yield), mp 139–142 °C: ^{1}H NMR (Me_2SO-d_6) δ 3.1 (m, 2 H, SCH_2), 3.6–3.8 (m, 4 H, SCH_2CH_2Br), 5.4 (m, 1 H, CHPh), 7.4–7.6 (m, 5 H, Ar), 8.35 (br, 3 H, exch, NH^+_3); IR (Nujol) ν_{max} 2960 cm^{-1} (NH_3); CIMS (NH_3), m/z (rel intensity) 262 [(MH + 2) – HBr], 260 (MH^+ – HBr).

2-[(2-Bromoethyl)sulfinyl]-1-phenylethylamine Hydrobromide. A stirred solution of 1-phenyl-2-[(2-bromoethyl)-thio]ethylamine hydrobromide (0.339 g, 1 mmol) in 2 mL of dry methanol was treated with a solution of 30% H_2O_2 (0.226 g, 2 mmol). The mixture was then stirred for 48 h. The solvent was removed in vacuo, and the crude material was recrystallized from chloroform to give the pure product as a yellow crystalline solid 0.3 g (84% yield), mp 96–100 °C: ^{1}H NMR ($CDCl_3$) δ 2.9–3.2 (m, 6 H, $CH_2SOCH_2CH_2Br$), 5.1 (m, 1 H, $CHPh(CH_2)$, 7.1 (m, 5 H, Ph), 8.1 (s, 3 H, exch $NH_3^+Br^-$); IR (Nujol) ν_{max} 1040 (s), 2912–3029 cm^{-1} ($NH_3^+Br^-$); MS, m/z (rel intensity) 196 (M^+ – HBr – Br).

General Procedure for Analysis of Aqueous Decomposition Products of Sulfinylnitrosoureas in Buffer or from Diazotization Reactions. Solutions of the sulfinylnitrosoureas ~25 mg (0.1 mmol/mL) in 0.5–1.0 mL of 40 mM potassium phosphate buffer (pH 7.2) in 3 mL air-tight Reactivials equipped with Teflon septums were thermostated at 37 °C. In the case of the amino precursors diazotization was carried out at 0 °C. At intervals samples of the gaseous fractions were withdrawn with a hypodermic syringe and analyzed by GC HP-5890 and the Hewlett-Packard GCMS with mass selective detector Model 5920 as described previously. Similar reaction conditions were employed but in the presence of 5 molar equiv of sodium bromide or sodium chloride where appropriate in the control reactions examining for possible halide exchange.

Acknowledgment. This work was supported by Grant 1RO1 CA21488-01 awarded by the National Cancer Institute, DHHS, to J.W.L., and by a contract with the National Foundation for Cancer Research. We thank Dr. Anne-Marie Sapse, City University of New York, for the preliminary ab initio calculations. We thank Dr. Tom Nakashima and his associates for the NMR measurements and Dr. Alan Hogg and his colleagues for the MS and CIMS spectra.

Six-Membered Ring-Fused Thiirene *S*-Oxides. Synthesis, Characterization, and Reactivity

Wataru Ando,* Yukio Hanyu, and Toshikazu Takata

Department of Chemistry, The University of Tsukuba, Sakuramura, Ibaraki 305, Japan

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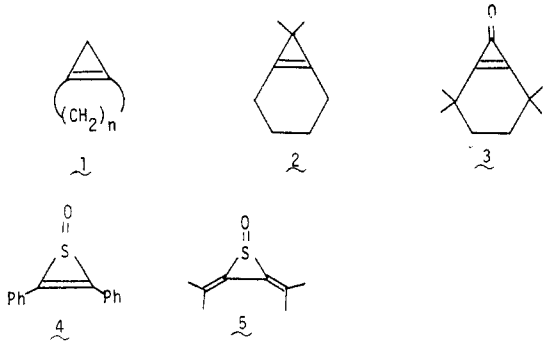
Alkyl-substituted thiirene *S*-oxides fused to six-membered rings have been synthesized by [2 + 4] cycloaddition of thiiranoradialene *S*-oxide with 4-substituted-1,2,4-triazoline-3,5-diones and to singlet oxygen. The fused thiirene *S*-oxides reacted with methanol or *p*-nitrophenyl isonitrile to afford products resulting from C–S bond cleavage. The distorted π-bond of a thiirene *S*-oxide released its strain in a cycloaddition with furan to yield a propellane thiirene *S*-oxide.

The bicyclo[*n*.1.0] olefin system **1** is of interest because of its unusual electron system.[1,2] The two reported examples of this system in which $n = 4$ are the annelated cyclopropene **2**, which has been observed only below –35 °C,[2a] and cyclopropenone **3**,[2n] which has been isolated.



1 2 3 4 5

There are no reports of this system in which $n < 4$, and the six-membered ring may be the lower limit for a cyclopropene fused to another ring.

Diphenylthiirene *S*-oxide (**4**) has been prepared by a modified Ramberg–Backlund reaction of bis(bromobenzyl) sulfone with triethylamine,[3] but alkyl-substituted thiirene *S*-oxides have not been reported. Recently, the authors synthesized the first hetero[3]radialene, thiiranoradialene *S*-oxide (**5**).[4] Although there has been considerable study of [2 + 4] cycloadditions of radialenes with dienophiles as a route to fused ring systems, no successful example is reported for [3]radialene[5] or its analogues.[6] This cycloaddition would provide a route to the highly strained bicyclo[4.1.0] olefins with a double bond at the bridge. We here describe the synthesis and properties of some six-membered ring-fused thiirene *S*-oxides.

Results and Discussion

Synthesis of Fused Thiirene *S*-Oxides. When **5** was treated with an equimolar amount of 4-methyl-1,2,4-triazoline-3,5-dione (MTAD) in CH_2Cl_2 at room temperature, the red color of MTAD rapidly disappeared and a single product **6a** was obtained as colorless crystals in quantitative yield.[7] Likewise, **5** added to 4-phenyl-1,2,4-triazo-

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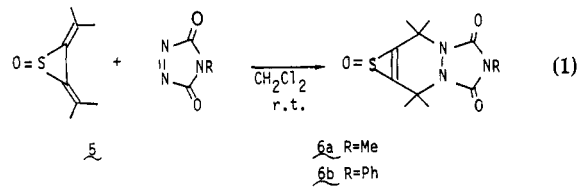
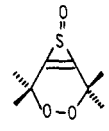
line-3,5-dione to give **6b** (eq 1). The products were



(1)

characterized as thiirene *S*-oxides by ^{1}H NMR, ^{13}C NMR, and IR spectra and elemental analyses. In the ^{13}C NMR spectra of **6a** and **6b** the resonances at 153.2 and 153.5 ppm, respectively, were assigned to the olefinic carbon by comparison with those found for **4** (137.3),[3] diisopropylcyclopropenone (160.9),[8] diphenylcyclopropenone (148.7),[9] and cyclopropenone **3** (169.0).[2n] In the IR spectra of **6a** and **6b** the stretching vibrational absorption due to the S–O bond appears at the unusually high frequency of 1115 cm^{-1}.

We explored the reaction of **5** with singlet oxygen, which has dienophilic reactivity similar to that of triazolinediones. Photosensitized oxygenation of **5** in benzene at room temperature gave a colorless crystalline product in 72% yield after purification by preparative HPLC. This product was characterized as a new thiirene *S*-oxide with a fused endoperoxide ring,[10] **7**, from spectroscopic data.



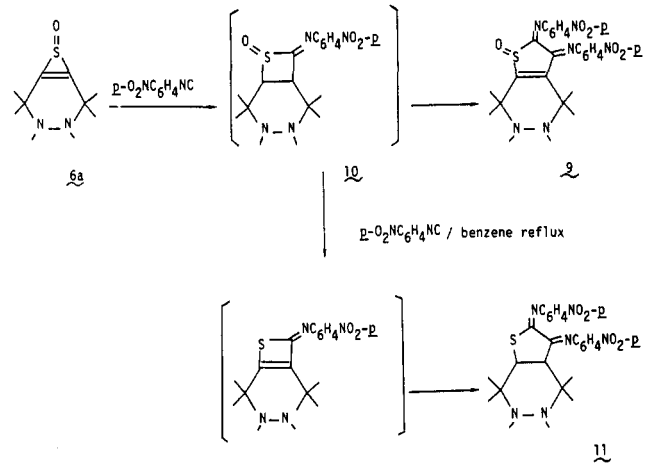
The high frequency of the IR absorption for S–O at 1115 cm^{-1}, as in **6**, and the highly downfield shifted olefinic ^{13}C NMR resonance at 155.5 ppm are characteristic of a fused thiirene *S*-oxide. In the ^{1}H NMR spectrum, two singlets at 1.63 and 1.67 ppm for four methyl groups also support the structure **7**. These signals suggest that **7** exists in a nonplanar conformation in which conformational interconversion is slow.

Compounds **6** and **7** are the first examples of alkyl-substituted thiirene *S*-oxides and are interesting as highly strained bicyclic olefins. Accordingly, we carried out an X-ray crystallographic analysis of **6a**.

Crystal Structure of the Fused Thiirene *S*-Oxide 6a. In the crystalline state of **6a** all bonds are approximately 0.01 Å shorter than those in **4**. This shortening may reflect the increase in π-bond character over the three-membered ring and the attached S–O bond, which may be attributed to the combined effects of ring fusion and alkyl substitution. The angle between the sulfoxide oxygen and the thiirene ring is 63.9°. Although the bond angle of C_1–S_1–C_2 of **6a** (42.8°) is comparable to that of **4** (42.9°), the C_4–C_1–C_2 and C_1–C_2–C_3 angles (130.1° and 128.0°) are ca. 20° smaller than those in diisopropylcyclopropeneone (151.9° and 152.7°).

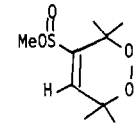
Another feature is the nonplanar structure around the bridge double bond of **6a**. In the crystalline state, the dihedral angle at the C=C bridge double bond is 15.5°. This phenomenon was suggested by Pople[11] and Wagner[12]

Scheme I



in their calculations on the [*n*.1.0] bicyclic olefin system and has been confirmed by Ando et al.[13] Thus the used thiirene *S*-oxide has highly strained σ and π bonds and should be more reactive than the nonfused **4**.

Chemical Properties of the Fused Thiirene *S*-Oxides. Treatment of **7** with excess methanol in chloroform resulted in the formation of sulfinic ester **8** (71%)



by nucleophilic attack of methanol on the sulfur atom. In contrast, **4** does not react with methanol under these conditions, although it does undergo ring opening with methoxide ion.[14] These results suggest that the reactivity of the thiirene *S*-oxide ring is increased by ring fusion.

Treatment of **6a** with 4 equiv of *p*-nitrophenyl isonitrile at room temperature (Scheme I) resulted in the formation of 2,3-diimino sulfoxide **9** (86%) as stable red crystals.[15] The formation of **9** can be explained by the insertion of 2 mol of the isonitrile into the C–S bond of **6a** through the intermediate imino thiet sulfoxide **10**. A similar reaction has been reported by Takizawa et al.[16] On the other hand, reaction of **6a** with 4 equiv of *p*-nitrophenyl isonitrile in refluxing benzene afforded the 2,3-diimino derivative **11** (66%), which is a stable red crystalline compound.[17] The structure of **11** was assigned on the basis of spectroscopic and elemental analysis and was confirmed by X-ray crystal analysis. Since **9** was not deoxygenated in the presence of excess *p*-nitrophenyl isonitrile in refluxing benzene, **11** is probably derived by deoxygenation of **10**.

When the thiirene *S*-oxide **7** was dissolved in excess furan at room temperature, a single crystalline product was

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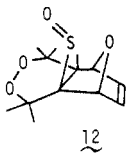
(15) Elemental analysis suggested the crystals (mp 82–83 °C) recrystallized from carbon tetrachloride contained 2 mol of carbon tetrachloride. However, crystals recrystallized from benzene–hexane (mp 205–270 °C) contained no solvent molecule.
(16) Obata, N.; Takizawa, T. *Tetrahedron Lett.* **1969**, 3403.
(17) The crystals (140–143 °C) recrystallized from carbon tetrachloride contained 2 mol of carbon tetrachloride. X-ray crystal analysis also indicated contamination by carbon tetrachloride but X-ray analysis of **12** could not be achieved owing to problem of analysis of reflections. Recrystallization from benzene–hexane gave crystals (mp 150–151 °C) containing no solvent molecules, which were used for the X-ray analysis.

obtained in 86% yield. The structure **12** assigned to this



12

product by spectroscopic and elemental analysis data was confirmed as a [2 + 4] cycloadduct by X-ray crystal analysis. The crystal structure of the adduct **12** clearly indicated that the cycloaddition proceeds stereospecifically by endo addition. This compound is the first example of a propellane containing the thiirane *S*-oxide moiety. The driving force for the formation of **12** is release of the ring strain of **7** by the cycloaddition. In contrast, **4** did not react with furan at 80 °C in a sealed tube.

X-ray crystal data for **12** suggest that the thiirane ring is slightly "lanky", as expected for a propellane thiirane *S*-oxide. In comparison with the structure of ethylene sulfoxide obtained by microwave analysis,[18] the bond length of S_1–C_1 (1.869 Å) or S_1–C_2 (1.885 Å) is ca. 0.05 Å longer, whereas C_1–C_2 (1.481 Å) is 0.02 Å shorter, and therefore the angle C_1–S_1–C_2 (46.4°) is 2° smaller. However, the S–O bond length (1.479 Å) is comparable to that of ethylene episulfide (1.483 Å), as suggested by its IR absorption at 1067 cm^{-1}.

Experimental Section

^1H NMR spectra were recorded at 60 MHz with a Varian EM-360A spectrometer; chemical shifts (δ) are expressed in parts per million downfield from internal tetramethylsilane. ^{13}C NMR spectra were recorded with JEOL FX-90Q spectrometer. IR spectra were obtained on a Hitachi 215 infrared spectrometer. Column chromatography was performed on Merck Kieselgel 60 (70–230 mesh). HPLC was carried out on a liquid chromatograph LC-08 (Nippon Bunseki Kogyo Co., Ltd.); column: JAIGEL-^1H (20 mm × 600 mm); carrier solvent, chloroform; RI detecter.

Thiiranoradialene *S*-Oxide (5). Synthesis of **5** was reported previously:[4] colorless crystals, mp 58.0–58.5 °C; ^1H NMR ($CDCl_3$) δ 2.17 (s, 6 H), 2.22 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 23.0 (q), 23.4 (q), 125.2 (s), 131.2 (s); IR (KBr) 1035 cm^{-1} ($\nu_{S=O}$).

Thiirene *S*-Oxide 6a. To a solution of **5** (156 mg, 1 mmol) in 10 mL of dichloromethane was added powdered 4-methyl-1,2,4-triazoline-3,5-dione (1113 mg, 1 mmol) at room temperature. After the red color due to the triazolinedione rapidly disappeared, the solution was concentrated in vacuo to yield **6a** quantitatively. The sample for X-ray crystal analysis was further purified by recrystallization from carbon tetrachloride at low temperature (ca. −10 °C): colorless crystals, mp 104–107 °C dec; ^1H NMR ($CDCl_3$) δ 1.87 (s, 6 H), 1.93 (s, 6 H), 3.10 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 22.7 (q), 23.3 (q), 25.1 (q), 64.7 (s), 153.2 (s), 154.0 (s); IR (KBr) 2975_w, 2925_w, 1698_s, 1460_s, 1115_s ($\nu_{S=O}$) cm^{-1}. Anal. Calcd for $C_{11}H_{15}N_3O_3S$: C, 49.05; H, 5.61; N, 15.60; S, 11.90. Found: C, 48.80; H, 5.56; N, 15.41; S, 12.07.

Thiirene *S*-Oxide 6b. Thiirene *S*-oxide **6b** was prepared in quantitative yield by the same procedure used for **6a**: colorless crystals, mp 104–107 °C dec; ^1H NMR ($CDCl_3$) δ 22.3 (q), 23.0 (q), 64.8 (s), 125.4 (d), 128.0 (s), 128.7 (d), 130.4 (s), 151.4 (s), 153.5 (s); IR (KBr) 3050_w, 2950_w, 2900_w, 1690_{sc}, 1400_s, 1115_s ($\nu_{S=O}$) cm^{-1}.

Thiirene *S*-Oxide 7. A solution of **5** (156 mg, 1 mmol) in 30 mL of benzene was irradiated in the presence of ca. 70 mg of tetraphenylporphyrin with a 500-W halogen lamp for 2 h at 20 °C. To monitor the reaction progress by ^1H NMR, aliquots were withdrawn from the reaction mixture at 30-min intervals. After completion of the reaction, the mixture was concentrated under reduced pressure. The residue was purified by high pressure liquid chromatography (eluent, toluene), giving almost pure **7** as colorless crystals (135 mg; 72%). The crude product was recrystallized from carbon tetrachloride at low temperature (ca. −10 °C): mp 103° C dec; ^1H NMr ($CDCl_3$) δ 1.63 (s, 6 H), 1.67 (s, 6 H); ^{13}C NMR ($CDCl_3$) 22.8 (q), 23.6 (q), 85.5 (s), 115.5 (s); IR ($CDCl_3$) 1115 ($\nu_{S=O}$) cm^{-1}.

X-ray Crystal Analysis of Thiirene *S*-Oxide 6a. The crystal has monoclinic space group $p2/n$ with a = 15.208 (2), b = 6.083 (1), and c = 16.139 (2) Å and β = 117.06 (1)° with Z = 4. Intensity data were collected on a four-circle diffractometer with graphite-monochromated Cu/Kα radiation. Of 2457 reflections obtained with $2\theta < 158°$, 1691 had intensities greater than $3\sigma F_o$ and were used for structure analysis. The structure was refined to a value of 0.058.

Reaction of 7 with Methanol. To solution of thiirene *S*-oxide **7** (188 mg, 1 mmol) in 10 mL of chloroform was added methanol (3 mL) at room temperature. After 3 h of stirring, the reaction mixture was concentrated and separated by high pressure liquid chromatography to give sulfinic ester **8** (156 mg, 71%): colorless crystals, mp 42.0–42.5 °C; ^1H NMR ($CDCl_3$) δ 1.39 (s, 3 H), 1.46 (s, 3 H), 1.49 (s, 3 H), 1.53 (s, 3 H), 3.65 (s, 3 H), 6.66 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 24.3 (q), 24.7 (q), 49.9 (q), 78.3 (s), 79.3 (s), 137.4 (d), 146.0 (s); IR (KBr) 1121_s ($\nu_{S=O}$) cm^{-1}; EIMS, m/e 226 (M^+). Anal. Calcd for $C_9H_{16}O_4S$: C, 49.07; H, 7.32. Found: C, 49.00; H, 7.38.

Reaction of 6a with *p*-Nitrophenyl Isonitrile at Room Temperature. To a solution of thiirene *S*-oxide **6a** (269 mg, 1 mmol) in 10 mL of benzene was added *p*-nitrophenyl isonitrile (592 mg, 4 mmol) at room temperature. After 1 day of stirring, the reaction mixture was concentrated under reduced pressure and the residue was separated by high pressure liquid chromatography. The product 2,3-diimino-2,3-dihydrothiophene *S*-oxide **9** (485 mg, 86%) was purified by recrystallization from carbon tetrachloride: red crystals (mp 82–83 °C; ^1H NMR ($CDCl_3$) δ 1.80 (s, 3 H), 1.90 (s, 3 H), 2.16 (s, 3 H), 2.24 (s, 3 H), 3.15 (s, 3 H), 7.10 (d, 2 H, J = 9.6 Hz), 7.18 (d, 2 H, J = 9.6 Hz), 8.38 (d, 4 H, J = 9.6 Hz); ^{13}C NMR ($CDCl_3$) δ 21.1 (q), 22.9 (q), 24.1 (q), 25.2 (q), 61.5 (s), 61.9 (s), 1179.8 (d), 120.2 (d), 125.1 (d), 144.4 (s), 146.1 (s), 146.5 (s), 149.8 (s), 150.3 (s), 153.6 (s), 153.8 (s), 154.1 (s), 159.3 (s), 159.8 (s); IR (KBr) 1705_s, 1580_s, 1340_s, 1105_m; EIMS, m/e 565 [M^+]. Anal. Calcd for $C_{25}H_{23}N_7O_7S + 2CCl_4$; C, 37.14; H, 2.65; N, 11.13. Found: C, 37.50; H, 2.74; N, 11.18.

Reaction of 6a with *p*-Nitrophenyl Isonitrile in Refluxing Benzene. To a refluxing solution of **6a** (269 mg, 1 mmol) in 10 mL of benzene was added *p*-nitrophenyl isonitrile (592 mg, 4 mmol). After being refluxed for 1 h, the reaction mixture was concentrated under reduced pressure and the residue was purified by high pressure liquid chromatography. 2,3-Diimino-2,3-dihydrothiophene **11** was recrystallized from carbon tetrachloride (365 mg, 65%): red crystals (mp 140–143 °C); ^1H NMR ($CDCl_3$) δ 1.81 (s, 6 H), 2.03 (s, 6 H), 3.16 (s, 3 H), 7.01 (d, 2 H, J = 9.6 Hz), 7.04 (d, 2 H, J = 9.6 Hz), 8.04 (d, 4 H, J = 9.6 Hz); ^{13}C NMR ($CDCl_3$) δ 22.4 (q), 24.0 (q), 25.0 (q), 60.7 (s), 62.0 (s), 116.5 (d), 119.7 (d), 125.1 (d), 129.5 (s), 143.4 (s), 145.7 (s), 153.5 (s), 153.8 (s), 155.2 (s), 156.1 (s); IR (KBr) 1705, 1575, 1335, 1100 cm^{-1}; EIMS, m/e 549 [M^+]. Anal. Calcd for $C_{25}H_{23}N_7O_6S + 2CCl_4$: C, 37.83; H, 2.70; N, 11.44. Found: C, 37.75; H, 2.70; N, 11.51. Compound **9** did not react with *p*-nitrophenyl isonitrile under these conditions.

X-ray Crystal Analysis of 11. The crystal has tricyclic space group ($P\bar{1}$) with a = 10.383, b = 10.241, and c = 13.393 Å and α = 84.88°, β = 89.77°, γ = 68.23° with Z = 2. Intensity data were collected on a four-circle diffractometer with graphite-monochromated Mo/Kα radiation. Independent reflections (1812) with 2θ values up to 40° [$F_o > 3F_o$] were used for structure analysis. The structure was refined to a final value of R = 0.115.

Reaction of 7 with Furan. Compound **7** (100 mg, 0.53 mmol) was dissolved in furan. After standing for 1 h, excess furan was removed under reduced pressure. The residue was purified by column chromatography (silica gel/dichloromethane–ethyl acetate) to give the pure adduct **12** (117 mg, 86%) which was recrystallized from carbon tetrachloride for X-ray analysis: colorless crystals (mp 113 °C dec): ^1H NMR ($CDCl_3$) δ 1.39 (s, 6 H), 1.90 (s, 6 H), 5.22 (s, 2 H), 6.71 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.0 (q), 26.9 (q), 62.7 (s), 80.1 (s), 81.6 (d), 137.8 (d); IR (KBr) 1067 ($\nu_{S=O}$) cm^{-1}; EIMS, m/e 208 [M^+ − SO]. Anal. Calcd for $C_{12}H_{16}O_4S$: C, 56.23; H, 6.29. Found: C, 56.29; H, 6.29.

X-ray Crystal Analysis of 12. The crystal has monoclinic space group $P2_1$ with a = 16.280 (4), b = 10.588 (6), and c = 16.117 (5) and β = 117.81 (2)° with Z = 8. Intensity data were collected

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on a Rigaku automated four-circle diffractometer with graphite-monochromated Mo/K_α radiation. Of 5837 reflections obtained with $2\theta < 55°$, 2467 with $|F| > 3(F)$ were used for structure analysis. The structure was refined to a final value of $R = 0.053$.

Acknowledgment. The author is especially appreciative of X-ray crystal analyses by Drs. M. Goto, National Chemical Laboratory for Industry, K. Ueno, Research Institute for Polymers and Textile, K. Kobayashi and T. Sakurai, the Institute of Physical and Chemical Research.

Supplementary Material Available: X-ray bond lengths and angles for crystals of compounds **6a**, **11**, and **12** (14 pages). Ordering information is given on any current masthead page.

Notes

Reaction of 1-Methyl-2,3-dinitropyrrole with Methoxide Ion

Audrey Di Lorenzo, Paolo Mencarelli,* and Franco Stegel*

Centro CNR di Studio sui Meccanismi di Reazione, Dipartimento di Chimica, Università di Roma La Sapienza, 00185 Roma, Italy

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The pattern of the reaction of nucleophilic reagents with dinitro derivatives of five-membered heterocyclic rings (such as thiophene[1-3] and pyrrole ring[4-6]) is dependent upon the structure of the substrate and the reaction conditions.

In previous papers we described the interaction of 2,4-,[4] 2,5-,[2] and 3,4-dinitro-substituted 1-methylpyrroles[5,6] with nucleophilic reagents. Of these compounds 1-methyl-2,5-dinitropyrrole is the only one that undergoes a direct aromatic substitution reaction. It was found that the reactivity of this para-like dinitro-substituted pyrrole is much lower than that of 2,5-dinitrothiophene and 2,5-dinitrofuran, and is comparable to that of *p*-dinitrobenzene, even if the reactivity ratios are dependent upon the nucleophile.

In order to complete the picture of the reactivity of 1-methyl dinitropyrroles toward nucleophilic reagents, we have now studied the course of the reaction of 1-methyl-2,3-dinitropyrrole (**1**) with methoxide ion in methanol, and have compared the reactivity of **1** with that of *o*-dinitrobenzene and 2,3-dinitrothiophene.

Results

Our first aim has been to ascertain the course of the reaction of **1**, and, more particularly, to determine whether a denitration reaction, similar to that reported for the reaction of 1-methyl-2,5-dinitropyrrole, was occurring. Indeed it was found that methoxide ion affords the substitution reaction only. The substitution occurs regiospecifically at the 2-position to yield 2-methoxy-1-methyl-3-nitropyrrole (**2**). The structure of the methoxy denitration product was deduced from its NMR spectral features and was confirmed from the fact that upon further nitration **2** yields 2-methoxy-1-methyl-3,5-dinitropyrrole, which had been previously obtained upon methoxy denitration of 1-methyl-2,3,5-trinitropyrrole.[7] In order to ascertain whether the regiospecificity could be affected by the nature of the nucleophile, the substitution was carried out also with *p*-methylbenzenethiolate ion in methanol, which gives a very small amount of substitution at the 3-position (<1%), in addition to substitution at the 2-position as the major reaction.

Table I. Kinetic and Activation Data for the Methoxy Denitration Reaction of Compound 1, 1-Methyl-2,5-dinitropyrrole, and Related Benzene Compounds in MeOH, at 25 °C

compd	k_2, M^{-1} s^{-1}	$\Delta H^{\ddagger}$,[a] kcal mol^{-1}	$-\Delta S^{\ddagger}$,[a] cal $°C^{-1}$ mol^{-1}
1	4.04×10^{-4}	20.2 (0.15)[b]	6.5 (0.46)
1-methyl-2,5-dinitropyrrole[c,d]	1.36×10^{-3}	20.4 (0.2)	3.4 (0.7)
o-dinitrobenzene[c,e]	7.10×10^{-5}	19.4 (0.4)	12.6 (1.3)
p-dinitrobenzene[c,e]	1.70×10^{-4}	21.8 (0.1)	2.5 (0.4)

[a] Standard deviation in parentheses. [b] $k_2 \times 10^3$, M^{-1} s^{-1} (°C): 2.17 (40.1), 4.18 (46.3), 8.5 (53.1), 16.1 (60.2). [c] Corrected for the statistical factor. [d] Reference 7. [e] Calculated from data reported by: Tommila E.; Murto, J. *Acta Chem. Scand.* **1962**, *16*, 53.

It may be of interest to compare the reactivity pattern of **1** with that of 2,3-dinitrothiophene.[8] In the latter substrate the denitration reaction occurs competitively at both 2- and 3-positions, the 2/3 ratio increasing in the presence of polarizable nucleophilic reagents.[8] In any case the substitution of 2,3-dinitrothiophene occurs mainly at the 3-position, at variance with what is observed in the reaction of **1**. The difference between the behavior of the pyrrole and the thiophene derivative can be related to the presence of different heteroatoms. It can be expected that the more electronegative nitrogen atom should favor specifically a nucleophilic attack to the adjacent reaction center. Moreover, the presence of the methyl group at position 1 of **1** can somewhat affect the reactivity of the pyrrole ring. The methyl group could lower the degree of conjugation of the 2-nitro group, which is the more sensitive to steric effects because it is situated between two rather bulky groups,[9] and decrease the rate of nucleophilic attack to the 3-position. At the same time the greater conjugation of the 3-nitro group in the initial state makes more difficult an attachment at that position with respect to the attack at the 2-position. The formation of the intermediate with sp^3 hybridization at the 2-position is expected to occur with steric release, and therefore could be further favored. According to this hypothesis it is reasonable that a small amount of the 3-substitution product

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