water, and the ether layer was dried over magnesium sulfate. Removal of the ether left 0.94 g (82%) of oil which, by preparative glpc on an Aerograph autoprep Model A-700 using a 10-ft 20% FFAP (free fatty acid phase) on Chromosorb W at 180°, was shown to consist almost entirely of III plus a small amount of neopentyl glycol. The sample of III was shown to be identical with that described above.

When 1.0 g of I was dissolved in the solution made by adding 0.14 g of sodium to 100 ml of pure methanol and the product isolated after 1 hr, there was obtained 0.97 g (85%) of a mixture similar to that described above, *i.e.*, mostly III and a small amount of neopentyl glycol.

Attempts to react the epoxy ketene ketal I with sodium and potassium *t*-butoxide in refluxing *t*-butyl alcohol, with piperidine or di-*n*-butylamine, with sodium amide (in ammonia or glyme), and with the sodium enolate of cyclohexanone failed. In all cases recovery of I was almost quantitative.

To a stirred solution of 1.0 g of I in 20 ml of dry benzene was added 0.80 g of anhydrous aluminum chloride in one portion. Two layers were formed but soon the mixture was homogeneous. After 1 hr at room temperature 15% hydrochloric acid was added. After a conventional work-up, removal of the benzene left an oily residue which on distillation yielded 0.79 g (65%) of 3-chloro-2,2-dimethylpropyl α-hydroxyisobutyrate (IV): bp 98–100° (10 mm); ir (neat) bands at 3625 and 1740 cm⁻¹; nmr bands (CDCl₃) at τ 5.98 (s, 2 H, CH₂Cl), 6.58 (s, 2 H, CH₂O), 6.66 (s, 1 H, OH), 8.58 [s, 6 H, COHC(CH₃)₂], and 8.97 [s, 6 H, (CH₃)₂CCl]. The analytical sample was obtained by preparative glpc on a 5-ft QF-1 on chromosorb W column at 120°.

Anal. Calcd for C₉H₁₇ClO₃: C, 51.8; H, 8.2. Found: C, 51.7; H, 8.3.

When a similar experiment was performed with anisole instead of benzene, the yield of IV (isolated) was 70%. In a similar experiment in anisole with boron fluoride etherate replacing the aluminum chloride, an aqueous work-up followed by extraction with ether afforded III in 70% yield. Treatment of I with anhydrous hydrogen fluoride (followed by an aqueous work-up) for 1 hr, benzoic acid in glyme for 1 day at 25°, and *p*-chlorophenol in glyme for 2 hr at reflux afforded III in 82–89% yields.

Registry No.—I, 25109-69-7; II, 25109-70-0; III, 25109-71-1; IV, 25109-72-2; 2,2-dimethyl-3-hydroxypropyl α-bromopropionate, 25109-73-3; 2,2-dimethyl-3-hydroxypropyl α-bromoacetate, 25109-56-2; 2,2-dimethyl-3-hydroxypropyl α-chloroisobutyrate, 25109-55-1.

Fluoronitroaliphatics. V. Carbonyl Additions of Fluorodinitromethane

HORST G. ADOLPH

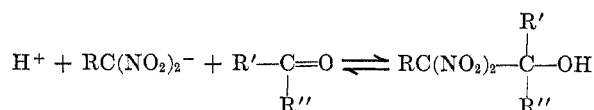*Advanced Chemistry Division, U. S. Naval Ordnance Laboratory, Silver Spring, Maryland 20910*

The addition of 1,1-dinitroalkanes and trinitromethane to carbonyl groups (Henry reaction) has been successful primarily with formaldehyde as the acceptor.[1] Far fewer additions to other carbonyl compounds giving isolable and stable product have been reported,[2] and some of these must, in the absence of a rigorous proof of structure, be regarded as unconfirmed in view of the ability of trinitromethane and probably other polynitroalkanes to form isolable complexes with some carbonyl compounds.[3]
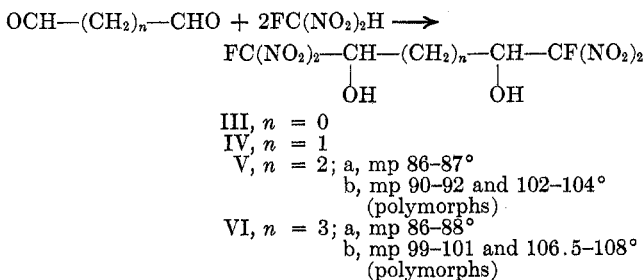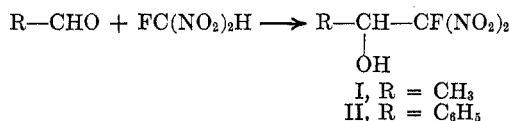
This frequent lack of stability or existence of adducts of polynitroalkanes to higher aldehydes and ketones is due to the reversibility of the Henry reaction and the fact that the equilibrium in these cases does not lie predominantly on the product side. A number of such

$$H^+ + RC(NO_2)_2^- + R'—C{=}O \rightleftharpoons RC(NO_2)_2—\underset{\underset{R''}{|}}{\overset{\overset{R'}{|}}{C}}—OH$$

equilibria have been studied by Rondestvedt and co-workers[4] and by Hall[5] who clearly demonstrated the dependence of the Henry equilibrium on the stability of the carbanion, $RC(NO_2)_2^-$ and on the degree of substitution at the carbinol carbon atom.

We wish now to report on a number of carbonyl additions of fluorodinitromethane, a new dinitroalkane whose preparation has been reported only recently.[6] Fluorodinitromethane was found to be the weakest acid[7] among all known 1,1-dinitroalkanes despite the presence of an additional strongly electron-withdrawing substituent. Its carbanion is the least stable known dinitrocarbanion.

Based on these and the above considerations, fluorodinitromethane should therefore form particularly stable carbonyl adducts. Qualitative observations demonstrating the unusual stability of 2-fluoro-2,2-dinitroethanol toward dissociation into formaldehyde and fluorodinitromethane in alkaline medium[6] are in agreement with this expectation. Regarding the addition to higher aldehydes, we find that fluorodinitromethane in buffered aqueous solution (pH 6.5–7.5) readily reacts with acetaldehyde, glyoxal, malondialdehyde, succindialdehyde, glutardialdehyed, and benzaldehyde to give isolable 1-fluoro-1,1-dinitro-2-alkanols I–VI in 50–80% yield.[8] Only one diastereomer of III

$$R—CHO + FC(NO_2)_2H \longrightarrow R—\underset{\underset{OH}{|}}{CH}—CF(NO_2)_2$$

I, R = CH₃
II, R = C₆H₅

$$OCH—(CH_2)_n—CHO + 2FC(NO_2)_2H \longrightarrow$$

$$FC(NO_2)_2—\underset{\underset{OH}{|}}{CH}—(CH_2)_n—\underset{\underset{OH}{|}}{CH}—CF(NO_2)_2$$

III, n = 0
IV, n = 1
V, n = 2; a, mp 86–87°
 b, mp 90–92 and 102–104° (polymorphs)
VI, n = 3; a, mp 86–88°
 b, mp 99–101 and 106.5–108° (polymorphs)

(1) P. Noble, Jr., F. G. Borgardt, and W. L. Reed, *Chem. Rev.*, **64**, 19 (1964); G. A. Shevkhgeimer, N. F. Pyatakov, and S. S. Novikov, *Usp. Khim.*, **28**, 48 (1958).

(2) P. Duden and G. Ponndorf, *Ber.*, **38**, 2031 (1905); N. Maraus and R. Zelinski, *J. Amer. Chem. Soc.*, **72**, 5329 (1950); H. Plaut, U. S. Patent 2,544,103 (1951); R. Schenk, Swedish Patent 135,832 (1952).

(3) For example, a 2:1 complex of trinitromethane and 2,2,4,4-tetramethyl-1,3-cyclobutanedione has been isolated as colorless crystals devoid of OH absorption in the infrared (private communication, L. A. Kaplan, this laboratory), and we have obtained strong indication of complex formation between fluorodinitromethane and acetone.

(4) C. S. Rondestvedt, Jr., M. Stiles, and A. L. Krieger, *Tetrahedron*, **19**, 197 (1963).

(5) T. N. Hall, *ibid.*, *Suppl.*, **No. 1**, 115 (1963); *J. Org. Chem.*, **29**, 3587 (1964); **30**, 3157 (1965).

(6) H. G. Adolph and M. J. Kamlet, *ibid.*, **34**, 45 (1969).

(7) V. I. Slovetskii, L. V. Okhobystina, A. A. Feinzil'berg, A. I. Ivanov, L. J. Birynkova, and S. S. Novikov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 2063 (1965); H. G. Adolph and M. J. Kamlet, *J. Amer. Chem. Soc.*, **88**, 4761 (1966).

(8) After completion of this manuscript our attention was directed to the work of Eremenko, *et al.*, who prepared III by the same method in ca. 5% yield, and I by the aqueous fluorination of potassium 1,1-dinitropropanol-2: L. T. Eremenko and G. V. Oreshko, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 380, 1765 (1969).

<div align="center">

TABLE I

PMR SPECTRA OF $FC(NO_2)_2CH(OH)R^a$

</div>

Compound	Solvent	>CH-	-OH	-R
I	CDCl₃	5.13 m, on irradiating OH, pair of q $J_{HF} = 17$ cps $J_{HH(CH_3)} = 6.5$ cps	2.83 d, $J_{HH(OH)} = 6$ cps	CH₃, 1.47 two d $J_{HF} = 1.2$ cps
	CD₃CN + ~10% D₂O	5.13 two q $J_{HF} = 20.5$ cps $J_{HH(CH_3)} = 6.5$ cps	3.30 s	CH₃, 1.38 two d $J_{HF} = 1.0$ cps
II	CDCl₃	6.10 d $J_{HF} = 19$ cps	2.04 s	C₆H₅, 7.37 s
III (single diastereomer)	CD₃NO₂	5.72 m (14 lines or more)	5.13 d (unresolved substructure) $J_{HH} = 8$ cps	...
IV (mixture of diastereomers)	CD₃NO₂	5.4 broad m	4.41 and 4.46	CH₂, 2.00 and 2.05
Va^b Vb	CD₃NO₂	5.16 broad m	4.15 s	CH₂, ~1.95 m
VIa^b VIb	CD₃NO₂	5.07 two t; on irradiating CH₂ region, d $J_{HF} = 19$ cps	3.95 s	CH₂, ~1.7 m

ᵃ Obtained on a Varian HA-100 spectrometer; chemical shifts in ppm relative to TMS (δ = 0.00) as internal standard. ᵇ Although the chemical shifts were essentially the same for the diastereomers a and b, the structure of the multiplets, particularly in the CH₂ region, was distinctly different.

was produced, but mixtures of diastereomers were obtained of the adducts IV–VI.

The stability of these alcohols is demonstrated by the fact that the diols V and VI are separable into their diastereomers by fractional recrystallization from chloroform. Thus, at least in this solvent no dissociation to fluorodinitromethane and aldehyde occurs. Thermally, I–VI dissociate with varying ease on heating to temperatures above 100°. The benzaldehyde adduct II is the least stable. It was, in fact, not obtained completely pure since it contains detectable (by nmr and ir) equilibrium concentrations of both fluorodinitromethane and benzaldehyde even at room temperature. All fluorodinitroalkanols I–VI are completely dissociated in 0.01 N aqueous hydroxide solutions and exhibit the characteristic uv absorption of fluorodinitromethane anion (λ_{max} 382 nm, ϵ 19,400).

The ir spectra of the alcohols I–VI show the expected nitro absorption at 1300 ± 20 and 1600 ± 20 cm⁻¹ and generally two or more OH bands between 3300 and 3550 cm⁻¹. III in the crystal (spectrum obtained in a fluorolube mull) exhibits only one fairly sharp OH band at 3450 cm⁻¹ which may indicate the presence of a highly symmetrical structure such as the *trans*-decalin type conformation of *meso*-III.
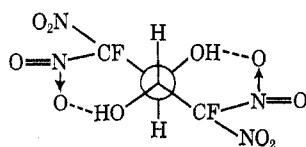
Also notable are the large differences in OH absorption, again in the crystal, between the diastereomers of V and VI: Va, three bands, 3200 (strong, broad), 3360 (medium, sharp), 3505 (medium, sharp) cm⁻¹; Vb (mp 102–104°), two bands, 3460 (medium, sharp),

3505 (medium, sharp) cm⁻¹; VIa, two bands, 3400 (strong, sharp), 3480 (medium, sharp) cm⁻¹; VIb (mp 106.5–108°); two bands, ca. 3350 (strong, broad), 3470 (medium, sharp) cm⁻¹. These and particularly the following additional differences in the ir spectra of the diastereomers are useful for monitoring the extent of their separation by fractional crystallization: Va has a band of medium intensity of 908 cm⁻¹ which is absent in Vb (Nujol mull); VIa has a moderately strong band at 1090 cm⁻¹, absent in VIb (Nujol mull).

The pmr spectra of the alcohols I–VI are recorded in Table I. Some of the compounds exhibit H–OH coupling, even in CDCl₃ (I), while others show no coupling even in CD₃NO₂ where such coupling has been shown to be induced in methanol.[9] Compound I exhibits long-range fluorine coupling to the methyl protons with a coupling constant of about 1 cps.

Experimental Section

General (Caution).—Fluorodinitromethane was prepared from 2-fluoro-2,2-dinitroethanol;[6] it is a skin irritant as well as an explosive and should be handled with *care*. Most of its derivatives also exhibit moderate to considerable sensitivity to initiation by impact, shock, friction, and other means.

Microanalyses and molecular weight determinations were by Professor Mary H. Aldridge, American University, Washington, D. C., and by Mr. D. J. Glover of this laboratory. The ir spectra were obtained on a Beckman IR 4 spectrometer with NaCl prisms. Melting points and boiling points are uncorrected.

1-Fluoro-1,1-dinitropropanol-2 (I).—A 38% aqueous solution of acetaldehyde, 5.2 g, was added to a well-stirred and cooled mixture of 3.7 g of fluorodinitromethane and 5 ml of water. A few drops of saturated sodium bicarbonate solution was added and the mixture stirred with continued cooling for 1 hr. It was then acidified with dilute sulfuric acid, the product extracted into methylene chloride, and the extract dried and distilled. Obtained was 4 g (79%), bp 40–42° (0.5 mm).

(9) N. F. Hepfinger and P. A. Clarke, *J. Org. Chem.*, **34**, 2572 (1969).

Anal. Calcd for $C_3H_5FN_2O_5$ (168.09): C, 21.43; H, 3.00; F, 11.30; N, 16.67. Found: C, 21.1; H, 3.1; F, 11.4; N, 16.4.

2-Fluoro-2,2-dinitro-1-phenylethanol (II).—To 50 ml of a NaOH–KH₂PO₄ buffer of pH 7[10] was added 2.1 g of freshly distilled benzaldehyde; the mixture was stirred and cooled in an ice bath, 5 g of fluorodinitromethane was added, and stirring and cooling were continued for 1 hr. Methylene chloride, 25 ml, was then added to the mixture, the phases were separated, and the organic phase was dried (MgSO₄) and freed from solvent *in vacuo* at ambient temperature. The residual pale yellow oil was shown by nmr (Table I) to be mainly II. However, small amounts (<10%) of benzaldehyde and fluorodinitromethane were also detected in the nmr spectrum and a carbonyl band (benzaldehyde) was present in the ir spectrum.

1,4-Difluoro-1,1,4,4-tetranitrobutane-2,3-diol (III).—Fifty milliliters of a NaOH–KH₂PO₄ buffer solution of pH 7[10] was cooled in an ice bath, and 17.7 g of a 30% aqueous solution of glyoxal was added with stirring, followed by 25 g of fluorodinitromethane. The mixture was stirred for 0.5 hr at 0–5°, then acidified with dilute sulfuric acid, saturated with NaCl, and extracted with four 25-ml portions of ether. The combined extracts were dried (MgSO₄) and the solvent was removed *in vacuo*. The residue was triturated with a small amount of methylene chloride; the mixture was chilled in the freezer and filtered to give 21.5 g of crude III, mp 175–180°. One recrystallization from methylene chloride or benzene gave 20.6 g (67%), mp 178–180° dec; ε in 0.01 *N* aqueous KOH (382 nm) 38,200.

Anal. Calcd for $C_4H_4F_2N_4O_{10}$ (306.10): C, 15.69; H, 1.31; F, 12.42; N, 18.31. Found: C, 15.8; H, 1.6; F, 12.1; N, 18.1

1,5-Difluoro-1,1,5,5-tetranitropentane-2,4-diol (IV).—A solution of 5.5 g of sodium malonaldehyde[11] in dilute sodium hydroxide (60 ml of water + 1.5 ml of 2 *N* sodium hydroxide) was cooled to about 0° in an ice–salt bath. With stirring and continued cooling, 15.5 g of fluorodinitromethane was added, most of which dissolved rapidly. A saturated solution of potassium dihydrogen phosphate was then added dropwise until the mixture had a pH of about 7. After 0.5 hr of stirring at 0° the solution was acidified with dilute sulfuric acid and extracted with four 50-ml portions of methylene chloride. The extract was dried (MgSO₄) and the solvent removed *in vacuo*. The remaining oil was held under a vacuum of 1 mm for several hours until it had solidified completely. The product was broken up under and digested thoroughly with 25 ml of chloroform and filtered, and the solid was washed with 5 ml of chloroform; 10.8 g of diol, mp 74–77°, was thus obtained. On chilling the filtrate another 0.6 g, mp 70–83°, was obtained; total crude yield, 57%. This material may be purified by vacuum sublimation (0.2 mm, 70°), followed by recrystallization from chloroform, mp 80–84° (mixture of diastereomers), ε in 0.01 *N* aqueous KOH (382 nm) 38,800.

Anal. Calcd for $C_5H_6F_2N_4O_{10}$: C, 18.76; H, 1.89; F, 11.87; N, 17.50; mol wt, 320.13. Found: C, 19.0; H, 2.0; F, 11.8; N, 17.6; mol wt (benzene), 312, 313.

1,6-Difluoro-1,1,6,6-tetranitrohexane-2,5-diol (V).—A mixture of 12 g of 2,5-dimethoxytetrahydrofuran, 80 ml of water, and 2 ml of 2 *N* sulfuric acid was stirred at 55° for 1 hr. The solution was then cooled below 5°, 20 g of fluorodinitromethane was added with stirring, and the mixture was brought to a pH of 7 with saturated sodium bicarbonate solution. Stirring and cooling in an ice bath was continued for 0.5 hr, after which time the reaction mixture was acidified with dilute sulfuric acid and extracted with four 30-ml portions of methylene chloride. The extract was dried, the solvent removed *in vacuo* (1 mm), and the semisolid residue triturated with 30 ml of chloroform. After standing in the refrigerator, 20.2 g of crude diol, mp 70–85°, was collected. After two recrystallizations from chloroform the material (15–17 g, 55–63%) melted at 80–100° (mixture of diastereomers), ε in 0.01 *N* aqueous KOH (328 nm) 38,000.

Anal. Calcd for $C_6H_8F_2N_4O_{10}$: C, 21.57; H, 2.41; F, 11.37; N, 16.77; mol wt, 345.15. Found: C, 21.8; H, 2.6; F, 10.7; N, 16.7; mol wt (chloroform), 335, 336.

Repeated fractional recrystallization of the mixture of diastereomers from chloroform gave two sharp melting fractions

which were readily distinguishable by their ir spectra (see above): Va, mp 86–87°; and Vb, mp 90–92°, 102–104° (isomorphs).

1,7-Difluoro-1,1,7,7-tetranitroheptane-2,6-diol (VI).—A solution of 40 g of 25% aqueous glutaraldehyde in 100 ml of water was cooled to 0° and 25 g of fluorodinitromethane was added. The mixture was stirred and cooled in an ice bath, and the pH was adjusted to 7 by dropwise addition of a saturated aqueous sodium bicarbonate solution. After stirring at about 0° for 0.5 hr, the solution was acidified with dilute sulfuric acid and extracted four times with a total of 200 ml of methylene chloride. Drying the extract and removing the solvent *in vacuo* gave 28.5 g of crude diol; after one recrystallization from chloroform the yield was 26 g (74%), mp 78–101°, ε in 0.01 *N* aqueous KOH (382 nm) 37,600.

Anal. Calcd for $C_7H_{10}F_2N_4O_{10}$: C, 24.15; H, 2.90; F, 10.91; N, 16.09; mol wt, 348.18. Found: C, 24.3; H, 2.9; F, 10.7; N, 15.8; mol wt (chloroform), 355, 357.

The pure diastereomers VIa and VIb were obtained by fractional recrystallization of the above mixture from chloroform. The higher melting isomer VIb, mp 99–101°, 106.5–108° (isomorphs), is the more abundant and less soluble and is isolated readily. Either of the isomorphic forms of VIb may be obtained by appropriately seeding saturated solutions of the material in chloforom. The second diastereomer, VIa, had mp 86–88°.

Registry No.—I, 22692-03-1; II, 25244-34-2; III, 25244-35-3; IV, 25244-36-3; V, 25244-37-5; VI, 25244-38-6; fluorodinitromethane, 7182-87-8.

Acknowledgment.—The author wishes to thank Dr. M. J. Kamlet for stimulating discussions and Dr. L. A. Kaplan for obtaining the nmr spectra.


Sensitized Photolysis of *cis,cis*-3,5-Cycloheptadienone. On the Intermediacy of *cis,trans*-3,5-Cycloheptadienone[1]

DAVID I. SCHUSTER[2] AND DAVID J. BLYTHIN

Department of Chemistry, New York University, New York, New York 10453

It was shown earlier that direct photolysis of *cis,cis*-3,5-cycloheptadienone (I) leads to decarbonylation and ring opening to a mixture of hexatrienes.[3,4] It is clear that this reaction originates from the excited singlet state (S₁) of I from the observations[4] that (a) triplet quenchers are without effect on this reaction, and (b) triplet sensitization gives a different reaction, isomerization of I to the valence tautomer II. By analogy

I   II   III
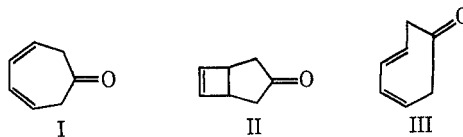
with the course of triplet-sensitized valence isomerization of *cis,cis*-1,3-cyclooctadiene,[5] it was postulated[4]

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(1) Part XXV of a series on the photochemistry of unsaturated ketones in solution. Part XXIV: D. I. Schuster and D. H. Sussman, *Tetrahedron Lett.*, No. 19, 1661 (1970).

(2) Alfred P. Sloan Fellow, 1967–1969.

(3) O. L. Chapman and G. W. Borden, *J. Org. Chem.*, **26**, 4185 (1961); O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *J. Amer. Chem. Soc.*, **84**, 1220 (1962).

(4) D. I. Schuster, B. R. Sckolnick, and F.-T. H. Lee, *ibid.*, **90**, 1300 (1968).

(5) R. S. H. Liu, *ibid.*, **89**, 112 (1967).

(10) Clark and Lubs: 29.63 ml of 0.1 *N* NaOH and 50 ml of 0.1 *M* KH₂PO₄ diluted to 100 ml.

(11) T. V. Protopopova and A. P. Skoldinov, *Zh. Obshch. Khim.*, **28**, 240 (1958); *Chem. Abstr.*, **52**, 12754 (1958).