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STEREOSELECTIVE [6 + 4] CYCLOADDITIONS OF METHYLFULVENE AND PHENYLFULVENE TO TROPONE

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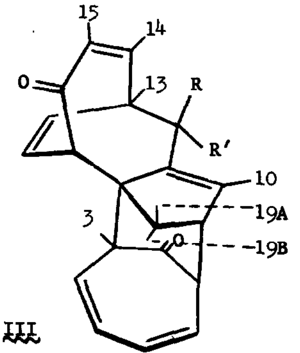
We recently reported the periselective formation of 2:1 adduct **IIIa** in the reaction of tropone with dimethylfulvene.[1] This observation of an unprecedented reaction of a fulvene as a 6π addend has led us to investigate further the mechanism of this reaction. The cycloadditions of 6-methyl-, 6-phenyl-, and 1,4-dideuterio-6-phenyl-, fulvenes with tropone provide evidence in support of our earlier mechanistic postulates.



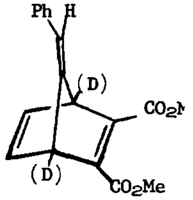
III

a; R=R'=Me
b; R=Me,R'=H
c; R=H,R'=Me
d; R=Ph,R'=H
e; R=H,R'=Ph

Reaction of 6-methylfulvene (1 mmol.) with tropone (3 mmol.) at 60° for 12 hours resulted in formation of a single 2:1 adduct, **IIIb**,[2] mp 176-176.5°, in 61% isolated yield. Irradiation of the methyl doublet centered at $\delta 0.79$ (C_6D_6) resulted in ~ 15% enhancements of the intensities of the resonances due to H-10 ($\delta 5.27$) and H-13 ($\delta 2.25$), consistent only with structure IIIb.[1b]

Reaction of 6-phenylfulvene (3 mmol.) with tropone (6 mmol.) in methanol at 60° resulted in formation of a single 2:1 adduct, **IIId**,[2] mp 160°, in 86% yield based upon recovered phenylfulvene and phenylfulvene dimers. Chemical shift differences produced by the anisotropy of the phenyl group allowed assignment of structure **IIId** rather than **IIIe** to the 2:1 adduct. In C_6D_6, the following chemical shift differences are observed: [proton, δ(IIIa)-δ(IIId)]; H-10, + 0.37; H-13, -0.54; H-14, -0.19; H-15, -0.13. The upfield shift of H-10 and downfield shifts of H-13, -14, and -15 induced by the benzene ring are compatible only with structure IIId with the aromatic ring "up", shielding H-10 and deshielding H-13, -14, and -15.

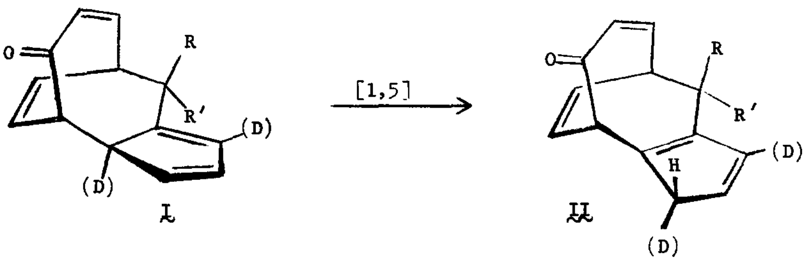
The stereochemistry of I was proven by reaction of 1,4-d$_2$-6-phenylfulvene with tropone. Acid-catalyzed deuterium exchange[3] in 6-(dimethylamino)fulvene resulted in deuterium incorporation predominantly at the 1- and 4-positions. After conversion of the partially deuterated aminofulvene into 6-phenylfulvene,[4] the positions of deuterium incorporation were proven by preparation of the dimethyl acetylenedicarboxylate adduct, VII, mp 91-91.5°.[2] Mass spectral analysis indicated the following amounts of deuterium incorporation in VII: d$_0$, 23%; d$_1$, 48%; d$_2$, 28%; d$_3$, 1%. Nmr analysis of VII indicated the following positions and amounts of deuterium incorporation in phenylfulvene: H-6, 0%; H-1, H-4, 44%, 52%; H-2 + H-3, 11% total.

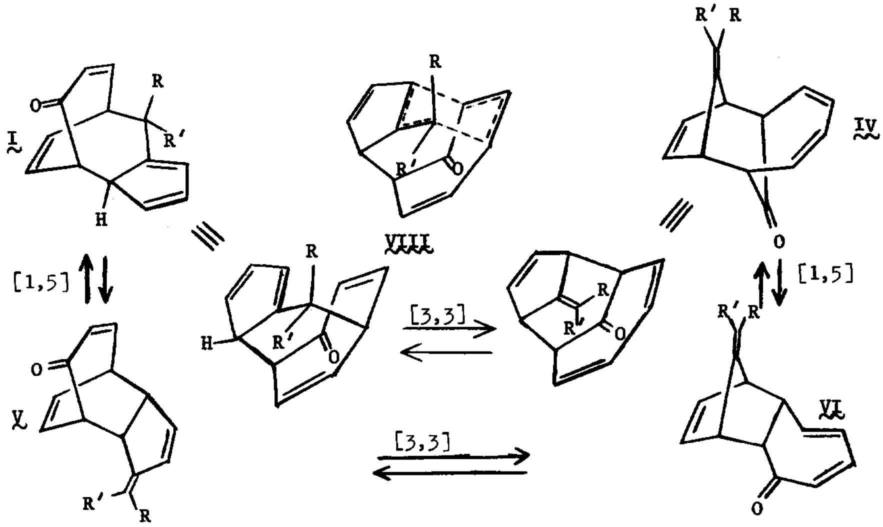


VII

Reaction of this partially deuterated phenylfulvene with tropone resulted in formation of IIId-d$_2$ in 52% yield. In the nmr spectrum of IIId-d$_2$ (100 MHz, C$_6$D$_6$), the resonances due to H-19B (δ1.97dd, J=12.0, 0.7 Hz) and H-10 (δ4.96m) were reduced in intensity to about one-half of the intensity in undeuterated IIId. The lack of scrambling of deuterium in the five-membered ring attests to the occurrence of a single concerted [1,5s] sigmatropic hydrogen shift before addition of the second tropone. Furthermore, the presence of deuterium at 19-B indicates that I is the exo adduct.

The proof of the stereochemistry of I does not rule out the initial formation of IV-VI followed by pericyclic rearrangement to I. However, the failure to observe long-lived intermediates in the dimethylfulvene reaction at 25°,[1a] coupled with the high temperatures required to effect known [1s,5s] sigmatropic carbon shifts in neutral systems,[5] make the intervention of undetected V or VI unlikely.





The intervention of the alternative [6 + 4] adduct **IV** is less easy to discount. Cope rearrangements generally occur only above 100°, but sterically favorable systems undergo [3s,3s] sigmatropic shifts readily at low temperatures.[6] Adduct **IV** would be ideally disposed to rearrange via the quasi-chair transition state **VIII**. An estimated lower limit on the order of hours for the half-life of the rearrangement of **IV** to I at 25° indicates that **IV** is in fact a plausible intermediate.

However, assuming **IV** were an intermediate in the formation of **I**, the Cope rearrangement of the adducts formed from methylfulvene and phenylfulvene would be expected to proceed most readily with the substituent (Me or Ph) in a quasi-equatorial rather than quasi-axial conformation.[7] The Cope rearrangements of **IVb** and **IVd** would be expected to produce **Ic** and **Ie** and, ultimately, **IIIc** and **IIIe**, respectively. Since these are not the isomers observed, the genesis of **I** from **IV** appears unlikely.

By contrast, the stereochemistry observed is compatible with the direct formation of **I** from tropone and the unsymmetrical fulvenes. The transition states leading to **Ib** and **Id** experience less steric repulsion between the fulvene substituent and tropone H-4 and -5 than the transition states leading to **Ic** and **Ie**. Furthermore, these transition states have the primary centers ideally aligned for bonding, while simultaneous secondary orbital interactions lead to large stabilization of this transition state relative to transition states for the other twenty-five possible adducts.

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