

PERICYCLIC REACTION OF OXEPIN WITH 3,4-DIAZACYCLOPENTADIENONE
AS AN ELECTRON-ACCEPTING HETERODIENONE SYSTEM

Takashi Ban and Ken Kanematsu*

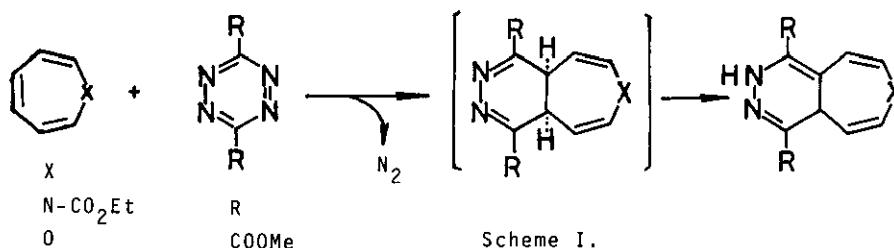
Institute of Synthetic Organic Chemistry, Faculty of Pharmaceutical
Sciences, Kyushu University 62, Fukuoka 812, Japan

Abstract---The cycloaddition reaction of oxepin with 2,5-diphenyl-3,4-diazacyclopentadienone prepared in situ from thermolysis of 1,3-bisdiazo-1,3-diphenyl-2-propanone gave anti-endo [4+2] π cycloadduct, which was found in the existence of equilibrium with the Claisen rearrangement product in solution by ^1H -NMR inspection.

A recent molecular orbital study¹ of the benzene oxide-oxepin valence isomerization has received considerable attention because of the interesting features of the cycloadditions of oxepin (1) and much efforts have been made to establish the capability for cycloaddition.

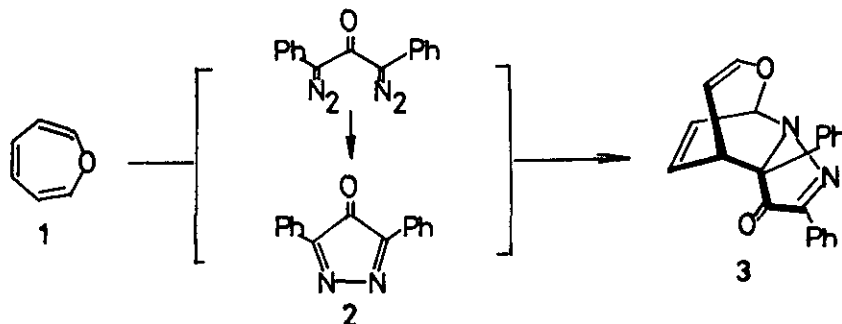
More recently, we found that the pericyclic reaction of oxepin (1) with electron-attracting cyclopentadienones such as 2,5-dimethoxycarbonyl-3,4-diphenylcyclopentadienone (CPC) gave the novel exo [6+4] π cycloadduct together with the facile tandem Cope-Claisen rearrangement product of the initially formed endo [2+4] π cycloadduct.²

In order to explore the scope and the mode of the cycloadditions, we turned to a study of the reaction between oxepin and cyclic heterodienone as a 4 π acceptor. In this connection, we reported previously the cycloaddition reaction of 1H-azepine with 2,5-diphenyl-3,4-diazacyclopentadienone (2) to afford the anti-endo [4+2] π cycloadduct.³ By contrast, Seitz and Kämpchen reported the [2+4] π cycloadditions of 1H-azepine and oxepin with the s-cis-azine system in 3,6-dimethoxycarbonyl-1,2,4,5-tetrazine. Both the azepine and oxepin react with their 4,5- π bond.⁴



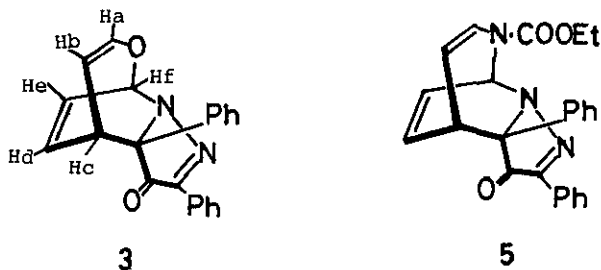
Related to these modes of cycloadditions, we now wish to report the result of cycloaddition of oxepin (1) and 2,5-diphenyl-3,4-diazacyclopentadienone (2) prepared in situ from thermolysis of 1,3-bisdiazo-1,3-diphenyl-2-propanone involving the isolation and characterization of the adduct.

When a solution containing a large excess of oxepin (1) and 1,3-diphenyl-1,3-bisdiazo-2-propanone in benzene was stirred at room temperature for 1 day, a crystalline 1:1 adduct (3) (mp 124-125°C, 54%) was afforded (Scheme II).

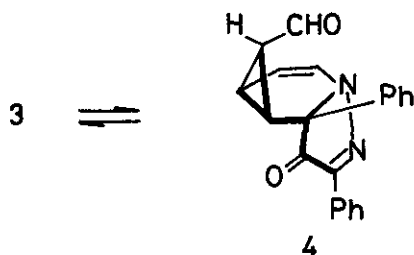


Scheme II.

The structure of 3 was assigned on the basis of the ^1H -NMR data in C_6D_6 by the double-resonance technique, in which characteristic signals of the olefinic protons exhibited at δ 4.36 (1H, Hb, t), 5.08 (1H, He, ddd), 5.55 (1H, Ha, dd), 6.06 (1H, Hd, ddd). Furthermore, the bridge head protons showed at δ 3.00 (1H, Hc, t) and 6.06 (1H, Hf, dd). The ^{13}C -NMR spectrum of the adduct also showed unsymmetrical structure (sp^3 carbons at 37.38, 80.16 and 86.25 ppm). The IR spectrum (Nujol) of 3 showed a characteristic enone carbonyl absorption in the five membered ring at 1725 cm^{-1} .³ The UV absorption at 402 nm (ϵ 3800) is in good agreement with that expected for the conjugated chromophore ($\text{N}=\text{C}-\text{C}=\text{O}$). These spectral data were grossly similar to those of the adduct 5 indicating their skeletal resemblance.³

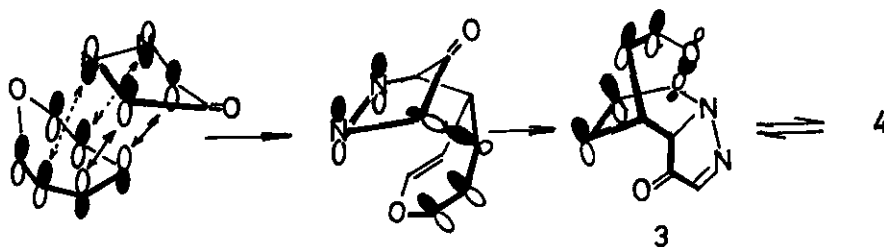


Interestingly, the ^1H -NMR spectrum of the adduct 3 was considerably changed. When the spectrum of 3 was taken in CDCl_3 at room temperature, the signals appeared at δ 8.42 (1H, d), 5.38 (1H, dd), 2.80 (1H, t), 2.32 (1H, ddd) and 2.12 (1H, dd). The signals at δ 8.42 and 2.80, 2.32, 2.12 indicated obviously the presence of the aldehyde moiety and the cyclopropane ring, which were possible only in the Claisen rearrangement of 3. Although the rearrangement product 4 was unsuccessful to isolate at present stage, the equilibrium of 3 and 4 was observed in 5:1 at room temperature after 3 h and 1:1 at 55°C by the ^1H -NMR inspection.



Scheme III.

The cycloadduct 5 was considerably stable for thermal or photochemical condition, but the cycloadduct 3 proceeds slowly to the Claisen rearrangement. In conclusion, the electron-attracting diazacyclopentadienone should be readily trapped by electron-donating oxepin to give the initially formed endo [2+4] π cycloadduct, owing to the greatly enhanced secondary orbital interactions, even in the existence of the valence-tautomeric equilibrium between the benzene oxide and the nonplanar conformational isomers. In addition, facile tandem Cope-Claisen rearrangement caused from the initially formed [2+4] π cycloadduct followed by the [3,3]sigmatropic shift to afford the anti-endo [4+2] π cycloadduct as depicted in Scheme IV. The same rearrangement should be observed in the cycloaddition of oxepine and CPC.² However, these results are in marked contrast to the adduct of oxepin and the s-tetrazine.⁴



Scheme IV.

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References

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