Steric Factors in (2+2)-Cycloadditions of Ketens to Olefins

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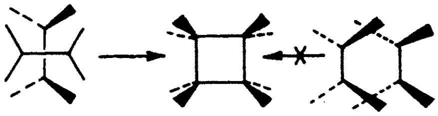
Summary The markedly reduced reactivity of *trans*- compared to *cis*-olefins in cycloadditions to ketens is cited as evidence for the suggested $({}_{\pi}2_s + {}_{\pi}2_a)$ concerted mode of addition.

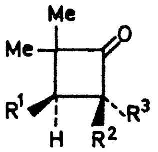
ORBITAL symmetry grounds have been used to predict that the cycloaddition of two ethylenic components to form a cyclobutane ring may proceed by a concerted route provided that the approach geometry is the tetrahedral one, (I), rather than a planar arrangement, (II).[1] The permitted route is designated $({}_{\pi}2_s + {}_{\pi}2_a)$ in the notation of Woodward and Hoffmann.

(I)

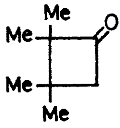


(II)

We now draw attention to evidence which substantiates this prediction in the case of cycloadditions of ketens to olefins. Considerable evidence has been put forward suggesting that such reactions are concerted.[2a–d] We find that dimethylketen reacts readily with *cis*-but-2-ene at 100°, the sole product being that with retained stereochemistry of the methyl groups, (III). The *trans*-olefin reacts more slowly by a factor of at least 3 to give mainly (IV) but with some (III). *cis*-Pent-2-ene likewise yields the isomers (V) and (VI) in the ratio 49 : 51% at a total rate almost identical with that for *cis*-but-2-ene, while *trans*-pent-2-ene under the same conditions gives no detectable product as also do 2-methylbut-2-ene and 2,3-dimethylbut-2-ene. Furthermore, isobutene while giving the adduct (VII) reacts with dimethylketen at a rate eight times slower than *cis*-but-2-ene. Other workers have reported similar findings; thus, dipenylketen adds to *cis*- and *trans*-allyl propyl ether at relative rates 184 : 1 respectively[2a] and ethoxy keten to *cis*- and *trans*-butenes 1·7 : 1.[3] Similar difficulties in adding *trans*- compared with *cis*- olefins to t-butylcyanoketen have been noted.[4]

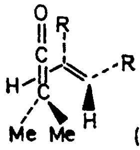


	R^1	R^2	R^3
(III)	Me	Me	H
(IV)	Me	H	Me
(V)	Me	Et	H
(VI)	Et	Me	H

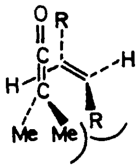


(VII)

These differences in reactivity are most convincingly viewed as arising from steric interactions between the reagents. In this respect no difference should exist between *cis*- and *trans*-olefin in the coplanar transition state but the tetrahedral approach requires a *trans*-olefin to present one bulky substituent group directly towards the keten, (VIII), while the *cis*-isomer can approach with hydrogens towards the keten, (IX).



(IX)



(VIII)

We believe that these interactions are responsible for the diminished reactivity towards ketens of *trans*-1,2- and 1,1-di-, tri-, and tetra-substituted ethylenes compared with mono- or *cis*-disubstituted, and that this is strong evidence for the correctness of the suggested geometry of approach in this reaction.

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[1] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, 1970.

[2] (a) R. Huisgen, L. Feiler, and P. Otto, *Chem. Ber.*, **1969**, **102**, 3444; (b) G. Binsch, L. Feiler, and R. Huisgen, *Tetrahedron Letters*, 1968, 4497; (c) R. Montaigne and L. Ghosez, *Angew. Chem.*, 1968, **80**, 194; (d) H. M. Frey and N. S. Isaacs, *J. Chem. Soc.* (*B*), 1970, 830.

[3] M. DoMinh and O. Strausz, *J. Amer. Chem. Soc.*, 1970, **91**, 1760.

[4] H. W. Moore, personal communication.