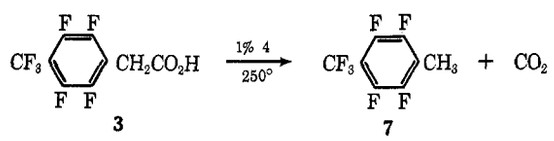
film on the inside of the condenser. It was swollen slightly with acetone but did not dissolve. An X-ray diffraction pattern shows well-defined lines indicating a high degree of crystallinity which is common with poly-*p*-xylylenes.[1] Whether the polymer units were joined head to tail or head to head and tail to tail was not determined. The polymer begins absorbing strongly in the ultraviolet at 300 nm.

Sodio ethyl cyanoacetate reacts readily with **1** to give ethyl (4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)cyanoacetate (**2**).[2] Only one isomer was isolated, presumably the para isomer. Toward nucleophilic substitution on an aromatic system, trifluoromethyl is strongly, perhaps exclusively, para directing.[3] The trifluoromethyl group also increases the rate of aromatic nucleophilic substitution relative to fluorine, 10^3 times,[4] which accounts for the ease with which **2** is prepared. Acidic hydrolysis of **2** to **3** was used instead of basic hydrolysis because of the sensitivity of the highly fluorinated nucleus to nucleophilic attack.

Pyrolysis of alkali salts of fluorinated aliphatic acids leads to olefins. For instance, pyrolysis of sodium heptafluorobutyrate gives hexafluoropropene in high yield.[5] In the present instance the reaction has been extended from a 1,2 elimination to a 1,6 elimination.

The free acid, **3**, was thermally stable to its boiling point at 250°. Addition of a small amount of **4** to the



boiling **3** caused loss of CO_2 to give **7**. Heating **4** in dimethylacetamide at 120° resulted in the formation of **7** also. The source of protons necessary to form **7** from **4** in the latter case was not investigated.

Experimental Section

Ethyl (4-Trifluoromethyl-2,3,5,6-tetrafluorophenyl)cyanoacetate (2).—Ethyl cyanoacetate (22.6 g, 0.20 mol) was added to 5.0 g (0.21 mol) of sodium hydride suspended in 75 ml of dimethylformamide keeping the reaction temperature at 25 ± 5°. When hydrogen evolution ceased, 23.6 g (0.10 mol) of octafluorotoluene (**1**) was added, maintaining the temperature at 25 ± 5°. The solution was stirred for 15 min after adding **1**. The reaction mixture was poured into 300 ml of ice water and extracted with 100 ml of ether. The ether phase was discarded; 30 ml of concentrated hydrochloric acid was added to the aqueous phase and extraction was performed with three 50-ml portions of ether. Evaporation of ether and distillation of residue gave 28 g (85% yield) of **2**, bp 107–113° (1.5 mm), mp 48–51°.

Anal. Calcd for $C_{12}H_5F_7NO_2$: C, 43.78; H, 1.84; F, 40.40; N, 4.26. Found: C, 44.08; H, 2.08; F, 39.86; N, 4.67.

(4-Trifluoromethyl-2,3,5,6-tetrafluorophenyl)acetic Acid (3).—Ethyl (4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)cyanoacetate (28 g, 0.085 mol) was added to 50 ml of water, 50 ml of acetic acid, and 80 ml sulfuric acid and the mixture was heated at reflux for 5 hr. The mixture was poured into 500 ml of water and cooled to 5° overnight. The solid was filtered off to give 20 g (85% yield) of product, mp 60–70°. Recrystallization from *n*-hexane gave 18 g of **3**, mp 77–80°.

Anal. Calcd for $C_9H_3F_7O_2$: C, 39.15; H, 1.09; F, 48.17. Found: C, 39.04; H, 1.22; F, 49.52.

Methyl (4-Trifluoromethyl-2,3,5,6-tetrafluorophenyl)acetate.—To a mixture of 35 ml of methanol, 20 ml of benzene, and 1 ml of concentrated H_2SO_4 was added 9.8 g (0.034 mol) of **3**. The mixture was heated to reflux and the water was collected in a Dean–Stark trap. When the reaction was finished the reaction mixture was cooled and extracted with water. The organic phase was dried over Drierite and distilled to give 6.0 g (0.021 mol, 60% yield) of methyl (4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)acetate, bp 90–100° (10 mm).

Anal. Calcd for $C_{10}H_5F_7O_2$: C, 41.39; H, 1.74; F, 45.84. Found: C, 41.37; H, 1.89; F, 45.74.

Potassium (4-Trifluoromethyl-2,3,5,6-tetrafluorophenyl)acetate (4).—(4-Trifluoromethyl-2,3,5,6-tetrafluorophenyl)acetic acid, 4.7 g (0.017 mol), was suspended in 25 ml of water, two drops of phenolphthalein indicator solution was added, and then 50% KOH solution was added to give a faint pink end point. The water was removed under reduced pressure at 25°. The dry residue was dissolved in 15 ml of acetone, filtered, and heated to boiling. Ethylene dichloride was added to the cloud point. Cooling gave 5.0 g (93%) of white needles, mp 222° dec. The salt was heated at 100° for 5 hr at 0.001 mm pressure and then analyzed.

Anal. Calcd for $C_9H_2F_7O_2K$: C, 34.40; H, 0.64; F, 42.33; K, 12.44. Found: C, 34.20; H, 0.57; F, 42.37; K, 12.48.

Poly-α,α,2,3,5,6-hexafluoro-*p*-xylylene (6).—Two grams of **4**, evacuated to a pressure of 0.01 mm, was heated in a 250° bath. The gases were led through a condenser cooled with Dry Ice. A thin film of polymer (0.1 g) formed on the inside of the condenser tube. The film was removed by wetting with acetone. It was 0.04 mm thick, clear, and pliable. An X-ray diffraction pattern on the film dried at 100° (0.001 mm) shows definite lines indicating crystallinity. Differential thermal analysis under nitrogen shows a small endothermic process starting at 421°. The sample showed no weight loss after 20 min at 400°. At 500° for 20 min it showed a 17% weight loss.

Anal. Calcd for $(C_8H_2F_6)_n$: C, 45.30; H, 0.95; F, 53.75. Found: C, 45.17; H, 0.83; F, 53.71.

α,α,α,2,3,5,6-Heptafluoro-*p*-xylene (7).—Ten grams (0.036 mol) of **3** was heated to 250° with no noticeable decomposition. It was allowed to cool and 0.10 g of **4** was added and then reheated to 250°. Seven grams of material distilled over at 135°. Redistillation gave 5.1 g (60%), bp 135–136° (705 mm), of **7**. The mass spectrum had a strong parent ion peak at *m/e* 232 and a base peak at *m/e* 163 (parent ion minus CF_3).

Anal. Calcd for $C_8H_3F_7$: C, 41.39; H, 1.31; F, 57.30. Found: C, 41.15; H, 1.39; F, 57.25.

One-half gram of **4** was heated to 120° in *N*,*N*-dimethylacetamide. Gas was evolved which gave a precipitate with barium hydroxide solution. After gas evolution ceased the mixture was poured into water and a dark liquid settled to the bottom. Vpc analysis (Dowfax 9N9 on Chromosorb W, 100°) showed only one volatile component, **7**. The mass spectrum was identical with that of **7** prepared in the previous experiment.

Registry No.—**2**, 32251-53-9; **3**, 32304-29-3; **3** methyl ester, 32251-56-2; **4**, 32251-54-0; **6**, 32218-15-8; **7**, 778-35-8.

(2) Ethyl (pentafluorophenyl)cyanoacetate has been prepared similarly from hexafluorobenzene but under much more vigorous conditions: German Patent 1,146,890 (April 11, 1963); *Chem. Abstr.*, **59**, 11331e (1963).

(3) D. J. Alsop, J. Burdon, and J. C. Tatlow, *J. Chem. Soc.*, 1801 (1962); J. Burdon, *Tetrahedron*, **21**, 3373 (1965).

(4) J. Burdon, W. B. Hollyhead, C. R. Patrick, and K. V. Wilson, *J. Chem. Soc.*, 6375 (1965).

(5) R. N. Haszeldine, *J. Chem. Soc.*, 4259 (1952).

The Configuration of D-Alanyl-D-cycloserine Confirmed

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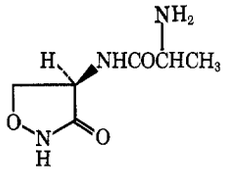
In an earlier report,[3] we described the synthesis of the dipeptide, D-alanyl-D-cycloserine (**1**), but the basis

(1) Abstracted from the M.S. thesis presented to the University of Georgia Graduate School by Mr. C. S. Levine.

(2) To whom inquiries should be directed.

(3) R. A. Payne and C. H. Stammer, *J. Org. Chem.*, **33**, 2421 (1968).

for the configurational assignment rested upon the exact position of the methyl resonance in the nmr spectrum of **1** and the melting point and optical rotation of



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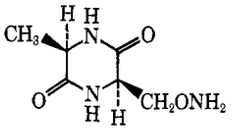

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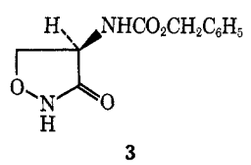
the piperazinedione, **2**, into which **1** is converted upon neutralization. The steric ambiguity of the earlier synthesis resulted from the fact that the blocked dipeptide from which **1** was obtained was one of a pair of diastereomers resulting from the coupling of *N*-carbobenzyloxy-DL-alanine with 2-trityl-DL-cycloserine. Racemic amino acids were used in this work because we had found no way to synthesize optically active cycloserine derivatives having the ring blocked. This report describes the synthesis of 2-carbobenzyloxy-D-cycloserine, which allows the unambiguous synthesis of **1**.

In our investigations of the carbobenzyloxylation of D-cycloserine, it was found that at high pH only the amine acylated product[4] (**3**) was obtained, while at a pH of ~8 both active sites reacted giving *N*,2-dicarbobenzyloxy-D-cycloserine (**4**), $[\alpha]^{25}D$ 32.8°. This compound was presumed to be optically pure since all its physical characteristics indicated it to be a single entity. This is the second[4] optically active ring-substituted cycloserine derivative to be prepared, but is the first to be useful in the synthesis of optically active peptides of cycloserine. Its usefulness derives from the fact that the amino group of **4** could be deblocked in 0.5 *N* HBr–acetic acid while the 2-carbobenzyloxy protecting group was retained *without* loss of optical activity.[5] Thus, the ring-protected derivative **5** became readily available for conversion to optically active cycloserine derivatives. Comparison of the nmr spectra of **3**, **4**, and **5** gave strong confirmation of the



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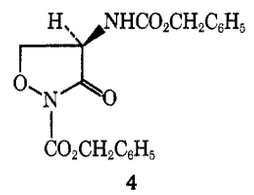

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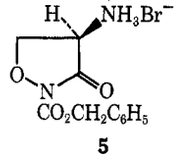
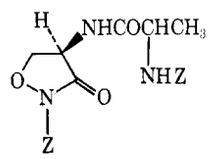


5

assigned structures. The carbobenzyloxy methylene groups of **4** appeared as singlets at δ 5.01 and 5.23 ppm while **3** and **5** showed singlets at δ 5.02 and 5.30 ppm, respectively. Consistent with these assignments was the infrared spectra and the fact that **3** is nitroprusside[6] positive and ninhydrin negative while **5** showed the opposite reactions with these reagents. The utility of **5** was confirmed when it was found that both **4** and **5** could be completely deblocked in liquid hydrogen fluoride according to the method of Sakakibara,[7] giving the parent cycloserine. The availability of **5** makes it possible to synthesize new cycloserine peptides and to check our earlier steric assignments.

The coupling of *N*-carbobenzyloxy-D-alanine with **5** was accomplished by the mixed anhydride procedure[8] and the dipeptide **6** was obtained in 65% yield. The required neutralization of the hydrobromide salt **5** with *N*-methylmorpholine prior to coupling was done at − 78° because it was found that the free amine rapidly dimerized, forming the biscarbobenzyloxy-2,5-piperazinedione (**7**). The structure of **7** was confirmed by carbobenzyloxylation of cycloserine dimer[9] in neutral to acidic aqueous solution.

The blocked dipeptide **6** was treated with anhydrous hydrogen fluoride, giving the ninhydrin-positive dipeptide as an extremely hygroscopic solid which gave a single spot on paper chromatography. Attempts to convert this product to the more tractable 2,5-piperazinedione **2** using a weakly basic ion exchange resin as was previously done[3] were unsuccessful. It was found alcoholic ammonia accomplished the neutral-



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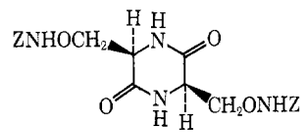

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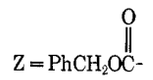

ization without destruction[10] of **2**. Warming of the free base in aqueous solution then afforded **2** in 62% yield. The physical properties of this product were essentially[11] identical with those previously[3] reported. A *p*-nitrobenzylidene derivative of **2** was prepared and found to be identical with that formed from the previously prepared material. This constitutes a proof of the configuration of a dipeptide previously synthesized and confirms the correctness of a configurational assignment based primarily on the chemical shift positions of the alanine methyl groups.[12]

Experimental Section

All melting points were measured on a Nagle–Kopfler micro hot stage. All infrared spectra were recorded on a Perkin-Elmer

(4) C. H. Stammer, C. C. Kartha, N. C. Chaturvedi, and J. D. McKinney, *J. Med. Chem.*, **13**, 1013 (1970).

(5) In ref 4, an optically active 2-trityl-D-cycloserine Schiff base was described. Hydrolysis of the Schiff base gave the ring-protected 2-trityl-cycloserine, but complete racemization occurred during the reaction. Thus, **5** is the only *useful* blocked cycloserine prepared so far.

(6) A specific color test for the N-*un*substituted isoxazolidone ring system; *cf.* L. R. Jones, *Anal. Chem.*, **28**, 39 (1956).

(7) S. Sakakibara, Y. Shimonishi, M. Okada, and Y. Kishida in "Proceedings of the Eighth European Peptide Symposium," H. C. Beyerman, Ed., Wiley, New York, N. Y., 1967, pp 44–49.

(8) N. Izumiya and J. P. Greenstein, *Arch. Biochem. Biophys.*, **52**, 203 (1954); G. W. Anderson, J. E. Zimmerman, and F. M. Callahan, *J. Amer. Chem. Soc.*, **89**, 5012 (1967).

(9) C. H. Stammer and J. D. McKinney, *J. Org. Chem.*, **30**, 3436 (1965).

(10) These aminoxymethyl-2,5-piperazinediones are very sensitive to base; *cf.* J. C. Miller, F. C. Neuhaus, F. O. Lassen, and C. H. Stammer, *J. Org. Chem.*, **33**, 3908 (1968).

(11) Reference 3 reports $[\alpha]^{25}D$ +21.3° (H_2O); the present work affords a purer material, $[\alpha]^{30}D$ +23.2° (H_2O).

(12) B. Halpern, L. F. Chew, and B. Weinstein, *J. Amer. Chem. Soc.*, **89**, 5051 (1967); B. Halpern, D. E. Nitecki, and B. Weinstein, *Tetrahedron Lett.*, 3075 (1967).

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

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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).