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CONCERNING THE PERISELECTIVITY OF THE CYCLOADDITION REACTION BETWEEN 8,8-DIMETHYLISOBENZOFULVENE AND TROPONE

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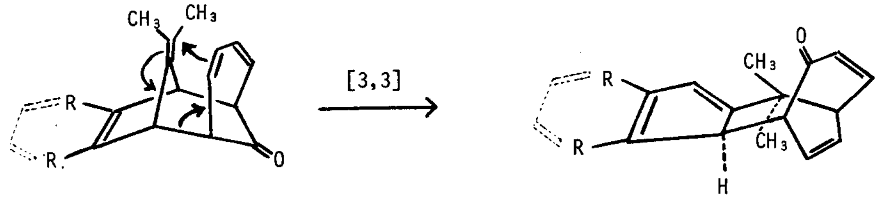
Regioselectivity and periselectivity (formation of one of the thermally allowed products) in cycloaddition reactions are of current interest and theoretical treatments of the former abound.[1] Periselectivity has been treated by one of us using Hückel based PMO theory.[2] The systems studied were quite varied[3] and the agreement with experiment was good. Some problems were encountered with systems containing heteroatoms (e.g., tropone, cyclopentadienone) but these have been eliminated by using data obtained from extended Hückel calculations.[5] However experiment and theory are not in accord in the reactions of 8,8-dimethylisobenzofulvene or 6,6-dimethylfulvene with tropone. Theory[2a,5] predicts the formation of the $[{}_{\pi}8_{s} + {}_{\pi}6_{s}]$ adduct (Ia) and the $[{}_{\pi}4_{s} + {}_{\pi}6_{s}]$ adduct (III) whereas experiment reveals the preferred formation of the $[{}_{\pi}8_{s} + {}_{\pi}6_{s}]$ adduct (II)[6] and the $[{}_{\pi}6_{s} + {}_{\pi}4_{s}]$ adduct (IV)[7] respectively. It has been stressed[2a] that the theoretical treatment can only predict products arising from kinetic control and that perhaps the products obtained from the above two reactions were in fact secondary products derived from (Ia) and (III) via sigmatropic shifts of order [3,3].[2a,6,8] It should be noted that these sigmatropic shifts relieve the bridgehead ring strain present in both (Ia) and (III) and should therefore be quite facile.



(Ia) R—R = —CH=CH—CH=CH—
(III) R = H

(II) R—R = —CH=CH—CH=CH—
(IV) R = H

In this letter we report that *in complete agreement with theory*[2a,5] *the reaction between 8,8-dimethylisobenzofulvene and tropone yields initially (Ia) which subsequently rearranges to the thermodynamically more stable isomer (II).*

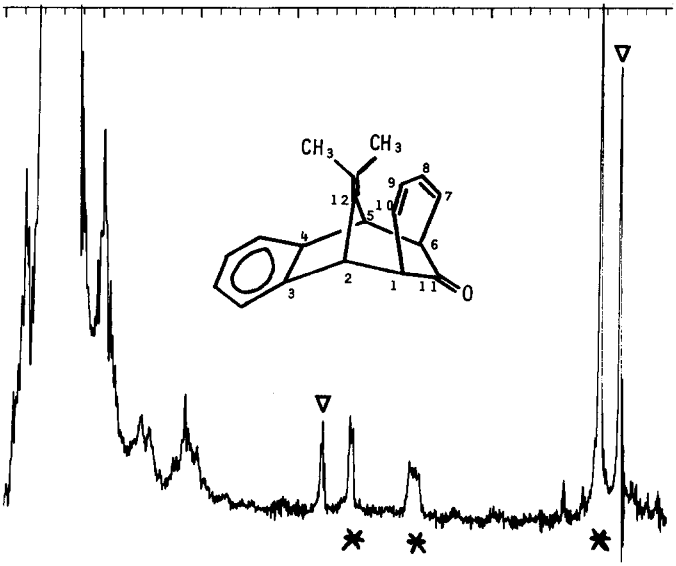
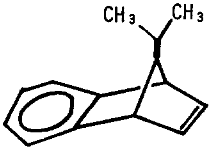


FIGURE 1.

Portion of the pmr spectrum (100M Hz) taken during the course of the reaction. The 8,8-Me_2IBF was generated from (VI) and 3,6-di(2'-pyridyl)-s-tetrazine using excess tropone as solvent and reactant. This spectrum clearly shows the high selectivity of the reaction. Traces of the 8,8-Me_2IBF dimers are the only other products formed.



(VI)

∇ resonances due to unreacted (VI)
* resonances due to (Ia) assignments listed in fig.2a) below.

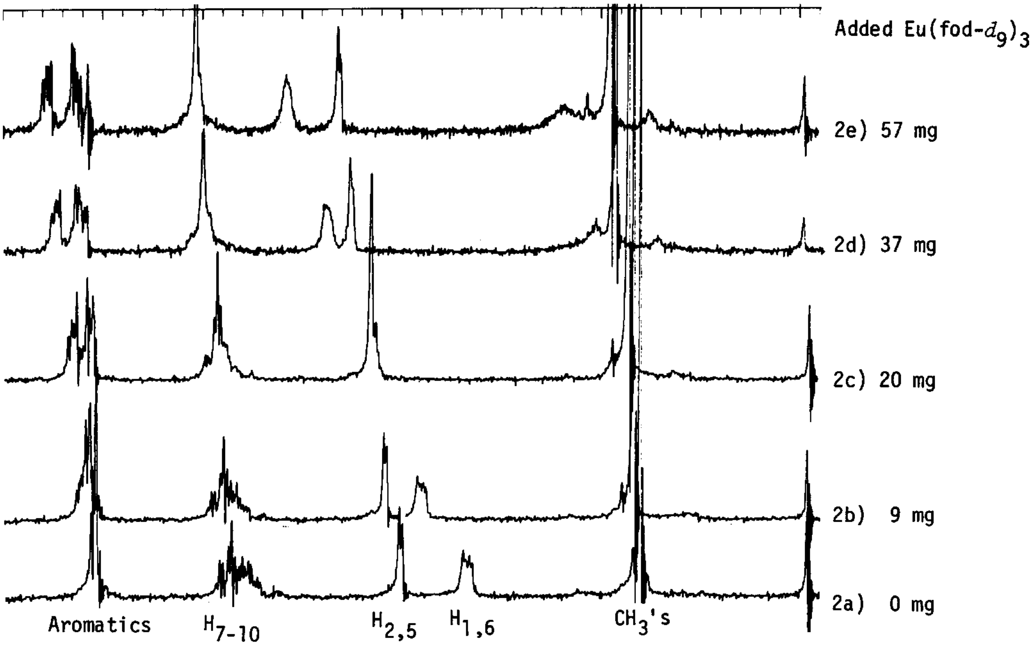
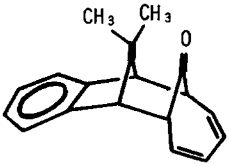


FIGURE 2. Pmr spectrum of (I). a) normal spectrum at 100M Hz in $CDCl_3$. b-e) added Eu(fod-d_9)$_3$.

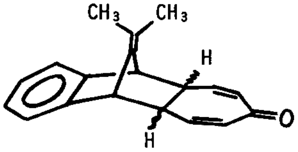
8,8-Dimethylisobenzofulvene, generated by our s-tetrazine route[9], was trapped using tropone[10] as solvent at 25°C. TLC and pmr of the reaction mixture revealed the formation of a single product in essentially quantitative yield. Isolation of the product was achieved using TLC (silica/$CHCl_3$)[11] and crystallisation from ethanol yielded a colourless compound, m.p. 136° (not sharp), analysis: C, 87.3%; H, 6.9% ($C_9H_{18}O$ requires C, 87.0%; H, 6.9%); m/e (parent), 262.

The pmr spectrum of compound (I) (Fig 2a) displays a sharp singlet for the two methyl groups. This singlet remains unaffected towards different solvents or the paramagnetic shift reagent $Eu(fod)_3$[12] (Fig. 2) thereby ruling out fortuitous magnetic equivalence of methyl groups in an asymmetrical cycloadduct. The entire spectrum is entirely consistent with a molecule possessing a plane of symmetry (note the AA'BB'pattern of the aromatic protons in the presence of $Eu(fod)_3$). The presence of aromatic protons restricts the number of possible structures of the compound to four, (Ia) (*exo*), (Ib) (*endo*), and (V) (*endo* and *exo*). The carbonyl stretching frequency of the compound occurred at 1720 cm^{-1} which unequivocally assigns the gross structure (I) to it.[13] The pmr spectra of (I) in the presence of $Eu(fod)_3$ (Fig. 2) strongly indicate that its stereochemistry is *exo*, i.e. (Ia). Complexation of the metal at oxygen in (Ia) should have a large effect on the aromatic protons and a minimal effect on the methyl groups. With (Ib) the opposite result should be observed. As may be seen, the methyl groups are moved downfield only slightly. Figure 1 shows the pmr spectrum of the reaction mixture.

(Ib)



(V)



Another strong indication that the compound (I) has the *exo* stereochemistry (Ia) comes from the observation that (I) rearranges smoothly and quantitatively to a compound identical in every respect with Tanida's observed product (II) prepared from the dimethylisobenzofulvene and tropone at 120°. Although (Ia) may rearrange to (II) via a concerted mechanism, for (Ib) to rearrange it must firstly dissociate into tropone and the isobenzofulvene. The latter alternative was ruled out since formation of dimer[2b,9d] was not detected even in trace quantities during the rearrangement.

Thus the formation of (Ia) as the kinetically controlled product is in agreement with theory. One naturally wonders now about the reaction of the dimethyl fulvene with tropone. There appears to be no reason why the fulvene should not add in the same way as the isobenzofulvene, and it is encouraging to find that the minor product formed in the reaction (a 4 + 2 adduct formed from the fulvene as the dienophile) is in fact the second favoured product[6a] according to theory[5,16].

References and Footnotes

1. (a) K.N. Houk, J. Sims, C.R. Watts and L.J. Luskus, *J.Amer.Chem.Soc.*, 95, 7301 (1973) and references therein; (b) N.D. Epiotis, *ibid.*, 95, 5624 (1973).
2. (a) M.N. Paddon-Row, *Aust.J.Chem.*, 27, 299 (1974); (b) preliminary report: M.N. Paddon-Row, P.L. Watson and R.N. Warrener, *Tetrahedron Letters*, 1033 (1973).
3. Houk and his coworkers have discussed the problem of periselectivity but to date they have restricted their attention to mainly the reactions of simple fulvenes.[4]
4. K.N. Houk and L.J. Luskus, *J.Org.Chem.*, 38, 3836 (1973); K.N. Houk, J.K. George and R.E. Duke, Jr., *Tetrahedron*, 30, 523 (1974).
5. (a) M.N. Paddon-Row, unpublished results; (b) adducts (I) and (III) are preferred using extended Hückel data. In ref. 2a the preferred adducts were derived from attack on the oxygen atom of tropone but it was noted that (I) and (III) were the next most favoured products.
6. (a) K.N. Houk, L.J. Luskus, and N.S. Bhacca, *J.Amer.Chem.Soc.*, 92, 6392 (1970); (b) K.N. Houk, L.J. Luskus, and N.S. Bhacca, *Tetrahedron Letters*, 2297 (1972).
7. H. Tanida, T. Irie, and K. Tori, *Bull.Chem.Soc.Japan*, 45, 1999 (1972).
8. For an alternative explanation of Houk's experimental results[6b], see ref 2(a) p.307.
9. (a) R.N. Warrener, *J.Amer.Chem.Soc.*, 93, 2346 (1971); (b) W.S. Wilson and R.N. Warrener, *J.C.S.Chem.Commun.*, 211 (1972); (c) G.M. Priestley and R.N. Warrener, *Tetrahedron Letters*, 4295 (1972); (d) P.L. Watson and R.N. Warrener, *Aust.J.Chem.*, 26, 1725 (1973).
10. A separate experiment showed that tropone was unreactive towards s-tetrazine under the same conditions.
11. Prolonged exposure of the product on the plate effected rearrangement to (II).
12. R.E. Rondeau and R.E. Sievers, *J.Amer.Chem.Soc.*, 93, 1522 (1971).
13. Bridgehead carbonyl groups in polycyclic molecules containing the [4.1.n...] unit (i.e. (I)) typically absorb in the 1720-1730 cm^{-1} region[14] whereas α,β-unsaturated ketones absorb in the 1660 cm^{-1} region.[15]
14. *inter alia:* R.C. Cookson, B.V. Drake, J. Hudec, and A. Morrison, *Chem.Commun.*, 15 (1966).
15. S. Itô, K. Sakan, and Y. Fujise, *Tetrahedron Letters*, 2873 (1970).
16. Sixteen possible modes of cycloaddition were considered.