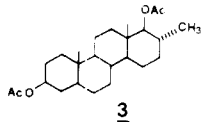
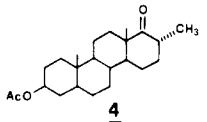
trobenzene at 85 °C (75% yield in 30 min). In toluene as solvent, no reaction occurred at 80 °C. At 100 °C, the formation of a mixture of products was ascertained, but the uranediol yield was only 20%.

The product [mp 209–211 °C (lit.[2] mp 211–213 °C); $[\alpha]_D$ 3.5° ($CHCl_3$) (lit.[5] $[\alpha]_D$ 3.7°)] has been unequivocally identified through its derivatives **3** and **4**. The former [mp 158–160



3



4

°C (lit.[6] mp 160 °C)] shows the same NMR spectrum reported in the literature[6] (see Experimental Section). Compound **4** [mp 169–171 °C (lit.[6] mp 171 °C); $[\alpha]_D$ −36° (lit.[6] $[\alpha]_D$ −38°)] was obtained through the oxidation of **2** with CrO_3, selective reduction with $NaBH_4$ at C-3, and acetylation of the corresponding alcohol.

The improvement of the above synthesis as compared to the previous procedure is relevant. The latter involved the formation of 5α-pregnane-3β,20β-diol 3-acetate 20-tosylate and rearrangement in formic acid at 23 °C to yield uranediol 3-acetate 17a-formate and uranediol.[3,6]

A relevant feature of the reported synthesis is that $Pd(PhCN)_2Cl_2$ reacts more rapidly at the C-20 alcoholic group than at C-3, although the C-3 position has been shown to be chlorinated by the complex.[7] This selectivity, necessary for the successful course of the reaction, is qualitatively shown by the reaction time for the uranediol synthesis (30 min) as compared to the formation time of the 3-chlorocholestanes (180 min).

In contrast, when $Pd(PhCN)_2Cl_2$ was made to react in the same experimental conditions with 5α-pregnane-3β,20α-diol and with its 3-acetate derivative, 17β-methyl-18-nor-5α,17α-pregn-13-en-3β-ol (or its 3-acetate derivative) was isolated in 90% yield, together with a small amount of 5α-pregn-17-en-3β-ol (5%). The difference in the course of the reactions of the two pregnane epimers and the relationship of the products structure to the C-20 configuration of the starting compound is completely similar to the results obtained by Hirschmann et al. in the formolysis of 3β-acetoxy-5α-pregnan-20α-yl tosylate and of its 20-epimer.[8] This analogy suggests that in the *D*-homoannulation promoted by the complex, the preliminary coordination of the C-20 hydroxyl group to Pd(II) occurs with the formation of a complex such as $Pd(PhCN)(ROH)Cl_2$. In the next steps, the complex anion $Pd(PhCN)(OH)Cl_2^-$ probably behaves as a good leaving group, just as the tosylate group in the Hirschmann synthesis does.[6,8]

Experimental Section

Uranediol (2). 5α-Pregnane-3β,20β-diol (**1**, 200 mg) was dissolved in nitrobenzene (5 mL) and $Pd(PhCN)_2Cl_2$ (240 mg) was added. The yellow-brown solution was warmed at 80 °C for 30 min with stirring. After the solution was cooled, diethyl ether was added and then water. The ethereal extracts were evaporated and the residue was chromatographed on a silica gel column by eluting with benzene–ether 7:3. A first band of unidentified products was obtained, then 140 mg of uranediol was recovered. The crystallization from $CHCl_3$–hexane afforded needles: mp 209–211 °C (lit.[2] mp 211–213 °C); $[\alpha]_D$ +3.5 (lit.[5] + $[\alpha]_D$ +3.7).

Anal. Calcd for $C_{21}H_{36}O_2$: C, 78.70; H, 11.32. Found: C, 78.75; H, 11.27.

Uranediol Diacetate (3). By acetylation with Ac_2O–piridine, **2** gave the diacetyl derivative **3**: mp 158–160 °C (from MeOH–CH_2Cl_2) (lit.[6] mp 160 °C); $[\alpha]_D$ 28.0° (lit.[6] $[\alpha]_D$ 30°). The NMR spectrum of **3** is as follows: 0.85 (s, 18-H), 0.79 (s, 19-H), 0.75 (d, 17-CH_3), 2.00 and 2.05 (s, 3-OAc, 17a-OAc), 4.33 (d, 17a-H).

Anal. Calcd for $C_{15}H_{40}O_4$: C, 74.20; H, 9.97. Found: C, 74.35; H, 10.02.

Uranol-17a-one Acetate (4). **2** (100 mg) dissolved in acetone (10 mL, distilled on $KMnO_4$) was treated for 2 min with stirring with 0.46 mL of an aqueous solution of H_2CrO_4 (8 N). After 5 min, the excess oxidant was destroyed with methanol. After addition of water and extraction with ether, the ethereal phase was washed with aqueous $NaHCO_3$ and then with water to neutrality. After evaporation of the solvent, the residue was chromatographed on a SiO_2 column by eluting with hexane–ether 4:1; 95 mg of the diketone was obtained. The diketone was selectively reduced with $NaBH_4$ (11 mg) in 14 mL of a mixture of CH_3OH–dioxane (1:1) (room temperature, 15 min). After hydrolysis and extraction with ether, the residue was chromatographed on a SiO_2 column by eluting with benzene–ether (4:1). The reaction product (30 mg) was acetylated by standard procedure to **4**. Crystals (from hexane–ether): mp 169–171 °C (lit.[6] mp 171 °C); $[\alpha]_D$ −36° (in $CHCl_3$) (lit.[6] $[\alpha]_D$ −32°).

17β-Methyl-18-nor-5α,17α-pregn-13-en-3β-ol (5). 5α-Pregnane-3β,20α-diol 3-acetate (100 mg) was dissolved in nitrobenzene (1.5 mL) and $Pd(PhCN)_2Cl_2$ (104 mg) was added. The yellow-brown solution was warmed at 85 °C for 2 h with stirring. After the solution was cooled, diethyl ether was added and then water. The residue from the ethereal extracts was chromatographed on a silica gel column by eluting with ether–hexane (5:1). The first band was the 3-acetate of **5** (25 mg); the second contained *trans*-3β-acetoxy-5α-pregn-17-ene (**6**). After eluting the residue with ether–hexane (3:7), a third yellow band was eluted, which afforded after evaporation a yellow-brown product. It was probably a complex between Pd(II) and the alkene **5** (as 3-acetate), since by treatment with $LiAlH_4$ **5** was quantitatively obtained. **5** was identified by mp [130–133 °C (lit.[8] mp 128.5–131 °C)], the NMR[8] and IR[8] spectra, and the catalytic hydrogenation to 17β-methyl-18-nor-5α,13ξ,14ξ,17α-pregnan-3β-ol [mp 119–121 °C from hexane; lit.[8] mp 122–123.5 °C)]. Crystals of **6** (from methanol) melted at 122–125 °C (lit.[9] mp 120–121.5 °C).

When 5α-pregnane-3β,20α-diol was submitted to the same reaction, the course was just the same. 5α-Pregn-17-en-3β-ol was identified by its mp, 135–136 °C (from methanol) (lit.[9] 136–137 °C).

Acknowledgment. This work is dedicated to Professor L. Panizzi on the occasion of his 70th birthday.

Registry No. —**1**, 516-53-0; **2**, 516-51-8; **3**, 4975-29-5; **4**, 2521-29-1; **5**, 33299-99-9; **5** acetate, 33300-00-4; **6**, 16374-33-7; 5d-pregnane-3β,20d-diol 3-acetate, 33299-98-8; $Pd(PhCN)_2Cl_2$, 14220-64-5.

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Nitration of 1-R-Pyrroles: Formation of Polynitro-1-R-pyrroles and Orienting Effects in the Reactions of 3-Nitro-1-R-pyrroles

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Received November 27, 1978

Electrophilic substitutions of the pyrroles[1] and five-membered heterocycles as a group[2] have been recently reviewed. We now report briefly two further aspects of the nitration of pyrrole derivatives.

A. Formation of Polynitropyrrole Derivatives. The formation of polyhalogenopyrroles upon electrophilic halogenation is well known[1] and is favored by the fact that the

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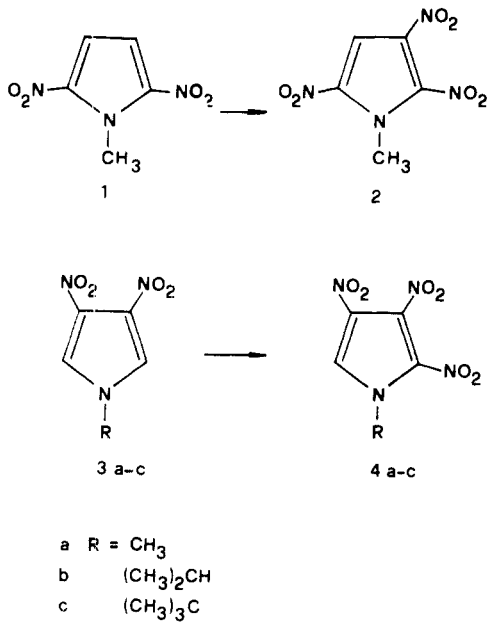
Scheme I



moderate deactivating effect of the halogen atoms is largely overwhelmed by the activating power of the heteroatom. We have now found that formation of polynitropyrroles occurs smoothly under relatively mild conditions and in good yields despite the presence of powerful electron-withdrawing substituents.

1. Formation of Trinitro Derivatives. The synthesis of each of the isomeric 1-methyltrinitropyrroles occurs in an unequivocal way from 2,5-dinitro- and 3,4-dinitro-1-methylpyrrole, respectively, in H_2SO_4 at 0 °C (Scheme I). Under the same reaction conditions, the nitration of other 3,4-dinitro-1-alkylpyrroles (**3b,c**) yields **4b** and **4c**, respectively, whereas the nitration of 2,4-dinitro-1-methylpyrrole yields a mixture of **2** and **4a** (ca. 3:2). So far 2,3,4-trinitrothiophene has been the only reported trinitro derivative of a five-membered heterocyclic ring.[3] Its synthesis did not involve the nitration of a dinitrothiophene. In principle the nitration of 3,4-dinitrothiophene could be feasible since 2-bromo-3,4-dinitrothiophene is nitrated satisfactorily to 2-bromo-3,4,5-trinitrothiophene.[3] However, attempts to obtain trinitrothiophenes by nitration of either 2,4- or 2,5-dinitrothiophenes were unsuccessful.[3] The higher reactivity of dinitropyrroles with respect to dinitrothiophenes is consistent with the trend of the relative reactivity of five-membered heteroaromatic rings in electrophilic substitution.[2]

2. Formation of a Tetranitro Derivative. 2,3,4,5-Tetranitro-1-methylpyrrole is obtained by nitration of **4a** in fuming H_2SO_4 at 65 °C. Hydrolysis of the nitrating mixture and workup operations were carried out under slightly acid conditions in order to avoid any nucleophilic reaction[4] on the tetranitro derivative. So far, this is the first five-membered heteroaromatic compound bearing four nitro groups bound to the carbon atoms.

B. Orientation in Nitration of 3-Nitro-1-R-pyrroles (5a–e). Often the main products are 2,4-dinitro derivatives (**6a–e**, Table I), whose formation would be consistent with the directing effect of the heteroatom and the nitro group. Other significant products are, however, 3,4-dinitro-1-R-pyrroles. Authentic samples of 3,4-dinitro-1-alkylpyrroles were prepared by cyclization of primary alkylamines, formaldehyde, and the dipotassium salt of 2,3,3-trinitropropanal.[5] 1-Aryl-3,4-dinitro derivatives obtained on nitration were characterized by comparison of their NMR spectra patterns with those of the 1-alkyl derivatives (presence of a low-field signal, corresponding to two equivalent pyrrole ring protons). This is, in our knowledge, the first example of electrophilic substitution yielding 3,4-substituted pyrroles. As the data of Table I show, the relative amount of the 3,4-dinitro compound increases steadily as the substituent at 1 becomes bulkier. However, the formation of these derivatives is bound also to the fact that in the pyrrole ring the α-orienting effect is not as strong as in the thiophene and in the furan rings.[6] The nitration of 3-nitropyrroles is similar to that of 3-X-thiophenes (X = CHO, CN, NO_2) in trifluoroacetic acid, yielding substantial amounts of 4-nitro-3-X-thiophenes.[7]

2,3,4-Trinitro derivatives and, in some cases, also minor amounts of 2,3,5-trinitro derivatives were identified among the reaction products. Since no unreacted 3-nitro derivative is detected at the end of the reaction and only 1 equiv of nitric acid or even slightly less is used in the nitration, it is likely that some of the substrate decomposes at the first stages of the reaction, so that the remaining part reacts with a small excess of the nitrating agent.

Table I. Relative Yields[a] in Nitration of 3-Nitro-1-R-pyrroles

	dinitro deriv.		trinitro deriv.	
R	2,4-dinitro	3,4-dinitro	2,3,4-trinitro	2,3,5-trinitro
methyl	74	13	9	4
isopropyl	66	23	11	1
tert-butyl	43	41	16	
p-nitrophenyl	75	15	10	
o-nitrophenyl	72	28		

[a] Determined by NMR or after chromatographic separation (see Experimental Section).

Table II. Nitration of 1-R-Pyrroles: Overall Yields and 2-Nitro/3-Nitro Ratios

R	% yield	2-nitro/3-nitro
methyl	34	3.15
isopropyl	62	0.56
tert-butyl	55	0.25
p-nitrophenyl	34	1.43
o-nitrophenyl	53	1.07

Experimental Section

Warning! All tri- and tetranitropyrroles must be considered potentially toxic and explosive and must be treated properly.

Trinitro-1-methylpyrroles. 2,5-,[8] 2,4-,[8] or 3,4-dinitro-1-methylpyrroles[5] (0.2–0.3 g) was dissolved in 10–15 mL of 96% H_2SO_4. A nitrating mixture made up with 1 equiv of 100% HNO_3 and 2–3 mL of 96% H_2SO_4 was added dropwise at 0 °C. The reactions of **1** and **3a** were complete within the time necessary for the addition (10–15 min). The trinitro derivatives were collected by filtration after pouring the reaction mixture into ice water.

1-Methyl-2,3,5-trinitropyrrole (**2**): yield 63%; mp 49–50 °C; mass spectrum, *m/e* 216 (M^+); NMR [$(CD_3)_2CO$] δ 4.20 (s, 3 H), 7.83 (s, 1 H).

1-Methyl-2,3,4-trinitropyrrole (**4a**): yield 75%; mp 111–112 °C; mass spectrum, *m/e* 216 (M^+); NMR [$(CD_3)_2CO$] δ 4.25 (s, 3 H), 8.43 (s, 1 H).

Under these reaction conditions the nitration of the less reactive 2,4-dinitro derivative was not complete within 1 h. The reaction mixture was characterized by TLC (silica gel, benzene) and NMR by comparison with authentic samples of the products. The product ratio was determined from the area ratio of the aromatic NMR signals of the products.

1-Methyl-2,3,4,5-tetranitropyrrole. HNO_3 (100%, 1.35 mL) was added dropwise with stirring and mild cooling (~10 °C) to a solution of 0.2 g of **3a** in 3 mL of fuming H_2SO_4 (20% SO_3). The reaction mixture was heated at 65 °C for 15 min, poured onto 50 g of ice, and extracted with ethyl acetate. The organic solution was dried. After the solvent was evaporated, the residue was purified by chromatography (silica gel, benzene); yield 45%; mp 101–102 °C; mass spectrum, *m/e*

261 (M^+); NMR (CD_3CN) δ 4.02 (s).

1-Isopropyl- (4b) and 1-*tert*-Butyl-2,3,4-trinitropyrroles (4c). The synthesis of **3b** and **3c** was carried out by the procedure described for **3a**, starting from the appropriate amines.[5]

3b: mp 95.5–96 °C; mass spectrum, *m/e* 199 (M^+); NMR [$(CD_3)_2CO$] δ 1.60 (d, J = 6.5 Hz, 6 H), 4.68 (septet, 1 H, J = 6.5 Hz), 8.06 (s, 2 H).

3c: mp 150–151 °C; mass spectrum, *m/e* 213 (M^+); NMR [$(CD_3)_2CO$] δ 1.75 (s, 9 H), 8.07 (s, 2 H).

The nitration of **3b** and **3c** in H_2SO_4 at 0 °C yielded **4b** (76%) and **4c** (66%), respectively.

4b: mp 139–140 °C; NMR [$(CD_3)_2CO$] δ 1.75 (d, J = 7 Hz, 6 H), 5.55 (septet, 1 H, J = 7 Hz), 8.53 (s, 1 H).

4c: mp 121.5–122 °C; NMR [$(CD_3)_2CO$] δ 1.88 (s, 9 H), 8.31 (s, 1 H).

Nitration of 3-Nitro-1-R-pyrroles. The starting materials were prepared from 1-R-pyrroles[9] upon nitration with 1 equiv of 100% HNO_3 in acetic anhydride at −20 (R = alkyl) or 0 °C (R = Ar).[8] The nitrations yielded mixtures of 2-nitro- and 3-nitro-1-R-pyrroles. These isomers were easily separated by chromatography (silica gel, benzene–ethyl acetate or petroleum ether–benzene) and identified from their NMR spectra. 2-Nitro derivatives were eluted more rapidly than 3-nitro derivatives. The relative ratios of 2- and 3-nitro isomers are reported in Table II together with the overall yields. 3-Nitropyrroles (0.50 g) were nitrated in H_2SO_4 at 0 °C or room temperature (R = *o*-nitrophenyl) with 1 equiv of 100% HNO_3. The crude reaction mixture (0.35–0.40 g) was poured into water and extracted with ether or ethyl acetate. When R was an alkyl group, the composition of the crude reaction mixture was determined by TLC and NMR spectroscopy. When R was an aryl group, the NMR spectrum of the crude reaction mixture was much less simple. Therefore, the reaction products were isolated by chromatography on silica gel with petroleum ether (30–50 °C) continuously enriched with benzene and characterized by their spectra. The relative rates of elution were as follows: 2,4-dinitro >2,3,4-trinitro >3,4-dinitro.

Melting Points and Spectral Features of Dinitro- and Trinitropyrroles (d, R = *p*-Nitrophenyl; e, R = *o*-Nitrophenyl).[10]

3d: mp 188–189 °C; NMR [$(CD_3)_2SO$] δ 8.08 (d, J = 10 Hz, 2 H), 8.40 (d, 2 H, J = 10 Hz), 8.90 (s, 2 H).

3e: mp 120–122 °C; mass spectrum, *m/e* 278 (M^+); NMR [$(CD_3)_2SO$] δ 7.7–8.5 (m, 4 H), 8.59 (s, 2 H).

4d: mp 60–63 °C; mass spectrum, *m/e* 323 (M^+); NMR [$(CD_3)_2CO$] δ 8.05 (d, J = 10 Hz, 2 H), 8.48 (d, 2H, J = 10 Hz), 8.55 (s, 1 H).

6b: mp 107–108 °C; NMR (CCl_4) δ 1.67 (d, 6 H, J = 7 Hz), 5.53 (septet, 1 H, J = 7 Hz), 7.62 (d, 1 H, J = 2 Hz), 7.73 (d, 1 H, J = 2 Hz).

6c: mp 141–142 °C; NMR (CCl_4) δ 1.78 (s, 9 H), 7.53 (d, 1 H, J = 2 Hz), 7.71 (d, 1 H, J = 2 Hz).

6d: mp 195–196 °C; NMR [$(CH_3)_2SO$] δ 7.86 (d, 2 H, J = 8 Hz), 7.95 (d, 1 H, J = 2 Hz), 8.33 (d, 2 H, J = 8 Hz), 8.58 (d, 1 H, J = 2 Hz).

6e: mp 154–155 °C; NMR [$(CD_3)_2SO$] δ 7.7–8.6 (m, 4 H), 8.13 (d, 1 H, J = 2 Hz), 8.69 (d, 1 H, J = 2 Hz).

Acknowledgments. The authors thank Professor G. Illuminati for helpful discussions.

Registry No.—**1,** 56350-95-9; **2,** 69726-47-2; **2b,** 69726-48-3; **3a,** 68712-54-9; **3b,** 69726-49-41; **3c,** 69726-50-7; **3d,** 69726-51-8; **3e,** 69726-52-9; **4a,** 69726-53-0; **4b,** 69726-54-1; **4c,** 69726-55-2; **4d,** 69726-56-3; **6a,** 2948-69-8; **6b,** 2881-71-2; **6c,** 69726-57-4; **6d,** 53256-10-3; **6e,** 69726-58-5; 1-methyl-2-nitropyrrole, 823-37-0; 1-isopropyl-2-nitropyrrole, 69726-59-6; 1-*tert*-butyl-2-nitropyrrole, 69726-60-9; 1-(*p*-nitrophenyl)-2-nitropyrrole, 69726-61-0; 1-(*o*-nitrophenyl)-2-nitropyrrole, 69726-62-1; 1-methyl-3-nitropyrrole, 823-72-3; 1-isopropyl-3-nitropyrrole, 69726-63-2; 1-*tert*-butyl-3-nitropyrrole, 69726-64-3; 1-(*p*-nitrophenyl)-3-nitropyrrole, 69726-65-4; 1-(*o*-nitrophenyl)-3-nitropyrrole, 69726-66-5; 1-methyl-2,3,4,5-tetranitropyrrole, 69726-67-6; 1-methylpyrrole, 96-54-8; 1-isopropylpyrrole, 7057-97-8; 1-*tert*-butylpyrrole, 24764-40-7; 1-(*p*-nitrophenyl)pyrrole, 4533-42-0; 1-(*o*-nitrophenyl)pyrrole, 33265-60-0.

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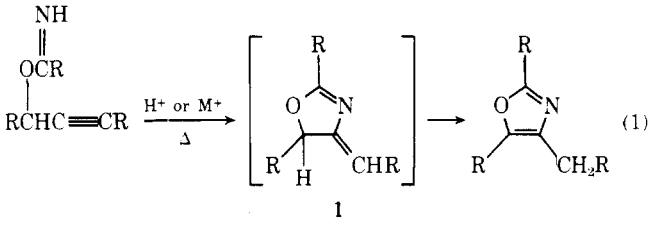
(10) In general, satisfactory analytical data could not be obtained for the polynitropyrroles.

Communications

4-Methylene-4,5-dihydrooxazoles: Isolation, Properties, and Use for the Preparation of Substituted Oxazoles

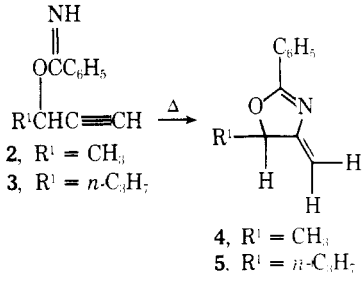
Summary: 4-Methylene-4,5-dihydrooxazoles are prepared from benzimidic esters of 1-alkyn-3-ols, and serve as useful intermediates for the synthesis of highly functionalized oxazoles.

Sir: Several natural products[1] and pharmacologically active compounds[2] contain oxazole rings. Substituted oxazoles also derive significant importance as azadiene components for Diels–Alder synthesis,[1,3,5] with their use in the total synthesis of pyridoxine (vitamin B_6)[1,4] being a notable example. One method of preparing substituted oxazoles, which is described most extensively in the patent literature, is the intramolecular cyclization of propargylic imidates (eq 1).[6] Concentrated sulfuric acid[6a] and Ag(I)[6b] and Hg(II)[6b] salts have been reported as catalysts for this conversion, which presumably[7] involves the intermediacy of a 4-alkylidene-4,5-dihydrooxazole (**1**). In this communication we report that when the solution thermolysis of benzimidic esters of 1-alkyn-3-ols is conducted under *basic* or *neutral* conditions the initially formed 4-methylene-4,5-dihydrooxazoles may be isolated in good yield (eq 2). We also report a preliminary study of the



(1)

1



(2)

2, $R^1 = CH_3$
3, $R^1 = n\text{-}C_3H_7$
4, $R^1 = CH_3$
5, $R^1 = n\text{-}C_3H_7$

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