verify the completion of reaction. The sample bulb was then closed off and removed for infrared analysis of the gaseous reaction products contained therein.

The *n* value of the reaction was calculated from the integrated electrolysis current (converted to equivalents by use of Faraday's law) and the known number of moles of material reacted.

Analytical Methods.—The gases were monitored by analyzing 0.2-ml samples with the gas chromatographic equipment described previously.[1] The relative molar responses of the fluoronitrogens to detection by thermal conductivity are the following: N_2 (1.00), CF_2N_2 (1.5), $F_2NCF{=}NF$ (1.85), $(F_2N)_2C{=}NF$ (2.22), and $(F_2N)_3CF$ (2.40). The final gaseous products were also analyzed by infrared and mass spectrometry with the apparatus described previously.[7] The iodine-containing solutions were analyzed by the conventional thiosulfate titration. Fluoride ion was determined by thorium nitrate titration. Cyanate degradation products were identified by comparing the infrared spectra of the solids in question to reference spectra of the solids obtained from aged solutions of cyanate, iodide, and fluoride.

Registry No.—Tris(difluoroamino)fluoromethane, 14362-68-6; tetrafluoroformamidine, 14362-70-0; pentafluoroguanidine, 10051-06-6.

Acknowledgment.—The authors thank G. B. Rathmann, J. G. Erickson, R. A. Mitsch, and C. D. Wright for their helpful suggestions. This work was sponsored by the Advanced Research Projects Agency and monitored by the Bureau of Naval Weapons.

The Reaction of Diazomethane with a Methylenecyclopropene

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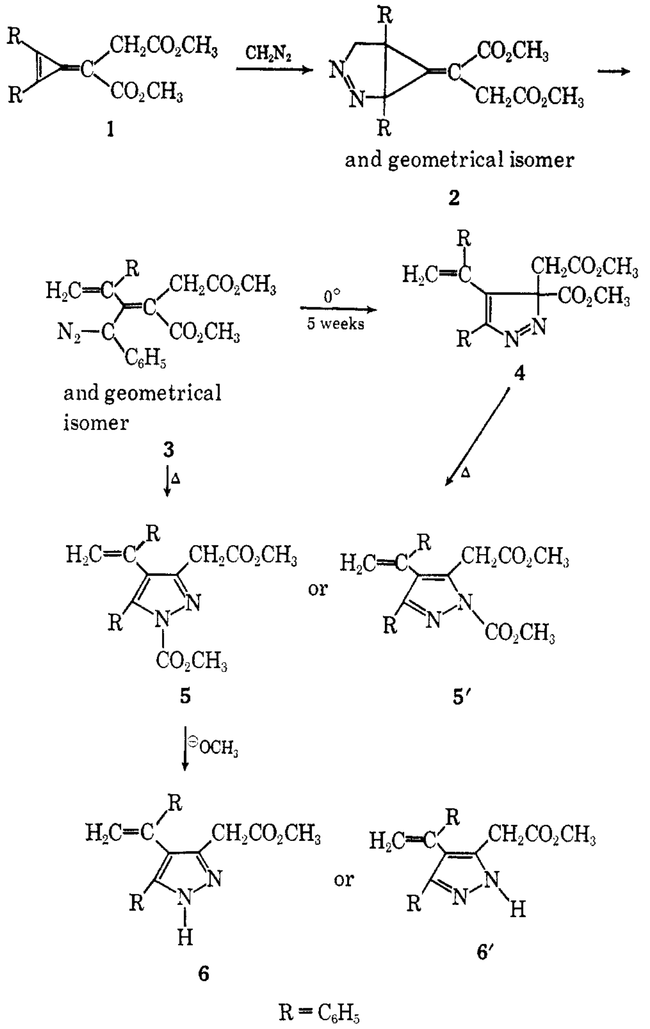
As a possible source of the highly strained spiropentene ring system,[2] the reaction of diazoalkanes with the *exo* double bond of a suitable methylenecyclopropene appeared attractive.[3] We therefore undertook an examination of the reaction of diazomethane with a methylenecyclopropene (**1**) which was available to us from previous work in these laboratories.[4] The purpose of this paper is to report our finding that this reaction does not proceed by attack of the diazomethane on the exocyclic double bond but, instead, by attack on the *endo* double bond to give the unstable ring-opened diazoalkene **3**, which isomerizes under very mild conditions to pyrazole **5** *via* what we believe to be the pyrazolenine **4**.

Since the expected products of reaction with either olefinic bond in **1** would be colorless, it was surprising to find that reaction of the yellow triafulvene with diazomethane produces a deep red, uncrystallizable oil.



Although its thermal instability precluded analyses, it is assigned structure **3** on the basis of the following spectrometric observations as well as elemental analysis of a subsequent rearrangement product (see below). Infrared absorptions suggested the presence of conjugated and unconjugated ester groups. Both infrared (absorption at 4.85 μ) and visible (absorption of 485 mμ) spectra argued for the phenyldiazomethane group.[5] Finally, a terminal methylene was suggested by infrared absorptions and confirmed by the nmr spectrum (see Experimental Section).

The probable route for the formation of **3** is *via* **2**. This suggestion finds sample precedents in the reports of Wiberg and Bartley,[6] and Izzo and Kende,[7] who found that cyclopropene and diphenylcyclopropenone were attacked by diazomethanes at the endocyclic double bond. However, whereas their intermediates opened to six-member heterocycles, **2** apparently undergoes what amounts to a diazo exchange between alkyl groups[8,9] to give the observed phenyldiazomethane.

Refluxing a carbon tetrachloride solution of the diazoalkane for 1 hr effected complete decolorization to give a single crystalline product (76%) which has been

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(1) (a) Danforth Fellow, 1960–1964. (b) This paper comprises a portion of the dissertation submitted by R. Scott Pyron in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Florida. (c) Alfred P. Sloan Fellow, 1963, 1967.

(2) W. M. Jones and M. Stowe, *Tetrahedron Letters*, 3459 (1964).

(3) T. V. Van Auken and K. L. Rinehart, Jr., *J. Am. Chem. Soc.*, **84**, 3736 (1962), and references included therein.

(4) W. M. Jones and J. M. Denham, *ibid.*, **86**, 944 (1964).

(5) G. L. Closs and R. A. Moss, *ibid.*, **86**, 4042 (1964).

(6) K. B. Wiberg and W. J. Bartley, *ibid.*, **82**, 6375 (1960).

(7) P. T. Izzo and A. S. Kende, *Chem. Ind.* (London), 839 (1964).

(8) D. G. Farnum and P. Yates, *Proc. Chem. Soc.*, 224 (1960).

(9) For a thorough discussion of diazo exchanges, see H. M. Walborsky and C. G. Pitt, *J. Am. Chem. Soc.*, **84**, 4831 (1962).