

# Double 1,3-Dipolar Cycloadditions of Meso-ionic Heterocycles with *N*-Phenylmaleimide

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Received December 7, 1989

3-Phenylsydnone and 2,4-diphenyl-3-methyloxazolium 5-oxide undergo double 1,3-dipolar cycloadditions with two molecules of *N*-phenylmaleimide to produce 4,8-iminobenzo[1,2-*c*:4,5-*c'*]dipyrrole-1,3,5,7-tetrone derivatives in a stereoselective manner.

*J. Heterocyclic Chem.*, **27**, 1519 (1990).

Recently we reported the 1,3-dipolar cycloaddition reactions of meso-ionic heterocycles to 2-substituted-1,4-benzoquinones producing 2*H*-isoindole-4,7-dione derivatives and 2*H*-indazole-4,7-dione derivatives (1:1 cycloadducts) [1,2].

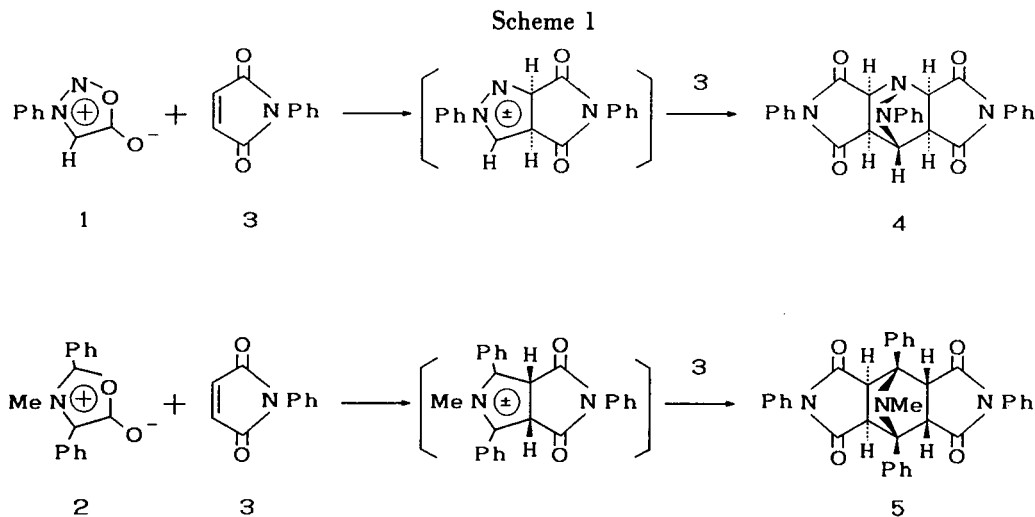
In this paper, the reactions of 3-phenylsydnone (**1**) and 2,4-diphenyl-3-methyloxazolium 5-oxide (**2**) with *N*-phenylmaleimide (**3**) leading to bicycloadducts were described. An equimolar mixture of **1** and **3** in *N,N*-dimethylformamide (DMF) was heated in a bath at about 140° for 8 hours to afford a light brown product in 79% yield (based on **3**) after the usual workup. The structure of this product was determined by elemental analysis and from their spectroscopic data as 8-aza-2,6,9-triphenylperhydro-4,8-iminobenzo[1,2-*c*:4,5-*c'*]dipyrrole-1,3,5,7-tetrone (**4**) consisting of one molecule of **1** and two molecules of **3** (1:2 adduct). In the nmr spectrum, a *singlet* signal at  $\delta$  5.64 ppm assignable to hydrogen at the 4-position in the *beta*-configuration is in reasonable agreement with the Karplus' correlation [3] between the vicinal hydrogen atoms at the 3a- and 4a-positions in the *alpha*-configuration being at right angles respectively. Furthermore *two doublet* signals at  $\delta$  4.58 (2H) and  $\delta$  3.64 (2H) ppm show that all four bridgehead hydrogen atoms, **3a**, **4a**, **7a** and **8a** are on the same side (*alpha*-configuration) shown in Scheme 1.

From the reaction of **2** with **3**, corresponding 9-methyl-2,4,6,8-tetraphenylperhydro-4,8-iminobenzo[1,2-*c*:4,5-*c'*]dipyrrole-1,3,5,7-tetrone (**5**) was obtained in 27% yield. Carrying out the reaction with a molar ratio of **2** and **3** of 1:2, the yield of **5** was increased to 75%. In this case, the *two singlet* signals at  $\delta$  4.40 and  $\delta$  3.37 ppm assignable to each of the two hydrogens at the 3a- and 8a-positions as well as at the 4a- and 7a-positions exhibit that the structure of **5** is not symmetrical as **4** shown in Scheme 1. If all four bridgehead hydrogen atoms, 3a, 4a, 7a and 8a are in the *alpha*- or *beta*-configuration, the signal should be a *singlet* because of the magnetic equivalence. Three signals in the <sup>13</sup>C nmr spectrum at 77.4, 53.9 and 51.1 ppm assignable to each two carbons at 3a- and 8a-, 4- and 8-, and 4a and 7a-positions are also compatible with this structure. The exclusive formation of unsymmetrical bicycloadduct **5** is considered that the first 1,3-dipolar cycloaddition of **2** to **3** was occurred at the opposite side to the case of **1** owing presumably to the substituent effects of **2**.

Isolation and stereochemistry of 1:1 cycloadducts of **1** and **2** with **3** are still under examination.

## EXPERIMENTAL

Melting points were determined on a Yanaco micro-melting



point apparatus and are uncorrected. The ir spectra were taken on a JASCO A-102 spectrometer using potassium bromide pellets. The  $^1\text{H}$  and  $^{13}\text{C}$  nmr spectra were recorded on a Varian XL-200 spectrometer in deuteriodimethyl sulfoxide using tetramethylsilane as the internal standard. Mass spectra were measured with M-2000 spectrometer. Elemental analyses were performed at Elemental Analysis Center in Kyoto University. For column chromatography, silica gel (Kieselgel 60, Merck, 70-230 mesh ASTM) and for preparative layer chromatography, silica gel pre-coated plates (2.0 mm Kieselgel 60, Merck) were used.

8-Aza-2,6,9-triphenylperhydro-4,8-iminobenzo[1,2-c:4,5-c']dipyrrole-1,3,5,7-tetrone (**4**).

A mixture of 1.30 g (8 mmoles) of **1** [**4**] and 1.39 g (8 mmoles) of **3** in 20 ml of DMF was heated at about  $140^\circ$  (bath temperature) for 8 hours. By pouring the mixture into water a light brown precipitate was deposited. The resulting precipitate was recrystallized from benzene, giving **4** as pale yellow crystal. From the mother liquor an additional amount of **4** was obtained by column or preparative layer chromatography with silica gel. The total yield of **4** was 79% based on **3**.

This compound had mp  $190.0-191.6^\circ$ ; ir: 1710 and 1780 (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr: 7.37 (m, 6H, arom), 7.15 (m, 4H, arom), 6.86 (m, 1H, arom), 6.71 (m, 4H, arom), 5.64 (s, 1H, H-4), 4.58 (d,  $J = 7$  Hz, 2H, H-7a and 8a), 3.64 (d,  $J = 7$  Hz, 2H, H-3a and 4a);  $^{13}\text{C}$  nmr: 174.2 (C=O), 172.7 (C=O), 144.2, 131.6, 129.1, 128.5, 128.3, 126.4 and 121.0 (Ph), 68.1 (C-7a and 8a or C-3a and 4a), 62.8 (C-4), 49.1 (C-3a and 4a or C-7a and 8a); ms: m/e 464 ( $M^+$ ).

*Anal.* Calcd. for  $\text{C}_{27}\text{H}_{20}\text{N}_4\text{O}_4$  (464.5): C, 69.82; H, 4.34; N, 12.06. Found: C, 70.13; H, 4.25; N, 11.95.

9-Methyl-2,4,6,8-tetraphenylperhydro-4,8-iminobenzo[1,2-c:4,5-c']dipyrrole-1,3,5,7-tetrone (**5**).

By treating an equimolar mixture of **2** [**5**] and **3** in a similar manner as described above colorless **5** was obtained in 27% yield. Carrying out the reaction with a molar ratio of **2** and **3** by 1:2, the yield of **5** was 75%.

This compound had mp  $204-206^\circ$ ; ir: 1785, 1772, 1723 and 1715 (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr: 7.95-7.80 (m, 4H, arom), 7.70-7.25 (m, 16H, arom), 4.40 (s, 2H, H-3a and 8a or H-4a and 7a), 3.27 (s, 2H, H-4a and 7a or H-3a and 8a), 1.93 (s, 3H, Me);  $^{13}\text{C}$  nmr: 175.6 and 172.9 (C=O), 135.2, 132.3, 132.0, 129.6, 129.0, 128.7, 128.3, 127.9, 127.7, 127.3 and 126.6 (Ph), 77.4, 53.9 and 51.1 (C-4 and 8, C-3a and 8a or C-4a and 7a), 30.3 (Me); ms: m/e 553 ( $M^+$ ).

*Anal.* Calcd. for  $\text{C}_{35}\text{H}_{27}\text{N}_3\text{O}_4$  (553.6): C, 75.93; H, 4.92; N, 7.59. Found: C, 75.63; H, 4.96; N, 7.47.

Acknowledgement.

The authors thank Mr. Nakata for his experimental assistance.

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