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 $R = 0.053$.

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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

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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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is formed in the reaction of 1 with the thiolate ion. In fact, since the thiolate ion is more polarizable than methoxide ion, the corresponding transition state for the formation of the intermediate σ adduct should be looser with thiolate ion than with methoxide ion, and therefore steric effects should be less important in the former.

Kinetic and activation data for the methoxy denitration of 1 are reported in Table I, together with related literature data for the methoxy denitration of 1-methyl-2,5-dinitropyrrole and *o*- and *p*-dinitrobenzene. These data show that the reactivity of the 2,3-dinitropyrrole derivative is lower by a factor of 3.4 than the reactivity of the 2,5-dinitropyrrole derivative. This behavior is similar to that of the related *o*- and *p*-dinitrobenzene in the same reaction, which shows a lower reactivity of the ortho derivative by a factor of 2.4.

In the methoxy denitration reaction the dinitropyrrole derivatives tested so far are nearly 1 order of magnitude more reactive that the corresponding benzene derivatives. The activation data are not very different and cannot give an unequivocal interpretation of the small rate differences observed in the methoxy denitration reaction. However, it can be observed that the reactions of the ortho-like compounds are characterized by a more negative activation entropy, which seems to be the more significant factor in determining the reactivity order between ortho- and para-like compounds.

Experimental Section

Melting points are uncorrected. ^{1}H NMR measurements were carried out with a WP 80 SY Bruker spectrometer, unless otherwise stated. Mass spectra were obtained with a VG 7070F instrument. The kinetic measurements were carried out spectrophotometrically in the thermostated cell compartment of a Cary 219 instrument. An excess of sodium methoxide was present, so that the reactions occurred under pseudo-first-order conditions. The kinetics were followed at the wavelength corresponding to the largest absorbance change in going from 1 to the substitution product (250 nm). Owing to the high methoxide ion concentration, the ionic strength was kept constant by adding $NaClO_4$.

1-Methyl-2,3-dinitropyrrole (1) was prepared by dinitration of 1-methylpyrrole and separated from its isomers according to a described procedure.[10]

2-Methoxy-1-methyl-3-nitropyrrole (2). Sodium methoxide (0.44 mol) was added to a solution of 1 (0.20 g, 0.11 mol) in 5 mL of methanol kept at 45 °C. After 90 min the excess of sodium methoxide was neutralized with dilute HCl. The solution was repeatedly extracted with ethyl ether. The ether solution was dried and evaporated to yield 0.17 g (yield 93%) of a white solid: mp (CCl_4) 82–82.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.48 (s, 3 H, NCH_3), 4.10 (s, 3 H, OCH_3), 6.17 (d, 1 H, J = 3.9 Hz); 6.57 (d, 1 H, J = 3.9 Hz); ^{13}C NMR ($CDCl_3$) δ 31.8 (NCH_3), 62.5 (OCH_3), 103.7 (C-4), 113.7 (C-5), 121.9 (C-3), 145.3 (C-2); UV (MeOH) λ_{max} 278, 334 nm; mass spectrum, calcd for $C_6H_8N_2O_3$ (M^+) m/e 156.05354, found 156.0538.

Nitration of 2 was carried out at 0 °C by adding 1 mL of a nitrating mixture (made up from 0.5 mL of 90% HNO_3 and 20 mL of acetic anhydride) to a solution of 80 mg of 2 in 5 mL of acetic anhydride. After 4 h the reaction mixture was poured into water and, after hydrolysis of the anhydride, extracted with ethyl ether (4 × 50 mL). The ether extracts were washed with a saturated $NaHCO_3$ solution, water, and finally dried (Na_2SO_4). The residue after evaporation of the solvent was chromatographed (silica gel, 9:1 benzene–ethyl acetate) to yield 30 mg of 2-methoxy-1-methyl-3,5-dinitropyrrole (mp 85–86 °C, lit.[7] 86–86.5 °C) together with some unreacted 2.

Reaction of 1 with Sodium *p*-Methylbenzenethiolate. Sodium methoxide (0.38 mL of a 4.64 M methanol solution) was added to a solution of 0.3 g of 1 and 0.27 g of *p*-methylbenzenethiol kept at 30 °C. After 10 min the reaction was complete. TLC analysis (silica gel, benzene) showed the presence of two compounds that were separated chromatographically (Merck 10401 Lichroprep Lobar, 4:1 benzene–ethyl acetate). The main product (0.375 g, yield 86%) was eluted first: mp 110–110.5 °C; ^{1}H NMR ($CDCl_3$) δ 2.20 (s, 3 H, Me-Ar), 3.62 (s, 3 H, MeN), 6.77 (d, 1 H, J = 3.32 Hz), 6.90 (d, 1 H, J = 3.32 Hz), 7.07 (pseudo-s, 4 H, (C_6H_4)); ^{13}C NMR ($CDCl_3$) δ 20.8 (MeAr), 35.2 (MeN), 128.1, 130.1, 130.9, 136.9 for the benzene ring, 106.9 (pyrrole C-4), 121.8 (pyrrole C-3), 123.8 (pyrrole C-5), 139.0 (pyrrole C-2); UV (MeOH) λ_{max} 238 nm; mass spectrum, calcd for $C_{12}H_{12}N_2O_2S$ (M^+) m/e 248.06206, found 248.0592.

The minor isomer (4 mg, yield 0.9%) did not lend itself to further purification and was characterized only through the following features: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.39 (s, 3 H), 3.97 (d, 1 H, J = 0.45 Hz), 5.46 (d, 1 H, J = 2.96 Hz), 6.65 (dd, 1 H, J = 0.45, 2.96 Hz), 7.25 (d, 2 H, J = 8.1 Hz), 7.50 (d, 2 H, J = 8.1 Hz); mass spectrum (M^+), m/e 248.

The structural assignment to the products of *p*-methylbenzenethiolate denitration was based upon the fact that both substitution products display a coupling constant which is in agreement with a 2,3-disubstitution pattern.[10] Moreover, the α hydrogen differs from the β hydrogen because of a weak coupling (nearly 0.5 Hz) which is usually responsible for a lower resolution in the former signal. This fact allows an easy identification of the substitution pattern when the effect of the substituents is considered.

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Registry No. 1, 72795-78-9; 2, 101493-73-6; 2-methoxy-1-methyl-3,5-dinitropyrrole, 89998-66-3; 1-methyl-2-((4-methylphenyl)thio)-3-nitropyrrole, 101493-74-7; *p*-methylbenzenethiol, 106-45-6.

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Regioselective Conversion of Allylic Alcohols to 1-Propenes via Organoiron Complexes

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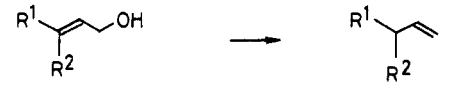
Regioselective reduction of 2-propen-1-ols (allylic alcohols) to 1-propenes with a transposition of the allylic double bond (eq 1) is an important process in synthetic



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chemistry. Recent development of this reaction involves the lithium aluminum hydride reduction of allylic phosphonates[1] and triphenylphosphonium salts[2] and protolysis of allylic stannanes,[3] which are derived from allylic alcohols. We describe here a general method for this purpose which utilizes the characteristics of iron carbonyl complexes.[4] This process involves the successive transformation of allylic alcohols 1, via allylic phosphates 2, (η^1-allyl)$Fe(CO)_2Cp$ (3), and (η^2-olefin)$Fe(CO)_2Cp$ complexes 4 to 1-propenes 5 (Scheme I). As an application of the

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