eV), m/e (relative intensity) 252 (100), 227 (27), 225 (22), 200 (8), 123 (4), 99 (7); high-resolution mass spectrum, calcd 252.0435, found 252.0434.

1,2-Dibromo-5,6-dicyanoacenaphthylene (8) and 1,2,5-Tribromo-6-cyanoacenaphthylene (9). 1,2,5,6-Tetrabromoacenaphthylene (1.809 g, 387 mmol), cuprous cyanide (2.77 g, 30.96 mmol), and N-methyl-2-pyrrolidinone (15 mL) under argon were stirred and heated to 118 °C over 30 min; the reaction was heated at 118 °C for 15 min. The reaction was worked up as for the preparation of 7.[20] The crude product was chromatographed on a 3 × 66 cm silica gel column (E. Merck, 70–230 mesh) with 10% methylene chloride/90% hexane as solvent; 250-mL fractions were collected. After four fractions the solvent was changed to 20% methylene chloride/80% hexane, after five more fractions the solvent was changed to 50% methylene chloride/50% hexane, and after fraction 30 the solvent was changed to 75% methylene chloride/25% hexane.

Fractions 13–25 yielded 0.536 g of 9 and fractions 34 and 35 yielded 0.282 g of 8. Fractions 34 and 35 were combined and recrystallized from methylene chloride to yield red crystals of 1,2-dibromo-5,6-dicyanoacenaphthylene (0.245 g, 18%): mp extensive softening 354–360 °C but not melted by 360 °C; IR (KBr) 2210 (C≡N), 1605, 1485, 1445, 1165, 848, 670, 500 cm^{-1}; high-resolution mass spectrum, calcd 359.8722, found 359.8722.

Fractions 13–25 were combined and recrystallized from methylene chloride to yield orange crystals of 1,2,5-tribromo-6-cyanoacenaphthylene (0.501 g, 31%): mp 319.5–323 °C; IR (nujol) 2209 (C≡N), 1480, 1415, 1202, 1160, 1140, 1050, 980, 825, 660 cm^{-1}; high-resolution mass spectrum, calcd 412.7872, found 412.7871.

1,2-Dibromo-5,6-dicyanoacenaphthylene (8). 5,6-Dicyanoacenaphthene (0.408 g, 2 mmol), N-bromosuccinimide (1.44 g, 8 mmol), dibenzoyl peroxide (11 mg), and carbon tetrachloride (25 mL) under argon were refluxed for 7 h. The carbon tetrachloride was removed under reduced pressure, leaving 1.77 g.

The crude mixture was chromatographed on a 4 × 43.5 cm silica gel column (E. Merck, 70–230 mesh) slurry packed with methylene chloride. The column was eluted with methylene chloride (250-mL fractions). Fractions 6 and 7 yielded 0.160 g of red crystals mixed in with light colored crystals of succinimide. Recrystallization from methylene chloride yielded 38 mg (5%) of 1,2-dibromo-5,6-dicyanoacenaphthylene: mp extensive softening 354–360 °C but not melted by 360 °C; IR (nujol) 2210 (C≡N), 1600, 1165, 670 cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 362 (45), 360 (100), 358 (47).

5,6-Dicyanoacenaphthene (10). 5,6-Dibromoacenaphthene (2.35 g, 7.53 mmol), cuprous cyanide (2.43 g, 27.10 mmol), and N-methyl-2-pyrrolidinone (35 mL) under argon were slowly heated to 160 °C over 1 h and then heated at 160 °C for 40 min. The reaction was worked up the same as that for 7. The crude reaction material (1.37 g) was chromatographed on a 3 × 65 cm column of silica gel (E. Merck, silica gel 60, 70–230 mesh) slurry packed with methylene chloride. The column was eluted with methylene chloride; 250-mL fractions were taken. Fractions 11–19 yielded 1.00 g of 5,6-dicyanoacenaphthene, which was recrystallized from methylene chloride to give white crystals of 10 (0.83 g, 54%, mp 310–311 °C, charred before melting): IR (KBr) 2210 (C≡N), 1590, 1432, 843 cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 204 (100), 203 (39), 202 (12), 149 (17), 85 (17), 71 (25), 57 (34); high-resolution mass spectrum, calcd 204.0685, found 204.0684.

5,6-Dinitroacenaphthene (15). The method of Sachs and Mosebach[21] was used to prepare 15: mp 219.5–222.5 °C (lit.[21] mp 220–224 °C).

1,2-Dibromo-5,6-dinitroacenaphthylene (16). 5,6-Dinitroacenaphthene (22.6 g, 93 mmol), N-bromosuccinimide (66.7 g, 375 mmol), and carbon tetrachloride (500 mL) under argon were brought to reflux, at which point several crystals of dibenzoyl peroxide were added.

Reflux was maintained for 6 days. The cooled dark red solution was washed with three portions (150 mL each) of aqueous concentrated sodium thiosulfate and then water. When any solids precipitated out, they were collected and saved for recrystallization. The red tar was washed with acetone, giving a red powder and a red solution. All red solids were recrystallized from toluene while all solutions were combined for chromatography on silica gel by eluting with benzene. The center-most portion of the red fraction gave quite pure compound which was also recrystallized from toluene. The yield was 5.0 g (12%); mp 283–284 °C; UV (THF) 231 (ε 2.9 × 10^4), 287 (ε 1.4 × 10^4), 346 (ε 1.4 × 10^4), 452 (ε 9.1 × 10^2) nm; IR (KBr) 3080 (w), 1530 (s), 1485 (m), 1445 (m), 1350 (s), 915 (m), 860 (m), 805 (m), 735 (m), cm^{-1}. Anal. Calcd for $C_{12}H_4Br_2N_2O_4$: C, 36.03; H, 1.01; Br, 39.96, N, 7.01. Found: C, 36.10; H, 1.01; Br, 40.17; N, 6.95.

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Registry No. 2, 7267-03-0; 3, 18105-07-2; 4, 86528-75-8; 5, 19190-91-1; 6, 56564-74-0; 7, 86528-76-9; 7 radical anion, 86528-83-8; 8, 86528-77-0; 8 radical anion, 86528-84-9; 9, 86528-78-1; 10, 86528-79-2; 10 radical anion, 86528-86-1; 11, 39653-72-0; 12, 69038-43-3; 12 radical anion, 86528-82-7; 13, 33239-23-5; 13 radical anion, 86528-81-6; 15, 4406-87-5; 16, 86528-80-5; 16 radical anion, 86528-85-0.

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Synthesis of Electron-Deficient Oxetanes. 3-Azidooxetane, 3-Nitrooxetane, and 3,3-Dinitrooxetane[1]

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A facile synthesis of 3-hydroxyoxetane is described and is based on the addition of acetic acid to epichlorohydrin, protection of the resulting primary alcohol as an acetal, basic acetate hydrolysis and ring closure, and removal of the protecting group. 3-Azidooxetane was prepared from 3-(tosyloxy)oxetane and sodium azide. Reduction of the azide with triphenylphosphine or hydrogen gave 3-aminooxetane, and oxidation of the amine with *m*-chloroperbenzoic acid gave 3-nitrooxetane. Oxidative nitration or reaction with tetranitromethane gave 3,3-dinitrooxetane. 3-Azidooxetane and 3,3-dinitrooxetane were polymerized with Lewis acids.

Recently we reported the synthesis of 3-fluoro-3-nitrooxetane by the base-catalyzed ring closure of the monotriflate derived from 2-fluoro-2-nitro-1,3-propanediol.[2] The "fluorine effect", or the destabilization of a nitronate

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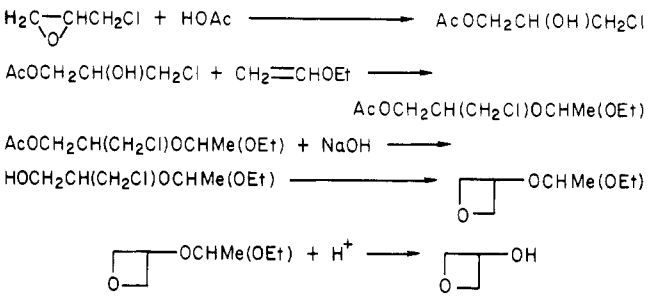
Scheme I



salt by an adjacent fluorine, enables this ring closure to take place despite the general tendency of 2-nitro alcohols to split off formaldehyde (reverse Henry reaction). The use of a less potent leaving group such as tosylate gave adducts of 1-fluoro-1-nitroethylene rather than the oxetane,[3] and even triflates from nonfluorinated nitro alcohols such as 2,2-dinitro-1,3-propanediol and 2-(hydroxymethyl)-2-nitro-1,3-propanediol gave no oxetanes.[2]

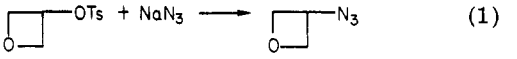
An alternative to this ring closure is the introduction of nitro groups by operating on oxetanes that contain other reactive functional groups. The conversion in high yield of 3-hydroxyoxetane to the tosylate has been reported, and the tosylate group has been displaced by halides.[4] The 3-hydroxyoxetane was obtained by the hydrolysis of 3-propenoxyoxetane, which, in turn, was prepared by the base-catalyzed rearrangement of 3-(allyloxy)oxetane. The latter compound, however, was obtained only in low yield by the cyclization of 2-(allyloxy)-3-chloropropanol,[5] a low-conversion chlorination product of allyl alcohol.[5,6]

We have developed a procedure suitable for the preparation of large quantities of 3-hydroxyoxetane from epichlorohydrin using the route outlined in Scheme I. The hydroxyl group of the acetic acid adduct of epichlorohydrin was blocked with a base-resistant protecting group. Ester hydrolysis and ring closure with aqueous base was followed by deblocking with acid.

The reaction of epichlorohydrin with acetic acid, catalyzed by ferric chloride, has been reported to give 3-chloro-2-hydroxy-1-propyl acetate in high yield.[7] This procedure was modified by eliminating the use of solvents and minimizing the amount of catalyst. The low iron level did not prevent monitoring the reaction by NMR, and the product was used without workup for the following step. The hydroxyl group was then protected with a vinylic ether.[8] Dihydropyran and ethyl vinyl ether gave similar results, and *p*-toluenesulfonic acid was used as a catalyst. No solvent was used, and to this point, we have a one-pot process. Next, aqueous sodium hydroxide hydrolyzed the ester and also closed the oxetane ring. The resulting crude 3-(1-ethoxyethoxy)oxetane was then treated with methanol and a catalytic amount of *p*-toluenesulfonic acid to give 3-hydroxyoxetane. Flash distillation gave 3-hydroxyoxetane of about 80% purity, and the pure alcohol could be isolated by fractionation. The impure material, however, was suitable for conversion to the tosylate with aqueous sodium hydroxide and tosyl chloride.[4] The overall yield of 3-(tosyloxy)oxetane based on epichlorohydrin was 29%.

Attempts to prepare 3-nitrooxetane from 3-(tosyloxy)-oxetane, 3-bromooxetane, or 3-iodooxetane by displacement reactions with silver nitrite or sodium nitrite were unsuccessful. Decomposition took place when reaction temperatures were high enough for the consumption of starting materials. It has been reported[4] that displacements of 3-(tosyloxy)oxetane with metal halides require temperatures of about 170 °C and that the reaction of 3-iodooxetane with diethylamine takes place at 200 °C.

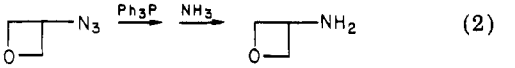
Azide salts, however, were found to react with 3-(tosyloxy)oxetane under relatively mild conditions to give 3-azidooxetane. A 50% yield was obtained with potassium azide at 87 °C in hexamethylphosphoramide and a 28% yield was obtained in refluxing acetonitrile in the presence of 18-crown-6. Polyethylene glycols were also reported to have crown-ether-type complexing ability,[9] and these materials were investigated as solvents for the displacement. Sodium azide and the tosylate (eq 1) gave an 86%



(1)

yield of 3-azidooxetane at 120–130 °C at 7–10 mmHg; under these conditions, the product was distilled from the reaction mixture as it was formed. The solvent did not codistill with the product when tetraethylene glycol or higher homologues were used. The azide was handled safely[10] by distilling the material directly into methylene chloride and by using the solution for subsequent reactions.

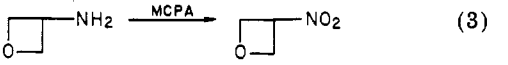
3-Aminooxetane was obtained in low yield from the reaction of 3-(tosyloxy)oxetane with liquid ammonia. A more satisfactory method, however, was the reduction of 3-azidooxetane. Azides have been converted to amines (eq 2) by a reaction with triphenylphosphine followed by ammonolysis,[11] and by this procedure, 3-azidooxetane gave



(2)

a 96% yield of 3-aminooxetane. This reduction was also carried out by hydrogenation at atmospheric pressure in methanol over 10% palladium on carbon, but the reaction was not realiably reproducible. The synthesis of 3-aminooxetane by the high-pressure hydrogenation of 3-oxetanone oxime has been reported in the patent literature.[12]

3-Aminooxetane was used as a starting material to prepare 3-nitrooxetane and 3,3-dinitrooxetane. The oxidation of cyclohexylamine with *m*-chloroperbenzoic acid to give nitrocyclohexane has recently been reported.[13] This reaction was found to give a 75% yield of 3-nitrooxetane from 3-aminooxetane (eq 3). The most generally



(3)

used method for converting a mononitro aliphatic compound to a *gem*-dinitro compound is the oxidative nitration reaction[14] using base, sodium nitrite, and silver nitrate (eq 4). 3,3-Dinitrooxetane was obtained in this way from 3-

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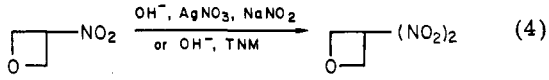
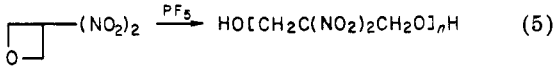
nitrooxetane but only in 22% yield. Nitronate salts have recently been nitrated with tetranitromethane.[15] Addition of this reagent to a solution of the salt of 3-nitrooxetane in aqueous methanol gave a 60% yield of 3,3-dinitrooxetane.



(4)

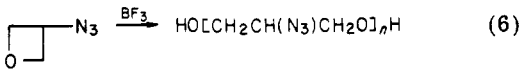
The polymerization of 3-fluoro-3-nitrooxetane was previously shown to be catalyzed by the strong Lewis acid catalyst, phosphorus pentafluoride, but not by boron trifluoride. 3,3-Dinitrooxetane was found to be even more resistant to cationic polymerization, requiring prolonged exposure to an atmosphere of phosphorus pentafluoride (eq 5) A polymer was obtained with a melting point of



(5)

200–202 °C. The polymer was insoluble in methylene chloride or ethyl acetate but was soluble in acetone. The molecular weight by vapor pressure osmometry was 2870.

3-Azidooxetane, which is not so highly deactivated by electron-withdrawing groups, was polymerized readily by boron trifluoride etherate, at temperatures as low as −30 °C (eq 6). Details are described in the Experimental Section.



(6)

Determination of the hydroxyl equivalent weight of polymers has generally provided difficulties.[16] We have used a simple procedure consisting of trimethylsilylation, removal of volatiles, and determination of silyl hydrogens by quantitative NMR.

Experimental Section

NMR and IR spectra were recorded with a Varian T-60 spectrometer and a Perkin-Elmer 700 spectrometer, respectively. A Varian 920 gas chromatograph was used for GLC separations, and a Mechrolab 301A vapor pressure osmometer was used for molecular weight determinations. Safety precautions for 3-azidooxetane are described in the text. Other azido and nitro compounds were handled with caution.

3-(Tosyloxy)oxetane. Epichlorohydrin (925 g, 10.0 mol) was added with stirring, over a 10-min period, to a solution of 1.5 g of ferric chloride in 612 g (10.02 mol) of glacial acetic acid. The mixture was heated at 65–70 °C for 24 h to give crude 3-chloro-2-hydroxy-1-propyl acetate: NMR ($CDCl_3$) δ 2.10 (s, 3 H, $COCH_3$), 3.80 (m, 6 H, $CH_2CH(OH)CH_2$); IR (film) 3500 (OH), 1735 cm^{-1} ($COCH_3$).

After 10 g of *p*-toluenesulfonic acid monohydrate was added to this crude material, 815 g (11.3 mol) of ethyl vinyl ether was added dropwise, with stirring, over a period of 2 h. The flask was cooled to maintain a reaction temperature of 35–37 °C. After the addition was completed, the mixture was heated at 35–40 °C for 16 h to give crude 3-chloro-2-(1-ethoxyethoxy)-1-propyl acetate.

This intermediate was added over a 1.5-h period with stirring to a solution of 1.1 kg (27.5 mol) of sodium hydroxide in 1.1 L of water at 105 °C, and the reaction mixture was refluxed for an additional 4-h period. The mixture was cooled and was washed with 1.5 L of water. The aqueous layer was washed with 1.5 L of methylene chloride, and the combined organic phases were stripped of solvent to give 1.2 kg of crude 3-(1-ethoxyethoxy)-oxetane.

Methanol (400 g) was added and the mixture was cooled to 15–18 °C. p-Toluenesulfonic acid monohydrate (10 g) was added with stirring. The reaction temperature increased over a 5-min period to 34 °C and then decreased to 25 °C in 30 min. The mixture was stirred for an additional 45-min period, and then 5 g of solid sodium bicarbonate was added. Distillation gave 280 g of 3-hydroxyoxetane, bp 45–50 °C (0.3 mm), of 80% purity (NMR).

This 3-hydroxyoxetane (3.07 mol) was stirred with 660 g (3.46 mol) of technical *p*-toluenesulfonyl chloride in 530 mL of water, and a solution of 194 g (4.84 mol) of sodium hydroxide in 200 mL of water was added over a period of 25 min. Ice-bath cooling was used to keep the reaction temperature below 70 °C. When the exothermic reaction subsided, the bath was removed, and the mixture was allowed to cool to 40 °C over a 1-h period. The product was isolated by filtration, washed with four 180 mL of warm (50 °C) water, and air-dried to give 649 g (93%) of 3-(tosyloxy)oxetane, mp 86–88 °C (lit.[4] 88.5–89 °C).

3-Azidooxetane. A stirred solution of 92 g (0.40 mol) of 3-(tosyloxy)oxetane and 40 g (0.48 mol) of sodium azide in 205 mL of polyethylene oxide (Carbowax 300) was heated to 120–130 °C over 30 min at 7–10 mmHg. The product distilled as it was formed, over a 1.5-h period, and was collected in a stirred receiver containing 200 mL of methylene chloride at −78 °C. The resulting methylene chloride solution contained 34 g (86%) of 3-azidooxetane, and an analytical sample was isolated by GC (9% QF-1 on Chromasorb W, 100 °C: ^1H NMR ($CDCl_3$) δ 4.70 (m, 4 H, CH_2), 4.76 (m, 1 H, CHN_3); IR (CH_2Cl_2) 3000, 2930 (CH), 2150 (N_3), 980 cm^{-1} (oxetane).

Anal. Calcd for $C_3H_5N_3O$: C, 36.36; H, 5.09; N, 42.41. Found: C, 36.29; H, 4.82; N, 43.06.

The product was handled safely as a methylene chloride solution (see discussion).

3-Aminooxetane. Triphenylphosphine (132.5 g, 0.50 mol) was added to a solution of 50 g (0.50 mol) of 3-azidooxetane in 800 mL of methylene chloride at 0–5 °C. The solution was allowed to stand for 0.5 h at 0–5 °C and for 3.5 h at room temperature. The solvent was removed under vacuum, and an ice-cooled solution of 800 mL of methanol saturated with ammonia was added to the residue. The resulting orange solution was stirred for 40 h at 0.5 °C. Distillation gave 32 g of 3-aminooxetane, bp 50–82 °C (60–70 mmHg) [lit.[12] 80–82 °C (100 mmHg)], and extraction of the distillation residue with ether followed by distillation gave an additional 3.2 g (96% total): ^1H NMR ($CDCl_3$) δ 2.03 (s, 2 H, NH_2), 4.0–4.8 (m, 5 H); IR (film) 3350 (NH_2), 3000, 2900 (CH), 1605 (NH_2), 970 cm^{-1} (oxetane); n^{26}_D 1.4500. Elemental analysis was carried out on the *p*-nitrobenzamide, mp 189–191 °C.

Anal. Calcd for $C_{10}H_{10}N_2O_4$: C, 54.03; H, 4.50; N, 12.60. Found: C, 54.02; H, 4.51; N, 12.32.

3-Nitrooxetane. A solution of 7.3 g (0.10 mol) of 3-aminooxetane in 100 mL of 1,2-dichloroethane was added over 1 h to a refluxing solution of 71 g (0.35 mol) of 85% *m*-chloroperbenzoic acid in 600 mL of 1,2-dichloroethane. The reaction mixture was heated at reflux for an additional 3-h period and was allowed to stand at ambient temperature for 16 h. The precipitated *m*-chlorobenzoic acid was filtered and was washed with 1,2-dichloroethane. The combined solutions were stripped of solvent under vacuum, and the residue was distilled in a Kügelrohr apparatus to give 6.35 g (62%) of 3-nitrooxetane at 77 °C (0.5–1.0 mmHg). An analytical sample was isolated by GC (9% QF-1 on Chromosorb W, 120 °C): NMR ($CDCl_3$) δ 4.87 (m, 4 H, CH_2), 5.23 (m, 1 H, $CHNO_2$); IR (CH_2Cl_2) 3000, 2940 (CH), 1550, 1370 (NO_2), 980 cm^{-1} (oxetane); n^{20}_D 1.4618; *d* 1.33.

Anal. Calcd for $C_3H_5NO_3$: C, 34.96; H, 4.89. Found: C, 34.77; H, 4.87.

3,3-Dinitrooxetane (Oxidative Nitration). A solution of 3.38 g (0.033 mol) of 3-nitrooxetane, 1.45 g (0.036 mol) of sodium hydroxide, and 2.56 g (0.036 mol) of sodium nitrite in 72 mL of water at 0–5 °C was added to a stirred solution of 12.2 g (0.072 mol) of silver nitrate in 25 mL of water at 0–5 °C. A black suspension formed immediately. After the reaction mixture was stirred at 0–5 °C for 2 h, 25 mL of saturated sodium chloride solution was added and stirring was continued for 30 min. The mixture was filtered through Celite, and the filter cake was washed with 10 mL of water and 100 mL of ether. The aqueous solution was washed with two 100-mL portions of ether, the combined ether solutions were dried and the solvent was removed. Column chromatography of the residue (silica gel, methylene chloride–hexane) gave 1.07 g (21.9%) of 3,3-dinitrooxetane: mp 70–71 °C

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(sublimed 100 °C): NMR ($CDCl_3$) δ 5.27 (s); IR (CH_2Cl_2) 3000, 2940 (CH), 1580, 1325 (NO_2), 1000 cm^{-1} (oxetane); d 1.65.

Anal. Calcd for $C_3H_4N_2O_5$: C, 24.34; H, 2.72. Found: C, 24.54; H, 2.80.

3,3-Dinitrooxetane (from Tetranitromethane). A solution of 1.03 g (0.010 mol) of 3-nitrooxetane and 2.0 g (0.010 mol) of tetranitromethane in 5 mL of methanol was added dropwise, with stirring over a 20-min period, to a solution of 0.42 g (0.010 mol) of sodium hydroxide in 1 mL of water and 2 mL of methanol at 0 °C. Stirring was continued for 30 min, and 10 mL of water was then added. The pH was adjusted to 9–10 with sodium hydroxide, and the mixture was extracted with ether (3 × 25 mL). The ether solution was washed with water and dried. Removal of the solvent gave 0.89 g (60%) of 3,3-dinitrooxetane identical with that above.

Polymerization of 3,3-Dinitrooxetane. A dry 100-mL flask, fitted with a syringe valve, was loaded with a solution of 0.113 g (0.76 mmol) of 3,3-dinitrooxetane in 0.5 mL of dry methylene chloride and was flushed with nitrogen. After 40 mL of nitrogen was removed by syringe, 40 mL (1.6 mmol) of phosphorus pentafluoride was added. After 30 h, solvent and catalyst were removed under vacuum. Extraction of the residue with 15 mL of methylene chloride gave 0.018 g (16%) of recovered 3,3-dinitrooxetane. The material insoluble in methylene chloride was extracted with 15 mL of ethyl acetate to give 0.024 g (21%) of white solid: M_r (ethyl acetate) 484; IR 3550 (OH), 1575, 1320 cm^{-1} (NO_2). The material insoluble in ethyl acetate was extracted with 15 mL of acetone to give 0.071 g (63%) of white solid: mp 200–202 °C; NMR (D_3CCOCD_3) δ 4.67 (br s); IR (acetone) 3600 (OH), 1565, 1320 cm^{-1} (NO_2); M_r (vapor pressure osmometry, acetone) 2870; d 1.59.

Polymerization of 3-Azidooxetane. A 50-mL magnetically stirred round-bottomed flask, fitted with a condenser and a drying tube, was loaded with 20 g of a 42% by weight solution of 3-azidoxetane in methylene chloride (0.085 mol), and was cooled to −30 °C. Freshly distilled boron trifluoride etherate (0.60 mL, 0.0052 mol) was added rapidly by syringe. After about 30 s the reaction temperature increased to the reflux temperature and a gelatinous polymer formed. The material was allowed to stand for 5 min at room temperature, and then 5 mL of water was added and the mixture was agitated to disperse the gel. Ethyl acetate (30 mL) was added and the mixture was stirred for 1 h. The organic layer was separated and dried over magnesium sulfate. Solvent was removed with a rotary evaporator (70 °C at 20 mmHg) to give a brown oil: NMR ($CDCl_3$) δ 3.58 (s); IR (CH_2Cl_2) 3000, 2900 (CH), 2150 (N_3), 1135 cm^{-1} (COC); M_r (vapor pressure osmometry, ethyl acetate) 2200; equiv wt (silylation) 1200.

The polymer dissolved in 20 mL of methylene chloride was poured into 20 mL of hexane with vigorous stirring. After 30 min the solvent was decanted from the precipitated oil, and the latter was dried at 70 °C under vacuum to give 7.4 g of material essentially identical with the unfractionated polymer.

The polymerization was also carried out at subambient temperatures with more dilute solutions. A solution of 1.0 g (0.0071 mol) of boron trifluoride etherate in 50 mL of methylene chloride was cooled to −30 °C, and a solution of 9.9 g (0.10 mol) of 3-azidooxetane in 100 mL of methylene chloride was added dropwise. The solution was stirred at −30 °C for 48 h. GLC analysis showed that less than 0.5% of the oxetane remained. Saturated sodium chloride solution (5 mL) was added, and the mixture was stirred for 30 min. The organic layer was allowed to come to ambient temperature and was washed with 100 mL of 5% potassium carbonate solution and 100 mL of water. The methylene chloride solution was dried over magnesium sulfate and was evaporated under vacuum. The residue was dissolved in 30 mL of methylene chloride, and the solution was filtered into 30 mL of rapidly stirred hexane. After 30 min the solvent was decanted and the remaining oil was washed with 30 mL of hexane. The product was dried at 70 °C under vacuum to yield 4.8 g (49%) of very viscous oil with M_r 2350 (VPO, ethyl acetate).

A similar reaction using 0.1 mol of 3-azidooxetane and 0.0052 mol of boron trifluoride etherate in 50 mL of methylene chloride, maintained at 0–5 °C, gave a 54.5% yield of product with a molecular weight of 2400.

Equivalent Weight Determination. A 50-mL round-bottomed flask equipped with a magnetic stirrer, a condenser, and a drying tube was loaded with approximately 0.2 g of 3-azidooxetane polymer, 5 mL of 1,2-dichloroethane, 2 mL of 1,1,1,3,3,3-hexamethyldisilazane and 0.5 mL of chlorotrimethylsilane. Volatile materials were removed at 70 °C under vacuum. The residue was dissolved in 1 mL of deuteriochloroform, and the proton NMR spectrum was recorded. The hydroxyl equivalent weight was calculated on the basis of the areas of the δ 3.3 signal (5 protons per monomer unit) and the δ 0 signal (9 protons per siloxy group). The same method was used for polymers with more complex NMR spectra by using weighed mixtures of the silylated polymer and a reference such as p-dichlorobenzene. The equivalent weight was calculated on the basis of the reference and siloxy signals.

Registry No. 3-Azidooxetane, 81764-67-2; 3-aminooxetane, 21635-88-1; 3-nitrooxetane, 86632-92-0; 3,3-dinitrooxetane, 81764-66-1; 3,3-dinitrooxetane homopolymer, 86611-87-2; 3-azidooxetane homopolymer, 85533-59-1; epichlorohydrin, 106-89-8; 3-chloro-2-hydroxy-1-propyl acetate, 24573-30-6; ethyl vinyl ether, 109-92-2; 3-chloro-2-(1-ethoxyethoxy)-1-propyl acetate, 85328-35-4; 3-(1-ethoxyethoxy)oxetane, 85328-36-5; 3-hydroxyoxetane, 7748-36-9; 3-(tosyloxy)oxetane, 26272-83-3; 3-[*N*-(*p*-nitrobenzoyl)amino]oxetane, 86632-93-1; tetranitromethane, 509-14-8.