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

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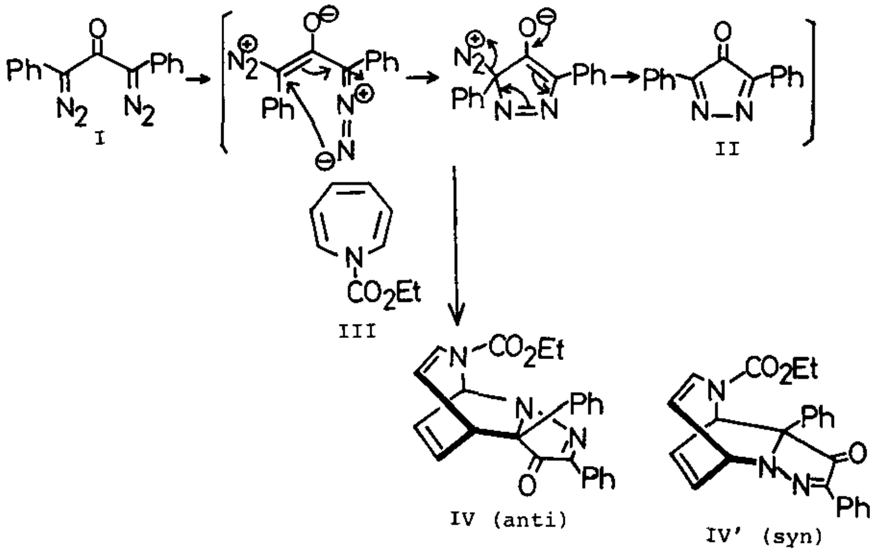
Abstract – The cycloaddition reaction of N-ethoxycarbonylazepine with 2,5-diphenyl-3,4-diazacyclopentadienone gave anti endo[4+2]π cycloadduct. The structure was determined by X-ray crystallographic study.

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 (2θ≧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.

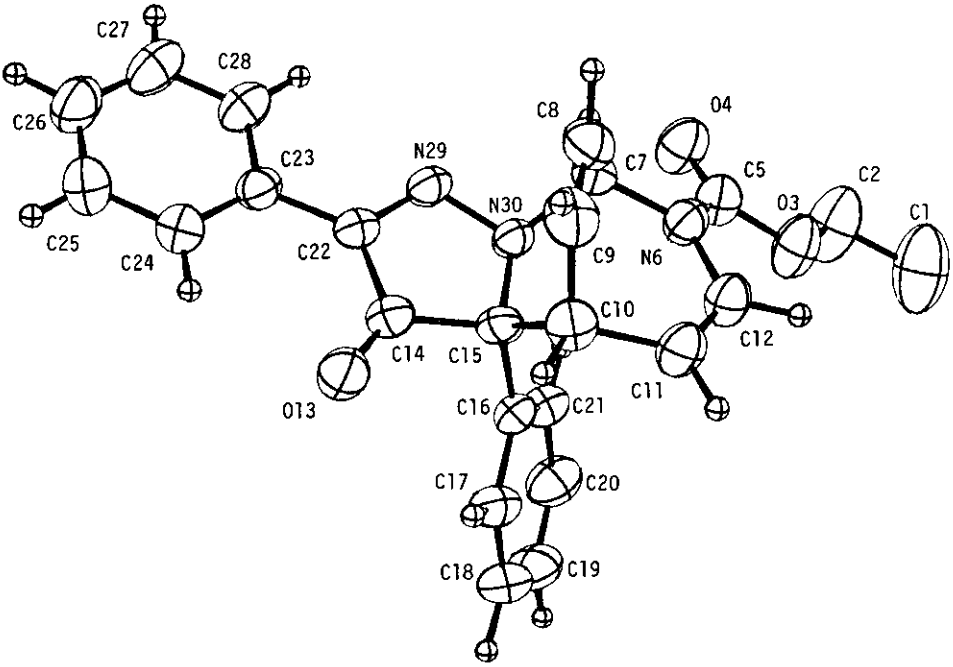


Figure 1 ORTEP drawing of IV

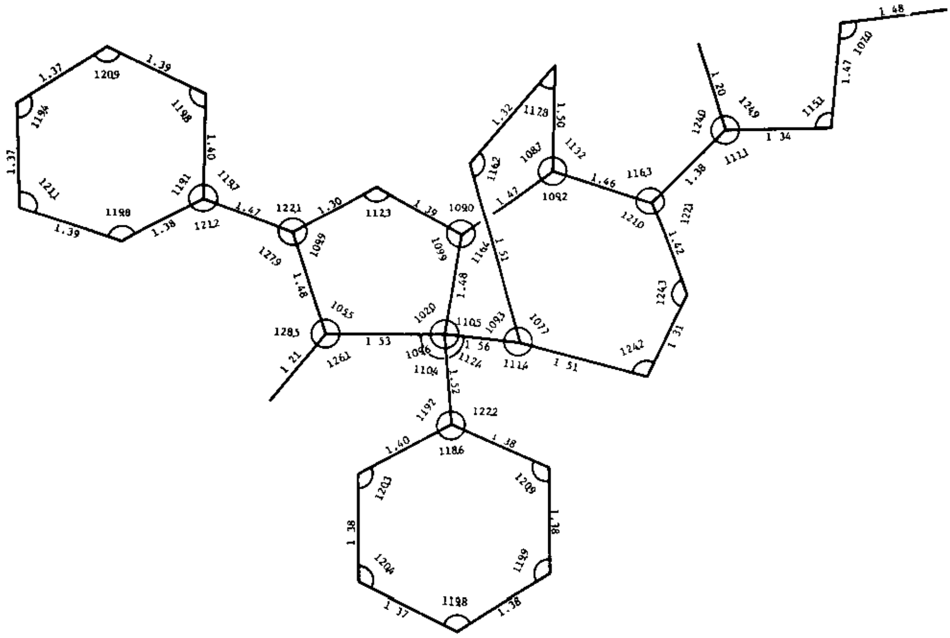
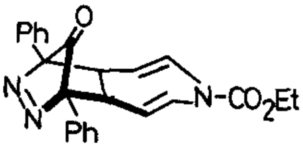


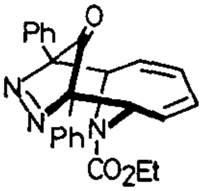
Figure 2 Distances and Angles of IV

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



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References

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