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EVIDENCE AGAINST THE $({}_{\pi}2_{s} + {}_{\pi}2_{a})$ MECHANISM FOR THE CYCLOADDITIONS OF ALLENES (1)

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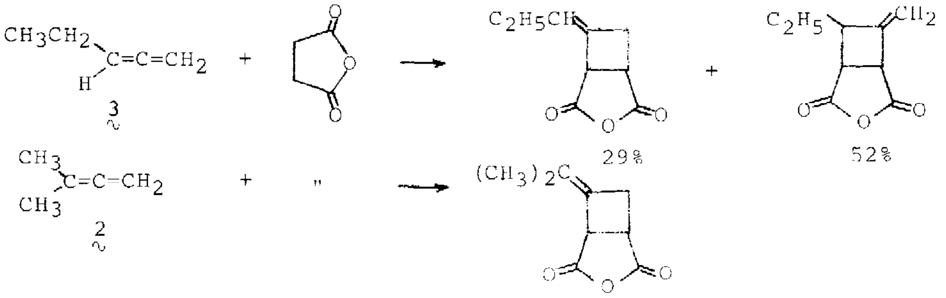
Abstract: The chemoselectivities in the $({}_{\pi}4_{s} + {}_{\pi}2_{s})$ cycloaddition reactions of tetraphenylcyclopentadienone (TPCD) with ethyl- and 1,1-dimethylallene have been determined and are compared with those observed for reaction with maleic anhydride.

Recently, a $[{}_{\pi}2_{s} + ({}_{\pi}2_{s} + {}_{\pi}2_{s})]$ pathway was suggested as a more favorable alternative to the $({}_{\pi}2_{s} + {}_{\pi}2_{a})$ pathway for concerted cycloaddition reactions of allenes (2). In this process both of the π-bonds of the allene are intimately involved in the reaction (2). The application of PMO theory to the two possible concerted pathways resulted in different predicted chemoselectivities for cycloaddition across the two double bonds of methyl- (**1**) and 1,1-dimethylallene (**2**). In the cycloaddition of **1** and **2** with an electron-deficient alkene $({}_{\pi}2_{s} + {}_{\pi}2_{a})$ or diene $({}_{\pi}4_{s} + {}_{\pi}2_{s})$ (i.e. a HOMO allene-LUMO alkene or diene controlled process) little difference in the reactivity of the two double bonds was predicted. In contrast, cycloaddition via the $[{}_{\pi}2_{s} + ({}_{\pi}2_{s} + {}_{\pi}2_{s})]$ process strongly favored addition across the least substituted double bond of **2** ($\Delta E \simeq 2.6$ kcal/mol), and slightly less so with **1** ($\Delta E \simeq 0.7$ kcal/mol). The predictions for the $[{}_{\pi}2_{s} + ({}_{\pi}2_{s} + {}_{\pi}2_{s})]$ process were amazingly consistent with the chemoselectivities observed in the cycloadditions of maleic anhydride with **2** and **3** (3) (Eq. 1 and 2). In order to experimentally determine the chemoselectivities expected of the $({}_{\pi}2_{s} + {}_{\pi}2_{a})$ process, the $({}_{\pi}4_{s} + {}_{\pi}2_{s})$ cycloaddition of **2** and **3** with tetraphenylcyclopentadienone (TPCD) has been investigated.

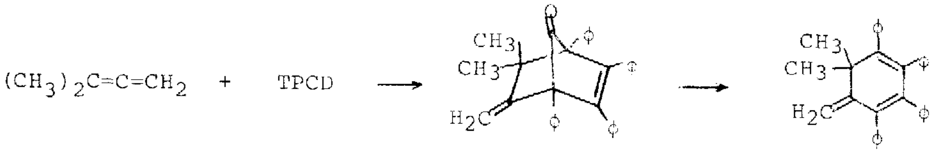
TPCD reacts quantitatively with **2** (C_6D_6 solution at 160°C for 22 hr in a sealed NMR tube) to produce a single, highly crystalline compound



Eq. 1

Eq. 2

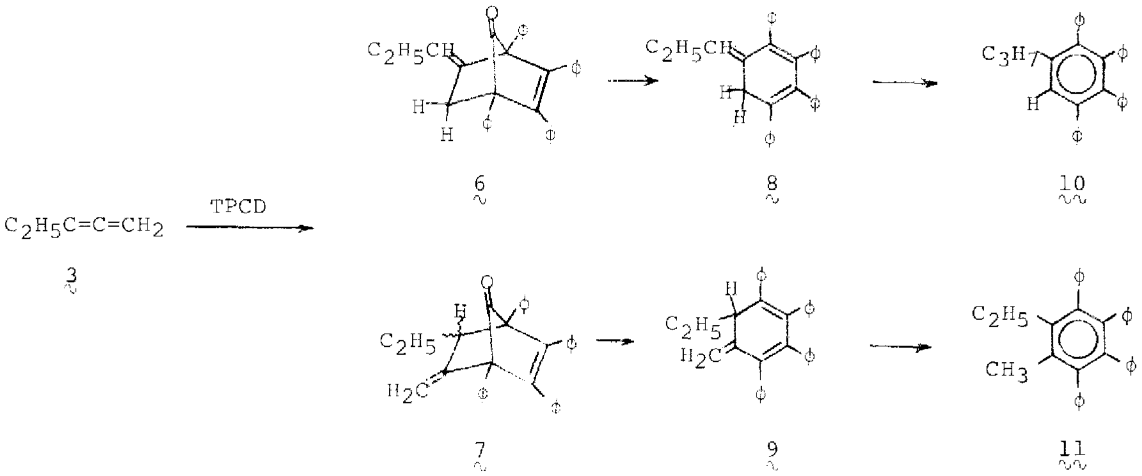
(mp 141-142°C from ethanol). Spectral data define the structure of the product as **4** formed by cycloaddition across the more highly substituted double bond followed by the loss of carbon monoxide from the intermediate adduct **5** [IR: no $\nu_{C=O}$, 902 cm^{-1} (=CH$_2$); NMR: (CDCl$_3$) δ 1.44 (s, 6H), 4.89 (br s, 1H), 5.41 (br s, 1H), 6.78 (m, 10H), and 7.1 (m, 10H); MS: exact mass calcd for $C_{33}H_{28}$, 424.219; found, 424.218].



5

4

Reaction of ethylallene (**3**) with TPCD results in the formation of a mixture of adducts which on silica gel preparative TLC gave two, rapidly moving, overlapping bands, and two more slowly moving, overlapping bands. The most rapidly moving fraction was obtained in ~90% purity (contaminated with **11**) and was recrystallized with great difficulty from methanol (mp 123-125°C). The structure of the adduct was assigned as **10** on the basis of NMR spectral data [(CDCl$_3$) δ 0.85 (t, J = 6.8 Hz, 3H), 1.66 (m, 2H), 2.49 (m, apparently due to slow, hindered rotation about the CH$_2$-ring bond, 2H), 6.84 (m, 10H), 7.13 (m, 10H), and 7.41 (s, 1H); MS: exact mass calcd for $C_{33}H_{28}$, 424.219; found, 424,221]. The second band was predominantly **11** which



could not be further efficiently purified by preparative TLC or recrystallization. The structure of the major component of this fraction is assigned as 11 [NMR: ($CDCl_3$) δ 0.54 (t, J = 6.7 Hz, 3H) 2.17 (s, 3H) 2.54 (m, 2H), 6.78 (m, 10H), and 7.17 (m, 10H); MS: parent ion m/e 424]. The third band contained varying amounts of 10 and a material assigned as a mixture of stereoisomers of 8 (vinyl H's at δ 5.86 and 6.14). Despite the much smaller rf value of this band relative to that of 10, 8 could not be isolated free of 10 indicating that 8 undergoes isomerization to 10 on TLC. In a similar manner, fraction 4 could not be obtained pure; always being contaminated with 11. THe structure of the major component of this band is assigned as 9 [NMR: ($CDCl_3$) δ 0.66 (t, J = 6.7 Hz, 3H). 0.96 (m, 2H), 3.76 (d, J = 2.4 Hz, 1H), 4.56 (d, J = 2.4 Hz, 1H), 6.82 (m, 10H), and 7.14 (m, 10H); MS: parent ion m/e 424]. 9 obviously undergoes isomerization on the silica gel to form 11. The relative amounts of 10, 11, 8, and 9 (by integration of the NMR spectrum of the crude reaction mixture) is ∿50 : 25 : 16 : 8, indicating the formation of 6 and 7 in a ratio of ∿2 : 1.

The chemoselectivity observed in the cycloaddition of 3 with TPCD is in good accord with that predicted by PMO calculations. (2) The chemoselectivity in the reaction of 2 with TPCD is enhanced by steric inhibition to the approach of the TPCD to either face of the unsubstituted double bond.

The dramatic differences between the chemoselectivities observed in the reactions with TPCD and maleic anhydride strongly indicate that the cycloaddition reactions with maleic anhydride do not occur via a $({}_{\pi}2_s + {}_{\pi}2_a)$ pathway. Despite the arguements put forth previously concerning the $({}_{\pi}2_s + {}_{\pi}2_a)$ concerted versus the two-step, diradical intermediate mechanisms for the cycloaddition reactions of allenes, sufficient data capable of discriminating between the concerted $[{}_{\pi}2_s + ({}_{\pi}2_s + {}_{\pi}2_s)]$ and the two-step, diradical-intermediate mechanisms is not yet available (see discussion and references cited in ref. 2). Such studies are currently being carried out in the author's laboratories.

References:

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