method of Dimroth, *et al.*,[7] and had mp 143–144° after crystallization from ethanol (lit.[7] mp 143°).

Bromination of 4-Benzyl-2,4,6-triphenyl-4*H*-pyran (2b). A. With 1 Molar Equiv of *N*-Bromosuccinimide.—(i) 4-Benzyl-2,4,-6-triphenyl-4*H*-pyran (**2b**, 0.5 g) and *N*-bromosuccinimide (0.25 g, ~10% excess) in carbon tetrachloride (20 ml) were refluxed for 2 hr and the reaction mixture was filtered. On evaporation of the filtrate an oil (0.535 g) was obtained. The oil was warmed with *n*-hexane, and the undissolved solid was filtered and identified as succinimide by mixture melting point with an authentic sample. On cooling the filtrate 4-benzyl-3-bromo-2,4,6-triphenyl-4*H*-pyran (**2c**), mp 120–122°, separated; after repeated crystallization from *n*-hexane it had mp 136–137°.

Anal. Calcd for $C_{30}H_{23}BrO$: C, 75.16; H, 4.80; Br, 16.70. Found C, 74.89; H, 4.90; Br, 16.60.

(ii) The above experiment was repeated but the mixture was refluxed for only 15 min. The 3-bromopyran **2c**, mp 136–137°, was again obtained. (iii) The 4*H*-pyran (**2b**, 0.214 g), *N*-bromosuccinimide (0.090 g), and benzoyl peroxide (3 mg) were stirred in carbon tetrachloride (10 ml) for 25 min, keeping the solution warm. The same product **2c** was obtained.

B. With 2 Molar Equiv of *N*-Bromosuccinimide.—The 4*H*-pyran (**2b**, 0.209 g), *N*-bromosuccinimide (0.186 g), and benzoyl peroxide (3 mg) in carbon tetrachloride (10 ml) were stirred for 45 min, keeping the solution warm. The nmr of the product (0.345 g) showed it to be a mixture, containing 4-benzyl-3-bromo-2,4,6-triphenyl-4*H*-pyran (**2c**) and a product which gave a singlet at τ 6.4.

C. With 3 Molar Equiv of *N*-Bromosuccinimide.—The 4*H*-pyran (**2b**, 1.32 g), *N*-bromosuccinimide (1.78 g), and benzoyl peroxide (18 mg) in dry carbon tetrachloride (50 ml) were warmed to initiate the reaction. The reaction mixture was kept warm and stirred for 1 hr. It was cooled and filtered and the filtrate was evaporated. The residual oil was dissolved in hot *n*-hexane. On cooling, crystals (0.2 g) separated which had mp 128–130°; mmp with **2c**, 134–135°. The mother liquors were evaporated. The nmr of the residue (1.15 g) showed the peaks for **2c** along with a singlet at τ 6.4.

The above residue was treated with *N*-bromosuccinimide (0.52 g) in carbon tetrachloride and the solution was refluxed for 2.5 hr. It was cooled and filtered. On evaporation of the filtrate an oil (1.32 g) was obtained. The nmr of the oil showed it to be a mixture containing **2c** and the compound, presumably **2d**, giving a singlet at τ 6.4, the latter being the major constituent.

Registry No.—**1a**, 1177-70-4; **1b**, 32247-00-0; **1c**, 32247-01-1; **2a**, 1177-68-0; **2b**, 1255-14-7; **2c**, 32247-04-4.

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Synthesis of Fluorodinitromethyl Epoxides

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General methods for the preparation of fluorodinitromethyl compounds have recently been described.[1] The synthesis of two fluorodinitromethyl epoxides, 1-fluoro-1,1-dinitro-3,4-epoxybutane (VI) and 2-fluoro-2,2-dinitroethyl glycidyl ether (IX), is described in this paper.

(1) M. J. Kamlet and H. G. Adolph, *J. Org. Chem.*, **33**, 3073 (1968).

1-Fluoro-1,1-dinitro-3,4-epoxybutane (VI) was prepared by the sequence of reactions shown below. The

$$CH_2{=}CHCH_2CH_2OH \xrightarrow{PBr_3} CH_2{=}CHCH_2CH_2Br \xrightarrow{AgNO_2}$$
I II

$$CH_2{=}CHCH_2CH_2NO_2 \xrightarrow[AgNO_3]{NaNO_2} CH_2{=}CHCH_2C(NO_2)_2H \xrightarrow{FClO_3}$$
III IV

$$CH_2{=}CHCH_2C(NO_2)_2F \xrightarrow[Na_2HPO_4]{CF_3CO_3H} CH_2{-}CHCH_2C(NO_2)_2F$$
V VI

initial reaction involved the conversion of 3-buten-1-ol (I) to 1-bromo-3-butene (II). 1-Nitro-3-butene (III) was prepared from II and silver nitrite. At least one fume-off was encountered during the distillation of III, illustrating the inherent instability of this type of compound. One of the by-products of this reaction has been tentatively identified from its infrared spectrum as 1-nitrito-3-butene. The conversion of III to 1,1-dinitro-3-butene (IV) involved the Shechter–Kaplan oxidative nitration reaction.[2] A fume-off was also encountered with the distillation of this compound. Initially it was thought that aqueous fluorination of IV to V would be the method of choice because of a shorter reaction time and easier work-up. However, aqueous fluorinations of both the sodium and potassium salts of IV resulted also in fluorination of the double bond. The desired reaction was accomplished by fluorinating with perchloryl fluoride, following the procedure of Kamlet and Adolph.[1] The conversion of V to 1-fluoro-1,1-dinitro-3,4-epoxybutane (VI) proved to be a clean high-yield reaction. It involves epoxidation with peroxytrifluoroacetic acid in the presence of the buffer disodium hydrogen phosphate.[3]

The approach to the synthesis of 2-fluoro-2,2-dinitroethyl glycidyl ether (IX)[4] utilized the dinitroethylation reaction.[5] This reaction consists of the 1,4 addition of active hydrogen compounds, such as aci-nitro compounds or alcohols, to 1,1-dinitroethylene. The 1,1-dinitroethylene is a reactive intermediate, which

$$[CH_2{=}C(NO_2)_2] + RH \longrightarrow RCH_2C(NO_2)_2H$$

has never been isolated but is generated *in situ* from 2-bromo-2,2-dinitroethyl acetate,[5-7] 1,2-dichloro-1,1-dinitroethane,[8] or 1,1,1-trinitroethane.[9]

2,2-Dinitroethyl allyl ether (VII) was prepared by the addition of allyl alcohol to 1,1-dinitroethylene, which was generated from 1,2-dichloro-1,1-dinitroethane and potassium iodide.[8] Fluorination of the sodium salt of VII with perchloryl fluoride gave 2-fluoro-2,2-dinitroethyl allyl ether (VIII), which was

(2) R. B. Kaplan and H. Shechter, *J. Amer. Chem. Soc.*, **83**, 3535 (1961).
(3) W. D. Emmons and A. S. Pagans, *ibid.*, **77**, 89 (1955).
(4) The preparation of this compound by the alkylation of 2-fluoro-2,2-dinitroethanol has recently been reported: V. Grakauskas, *J. Org. Chem.*, **35**, 3030 (1970).
(5) M. B. Frankel, *ibid.*, **23**, 813 (1958).
(6) H. Feuer, G. Leston, R. Miller, and A. T. Nielsen, *ibid.*, **28**, 339 (1963).
(7) L. J. Winters and W. E. McEwen, *Tetrahedron*, **19** (1), 49 (1963).
(8) H. E. Ungnade and L. W. Kissinger, *J. Org. Chem.*, **31**, 369 (1966).
(9) L. Zelden and H. Shechter, *J. Amer. Chem. Soc.*, **79**, 4708 (1957).

epoxidized to 2-fluoro-2,2-dinitroethyl glycidyl ether (IX).

$$ClCH_2C(NO_2)_2Cl + 2KI \longrightarrow [CH_2{=}C(NO_2)_2] + 2KCl + I_2$$

$$[CH_2{=}C(NO_2)_2] + HOCH_2CH{=}CH_2 \longrightarrow CH_2{=}CHCH_2OCH_2C(NO_2)_2H$$

VII

$$VII \xrightarrow[NaOH]{FClO_3} CH_2{=}CHCH_2OCH_2C(NO_2)_2F \xrightarrow[Na_2HPO_4]{CF_3CO_3H}$$

VIII

$$CH_2\text{—}CHCH_2OCH_2C(NO_2)F$$

$$\diagdown\diagup O$$

IX

A by-product was isolated in the distillation of VIII as a volatile forerun. It was identified as 2-fluoro-2,2-dinitroethyl methyl ether (X) by its infrared spectrum and elemental analysis. Compound X was probably formed by cleavage of the ether linkage of VIII with subsequent formation of the methyl ether by reactions with the methanol solvent.

$$CH_2{=}CHCH_2OCH_2C(NO_2)_2F + FClO_3 \xrightarrow[CH_3OH]{H_2O}$$

VIII

$$CH_3OCH_2C(NO_2)_2F$$

X

As was mentioned previously, the reactive intermediate, 1,1-dinitroethylene, can also be generated from 1,1,1-trinitroethane.[9] It was found that 1,1,1-trinitroethane could be prepared in 71% yield from potassium nitroform and methyl iodide. This obviates the necessity of using the hazardous and expensive silver salt of nitroform.[10] Treatment of 1,1,1-trinitroethane with a solution of potassium hydroxide in allyl alcohol gave the potassium salt of allyl 2,2-dinitroethyl allyl ether, which was then subsequently acidified, fluorinated, and epoxidized to the desired monomer IX in the manner described previously.

Experimental Section

General (Caution).—Most of the products described in this paper are explosives of moderate to considerable sensitivity to initiation by impact, shock, fraction or heat. They should therefore be *handled with care*. All distillations should be well shielded. Furthermore, many dinitrofluoromethyl compounds show varying degrees of toxicity. Precautions for fluorinating with perchloryl fluoride are previously described.[1]

Elemental analyses have been reviewed and are in accord with theory. Melting and boiling points are uncorrected.

1-Bromo-3-butene (II).—Phosphorus tribromide, 360 g (1.33 mol), was cooled to −5° and a solution of 257 g (3.56 mol) of 3-buten-1-ol in 120 g (1.52 mol) of pyridine was added dropwise in 1.5 hr with good mechanical stirring. The addition was exothermic and a white solid precipitated. The mixture was stirred for another hour at −5° and allowed to warm to ambient temperature. The reaction flask was connected to a receiver which was immersed in a Dry Ice–acetone bath and the product was stripped off under a vacuum of 2 mm. The product was dissolved in methylene chloride, washed with 5% $NaHCO_3$ and water, dried, and fractionated through a spinning band column. The yield of 1-bromo-3-butene was 261.9 g (54.5%), bp 97.5°, $n^{28}D$ 1.4589.

1-Nitro-3-butene (III).—To a well-stirred mixture of 377 g (2.44 mol) of silver nitrite in 500 ml of dry methylene chloride was added dropwise 288.3 g (2.13 mol) of 1-bromo-3-butene while maintaining the temperature at approximately 15° (this reaction was carried out in the dark to its completion). After the addition was complete (30 min), the reaction mixture was allowed to warm to room temperature and stirring was continued until the supernatant liquid showed a negative test for bromide. This required approximately 4 days. The gray solid was removed by filtration and washed well with methylene chloride. The solvent was removed under vacuum and the orange liquid residue was fractionated through a small Vigreux column to yield 25 g of low-boiling material, $n^{25}D$ 1.4275, presumably the 1-nitroso-3-butene, and 126.3 g (62% yield) of 1-nitro-3-butene, bp 55° (19 mm), $n^{25}D$ 1.4308.

1,1-Dinitro-3-butene (IV).—To 25.2 g (0.63 mol) of sodium hydroxide dissolved in 225 ml of water was added 62.1 g (0.615 mol) of 1-nitro-3-butene dropwise while maintaining the temperature at 3°. After the addition was complete, 42.5 g (0.615 mol) of sodium nitrite was added and the reaction mixture was stirred for approximately 30 min while warming to room temperature.

This freshly prepared solution was then added quickly with good stirring to a solution of 209 g (1.23 mol) of silver nitrate, 450 ml of water, and 450 ml of ether at 3°. (Just prior to this addition a few drops of sodium hydroxide were added to the silver nitrate solution until the appearance of silver oxide was noted.) A heavy cream-colored solid was formed immediately and the temperature rose to 15°. The solid decomposed rapidly with blackening. The cooling bath was then removed and the mixture was stirred for 1 hr. The silver was filtered and washed well with ether. The ether layer was separated and the aqueous layer was extracted several times with ether. The combined ether portions were dried over magnesium sulfate and the excess solvent was removed at reduced pressure. The resulting orange liquid residue was fractionated through a small Vigreux column yielding 38 g (43% yield) of 1,1-dinitro-3-butene, bp 63.5–65° (1.5 mm), $n^{25}D$ 1.4504.

1-Fluoro-1,1-dinitro-3-butene (V).—Into a 250-ml round-bottom flask equipped with a Dry Ice condenser, thermometer, and gas inlet was placed 2 g of sodium hydroxide in 15 ml of water, 7.3 g (0.05 mol) of 1,1-dinitro-3-butene, and 35 ml of methanol. This mixture was stirred at room temperature for 1 hour. After purging the system with nitrogen, perchloryl fluoride was admitted slowly above the liquid until refluxing began; this required approximately 40 min. The rate of perchloryl fluoride admission was then set so that the reaction temperature remained approximately at 20° (cooling was regulated by the reflux rate). After a reaction time of approximately 2 hr, 50 ml of water was added; the hazy solution became clear. The solution was extracted with three 50-ml portions of methylene chloride and the combined methylene chloride extracts were then washed with three 50-ml portions of water. After drying the methylene chloride solution over magnesium sulfate, solvent was removed under reduced pressure and the residual yellow liquid was fractionated through a small Vigreux column to yield 4.1 g (50% yield) of 1-fluoro-1,1-dinitro-3-butene, bp 47° (9 mm), $n^{25}D$ 1.4210.

1-Fluoro-1,1-dinitro-3,4-epoxybutane (VI).—A solution of peroxytrifluoroacetic acid was prepared from 1.72 ml (0.0615 mol) of 90% hydrogen peroxide, 10.4 ml (0.074 mol) of trifluoroacetic anhydride, and 15 ml of methylene chloride. This reagent was added over a 20-min period to a well-stirred, boiling mixture of 8.1 g (0.049 mol) of 1-fluoro-1,1-dinitro-3-butene, 50 ml of methylene chloride, and 28 g (0.197 mol) of disodium phosphate (predried under vacuum oven overnight at 50°). After this mild exothermic reaction had subsided, the solution was heated under reflux for 2.5 hr. The resulting mixture was stirred with 100 ml of water until all of the inorganic salts had dissolved. The organic layer was separated and the aqueous layer was extracted with two 20-ml portions of methylene chloride. The combined methylene chloride extracts were washed with 25 ml of 10% sodium bicarbonate solution and dried over magnesium sulfate. The solvent was removed at reduced pressure and the residual liquid was fractionated through a small Vigreux column to yield 1.77 g of unreacted 1-fluoro-1,1-dinitro-3-butene and 5.79 g (83% yield) of 1-fluoro-1,1-dinitro-3,4-epoxybutane, bp 55° (0.45 mm), $n^{25}D$ 1.4365.

2,2-Dinitroethyl Allyl Ether (VII). From 1,2-Dichloro-1,1-dinitroethane.—To a mixture of 219 g (1.32 mol) of potassium iodide, 85.5 g (1.48 mol) of allyl alcohol, and 200 ml of methylene chloride was added dropwise 50 g (0.264 mol) of 1,2-dichloro-1,1-dinitroethane[8] over a period of 15 min. The reaction mixture, which became deep red in color, was stirred overnight at room temperature. Water (200 ml) was then added to dissolve the inorganic salts and the layers were separated. The water layer was extracted with methylene chloride and the combined methylene chloride portions were washed thoroughly with 10% sodium thio-

(10) G. S. Hammond, *et al.*, *Tetrahedron Suppl.*, **1**, 177 (1963).

sulfate solution followed by a water wash. The methylene chloride solution was dried over magnesium sulfate. Excess solvent was removed under reduced pressure yielding a mixture of white solid and red oil. The white solid (48.4 g) was removed by recrystallization from carbon tetrachloride and identified as 1,2-diiodo-3-hydroxypropane (mp 47°). The red oil (54 g) was contained in the carbon tetrachloride and subsequently isolated by removal of the solvent under vacuum. It was identified by its infrared spectrum as crude allyl 2,2-dinitroethyl ether. An initial attempt to purify the product by distillation resulted in an explosion.

The crude allyl 2,2-dinitroethyl ether was purified by conversion to the potassium salt and subsequent acidification. To a solution of 46.6 g (0.264 mol) of crude allyl 2,2-dinitroethyl ether dissolved in 60 ml of ether was added 14.8 g (0.264 mol) of potassium hydroxide in 50 ml of methanol. A heavy yellow solid formed immediately; the temperature rose slightly but was easily controlled at 20° with an ice bath. The reaction mixture was cooled to 0° and filtered, yielding 40 g of potassium 2,2-dinitroethyl allyl ether, mp 130–133.5°. A recrystallization from methanol yielded potassium 2,2-dinitroethyl allyl ether as yellow needles in 67% yield, mp 140–141°. The potassium 2,2-dinitroethyl allyl ether was dissolved in water and acidified to pH 1 with dilute hydrochloric acid. The resulting insoluble yellow oil was extracted with methylene chloride and the methylene chloride extracts were washed with water. After drying over magnesium sulfate, the methylene chloride was removed under reduced pressure yielding 2,2-dinitroethyl allyl ether in 96% yield as a pale yellow oil, $n^{27.5}$D 1.4527, d^{25} 1.3). The overall yield from 1,2-dichloro-1,1-dinitroethane was 36%.

From 1,1,1-Trinitroethane.—To a solution of 98.3 g (85%, 1.49 mol) of potassium hydroxide in 183 ml of water and 426 ml of ethanol was added dropwise 720 g (1.43 mol) of 30 wt % aqueous nitroform while maintaining the temperature at 15–20°. After the addition was complete (1 hr), the resulting solid potassium nitroform was filtered and washed well with cold water and then cold ethanol. The moist salt was then refluxed for 10 hr with 217.2 g (1.53 mol) of methyl iodide in 1300 ml of acetone. The resulting yellow solid was removed by filtration and washed with acetone. The filtrate and washes were combined and solvent was removed under reduced pressure. The red residue was taken up in 350 ml of methylene chloride and washed with aqueous sodium thiosulfate until the red color was removed. The methylene chloride portion was dried over magnesium sulfate and then concentrated until solid began to come out of solution. Hexane was added and the solid was allowed to crystallize, yielding 166 g (71%) of 1,1,1-trinitroethane, mp 52.5–54°.

To a solution of 32.7 g (85%, 0.5 mol) of potassium hydroxide in 400 ml of allyl alcohol was added dropwise 41.3 g (0.25 mol) of 1,1,1-trinitroethane in 100 ml of allyl alcohol over a 1-hr period while maintaining the temperature at 15–20°. Orange solid appeared immediately. The reaction mixture was stirred for an additional hour at room temperature after the addition was completed. The solid was filtered and washed with cold methanol, yielding 67.5 g of potassium 2,2-dinitroethyl allyl ether. A recrystallization from methanol yielded 35.8 g (67% yield) of potassium 2,2-dinitroethyl allyl ether as fine yellow needles, mp 137–138°. The preparation of allyl 2,2-dinitroethyl ether from the potassium salt was exactly the same as described previously in the 1,2-dichloro-1,1-dinitroethane experiment.

2-Fluoro-2,2-dinitroethyl Allyl Ether (VIII).—The sodium salt was formed *in situ* from 4.11 g (0.023 mol) of 2,2-dinitroethyl allyl ether and 0.94 g (0.023 mol) of sodium hydroxide. The solvent consisted of 15 ml of water and 35 ml of methanol. Perchloryl fluoride was added above the surface of the orange reaction mixture at such a rate that the temperature was maintained at approximately 20°. Total reaction time was approximately 4 hr. Water (50 ml) was then added and the reaction mixture was extracted with three 60-ml portions of methylene chloride. The combined methylene chloride extracts were then washed with three 30-ml portions of 3% sodium hydroxide and finally with water. After drying over magnesium sulfate, the solvent was removed under reduced pressure. The remaining liquid residue was distilled through a small Vigreux column to yield 0.62 g (16%) of 1,1-dinitro-1-fluoro-2-methoxyethane, bp 60–61.5° (12 mm), n^{28}D 1.4030, and 2.4 g (53%) of 2,2-dinitro-2-fluoroethyl allyl ether, bp 41° (1 mm), n^{25}D 1.4245.

2-Fluoro-2,2-dinitroethyl Glycidyl Ether (IX).—A solution of peroxytrifluoroacetic acid was prepared at 0° from 1 ml (0.036 mol) of 90% hydrogen peroxide, 6 ml (0.043 mol) of trifluoroacetic anhydride, and 10 ml of methylene chloride. This reagent was added over a 35-min period to a well-stirred boiling mixture of 4.06 g (0.021 mol) of 2,2-dinitro-2-fluoroethyl allyl ether, 25 ml of methylene chloride, and 15.7 g (0.111 mol) of disodium hydrogen phosphate (predried in vacuum oven overnight at 50°). After the mild exothermic reaction had subsided, the solution was heated under reflux for 2 additional hr. The resulting mixture was stirred with 75 ml of water until all of the inorganic salts had dissolved. The organic layer was separated and the aqueous layer was extracted with three 40-ml portions of methylene chloride. The combined methylene chloride portion was washed with 50 ml of 10% sodium bicarbonate solution and dried over magnesium sulfate. The solvent was removed at reduced pressure and the residual liquid was fractionated through a small Vigreux column to yield 0.27 g of unreacted 2-fluoro-2,2-dinitroethyl allyl ether and 3.92 g (95% yield) of 2-fluoro-2,2-dinitroethyl glycidyl ether, bp 70° (0.4 mm), n^{25}D 1.4362, d^{25} 1.45.

Registry No.—II, 5162-44-7; III, 32349-29-4; IV, 10229-09-1; V, 19273-49-5; VI, 32349-32-9; VII, 32349-33-0; VIII, 25171-99-7; IX, 25184-14-9.

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