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MOLECULAR DESIGN BY CYCLOADDITION REACTIONS. XI.
CYCLOADDITION OF TROPONE AND DIPHENYLFULVENE

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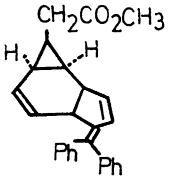
Cycloaddition reaction of tropone and 6,6-diphenylfulvene gave only 1:1 adduct in 60% yield. The structure of the adduct was established by spectral data and by chemical conversions. Mechanism for the formation of the [4+2]adduct is discussed.

The competition between thermally allowed [4+2] and [6+4]cycloadditions has recently aroused much interest. Houk *et al.* reported the periselective formation of [6+4]adduct in the reaction of tropone with dimethylfulvene, which immediately undergoes a [1,5]hydrogen shift to yield the rearranged 1:1 adduct followed by addition of a second molecule of tropone.2) While it is concluded that the steric effects play an important role in the [6+4]cycloadditions of tropone to 6-substituted fulvenes (IIb-d) by the kinetic study.3)

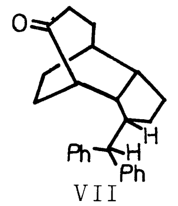
In order to get further information about effects of the substituent at the fulvene moiety and mechanism of this reaction, we have investigated the cycloaddition of tropone to 6,6-diphenylfulvene.

Reaction of tropone (I) with 6,6-diphenylfulvene (IIa) in chlorobenzene at 140°C in a sealed tube afforded only a 1:1 adduct (IIIa) (mp 184-186°C, $C_{25}H_{20}O$) in the yields of 57-60%. The ir spectrum of IIIa showed characteristic α,β-unsaturated carbonyl bands at 1650 (C=O) and 1625 (C=C) cm^{-1}. The structure of the adduct (IIIa) was eventually proved by a complete analysis of the nmr spectrum and also established by chemical conversions. The absence of appreciable couplings between H-1 and H-8 and between H-5 and H-12 indicated the bridgehead protons (H-8 and H-12) to be *exo* to the bicyclo[3.2.2]-nonadienone system, thus readily ruling out structures, [6+4] adducts (IV) and (V). Furthermore, the coupling pattern in the olefinic region is similar to that of the bicyclo[3.2.2]nonadienone moiety.4) In addition, the orientation of the fulvene moiety in the adduct could be determined as follows; one proton in the four methine protons appeared the highest field (δ 3.24) as doublet ($J_{12,8}$ = 8.7 Hz) due to the anisotropy of carbonyl group.4)

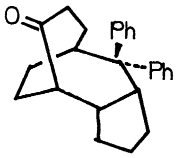
Irradiation of the adduct (IIIa) in methanol at room temperature gave a photo-[3.3]rearrangement product (VI) as a yellow oil in quantitative yield. The nmr spectrum of VI is similar to those of the photo[3.3]rearrangement products as previous reported by us.4) Catalytic hydrogenation of IIIa over palladium on charcoal in ethanol yielded a fully saturated octahydro compound (VII), mp 174-175°C, M^+ m/e 344, $C_{25}H_{28}O$. The nmr spectrum of VII exhibited a benzyl proton at δ 3.67 as a doublet (J= 10.9 Hz), which supported strongly the [4+2]type structure of the adduct (VII), and thus the [6+4]adduct (VIII) was ruled out.



VI



VII

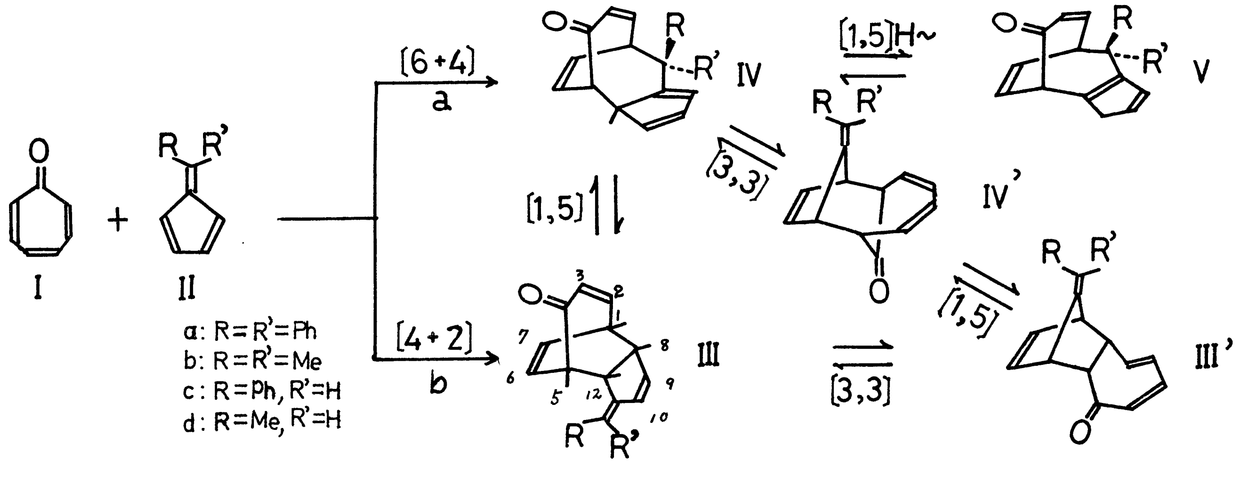


VIII

On the basis of the above facts, the adduct was assigned as structure IIIa, that of the [4+2]π cycloadduct with *endo* configuration, which is only one of possible fifty 1:1 adducts and twenty-six of which are thermally allowed.[2)]

Further attempts to effect the isolation of [6+4]cycloadduct even in the presence and/or absence of excess tropone under more drastic conditions were unsuccessful and only the [4+2]adduct (IIIa) was detected. By contrast, it is surprising that the reactions of tropone with 6,6-dimethyl, 6-methyl and 6-phenylfulvenes resulted in the formation of the corresponding [6+4]adducts in good yields.[2,3)]

Thus, mechanistic speculation leads to consideration paths a and b, with the initial formations of the alternative [6+4]adducts (IV) and (IV') followed by successive sigmatropic shifts or with directly formation of the [4+2]adduct by Alder rule. Although there are no isomers detected, the formation of the 1:1 adduct resulting from exclusive *endo*[4+2]cycloaddition is presumably controlled by the steric effects of the two bulky phenyl groups, and the *exo*[6+4] mode would be inhibited by such effects. On the other hand, the *endo*[6+4]cycloaddition might be sterically possible, but would involve unfavorable secondary orbital interaction in the transition state.



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