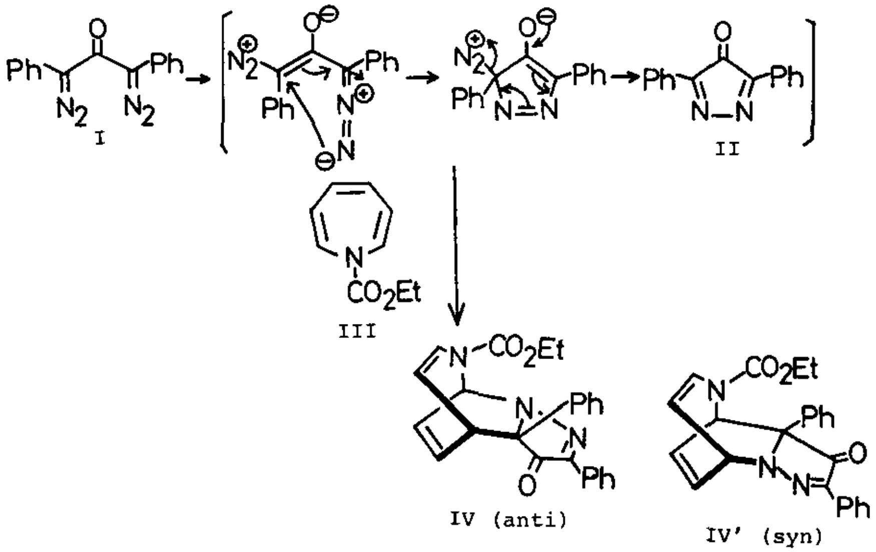
HETEROCYCLES, Vol.12, No.4, 1979

X-RAY STRUCTURE DETERMINATION OF A CYCLOADDUCT OF 1H-AZEPINE AND DIAZACYCLOPENTADIENONE

Kazunobu Harano, Takashi Ban, and Ken Kanematsu*
Faculty of Pharmaceutical Sciences, Kyushu University,
Maedashi, Higashiku, Fukuoka, 812, Japan.

Abstract – The cycloaddition reaction of N-ethoxycarbonylazepine with 2,5-diphenyl-3,4-diazacyclopentadienone gave anti endo$[4+2]\pi$ cycloadduct. The structure was determined by X-ray crystallographic study.

Thermolysis of 1,3-bisdiazo-1,3-diphenyl-2-propanone (I) provided a simple route to 2,5-diphenyl-3,4-diazacyclopentadienone (II) which is served as a convenient heterodienone component in spite of an unstable intermediate. This fascinating intermediate has been shown to act as both a dienophile with 2,3-dimethyl-1,3-butadiene and a diene with norbornene in pericyclic reactions.[1] These interesting features of the cycloaddition reactions of the diazacyclopentadienone prompted us to examine the mode of cycloaddition of I with *seven-membered ring* unsaturated compounds; e.g., azepine, diazepine, cycloheptatriene and tropone.



Of those, N-ethoxycarbonylazepine (III) reacted with I to give 1:1 cycloadduct (IV) in a moderate yield. In this communication we present the results of structure confirmation of the adduct (IV).

The ^{13}C-NMR spectrum in C_6D_6 of IV shows five detectable signals of sp^3 carbons, of which, signals at 38.85, 68.96, and 80.16 ppm are ascribable to the structure of [4+2]π cycloadduct. The UV absorption at $\lambda^{max}_{benzene}$ 400 nm (ε 4000) is in good agreement with that expected for the conjugated chromophore (N=C-C=O).

From these data, the structure of IV was considered to be [4+2]π cycloadduct instead of [6+4]π cycloadduct. However, there are some obscurity in regiochemistry of IV. Assignment of the conjugated carbonyl absorption at 1725 cm^{-1} by IR spectrum is uncertain for that expected structure. Thus, IV was submitted to single-crystal X-ray analysis.

Single crystals of IV were obtained from ethanol-acetone solution by slow evaporation at room temperature. Unit cell dimensions were obtained from least-squares refinement of the 2θ angles of 15 reflections measured on a Syntex P$\bar{1}$ automated diffractometer (Mo, λ=0.71069 Å). The crystals are triclinic, space group P$\bar{1}$, there are two molecules in the unit cell of dimensions a=9.9201, b=12.5030, c=9.1718 Å, α=106.40, β=105.46, γ=97.41°. Intensity data were collected using the θ-2θ scan technique and of the 3530 independent reflections within the range of the diffractometer ($2\theta \geqq 55°$), 2792 were observed. The orientation of the major part of the molecule was found by direct phasing$^{2)}$, but difficulty was experienced in finding a correct phasing model owing to two overlapping molecules. The middle positions of the both models were used for phase determination (29 atoms). The position of remaining atom was obtained from a difference Fourier map.

Refinements were carried out by the block-diagonal least-squares method$^{3)}$ using isotropic temperature factors for the hydrogen with exception of the hydrogen atoms of ethyl group with high temperature factors and anisotropic temperature factors for the remaining atoms. Final R value was 0.053 for the observed reflection.

Thus, the molecular structure shown in the Figure establishes that IV has the structure of anti-endo[4+2]π cycloadduct from III (4π) and II (2π).

The C_{15}-C_{14}-C_{22} angle is 4° smaller in the diazacyclopentenone than in the cyclopentenone.$^{4)}$ This difference might be due to the short bond distance of N-N bond of the diazacyclopentenone as compared with a corresponding cyclopentenone, which gives rise to a higher C=O stretching frequency at 1725 cm^{-1} in the IR spectrum.

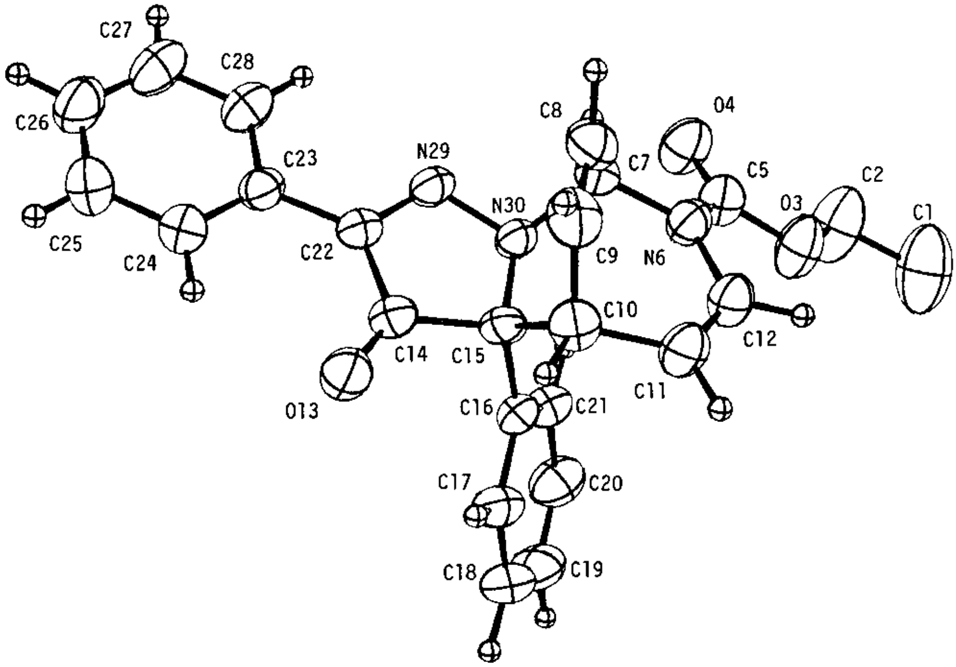


Figure 1 ORTEP drawing of IV

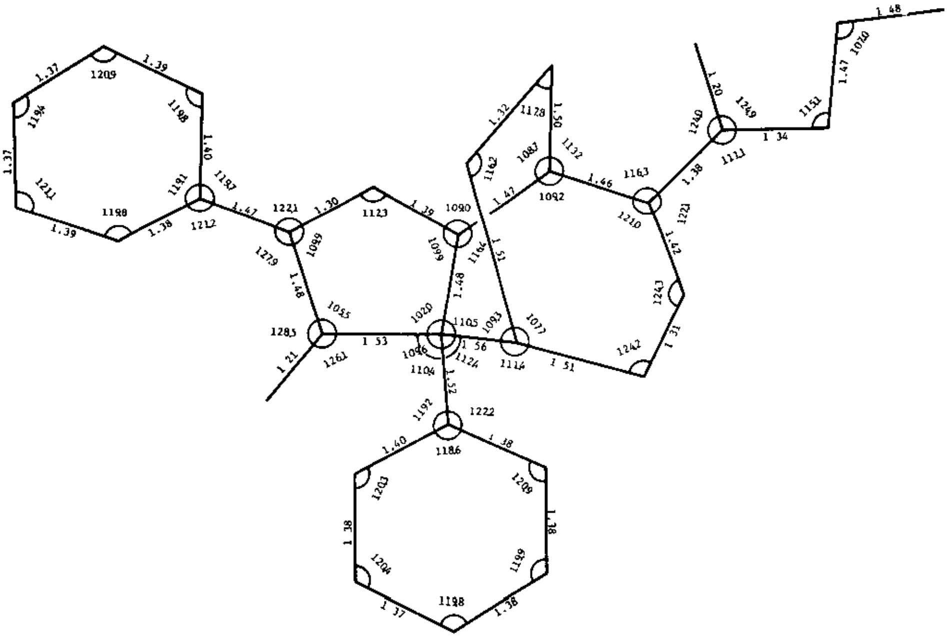
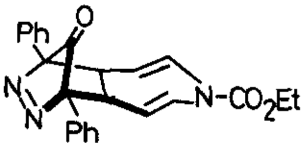


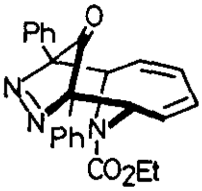
Figure 2 Distances and Angles of IV

In consideration of the molecular structure of IV, we can consequently explain the PMR spectrum by spin-spin decoupling experiments and study of the solvent-induced shifts of the resonance of olefinic protons. The six methine protons in the PMR spectrum ($CDCl_3$ with TMS as internal standard) are ascribed as follows : δ 3.45 ppm (dd, $J_{10,11}=J_{7,10}=7Hz$, H_{10}) ; 4.88 (dd, $J_{11,12}=7Hz$, H_{11}) ; 5.64 (dd, $J_{8,9}=8Hz$, $J_{7,8}=6Hz$, H_8) ; 6.39 (d, H_{12}) ; 6.48 (dd, H_9) ; 6.84 (brd, H_7).

It is to be noted that 1H-azepine exhibits the marked polyene character and has been shown to undergo a wide range of cycloaddition reactions wherein the triene system acts as a 2π, 4π, or 6π component.5) Therefore, the adduct is able to consider one of [4+2]π (IV), another type of [4+2]π (V) from azepine(2π) and diazacyclopentadienone(4π), and [6+4]π cycloadduct (VI) from azepine(6π) and diazacyclopentadienone(4π) in thermal conditions. However, in this case, the [4+2]π adduct (IV) is an isolable product and the regiochemistry is anti and endo showing a high degree of reactivity and regioselectivity.



V



VI

Acknowledgements We thank Drs. I. Ueda and S. Kono (College of General Education, Kyushu University) for their helpful suggestions during the crystallographic analysis. This investigation was supported in part by the Grant-in-Aid for Chemical Research in Development and Utilization of Nitrogen-Organic Resources.

References

1) B. M. Trost and P. J. Whiteman, J. Am. Chem. Soc. , 1974, 96, 7421.
2) G. Germain, P. Main, and E. W. Woolfson, Acta Cryst. , 1970, B24, 274.
3) All the calculations were performed on the FACOM M-190 computer in the Computer Center of Kyushu University with the Universal Crystallographic Computation Program System UNICS II (Sakurai, Iwasaki, Kobayashi, Bando, and Nakamichi, 1974).
4) K. Harano, T. Ban, M. Yasuda, and K. Kanematsu, Tetrahedron Lett. , 1978, 4037.
5) W. S. Murphy, K. P. Raman, and B. J. Hathaway, J. Chem. Soc. Perkin I, 1977, 2521, and references cited therein.

Received, 21st November, 1978