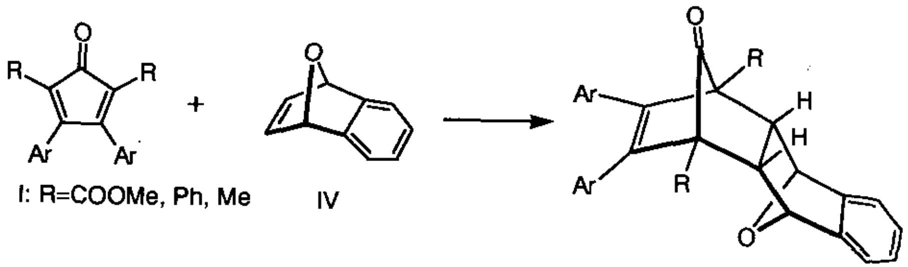
CYCLOADDITION REACTION OF 4-OXO-4*H*-PYRAZOLE 1,2-DIOXIDES WITH EPOXYNAPHTHALENE. X-RAY ANALYSIS OF THE CYCLOADDUCT AND SOME COMMENTS ON CYCLOADDITION BEHAVIOR

Kazunobu Harano, Yasuyuki Yoshitake, Masashi Eto and Takuzo Hisano*
Faculty of Pharmaceutical Sciences, Kumamoto University, 5-1 Oe-honmachi, Kumamoto 862, Japan

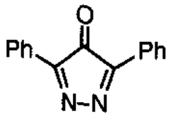
Abstract - The crystal structure of the cycloadduct of 2,5-bis(methoxycarbonyl)-4-*exo*-4*H*-pyrazole 1,2-dioxide with epoxynaphthalene was elucidated. The result indicates that the cycloadduct resulted from the direct 1,3-dipolar cycloaddition.

Cyclopentadienones show high reactivity toward various dienophiles and can serve as excellent trapping agents for unactivated olefinic compounds. Kanematsu and coworkers performed basic studies on cycloaddition of several cyclopentadienone (I) and diazacyclopentadienone (II) with various unsaturated compounds and clarified important controlling factors intervened in the cycloadditions.[1] The cyclopentadienones (I) underwent stereospecific Diels-Alder (DA) reaction with epoxynaphthalene (IV) to give the *endo-exo* adducts, wherein I approaches to IV from the less hindered *exo* site, in which the π-HOMO of the ethylenic group extends in the *exo* direction by interaction with the strained σ-bonds connecting to the bridgehead oxygen and by through-space interaction with the π-orbitals of the benzene moiety through the n-orbitals of the ether oxygen.

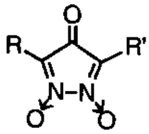


I: R=COOMe, Ph, Me

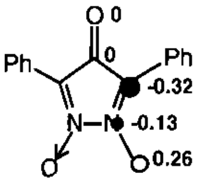
IV



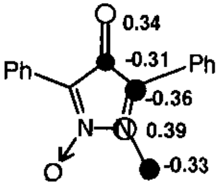
II



IIIa: R=R'=COOMe
IIIb: R=R'=Ph
IIIc: R=Ph,R'=Me



HOMO
-9.64 eV

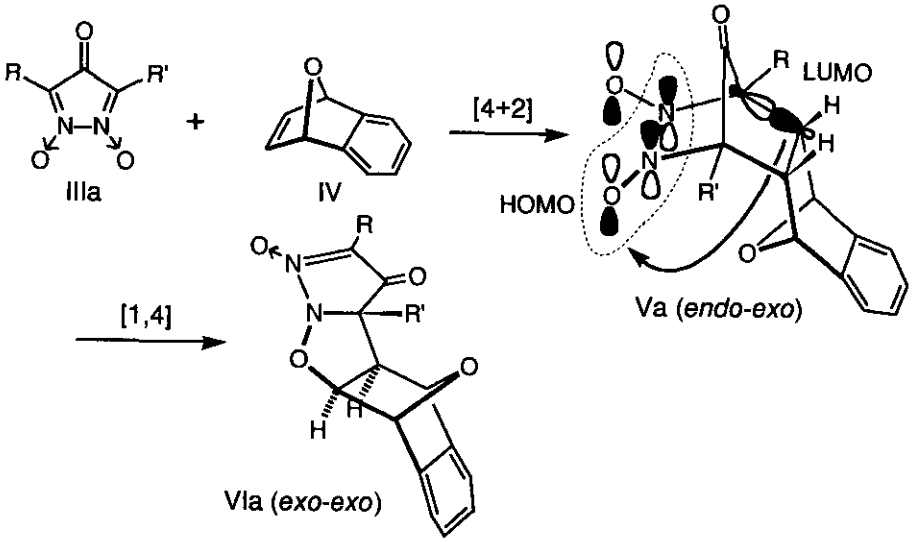


LUMO
-1.95 eV

Freeman *et al.* reported that 4-oxo-4*H*-pyrazole 1,2-dioxides (III) underwent cycloaddition with acrylonitrile, methyl acrylate and n-butyl vinyl ether to give the 1,3-dipolar cycloadducts.[2a] However, stereochemistry of their cycloadducts has not been reported.[2b]

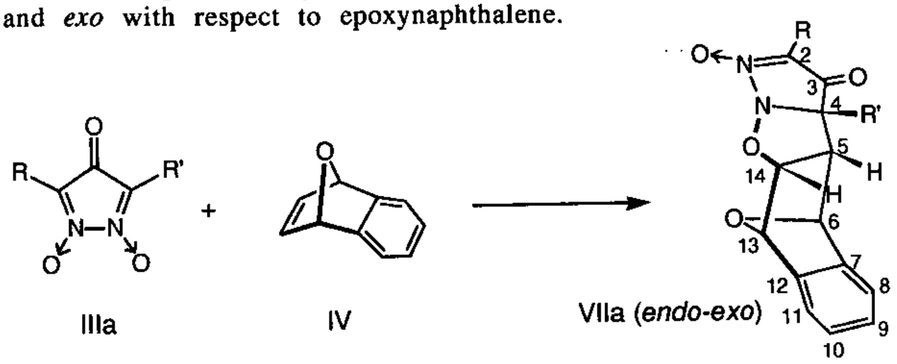
We now report cycloaddition behavior of some 4-oxo-4*H*-pyrazole 1,2-dioxide (III) toward epoxynaphthalene.

The frontier MO's of 4-oxo-4*H*-pyrazole 1,2-dioxides (IIIa-c) calculated by MNDO[3] are closely similar to those of cyclopentadienones, suggesting that III acts as a diene. If the dioxides (III) undergo Diels-Alder (DA) cycloadditions to olefins, the products (VI) hitherto obtained[2a] are considered to be derived from allowed six-electron [1s,4s]-sigmatropic rearrangement[4] of the primary Diels-Alder (DA) adducts (V).



To clarify this point, we carried out the cycloaddition of 2,5-bis(methoxycarbonyl)-4-oxo-4*H*-pyrazole 1,2-dioxide (IIIa) with epoxynaphthalene (IV). The reaction took place under mild reaction conditions (40 °C) to give pale yellow crystals (VIIa). The pmr and cmr spectral data support the formation of 1:1 cycloadduct.[5] To get a definitive evidence for the *endo/exo* nature of VIIa, a single crystal X-ray analysis was undertaken. The single crystals suitable for X-ray diffraction were obtained from slow evaporation of the benzene solution at room temperature. The crystals are monoclinic, space group $P2_1/n$, which was judged from systematic absence of reflections and there are four molecules in the unit cell of dimensions a=12.747(5), b=10.596(11), c=12.401(5)Å, β=91.47(3)°.[6] The structure was solved by the direct method using the MULTAN78 series of program[7] and refined by the block-diagonal least-squares method using UNICS III program.[8] Hydrogen atoms were located at calculated idealized positions and refined using isotropic temperature factors. The refinement converged to R=0.049. The ORTEP[9] drawing of VIIa is depicted in Figure.

As can be seen in Figure, the cycloadduct (VIIa, *endo-exo*) is *endo* with respect to the pyrazole and *exo* with respect to epoxynaphthalene.



IIIa

IV

VIIa (*endo-exo*)

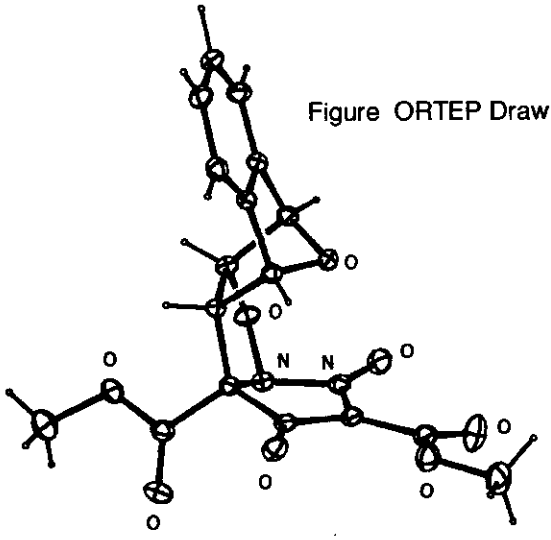


Figure ORTEP Drawing of VIIa

If III acts as a diene, the DA reaction of IIIa with IV would give the *endo-exo* adduct (V), which in turn undergoes [1,4]-sigmatropic rearrangement to give the *exo-exo* adduct (VI). The X-ray structure is clearly inconsistent with the one derived from the consecutive pathway. In conclusion, the cycloadduct is considered to be derived from the direct 1,3-dipolar cycloaddition.

Similarly, the cycloadditions of IIIb,c with IV gave the *endo-exo* type cycloadducts (VIIb,c). The pmr and cmr spectral data show similar spectral behavior to those of VIIa (see Reference 5).

The kinetic study of the cycloaddition of IIIa-c with various olefins will be reported in the near future.

ACKNOWLEDGMENT

We thank Prof. T. Sakurai (Shinshu University) and Prof. S. Kawano (College of Kyushu Jogakuin) for providing their revised X-ray crystallography programs.

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5. The physical properties and spectral data of the cycloadducts are as follows;**VIIa**: mp 169-170°C (decomp.). Yield 70%. Pmr ($CDCl_3$): 3.87 (3H, s, C4-COOMe), 3.92 (1H, d, J=6.4 Hz, C5-H), 3.94 (3H, s, C2-COOMe), 4.99 (1H, d, J=6.4 Hz, C14-H), 5.31 (1H, br s, C6-H), 5.39 (1H, br s, C13-H), 7.22-7.36 (4H, m, aromatic CH). Cmr ($CDCl_3$): 183.2 (s, C-3), 164.8 (s, C2-$\underline{C}$O), 156.2 (s, C4-$\underline{C}$O), 143.3 (s, C-12) 140.3 (s, C-7), 94.1 (d, C-14), 82.1 (s, C-4), 81.9 (d, C-13), 79.3 (d, C-6), 54.4 (q, C2-COO$\underline{Me}$), 53.9 (d, C-5), 52.8 (q, C4-COO$\underline{Me}$)
   VIIb: mp 203°C (decomp.). Yield 76%. Pmr ($CDCl_3$); 3.47 (1H, d, J=6.6 Hz, C5-H), 5.12 (1H, d, J=6.6 Hz, C14-H), 5.34 (1H, s, C6-H), 5.51 (1H, s, C13-H), 7.19-7.74 (8H, m, aromatic CH), 8.21-8.23 (2H, m, aromatic CH). Cmr ($CDCl_3$): 189.6 (s, C-3), 144.2 (s, C-12), 141.2 (s, C-7), 135.7 (s, C-2), 92.9 (d, C-14), 81.5 (d, C-13), 80.9 (s, C-4), 79.6 (d, C-6), 59.2 (d, C-5),
   VIIc: mp 229-230°C (decomp.). Yield 46%. Pmr ($CDCl_3$):1.68 (3H,s,C4-Me), 2.87 (1H, d, J=6.4 Hz, C5-H), 5.00 (1H, d, J=6.4 Hz, C14-H), 5.25 (1H, s, C6-H), 5.35 (1H, s, C13-H), 7.14-7.50 (7H, m, aromatic CH), 8.34-8.37 (2H, m, aromatic CH). Cmr ($CDCl_3$): 192.7 (s, C-3), 144.2 (s, C-12),141.0 (s, C-7), 93.2 (d, C-14), 82.1 (d, C-13), 79.8 (d, C-6), 76.4 (s, C-4), 59.0 (d, C-5), 21.4 (q, C4-Me)
6. The details of the X-ray analysis will be reported in a separate paper.
7. P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, "MULTAN78, A System of Computer Programs for the Automatic Solution of Crystal Structure from X-Ray Diffraction Data," Univ. of York, England, 1978.
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Received, 28th May, 1992