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Oxidation of Furan, Pyrrole, Thiophene, Benzo[*b*]furan, and Benzo[*b*]thiophene with Oxodiperoxomolybdenum (VI), $MoO_5 \cdot HMPA$

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The oxidation of 2,5-diphenylfuran (**1**) with (hexamethylphosphoramide)oxodiperoxomolybdenum (VI), $MoO_5 \cdot HMPA$, gave *cis*-1,4-diphenyl-2-butene-1,4-dione (**2**) and its *cis*-epoxide **3**. 2,3-Diphenylpyrrole (**4**) was similarly treated with $MoO_5 \cdot HMPA$ to give the dimeric product **6**, together with the *cis*-epoxide **3** and the *trans*-olefin **5**. In the case of 2,5-diphenylthiophene (**8**), the oxidation with $MoO_5 \cdot HMPA$ occurred at the sulfur atom of **8** to give thiophene 1,1-dioxide **9**. The oxidation of benzo[*b*]furan (**10**) and benzo[*b*]thiophene (**16**) with $MoO_5 \cdot HMPA$ is also described.

Keywords——furan; pyrrole; thiophene; benzo[*b*]furan; benzo[*b*]thiophene; peroxomolybdenum complex; oxidation; epoxidation; dimerization

(Hexamethylphosphoramide)oxodiperoxomolybdenum (VI), $MoO_5 \cdot HMPA$, is a highly effective reagent for the selective epoxidation of olefins.[1] However, little information is available concerning the behavior of $MoO_5 \cdot HMPA$ towards heteroatom-substituted olefins, which are present as partial structures of many heterocyclic compounds. Frimer[2] reported that the oxidation of 3,4-dihydro-2*H*-pyran with $MoO_5 \cdot HMPA$ affords 4-formyloxybutanal. In a continuation of our studies on the oxidation of indoles with $MoO_5 \cdot HMPA$,[3,4] we have examined the behavior of $MoO_5 \cdot HMPA$ towards five-membered heterocycles such as furan, pyrrole, thiophene, benzo[*b*]furan, and benzo[*b*]thiophene.

Treatment of 2,5-diphenylfuran (**1**) with $MoO_5 \cdot HMPA$ in dry methylene chloride at room temperature for a week gave *cis*-1,4-diphenyl-2-butene-1,4-dione (**2**)[5] and *cis*-2,3-epoxy-1,4-diphenylbutane-1,4-dione (**3**)[5] in 18% and 21% yields, respectively, together with recovered **1** in 30% yield. The formation of the *cis*-olefin **2** may be explained in terms of the epoxidation of **1**, leading to an intermediate epoxide which rearranges, by analogy with the mechanism proposed for the oxidation of furans with the peracid.[6] The epoxide **3** is formed by the stereospecific epoxidation of **2** with $MoO_5 \cdot HMPA$.[5]

The oxidation of 2,5-diphenylpyrrole (**4**) with $MoO_5 \cdot HMPA$ for two weeks gave the *trans*-olefin **5**[7] (6%), the *cis*-epoxide **3** (6%), and the dimeric product **6** (14%), together with recovered **4** (25%). The proposed structure of **6** is based on the spectroscopic data: the parent ion in the mass spectrum (MS) appears at *m/e* 452, indicating that **6** is dimeric. The infrared (IR) spectrum shows absorptions at 3448 (NH of a pyrrole), 3264, and 1656 cm^{-1} (NH and C=O of pyrrolin-4-one).[8] The proton nuclear magnetic resonance (^1H-NMR) spectrum shows two doublets at δ 5.34 (1H, $J=1.1$ Hz, =CH–CO–) and δ 6.19 (1H, $J=2.9$ Hz, a pyrrole ring proton). The formation of the dimer **6** can be rationalized as illustrated in Chart 1; a similar dimerization is observed in the oxidation of 2-phenylindole with $MoO_5 \cdot HMPA$ to give the dimeric product **7**.[4]

In the case of 2,5-diphenylthiophene (**8**), the oxidation with $MoO_5 \cdot HMPA$ occurred

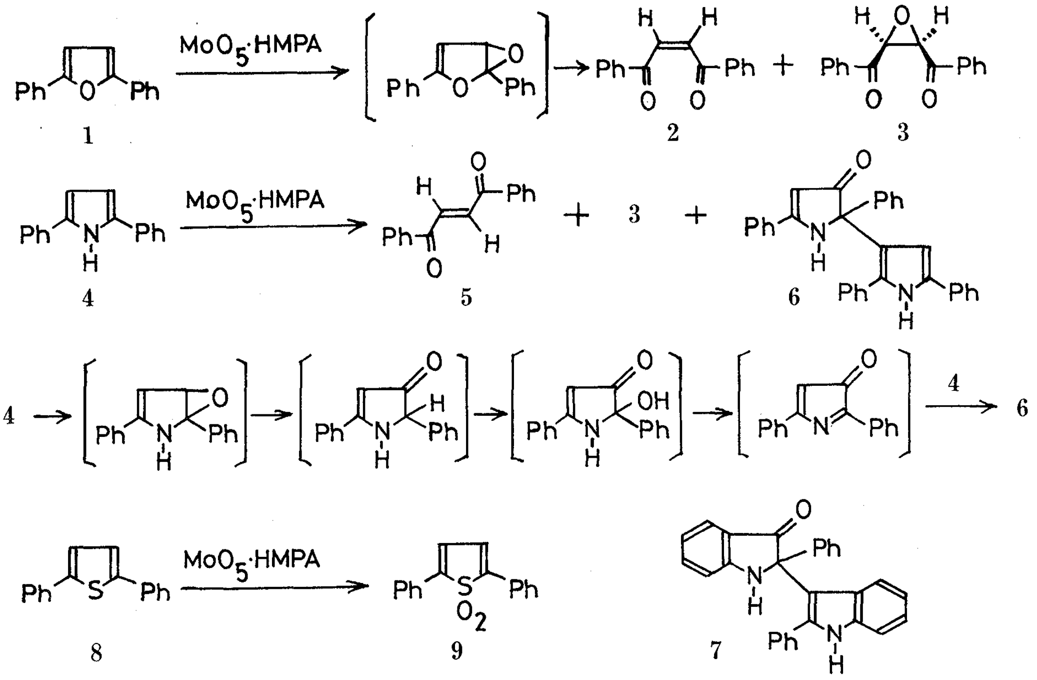

Chart 1

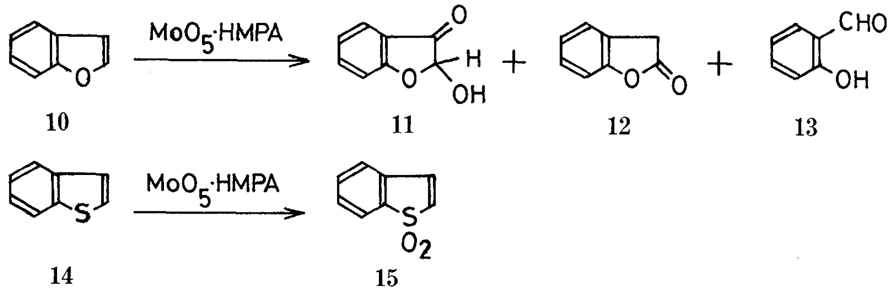

Chart 2

predominantly at the sulfur atom of **8** to give 2,5-diphenylthiophene 1,1-dioxide (**9**)[9] in 37% yield, together with recovered **8** in 60% yield.

The oxidation of benzo[*b*]furan (**10**) with $MoO_5 \cdot HMPA$ gave 2-hydroxy-3(2*H*)-benzofuranone (**11**)[10] (18%), 2(3*H*)-benzofuranone (**12**)[11] (7%), and salicylaldehyde (**13**) (12%), together with recovered **10** (15%). The formation of **11** is analogous to that of 1-acetyl-2-hydroxyindoxyl in the oxidation of 1-acetylindole with $MoO_5 \cdot HMPA$.[4] The oxidation of benzo[*b*]thiophen (**14**) with $MoO_5 \cdot HMPA$ was similar to that of **8**, giving benzo[*b*]thiophene 1,1-dioxide (**15**)[12] in 86% yield. The reaction of **17** with $MoO_5 \cdot HMPA$ did not occur.

These results indicate that the MoO_5 oxidation of five-membered heterocycles gives a variety of products depending on the precise properties of the heteroatoms.

Experimental

All melting and boiling points are uncorrected. IR spectra were recorded on Hitachi 260-10 and 270-30 spectrophotometers. ^1H- and ^{13}C-NMR spectra were measured with JEOL JNM-PMX 60 and GX-400 spectrometers, respectively, using tetramethylsilane as an internal standard. Ultraviolet (UV) absorption spectra were recorded on a Hitachi 124 spectrometer. Mass spectra were obtained with a JEOL D-300 spectrometer operating at 70 eV. Column chromatography was carried out on silica gel (80—100 mesh, Kanto Chemical Co., Inc.).

Materials——(Hexamethylphosphoramide)oxodiperoxomolybdenum (VI), $MoO_5 \cdot HMPA$, was prepared by the method of Mimoun and co-workers.[13] 2,5-Diphenylfuran (**1**),[14] -pyrrole (**4**)[15] and -thiophene (**8**),[15] and benzo[*b*]furan (**10**)[16] were prepared according to the literature. Benzo[*b*]thiophene (**14**) was obtained from Tokyo Kasei Kogyo Co., Ltd.

Oxidation of 2,5-Diphenylfuran (1) with $MoO_5 \cdot$HMPA——A solution of **1** (0.440 g, 2 mmol) and $MoO_5 \cdot$HMPA (0.780 g, 2.2 mmol) in dry CH_2Cl_2 (25 ml) was stirred at room temperature under argon for a week. After removal of the solvent under reduced pressure, the residue was chromatographed on a silica gel column. Elution with C_6H_6 gave recovered **1** (0.133 g, 30%). Elution with CH_2Cl_2–C_6H_6 (9 : 1) gave *cis*-1,4-diphenyl-2-butene-1,4-dione (**2**) (87 mg, 18%) and *cis*-2,3-epoxy-1,4-diphenylbutane-1,4-dione (**3**) (0.106 g, 21%). The products, **2** and **3**, were identified by direct comparison of their physical and spectral data with those of the previously obtained samples.[5]

2: mp 131—134 °C (from C_6H_6) [lit.[5] mp 133.5—134.5 °C]. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1660 (C=O).

3: mp 129—131.5 °C (from ethyl acetate) [lit.[5] mp 127.5—128.5 °C]. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1680 (C=O).

Oxidation of 2,5-Diphenylpyrrole (4) with $MoO_5 \cdot$HMPA——Using a procedure similar to that described above for the oxidation of **1**, **4** (1.55 g, 7.1 mmol) was treated with $MoO_5 \cdot$HMPA (2.78 g, 7.8 mmol) in dry CH_2Cl_2 (57 ml) for two weeks. The reaction mixture was purified by column chromatography on silica gel with CH_2Cl_2 as an eluent to give recovered **4** (0.39 g, 25%), *trans*-1,4-diphenyl-2-butene-1,4-dione (**5**) (0.10 g, 6%), the *cis*-epoxide **3** (0.10 g, 6%), and 5-(2,5-diphenylpyrrol-3-yl)-2,5-diphenyl-2-pyrrolin-4-one (**6**) (0.19 g, 12%). The olefin **5** was identified by direct comparison of its physical and spectral data with those of the previously obtained sample.[5]

6: mp 150.5—153 °C (from acetone–C_6H_6). *Anal.* Calcd for $C_{32}H_{24}N_2O$: C, 84.93; H, 5.35; N, 6.19. Found: C, 84.65; H, 5.10; N, 5.94. IR ν_{max}^{KBr} cm^{-1}: 3448 (NH of pyrrole), 3254 (NH), and 1656 (C=O). ^{1}H-NMR (DMSO-d_6) δ: 5.34 (1H, d, J=1.1 Hz, =CH–CO, exchangeable with D_2O), 6.19 (1H, d, J=2.9 Hz, –HC=), 7.0—7.8 (20H, m, Ar-H), 9.05 (1H, s, NH, exchangeable with D_2O), and 11.30 (1H, s, NH, exchangeable with D_2O). ^{13}C-NMR (DMSO-d_6) δ: 71.87 (s, C(5)), 93.02 (d, C(3)), 108.04 (d, C(4′)), 172.12 (s, C(2)), 200.60 (s, C(4)), 120.97, 129.79, 129.81, 131.55, 132.24, 133.06, 140.55 (7s), 123.46, 125.49, 126.48, 126.74, 126.92, 127.01, 127.13, 127.50, 128.15, 128.19, 128.22, 128.50, 128.56, 129.29, 131.68 (15d). UV λ_{max}^{EtOH} nm (log ε): 237 (4.31), 247 (4.31), 308 (4.40). MS *m/e*: 452 (M^+).

Oxidation of 2,5-Diphenylthiophene (8) with $MoO_5 \cdot$HMPA——Using a procedure similar to that described above for the oxidation of **1**, **8** (0.210 g, 0.89 mmol) was treated with $MoO_5 \cdot$HMPA (0.342 g, 0.96 mmol) in dry CH_2Cl_2 (15 ml) for a week. The reaction mixture was purified by column chromatography on silica gel with C_6H_6 as an eluent to give 2,5-diphenylthiophene 1,1-dioxide (**9**) (88 mg, 37%), together with recovered **8** (0.126 g, 60%).

9: mp 179—182 °C (from CH_3OH) [lit.[9] mp 178—179 °C]. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1304 and 1140 (SO_2). ^{1}H-NMR ($CDCl_3$) δ: 6.97 (2H, s, –S–C=CH–), 7.3—7.9 (10H, m, Ar-H).

Oxidation of Benzo[*b*]furan (10) with $MoO_5 \cdot$HMPA——Using a procedure similar to that described above for the oxidation of **1**, **10** (0.472 g, 4 mmol) was treated with $MoO_5 \cdot$HMPA (1.562 g, 4.4 mmol) in dry CH_2Cl_2 (40 ml) for a week. The reaction mixture was purified by column chromatography on silica gel. Elution with C_6H_6 gave salicylaldehyde (**13**) (59 mg, 12%) and 2(3*H*)-benzofuranone (**12**) (38 mg, 7%), together with recovered **10** (69 mg, 15%). Elution with CH_2Cl_2–ethyl acetate (8 : 1) gave 2-hydroxy-3(2*H*)-benzofuranone (**11**) (0.110 g, 18%). **13**, bp 36 °C (4 mmHg), was identified by direct comparison of its physical and spectral data with those of a commercial sample.[17]

11: mp 108.5—110 °C (from ether) [lit.[10] mp 104—105 °C]. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3250 (OH) and 1730 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 5.33 (1H, br, OH, exchangeable), 5.57 (1H, s, –O–CH–CO–), 6.8—7.2 (2H, m, Ar-H), 7.4—7.8 (2H, m, Ar-H). MS *m/e*: 150 (M^+).

12: mp 44—47 °C (from ligroin) [lit.[11] mp 49—50 °C]. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1800 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 3.70 (2H, s, –CH_2–Ar) 7.0—7.35 (4H, m, Ar-H).

Oxidation of Benzo[*b*]thiophene (14) with $MoO_5 \cdot$HMPA——Using a procedure similar to that described above for the oxidation of **1**, **14** (0.268 g, 2 mmol) was treated with $MoO_5 \cdot$HMPA (0.780 g, 2.2 mmol) in dry CH_2Cl_2 (20 ml) for 6 d. The reaction mixture was purified by column chromatography on silica gel with CH_2Cl_2–C_6H_6 (1 : 1) as an eluent to give benzo[*b*]thiophene 1,1-dioxide (**15**) (0.290 g, 87%), mp 140 °C [lit.[12] mp 142—143 °C]. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1280 and 1145 (SO_2). ^{1}H-NMR ($CDCl_3$) δ: 6.68 (1H, d, J=7 Hz, –CH=), 7.18 (1H, d, J=7 Hz, –CH=), and 7.2—7.8 (4H, m, Ar-H). MS *m/e*: 166 (M^+).

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