Infracord Model 257; the nmr spectra were recorded on an Hatachi HA 100 and optical rotations were determined on a Rudolph Model 80 polarimeter.

N,2-Dicarbobenzyloxy-D-cycloserine (4). A. From D-Cycloserine.—To a solution of 10.2 g (100 mmol) of D-cycloserine in 250 ml of 1 *N* $NaHCO_3$ (250 mmol) in a three-necked flask equipped with a mechanical stirrer and a delivery funnel and cooled in an ice bath, 42 g (240 mmol) of benzyl chloroformate was added dropwise over a period of 25 min. The ice bath was removed and the reaction mixture was stirred for 2 hr at room temperature. The mixture was filtered and the white solid was washed with 25 ml of ether and dried *in vacuo* overnight to yield 15.0 g of *N*,2-dicarbobenzyloxy-D-cycloserine. To the filtrate 5.0 g (15 mmol) of benzyl chloroformate was added and shaken vigorously by hand for 20 min. Filtration gave a solid which was washed with 25 ml of ether to give another 8.9 g of product. The total yield was 23.9 g (64.5%); mp 125–128°. Recrystallization from ethyl acetate afforded 20.5 g of *N*,2-dicarbobenzyloxyl-D-cycloserine: mp 127–128°; ir (KBr) 3350 (NH), 1800 (C=O), 1700 (C=O), 1760 cm^{-1} (C=O); nmr (DMSO-d_6) δ 4.3 (m, 3 H, $-CH_2CH-$), 5.01 (s, 2 H, $-CH_2C_6H_5$), 5.22 (s, 2 H, $-CH_2C_6H_5$), 7.28 (s, 5 H, 501 (s, 2 H, $-CH_2C_6H_5$), 5.33 (s, 2 H, $-CH_2C_6H_5$), 7.28 (s, 5 H, $-C_6H_5$), 7.33 ppm (s, 5 H, $-C_6H_5$); $[\alpha]^{25}D$ 36.9° (*c* 2, H_2O).

Anal. Calcd for $C_{19}H_{18}N_2O_6$: C, 61.60; H, 4.90; N, 7.56. Found: C, 61.35; H, 4.94; N, 7.54.

B. From 2-Carbobenzyloxy-D-cycloserine Hydrobromide.—To a mixture of 413 ml (2.43 mmol) of benzyl chloroformate and 50 ml of distilled water in a 250-ml round-bottomed flask equipped with a ground glass stopper, 632 mg (2 mmol) of 2-carbobenzyloxy-D-cycloserine hydrobromide was added. After shaking the flask vigorously for 5 min, 2 ml of 1 *N* $NaHCO_3$ (2 mmol) was added and shaking was continued. After 10 min, the reaction mixture was treated with 1 ml of 1 *N* $NaHCO_3$ (1 mmol) and after 10 min 336 mg of a white solid was collected on a filter. The filtrate was treated with ten drops of benzyl chloroformate and 1 ml of 1 *N* $NaHCO_3$ (1 mmol), shaken vigorously for 10 min, and extracted with 100 ml of hot ethyl acetate. The ethyl acetate solution was dried over anhydrous Na_2SO_4 and evaporated *in vacuo* to give a brown oil, which when triturated with anhydrous ether gave 117 mg of a white solid. The two amide products were combined to give 453 mg (61%) of **4**: mp 124–127°; $[\alpha]^{25}D$ +32.8° (*c* 2, H_2O); ir identical with that of an authentic sample.

2-Carbobenzyloxy-D-cycloserine Hydrobromide (5).—A solution of 4.4 g (12 mmol) of *N*,2-dicarbobenzyloxy-D-cycloserine (4) and 50 ml of glacial acetic acid in a 250-ml round-bottomed flask equipped with a magnetic stirrer and a drying tube was treated with 50 ml of 1 *N* HBr in acetic acid. The reaction solution was stirred for 5 hr at room temperature and was slowly poured into 500 ml of anhydrous ether and stirred magnetically for 10 min to yield 3.56 g (94%) of 2-carbobenzyloxy-D-cycloserine hydrobromide after filtration and drying *in vacuo:* mp 128–131° dec; ir (KBr) 2800 ($-NH_3^+Br$), 1770 (C=O), 1760 cm^{-1} (C=O); nmr (DMSO-d_6) δ 4.3 (m, 3 H, $-CH_2CH-$) 5.30 (s, 2 H, $-CH_2C_6H_5$), 7.28 ppm (s, 5 H, $-C_6H_5$). An analytical sample was prepared by recrystallization from methanol and ether, mp 131–133°.

Anal. Calcd for $C_{11}H_{13}N_2O_4Br$ (316): C, 41.65; H, 4.10; N, 8.33. Found: C, 40.71; H, 4.16; N, 8.74.

N-Carbobenzyloxy-D-alanyl-2-carbobenzyloxy-D-cycloserine (6).—A solution of 3.35 g (15 mmol) of *N*-carbobenzyloxy-D-alanine[13] and 1.65 ml (15 mmol) of *N*-methylmorpholine in 75 ml of tetrahydrofuran (dried over CaH_2) in a 200 ml round-bottomed flask equipped with a thermometer and magnetic stirrer, and cooled in a Dry Ice–acetone bath, was treated with 15 mmol of isobutyl chloroformate. After stirring for 30 sec, a cold solution of 4.74 g (15 mmol) of 2-carbobenzyloxy-D-cycloserine hydrobromide and 1.65 ml (15 mmol) of *N*-methylmorpholine in 35 ml of tetrahydrofuran was added. The Dry Ice–acetone bath was removed, the reaction mixture was stirred for 15 min and filtered, and the filtrate was evaporated *in vacuo* at 36° to give a brown oil. It was dissolved in 100 ml of ethyl acetate and the solution was washed with 100 ml of H_2O, 100 ml of 1 *N* HCl, 100 ml of H_2O, and 100 ml of 1 *N* $NaHCO_3$, and dried over anhydrous Na_2SO_4. The solution was evaporated *in vacuo* at 40° to yield 5.93 g of crude **6**: mp 137–146°; $[\alpha]^{30}D$ +19.3° (*c* 2, THF). Recrystallization from absolute ethanol afforded 4.33 g (65%) of **6**: mp 149–151°; ir (KBr) 3310, 3280 (NH), 1770 (C=O), 1695. (C=O), 1665 cm^{-1} (C=O);

Anal. Calcd for $C_{22}N_{23}N_3O_7$ (441.4): C, 59.86; H, 5.25; N, 9.52. Found: C, 59.63; H, 5.17; N, 9.59.

DD-*cis*-3-Aminoxymethyl-6-methyl-2,5-piperazinedione (2).—A mixture of 2.23 g (5 mmol) of *N*-carbobenzyloxy-D-alanyl-2-carbobenzyloxy-D-cycloserine (6) and 1.10 g (10 mmol) of anisole in a 50-ml Nalgene erlenmeyer flask equipped with a magnetic stirrer and cooled in an ice bath was treated with 10 ml of anhydrous hydrogen fluoride. The reaction mixture was stirred for 30 min at 0° and was evaporated in a stream of dry nitrogen gas. The remaining gum was washed with several 10-ml portions of anhydrous ether and dried *in vacuo* for 4 days to yield 893 mg (92%) of the hygroscopic D-alanyl-D-cycloserine hydrofluoride. A mixture of this solid and 10 ml of absolute ethanol was treated with ammonia gas for 10 min, evaporated in a stream of dry nitrogen, and dried overnight *in vacuo*. The remaining solid was dissolved in 5 ml of hot H_2O, 20 ml of ethanol, and 5 ml of 2-propanol. After cooling, the solution was filtered and evaporated *in vacuo* at 53° leaving 534 mg of crude **2**, mp >200°. Recrystallization from methanol and water gave 450 mg of **2**: mp >360; ir (KBr) 3310 (NH), 1670 (C=O), 1340 cm^{-1} (CO); $[\alpha]^{25}D$ +23.9° (*c* 2, H_2O); identical with previous sample.[3]

cis-3-[*N*-(4-Nitrobenzylidene)aminoxymethyl]-6-methyl-2,5-piperazinedione.—A suspension of 17.3 mg (0.1 mmol) of **2** and 15.2 mg (0.1 mmol) of *p*-nitrobenzaldehyde in 0.2 ml of H_2O and 5 ml of methanol was stirred magnetically in a 10-ml round-bottomed flask for 1 hr at room temperature. After the solution was evaporated *in vacuo* the residue was dissolved in 3 ml of hot DMF and the mixture was centrifuged. The supernatant liquid was treated with 10 ml of H_2O. The precipitated solid was recrystallized from DMF–H_2O and washed with ethanol to give 25 mg of *cis*-3-[*N*-(4-nitrobenzylidene)aminoxymethyl]-6-methyl-2,5-piperazinedione: mp 244–246°; ir (Nujol) 3198 (NH), 1675 cm^{-1} (C=O); identical with previously prepared sample.[3]

D-Cycloserine Hydrofluoride. A. From *N*,2-Dicarbobenzyloxy-D-cycloserine (4).—A mixture of 370 mg (1 mmol) of *N*,2-dicarbobenzyloxy-D-cycloserine and 216 mg (2 mmol) of anisole in a 15-ml Nalgene centrifuge tube was treated with 5 ml of anhydrous hydrogen fluoride. The mixture was stirred with a nagalene stirring rod for 25 min in an ice bath 0° and evaporated in a stream of dry nitrogen. The remaining pink oil was washed with three 5-ml portions of anhydrous ether and the white, gummy residue was dried *in vacuo* for 2 days resulting in 132 mg of D-cycloserine hydrofluoride (95%): ir (KBr) 3400 ($-N^+H_3F^-$) and 1750 cm^{-1} (C=O). This product was identical with a sample prepared from D-cycloserine by treatment with anhydrous hydrogen fluoride.

Registry No.—**1**, 32296-73-4; **2**, 16562-03-1; **4**, 32296-75-6; **5** (HBr), 32296-76-7; **6**, 32296-77-8; *cis*-3-[*N*-(4-nitrobenzylidene)aminoxymethyl]-6-methyl-2,5-piperazinedione, 32296-78-9; D-cycloserine hydrofluoride, 32367-42-3.

(13) Prepared in 71% yield, mp 86–87°, $[\alpha]^{25}D$ +15.6°, by the procedure of M. Bergmann and L. Zervas, *Ber.*, **65**, 1192 (1932).

Nuclear Bromination of Thiopyrans and Pyrans by *N*-Bromosuccinimide

ULLI EISNER* AND THAIYA KRISHNAMURTHY

Department of Chemistry, Howard University, Washington, D. C. 20001

Received February 23, 1971

N-Bromosuccinimide is a reagent which selectively brominates allylic and benzylic positions.[1] However, a number of exceptions have been reported[2–6] where

(1) L. Horner and E. H. Winkelmann in "Newer Methods of Preparative Organic Chemistry," Vol. 3, W. Foerst, Ed., Academic Press, New York, N. Y., 1964, p 151.

(2) N. B. Chapman and J. F. A. Williams, *J. Chem. Soc.*, 5044 (1952).

(3) H. Pines, A. Alul, and M. Kolobielski, *J. Org. Chem.*, **22**, 1113 (1957).

(4) K. Dittmer, R. P. Martin, W. Herz, and S. J. Cristol, *J. Amer. Chem. Soc.*, **71**, 1201 (1949).

(5) W. J. Bailey and J. Bello, *J. Org. Chem.*, **20**, 525 (1955).

(6) M. F. Grundon and K. J. James, *Chem. Commun.*, 1427 (1970).

N-bromosuccinimide was shown to brominate nuclear rather than benzylic positions. Chapman and Williams[2] showed that bromination of 2-methylnaphthalene gave 1-bromo-2-methylnaphthalene unless the *N*-bromosuccinimide was carefully purified; in the latter case, bromination took place in the side chain.

We were interested in the synthesis of benzylic bromides in the thiopyran and pyran series. The starting material, 2-benzyl-2,4,6-triphenyl-2*H*-thiopyran (**1a**), was prepared[7] by the action of benzylmagnesium chloride on triphenylthiopyrylium perchlorate and separation of the resulting mixture of isomers by Soxhlet extraction with ethanol. Under the same conditions triphenylthiopyrylium iodide[8] gave exclusively the 4*H*-thiopyran **2a**. The nmr spectra given are in Table I. Assignment of the signals for the protons at

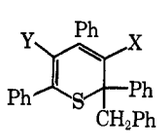
TABLE I

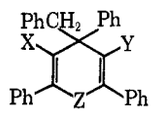
NMR SPECTRA OF SUBSTITUTED PYRANS AND THIOPYRANS[a]

Compd	H-3	H-5	Benzylic protons
1a	3.18 (s)	3.90 (s)	6.45 (s)
2a	4.04 (s)	4.04 (s)	6.67 (s)
1b		4.16 (s)	6.21, 6.48 (dd, J = 13.5 Hz)
1c			6.29, 6.41 (dd, J = 13.5 Hz)
2b	4.49 (s)	4.49 (s)	6.72 (s)
2c	4.77 (s)		6.24, 6.94 (dd, J = 13 Hz)

[a] In $CDCl_3$; chemical shifts in τ.

C-3 and C-5 in **1a** were made by means of the nuclear Overhauser effect (NOE); irradiation of the benzylic protons resulted in an enhancement of the signal at τ 3.18. Long-range coupling (J = 0.15 Hz) between the protons at C-3 and C-5 was confirmed by double resonance.





1a, X = Y = H
b, X = Br; Y = H
c, X = Y = Br
d, X = Cl; Y = H

2a, X = Y = H; Z = S
b, X = Y = H; Z = O
c, X = Br; Y = H; Z = O
d, X = Y = Br; Z = O

Treatment of **1a** with 1 molar equiv of *N*-bromosuccinimide in the presence of benzoyl peroxide gave a colorless solid, $C_{30}H_{23}BrS$, the nmr spectrum of which (see Table I) showed it to be the 3-bromo derivative **1b**. The benzylic protons in **1b**, unlike those in **1a**, are nonequivalent.

When the experiment was repeated with purified reagents according to the method of Chapman and Williams[2] the same compound **1b** was obtained.

When the thiopyran **1a** was treated with 3 equiv of *N*-bromosuccinimide a dibromo derivative, $C_{30}H_{22}Br_2S$, was obtained. The nmr spectrum (Table I) clearly showed it to have structure **1c**; the benzylic protons were again nonequivalent. The dibromo derivative **1c** was recovered unchanged on treatment with 2 molar equiv of *N*-bromosuccinimide.

4-Benzyl-2,4,6-triphenyl-4*H*-pyran **2b** (for nmr see Table I) on treatment with 1 molar equiv of *N*-bromosuccinimide under various conditions yielded a solid, $C_{30}H_{23}BrO$. The nmr spectrum (Table I) showed that again substitution of bromine had taken place in the ring with the formation of **2c**.

The action of 2, 3, or more equiv of *N*-bromosuccinimide on **2b** produced mixtures from which the monobromo derivative **2c** could be isolated. The nmr of the residue, which showed a singlet at τ 6.4 as well as the signals corresponding to **2c**, indicated the formation of the dibromo derivative **2d**.

Attempted benzylic chlorination of **1a** with *N*-chlorosuccinimide or with trichloromethanesulfonyl chloride led to complex mixtures, the nmr of which suggested the presence of the monochloro derivative **1d**.

Experimental Section

Melting points were determined on a Thomas–Hoover capillary melting point apparatus. Nmr spectra were recorded on a Varian A-60 instrument.

2,4,6-Triphenylthiopyrylium Iodide.—2,4,6-Triphenylpyrylium perchlorate[9] (15.4 g) in acetone (500 ml) was treated with sodium sulfide (20 g) in water (200 ml), stirred for 5 min, treated with 26% hydriodic acid (200 ml), and stirred for 30 min. The reaction mixture was diluted with water (500 ml) and extracted with chloroform (two 200-ml portions). The chloroform extract was concentrated and treated with ether (500 ml) to precipitate the iodide (10.8 g), which had mp 204–205° (lit.[8] mp 205–206°).

Preparation of 2-Benzyl-2,4,6-triphenyl-2*H*-thiopyran (1a) and 4-Benzyl-2,4,6-triphenyl-4*H*-thiopyran (2a). A. From 2,4,6-Triphenylthiopyrylium Perchlorate.—The method of Dimroth, *et al.*,[7] was used. The crude mixture of thiopyrans (6.3 g), mp 132–140°, was separated by Soxhlet extraction with ethanol. The residual 2-benzyl-2,4,6-triphenyl-2*H*-thiopyran (**1a**, 2.40 g) had mp 158–159°, raised to 159–160° on crystallization from ethyl acetate (lit.[5] mp 160°).

The above procedure was repeated and the extract was evaporated to dryness. The residual 4-benzyl-2,4,6-triphenyl-4*H*-thiopyran (**2a**) had mp 116–117° after one crystallization from ethanol (lit.[7] mp 117°).

B. From 2,4,6-Triphenylthiopyrylium Iodide.—The method of Dimroth, *et al.*,[7] was followed using the iodide (8.2 g) and benzylmagnesium chloride [from benzyl chloride (9 g) and magnesium (1.35 g)]. The crude solid (6.25 g), mp 93–95°, was shown by nmr to consist mainly of the 4H isomer **2a**.

2-Benzyl-3-bromo-2,4,6-triphenyl-2*H*-thiopyran (1b).—2-Benzyl-2,4,6-triphenyl-2*H*-thiopyran (0.16 g) was treated with *N*-bromosuccinimide (0.067 g, 1 molar equiv) and benzoyl peroxide (1 mg) in dry carbon tetrachloride (10 ml). The reaction mixture was warmed to initiate the reaction and stirred for 15 min, keeping the solution warm. It was cooled and filtered. The filtrate was evaporated and the residue was chromatographed on a silica gel column using 40% benzene in petroleum ether (bp 30–60°) as the eluent. This afforded 2-benzyl-3-bromo-2,4,6-triphenyl-2*H*-thiopyran (**1b**), which had mp 163–164° after crystallization from *n*-hexane.

Anal. Calcd for $C_{30}H_{23}BrS$: C, 72.73; H, 4.65. Found: C, 72.33; H, 4.88.

The experiment was repeated using *N*-bromosuccinimide which had been kept at 0.05 mm for 16 hr.[2] The nmr of the crude product was identical with that of **1b**. After crystallization from benzene–petroleum ether, **1b**, mp 160–162°, was isolated in 70% yield.

2-Benzyl-3,5-dibromo-2,4,6-triphenyl-2*H*-thiopyran (1c).—The 2*H*-thiopyran (**1a**, 1 g) was treated with *N*-bromosuccinimide (1.42 g, ~3 mol equiv) and benzoyl peroxide (14 mg) in the usual manner. The 3,5-dibromo-2,4,6-triphenyl-2*H*-thiopyran (**1c**) which separated was crystallized from cyclohexane–petroleum ether and had mp 199–200°.

Anal. Calcd for $C_{30}H_{22}Br_2S$: C, 62.72; H, 3.83; Br, 27.87. Found: C, 62.63; H, 4.08; Br, 27.62.

The dibromo derivative **1c** was treated with 2 molar equiv of *N*-bromosuccinimide and refluxed in carbon tetrachloride for several hours, when it was recovered unchanged.

4-Benzyl-2,4,6-triphenyl-4*H*-pyran (2b) was prepared by the

(7) K. Dimroth, K. Wolf, and H. Kroke, *Justus Liebigs Ann. Chem.*, **678**, 183 (1964).

(8) K. Kanai, M. Umehara, H. Kitano, and K. Fukui, *Nippon Kagaku Zasshi*, **84**, 432 (1963); *Chem. Abstr.*, **59**, 13934*f* (1963).

(9) R. Wizinger, S. Losinger, and P. Ulrich, *Helv. Chim. Acta*, **39**, 5 (1956).

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.

Acknowledgment.—We are indebted to Professor L. M. Jackman, Penn State University, for helpful discussions and to Mr. E. Sokoloski, NHLI, National Institutes of Health, for measuring the NOE.

Synthesis of Fluorodinitromethyl Epoxides

EDWARD F. WITUCKI, GERALD L. ROWLEY, MICHAEL WARNER, AND MILTON B. FRANKEL*

Advanced Programs, Rocketdyne, a Division of North American Rockwell Corporation, Canoga Park, California 91304

Received April 16, 1971

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).