yl sulfoxide with 3.5 g (0.03 mol) of tetramethylguanidine. A total of 1.5 ml (0.01 mol) of *t*-Boc azide was added immediately, and the solution was stirred at 40° for 3 weeks with the addition of 0.4 ml of *t*-Boc azide every 3 days. The solution was then diluted with 150 ml of H_2O, brought to pH 2.5 with the addition of solid $NaHSO_4$, and extracted five times with ethyl acetate. The extracts were combined, dried with Na_2SO_4, and evaporated under reduced pressure. The viscosity of the residual oil was reduced by the addition of a small amount of ethyl acetate, and an excess of dicyclohexylamine was added. The resultant crystalline salts were collected by filtration and recrystallized from ethyl acetate. The yield of **5** was 70% (3.22 g), and its physical characteristics follow: mp 230–231°; BAW R_f 0.81, BP R_f 0.70; $[\alpha]^{25}D$ +16.8° (2% acetic acid in ethanol, *c* 0.46). Anal. Calcd for $C_{27}H_4N_2O_4$: C, 70.43; H, 9.57; N, 6.09. Found: C, 70.41; H, 9.68; N, 6.04. The yield of **6** was 13% (0.533 g), and its physical characteristics follow: mp 181–182°; BAW R_f 0.74, BP R_f 0.72; $[\alpha]^{25}_{300}$ +32.6° (ethanol, *c* 2.06). Anal. Calcd for $C_{23}H_{44}N_2O_4$: C, 66.97; H, 10.79; N, 6.74. Found: C, 66.91; H, 10.68; N, 6.78.

Registry No.—DL-**1**, 1132-26-9; D-**1**, 17350-84-4; L-**1**, 23239-35-2; DL-**2**, 26287-62-7; D-**2**, 53940-82-2; L-**2**, 53940-83-3; DL-**3**, 53940-84-4; D-**3**, 53940-85-5; DL-**4**, 53940-86-6; D-**4**, 53940-87-7; **5**, 53940-89-9; **6**, 53940-91-3; *t*-Boc azide, 1070-19-5.

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Ring Opening of 3-Chloro-4-nitroisothiazole with Amines

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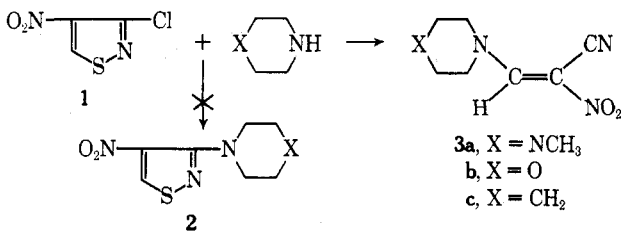
In an attempt to prepare 3-(*N*-methylpiperazino)-4-nitroisothiazole (**2a**), 3-chloro-4-nitroisothiazole (**1**)[1] was treated with *N*-methylpiperazine. Unexpectedly, a ring opening occurred leading to the enamine **3a** rather than **2** (Scheme I). The evidence for this is as follows.

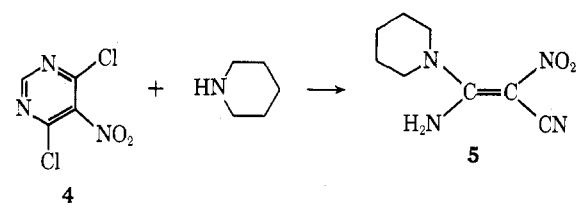
Scheme I



The product did not contain sulfur and analyzed as $C_8H_{12}N_4O_2$. The ir spectrum showed a C≡N band (2200 cm^{-1}), a strong C=C band (1620 cm^{-1}), and an NO_2 band (1280 and 1490 cm^{-1}) which had been shifted to longer wavelength owing to conjugation with an amino group. A normal C=C—NO_2 should have peaks at 1524 ± 4 and 1353 ± 6 cm^{-1}.[2] The NMR chemical shift of the olefinic proton (δ 8.50) enabled us to assign the configuration of **3a** as having a trans relationship between the amine and NO_2 nitrogens. Matter et al.[3] have shown that the equation $\delta = 5.25 + Z_{gem} + Z_{trans} + Z_{cis}$ is useful in determining the chemical shift of protons on substituted ethylenes where *Z*'s are parameters for various substituents listed in his paper. Together with the parameter for NO_2 determined by Descotes et al.,[4] one can calculate the chemical shift for the olefinic proton of **3a** as follows. δ = 5.25 + 1.17 (conjd NR_2) + 0.55 (*trans*-CN) + 1.67 (*cis*-NO_2) = 8.64. The calculated chemical shift for the other isomer is δ = 5.25 + 1.17 + 0.75 (*cis*-CN) + 0.46 (*trans*-NO_2) = 7.63. Clearly the observed value (8.50) is closer to that calculated for **3a** than its isomer.

There are no other 3-amino-2-nitroacrylonitriles reported in the literature, the nearest analog being **5**.[5] This compound, prepared by ring opening of the dichloronitropyrimidine **4** (Scheme II), shows ir maxima at 1643 cm^{-1} (C=C).

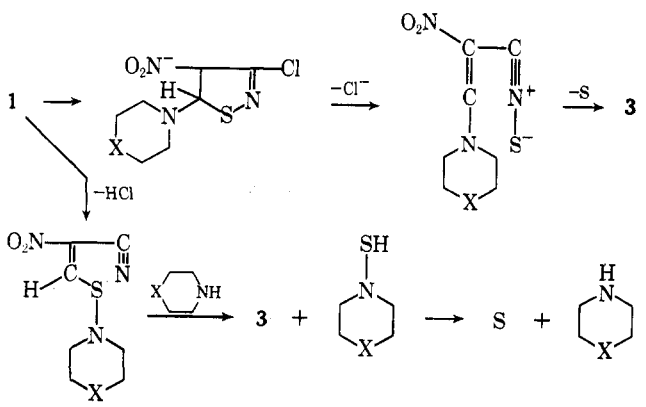
Scheme II



The monobasic amines, morpholine and piperidine, react in a like manner if triethylamine is present.

Two possible mechanisms for the formation of **3** are given in Scheme III. The first involves a nitrile sulfide in-

Scheme III



termediate. The species has been proposed by Howe and Franz as an intermediate in the decomposition of 1,3,4-oxathiazol-2-ones.[6] The second involves nucleophilic attack on sulfur.[7] Several ring openings of isothiazoles have been shown to involve attack on the ring sulfur.[8-11] At this point it is not possible to decide between the two mechanisms.

Experimental Section

3-(4-Methyl-1-piperazino)-2-nitroacrylonitrile (3a). To 5.00 g of 3-chloro-4-nitroisothiazole[1] in 25 ml of isopropyl alcohol at 0°, 3.25 g of *N*-methylpiperazine in 10 ml of isopropyl alcohol was added dropwise. The solution was kept at room temperature overnight. A pale yellow solid (mp 119°, sulfur, 600 mg) was filtered. The solution was concentrated and cooled, giving 3.32 g of **3a:** mp 83–85°; NMR ($CDCl_3$) δ 2.33 (3 H, s), 2.55 (2 H, t), 2.61 (2 H, t), 3.70 (2 H, t), 4.00 (2 H, t), 8.50 (1 H, s); ir, see text. Anal. Calcd for $C_8H_{12}N_4O_2$: C, 48.98; H, 6.17; N, 28.56. Found: C, 48.80; H, 5.90; N, 28.37; S, 0.0.

3-(1-Morpholino)-2-nitroacrylonitrile (3b). To 5.00 g of 3-chloro-4-nitroisothiazole in 25 ml of benzene at 0°, 2.80 g of morpholine in 5 ml of benzene was added slowly followed by 3.16 g of triethylamine. An exothermic reaction occurred and a solid formed. After 1 hr the solution was treated with dilute HCl and benzene, and the solid was filtered and crystallized from dimethoxyethane to give sulfur (mp 118°, insoluble in DME), and 3.02 g of **3b,** mp 143–145°. Anal. Calcd for $C_7H_9N_3O_3$: C, 45.90; H, 4.90; N, 22.94. Found: C, 45.76; H, 4.82; N, 22.84.

3-(1-Piperidino)-2-nitroacrylonitrile (3c). 3-Chloro-4-nitroisothiazole (5.00 g) and piperidine (2.80 g) were allowed to react as above. The product was soluble in benzene but was crystallized from isopropyl alcohol and then methanol to give 3.54 g of **3c,** mp 116–118°. Anal. Calcd for $C_8H_{11}N_3O_2$: C, 53.03; H, 6.12; N, 23.19. Found: C, 52.80; H, 6.16; N, 23.48.

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Registry No.—1, 14217-68-6; **3a,** 54062-82-7; **3b,** 54062-83-8; **3c,** 54062-84-9; *N*-methylpiperazine, 109-01-3; morpholine, 110-91-8; piperidine, 110-89-4.

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Monoesters of Cyclohexane-1β,3β,5β-triol

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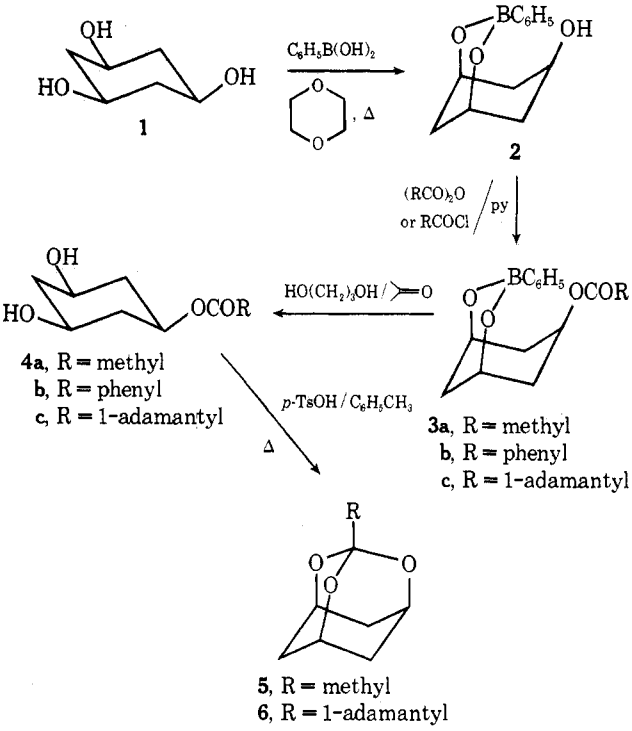
We required a series of the title compounds in order to study their cyclization to the corresponding trioxaadamantanes. This ring system, hitherto prepared[2] from cyclohexane-1β,3β,5β-triol (α-phloroglucitol, **1**) (Scheme I) and a trialkyl ortho ester, is reported[3] to be stable toward Grignard reagents and has seen limited use as a carboxylic acid protecting group.[4] We describe herein the synthesis of three monoesters of **1** and some preliminary cyclization results.

Scheme I



Starting triol **1** was obtained highly stereoselectively by high-pressure hydrogenation[2] of 1,3,5-trihydroxybenzene (phloroglucinol) over a rhodium catalyst. Efforts to conveniently prepare monoesters of **1** by direct acylation with 1 equiv of acylating agent in pyridine were thwarted by the qualitative observation that partially acylated phloroglucitols appeared to be more susceptible to further acylation than **1** itself. Likewise, partial saponification of fully acylated derivatives (for example, α-phloroglucitol tribenzoate) with 2 equiv of base produced mixtures in which the desired monoacyl product did not predominate.

Success was achieved through reaction of **1** with phenylboronic acid[5] in refluxing dioxane, producing α-phloroglucitol phenylboronate (**2**) in 99% yield. This last substance was treated with 1 equiv of the acid chloride or anhydride in pyridine, leading to the corresponding acyl derivatives **3** in good yields (79–99%). The phenylboronate group was then cleaved using propane-1,3-diol in acetone,[5] affording the title compounds **4** in yields of ca. 80%.

While monoacetate **4a** could be cyclized to trioxaadamantane **5** in 40% yield with refluxing toluene containing toluenesulfonic acid, esters **4b** and **4c** proved much more resistant to cyclization. For example, reaction of **4c** with toluenesulfonic acid in boiling xylene afforded trioxaadamantane **6** [mp 142–144°, tentative assignment based on a high-resolution mass spectrum, *m/e* 276.176 (calcd, 276,173)] in less than 1% yield.

Experimental Section

Melting points were determined on a Kofler hot stage or in a sealed capillary in an oil bath and are uncorrected. Infrared spectra were recorded with a Beckman IR-5 spectrophotometer. NMR spectra were recorded on a Varian A-60, HA-100, or XL-100 high-resolution spectrometer. Chemical shifts are reported in parts per million downfield from internal Me_4Si. Mass spectra (70 eV) were determined on a CEC 110-2B double-focusing mass spectrometer equipped with a direct inlet. Elemental analyses were performed at the University of Oregon by Dr. S. Rottschaefer.