

it appears that all peptide bonds are routinely hydrolyzed. Amino acid analysis was performed with a Beckman amino acid analyzer which has an estimated accuracy of 5%.

Registry No.—DMF, 68-12-2; methylene chloride, 75-09-2.

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Synthesis of

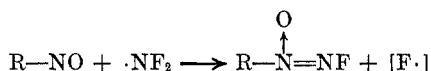
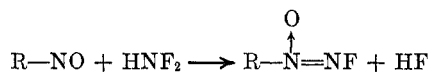
α,α -Dinitro-*N'*-fluorodiimide N-Oxides¹

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Syntheses of *N'*-fluorodiimide N-oxides have been reported by reactions of tetrafluorohydrazine²⁻⁶ or di-



fluoramine^{3,7} with nitroso compounds. Pseudonitroles gave α -nitro-*N'*-fluorodiimide N-oxides,^{3,7} but α,α -dinitro-*N'*-fluorodiimide N-oxides have not been prepared directly; α,α -dinitro nitroso compounds are unknown.

In the present work, 1,1-dinitrobutyl-*N'*-fluorodiimide N-oxide was isolated from the reaction of the sodium salt of 1,1-dinitrobutane with tetrafluorohydrazine in methanol. The product was identified by analysis, and ir and nmr spectra. Most significantly, the ¹⁹F signal, -125 ppm from trifluoroacetic acid, was in the region reported for other *N'*-fluorodiimide N-oxides. The mechanism for this reaction may involve 1,1-dinitro-1-nitrosobutane as a transient intermediate. The nitrosating agent may be nitrous acid resulting from the Neff reaction of the starting material; 1,1-dinitrobutane was also formed. An acid source is the abstraction of hydrogen from the solvent to give difluoramine which is readily dehydrofluorinated.

Preliminary work on this reaction was done with the salt of 1,1-dinitroethane, but the product was such a sensitive explosive that characterization could not be completed. The salt of nitroform did not react under

these conditions. Sodium 2-propanenitronate on the other hand yielded only the coupling product, 2,3-dimethyl-2,3-dinitrobutane, as reported by Freeman.⁸

Experimental Section

Caution. Explosion shielding and remote manipulation are required for the N₂F₄ reaction and for product isolation.

1,1-Dinitrobutyl-*N'*-fluorodiimide N-Oxide.—A Fischer-Porter aerosol tube containing a solution of 14.8 g (0.10 mol) of 1,1-dinitrobutane and 0.10 mol of sodium methoxide in 45 ml of methanol was evacuated at liquid nitrogen temperature and filled with nitrogen several times. The tube was charged with 0.2 mol of tetrafluorohydrazine and the mixture was stirred for 20 hr at ambient temperature. The excess tetrafluorohydrazine was removed and most of the solvent was removed under vacuum. Methylene chloride (50 ml) was added and the solution was filtered and distilled to give 6.5 g of liquid, bp 46° (0.35 mm), which contained some 1,1-dinitrobutane. Chromatography with a 2 × 38 cm column of neutral active alumina and methylene chloride resulted in retention of the 1,1-dinitrobutane on the column as a bright yellow complex. Distillation of the eluent gave 1.3 g (6.2% yield) of 1,1-dinitro-1-butyl-*N'*-fluorodiimide N-oxide, bp 34–35° (0.15 mm).

Anal. Calcd for C₄H₇N₄FO₃: C, 22.86; H, 3.33; N, 26.7; F, 9.05. Found: C, 23.20; H, 3.17; N, 26.63; F, 9.0.

The proton nmr spectrum consisted of a triplet (*J* = 8 Hz) at δ 1.12 for CH₃, a multiplet at δ 1.9 for CH₂CH₂, and a triplet (*J* = 8 Hz) at δ 3.12 for the other methylene. The fluorine spectrum consisted of a broadened singlet at -125 ppm from external trifluoroacetic acid. The infrared spectrum consisted of bands at 3.42 (m), 3.53 (m), 6.4 (vs), 6.9 (m), 7.01 (m), 7.3 (m), 7.54 (s), 9.05 (w), 10.8 (w), 11.7 (m), 12.4 (m), and 13.2 μ (m).

Registry No.—1,1-Dinitrobutyl-*N'*-fluorodiimide N-oxide, 24903-89-7.

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Radical Anions Produced by Electrochemical Reduction of 1,3 Diketones¹

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The half-life of radicals obtained by electrolysis of enolized 1,3 diketones is short because of rapid coupling reactions.² In DMSO as solvent, the reduction of the enolate anion of a 1,3 diketone causes decomposition via cleavage reactions.^{2b} This latter fact appears to be inconsistent with one aspect of the pioneering work of Bauld and coworkers on the electron spin resonance (esr) spectra of dianion radicals.³⁻⁶ These workers reported⁶ esr data for the dianion radical formed by the electrochemical reduction of the dibenzoylmethide ion in DMF. On the basis of our observations of the electrochemical behavior of 1,3 diketones, we suggest that

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