# On the Mechanism of the *meta* Photocycloaddition of Ethylenes to Benzenoid Compounds

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cis-Cyclo-octene undergoes locoselective *meta* photocycloaddition to isopropylbenzene, t-butylbenzene, *p*-methylcumene, anisole, and *p*-methylanisole. The results are discussed in terms of substituent stabilisation of the intermediates produced either by *meta* ethylene cycloaddition to the S_1 arene or by *meta* bonding in the photo-excited benzene derivative. The mechanistic pathway preferred appears to be influenced by steric effects of the arene and ethylene substituents.

SINCE the first reports of *meta* photocycloaddition of ethylenes to the benzene ring to yield compounds of type (1),[1] the scope,[2-11] synthetic potential,[2,7,11] and orbital symmetry features [2,12,13] of this remarkable process have been described in many publications.[14]
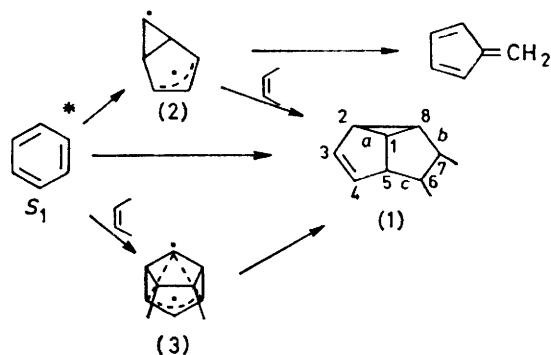

SCHEME 1

Aspects of the addends which affect the relative efficiency of the *meta* and *ortho* cycloadditions have also been discussed.[2,4,8,9,15,16] It has been noted that S_1 benzene is potentially *meta* bonding [17] and that from orbital symmetry considerations, the 'allowedness' of the *meta* cycloaddition is insensitive to the mechanistic details of the process; [2,13] thus bond *a* in the adduct may be formed prior or subsequent to bonds *b* and *c* [*i.e.* formation of intermediates (2) and (3) respectively] or the three may be formed synchronously (see Scheme 1).
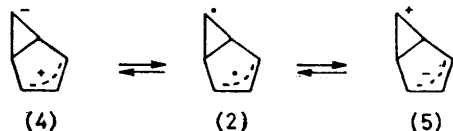

The lack of significant fluorescence quenching of benzene by alkenes [18] and the quenching of fulvene formation from irradiated benzene in the presence of an ethylene [1b] suggests that the *meta* cycloadducts arise by addition of the ethylene to the species (2); this may be formed in its singlet state adiabatically from benzene [17,19,20] and may be better represented as a hybrid between dipolar canonical forms, with form (4) being likely to make the greatest contribution to the hybrid.

From studies of the intramolecular *meta* photocyclo-addition of *cis*- and *trans*-6-phenylhex-2-ene it was suggested, however, that the reaction proceeded by way of an excited-state complex.[21] This proposal has been reinforced by Srinivasan and his co-workers who rationalise the locospecific *endo* 2,6-addition of various alkenes to methyl [5,6] and methoxy [7] benzenes by the involvement of an *endo* sandwich exciplex, for example (6) from toluene and cyclopentene, which yields the addition intermediate (7) and thence exclusively the
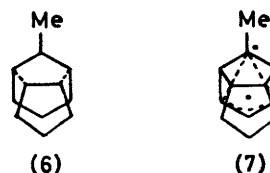
1-methyl-substituted derivative of (1); thus it was considered that the 'last bond to close is the cyclo-propane which seems to form in either way.' [7] On the other hand if a species such as (2) were involved in the *meta* cycloaddition of ethylenes to substituted benzenes to any extent, then as a result of stabilisation of radical/charge centres by the substituents, the 3-, 5-, and 8-substituted isomers of the adduct (1) may be expected
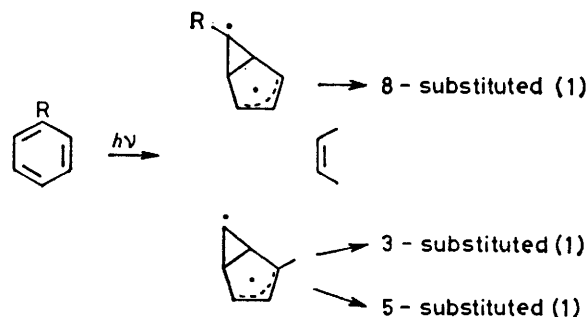
SCHEME 2

to be formed as shown in Scheme 2. With substituted benzenes, the concerted mechanism involving synchronous formation of bonds *a*, *b*, and *c* may be expected to show little selectivity in the formation of substituted isomers of (1).

The purpose of the present work was to determine if

both intermediates (2) and (3) may be involved in the mechanistic pathway of this intriguing and general photoprocess, and to achieve this we have studied the orientational selectivity of the addition of *cis*-cyclo-octene to isopropylbenzene, t-butyl benzene, *p*-methyl-cumene, anisole, and *p*-methylanisole. This particular alkene was chosen for detailed study since in its photo-addition with toluene the 5-methyl isomer of (1) was formed specifically,[22] and hence this provided the only indication that the pathway involving (3) as an inter-mediate was not the exclusive route to *meta* cyclo-adducts (1).[5-7]

RESULTS AND DISCUSSION

The adducts were prepared by irradiation of equi-volume solutions under air at 20 °C. Minor amounts of photoproducts other than *meta* cycloadducts were formed in most cases but concentrations of these were too low to affect seriously spectral analysis, and separ-ation of isomers could be achieved by preparative g.l.c. with Carbowax 20m as the liquid phase. The results are summarised in Table 1.[23] Estimates of the relative

TABLE 1

*meta* Photocycloaddition modes of *cis*-cyclo-octene to benzenoid compounds

| Arene	Product isomer of (1) (approximate respective ratios)
Toluene [a]	5-Methyl
Isopropylbenzene	1-Isopropyl, 3-isopropyl (2 : 1)
t-Butylbenzene	1-t-Butyl, 3-t-butyl (1 : 1.5)
p-Methylcumene	1-Methyl-3-isopropyl, 1-isopropyl-3-methyl (5 : 1)
Anisole	8-Methoxy
p-Methylanisole	1-Methoxy-3-methyl

[a] Ref. 22.

yields of the isomers in mixtures were made from 220-MHz spectra of undistilled products and supported by g.l.c. analysis. The structures of the adducts were assigned from spectral data and in particular the posi-tions of the substituents were deduced from [1]H n.m.r. spectra (100 and 220 MHz) and their comparison with that of *cis*-cyclo-octene with benzene[4,24] and those of other *meta* cycloadducts of known structure.[3-11] For example the 8-position of the methoxy-group in the *meta* cycloadduct from *cis*-cyclo-octene and anisole was assigned as follows. The spectrum consists of seven sets of resonances at δ 5.45—5.75 (ethenyl 3- and 4-H), 3.24 (methoxy), 2.85—3.15 (5-H), 2.35—2.85 (6- and 7-H), 2.15—2.35 (1-H), 1.75—1.95 (2-H), and 0.75—2.15 (-CH_2- of cyclo-octane). The ethenyl resonance was identical to that of the *meta* cycloadduct of benzene and *cis*-cyclo-octene. Thus the lower-field resonance (3-H) was comprised of a pair of doublets ($J_{3,4}$ 5.5, $J_{3,2}$ 2, $J_{3,5}$ 0 Hz) and the upfield resonance (4-H) was a pair of multiplets ($J_{4,3}$ 5.5, $J_{4,5}$ 2, $J_{4,2}$ *ca.* 1 Hz). Spin de-coupling revealed that the allylic protons resonated at δ 1.86 (2-H) and 3.01 (5-H). The presence of the 1-H proton was shown by the triplet ($J_{1,2} = J_{1,5} = 7$ Hz) centred at δ 2.23. Thus the methoxy-substituent must reside on the 8-position. Assignment of the positions

of the substituents in the other adducts followed this approach. As with *meta* cycloadducts from other systems,[7] however, [1]H n.m.r. spectroscopy was of little use in assigning stereochemistry but from the general thermal stability of the present products,[25] the *endo* stereoisomer was considered to be the major if not exclusive isomer.

In principle, with the monosubstituted and unsym-metrically *para* disubstituted arenes studied here, there are six substituted positional isomers of (1) which may be formed with an ethylene. If addition occurred ex-clusively by initial formation of (3) from the exciplex then
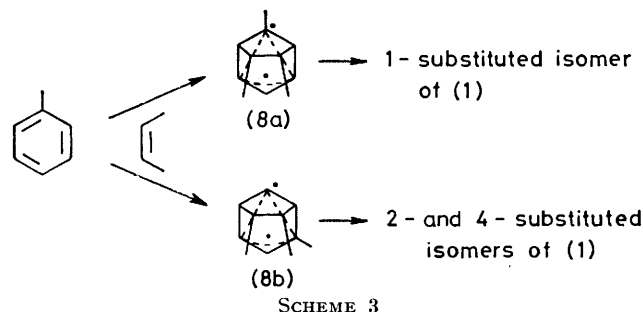
SCHEME 3

assuming the substituent will reside on positions to give maximum stabilisation of the radical/charge centre only the 1-, 2-, and 4-isomers may be expected from mono-substituted arenes as shown in Scheme 3. That the latter two isomers are not observed in the present systems, or those involving cyclopentene with toluene[6] and anisole[7] (but see later) and cycloheptene and ani-sole,[7] is further evidence for an *endo* approach of the addends and addition to give (3), as steric interaction of the arene and ethylene substituents in (8b) would make this less favoured than (8a). Further, for similar steric reasons with the *para* substituted compounds it would be expected that in the formation of (1) *via* (3) the isomer formed preferentially would be that with the bulkier group in the 1- rather than the alternative 3-position as shown in Scheme 4.


SCHEME 4
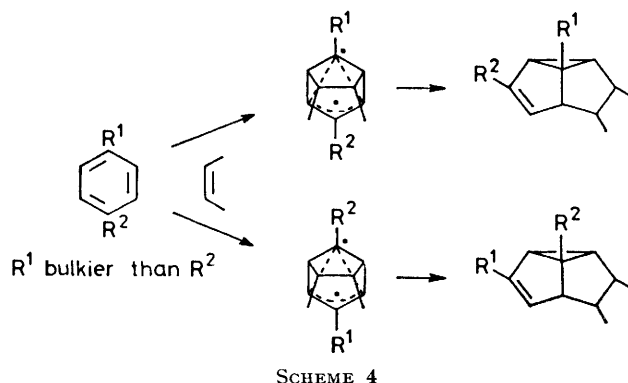
Inspection of the data in Table 1 reveals that the *meta* photocycloaddition of *cis*-cyclo-octene to the arenes cannot be rationalised simply in terms of previous mechanistic proposals[5-7] and the intermediate (3). Nonetheless, it is not a random addition but is highly

selective giving not more than two of the possible six isomers. Although the 1-substituted isomer of (1) was formed from both isopropyl- and t-butyl-benzene, the 3-isomer comprised 30% of the adduct mixture in the former case and was the major product in the latter, and whereas involvement of (8a) can account for formation of the former isomers, it is highly improbable, both on steric grounds and stabilisation of radical centres, that the analogous species (9) would be involved in the formal 3,5-orientation of the addends. The formation of the 3-substituted isomers of (1) can, however, be
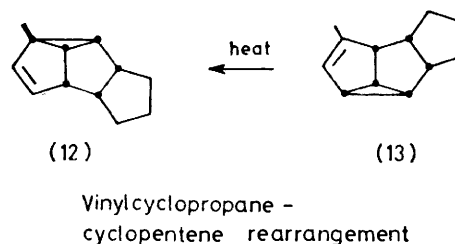

(9)   3 - Isomer

rationalised by the involvement of a species such as singlet prefulvene (2) (see Scheme 2) (*i.e.* prior formation of bond *a*) which is then trapped by the alkene in a concerted manner. Formation of (2) may not be greatly affected by steric factors but its relative involvement compared to (3) in the production of (1) appears to increase with the steric bulk of the substituent. Further this mechanism can accommodate the observed preferred 3,5- rather than 2,6-attack, of *cis*-cyclo-octene to *p*-methylcumene; as noted above 2,6-attack would be expected in this case if (3) were the sole reaction intermediate. For the alkyl benzenes, formation of (2) (Scheme 2) with the substituent or the more bulky substituent in the 5-membered ring seems to be preferred since no 8-substituted isomer of (1) was detected. Toluene and *cis*-cyclo-octene yield the 5-substituted isomer of (1) but with bulkier groups than methyl, it appears that the approach of the ethylene changes from that depicted in (10) to that in (11); from space-

(10) R¹ = Me, R² = H
(11) R¹ = H, R² = Prⁱ or Buᵗ
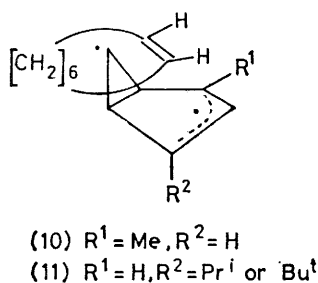
filling molecular models, this can be understood in terms of steric interactions between the alkyl substituent and the ethenyl hydrogen of the *cis*-cyclo-octene.

We examined the reaction of *cis*-cyclo-octene with anisole to determine if a polar substituent would affect the above considerations based on steric factors of the substituents. Irradiation of this system gave a mixture of products of which the major constituted approximately 90% and to which the 8-methoxy-structure of (1) was assigned as outlined above. The minor components were not analysed in detail but that formed in the greater

amount (*ca.* 3 : 1) appeared to be a *meta* cycloadduct which had eliminated methanol whereas the other had molecular weight and mass-spectral fragmentations indicative of a positional isomer of the major product. These results are in marked contrast to those reported for this arene with cyclopentene and cycloheptene both of which are reported to yield the 1-methoxy-substituted isomer of (1), again, it is proposed, *via* 2,6-*endo* attack and involving (8a). We have re-examined the anisole–cyclopentene system and confirm the results of Srinivasan and his co-workers but we have also observed the formation of minor amounts (*ca.* 8% of the major isomer) of two further *meta* cycloadducts to which we assign, from spectroscopic data of their mixture and the thermal conversion of one into the other, the 2- and 4-methoxy-substituted compounds (12) and (13) respectively. The

(12)   (13)

Vinyl cyclopropane –
cyclopentene rearrangement

observation of these two isomers as minor reaction products in the present work is rationalised by the involvement and substituent stabilisation of the diradical intermediate (8b) which, as noted above, on steric grounds may be expected to be less favoured than (8a) which yields the isomer produced in major amounts. Formation of the 8-methoxy-isomer of (1) from anisole and *cis*-cyclo-octene is considered to arise from addition of ethylene to the 6-methoxy-derivative of the diradical (2) (Scheme 2) rather than its polarised forms since the OMe group would not significantly stabilise the negative charge on the cyclopropane ring of (3) and reversal of polarity to (5) seems highly unlikely in view of the stability of cyclopropyl cations compared to that of the anions. The alternative mechanism involving a 1,3-ethylene addition to give (14) would also have yielded

(14)
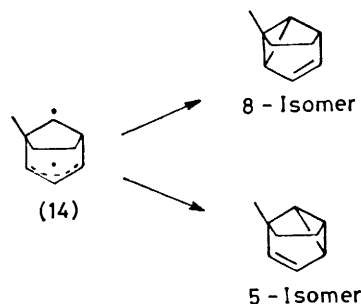
8 - Isomer

5 - Isomer

the 5-isomer and indeed the lack of reaction of *o*-dimethoxybenzene with cyclopentene is suggested to arise from steric problems in such 1,3-attack leading to intermediates of type (14). It is of interest to note

here that the *meta* addition of thiochrome 1,1-dioxide to anisole is reported to be 3,5;[26] we consider that this reaction is again better rationalised in terms of attack of ethylene on to the species analogous to (11) than by involvement of (9) whether this latter has *exo* or *endo* stereochemistry.

The addition of cyclopentene to *p*-methylanisole is specifically 2,6 and surprisingly, in view of the results with the photoaddition of *cis*-cyclo-octene to toluene and anisole, we have observed that the major products from this *p*-substituted arene and *cis*-cyclo-octene also reflect a 2,6-mode of addition. Thus the two major products formed in an approximately 2 : 1 ratio have essentially identical [1]H n.m.r. spectra which show the presence of one ethenyl proton, the methoxy-group on a saturated carbon, and the methyl group on an ethylene bond; in view of the relative thermal labilities of the products, we assign the *exo* and *endo* 1-methoxy-3-methyl isomer structures (15) and (16) respectively to the minor and

(15) $R^1-R^1 = -[CH_2]_6-$, $R^2=H$
(16) $R^1=H$, $R^2-R^2 = -[CH_2]_6-$
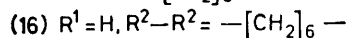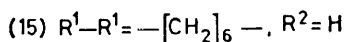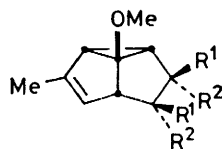
major adducts. The isomer arising from 3,5-addition to *p*-methylanisole, unlike that from *p*-methylcumene, was not detected.

A preliminary study of cyclopentene and vinyl acetate with the above benzene derivatives was also undertaken but the adducts of the former ethylene with cumene, t-butylbenzene, and *p*-methylcumene were produced in low yields and accompanied by significant amounts of by-products, and spectral interpretations of the adducts from vinyl acetate were complicated by the formation of regioisomeric mixtures. However, it was possible to deduce in the latter case that (a) the addition was loco-specifically 2,6 to toluene, (b) the ratio of 1-substituted-(1) to the 3-isomer was 4 : 1 and 3 : 1 respectively from cumene and t-butylbenzene, and (c) the ratio of 1-methyl-3-isopropyl-(1) to 1-isopropyl-3-methyl-(1) was 2 : 1 from *p*-methylcumene.

The present study has shown that the orientation of *meta* cycloaddition of ethylenes to benzenoid compounds cannot be accounted for universally by a mechanism involving a sandwich exciplex and the intermediate (3). The results with *cis*-cyclo-octene as addend can best be rationalised in terms of the involvement of primary *meta* bonding in the arene to yield such a species as (2). The extent of involvement of this latter species is variable but steric and electronic features of the addends seem to play important roles in the choice of reaction pathway for a particular system, and it is surprising that in some systems one mechanism operates to the apparent total exclusion of the other.

EXPERIMENTAL

The irradiation source in all experiments comprised Hanovia 15-W low-pressure mercury-arc lamps. The general procedure involved the irradiation in quartz tubes of varying capacity (50—300 ml) of equivolume mixtures of the arene and the ethylene at 20 °C. Degassing the solutions under nitrogen had no detectable effect. The reactions were monitored by g.l.c. and when sufficient product was judged to be formed or occluded polymer on the quartz tubes had essentially stopped the reaction, the starting materials were removed under vacuum to give the crude products, the [1]H n.m.r. spectra of which from isopropylbenzene, t-butylbenzene, and *p*-methylcumene were used to assess the ratio of products. The products were vacuum-distilled and the adduct isomers separated by preparative g.l.c. (Carbowax 20M) where required.

The structures of the products were assigned using mass spectroscopy (1 : 1 adducts of starting materials), absorption in the ultraviolet region between 215 and 240 nm (vinyl cyclopropane chromophore), absorptions in the infrared spectrum at 3 050—3 010 cm^{-1} (ethenyl CH, and cyclopropyl C–H stretching) and 1 620—1 590 cm^{-1} (C=C in cyclopentene ring), and [1]H n.m.r. spectra (tetramethylsilane as internal standard). The ethenyl and substituent proton resonances are shown in Table 2. Similar data were

TABLE 2
Ethenyl and substituent [1]H n.m.r. signals of adducts

Arene	Isomer of (1)	δ Values (CDCl$_3$)
Isopropylbenzene	1-Isopropyl	5.75—5.5 (2 H, two ABq allylic couplings, 3-H, 4-H), 0.93 (6 H, d, *J* 6 Hz, Me of isopropyl) (2.0—2.3 region, no evidence for 1-H triplet)
	3-Isopropyl	5.08 (1 H, br s, 4-H), 1.03 (6 H, d, *J* 6 Hz, Me of isopropyl on C=C)
t-Butylbenzene	1-t-Butyl	5.72—5.5 (2 H, two ABq allylic couplings, 3-H, 4-H), 0.87 (9 H, Bu^t on saturated C) (absence of 1-H triplet at *ca.* 2.0—2.3)
	3-t-Butyl	5.08 (1 H, br s, 4-H), 1.10 (9 H, Bu^t on C=C)
p-Methylcumene	1-Methyl-3-isopropyl	5.02 (1 H, br s, 4-H), 1.32 (3 H, s, Me, on saturated C), 1.06 (6 H, d, *J* 6 Hz, Me$_2$ of isopropyl on C=C)
	3-Methyl-1-isopropyl	4.94 (1 H, br s, 4-H), 1.73 (3 H, t, Me on C=CH), 0.88 (6 H, d, *J* 6 Hz, Me of isopropyl on saturated C)
Anisole	8-Methoxy	See text
p-Methylanisole	1-Methoxy-3-methyl	5.17 (1 H, br s, 4-H), 3.35 (3 H, s, OMe on saturated C), 1.75 (3 H, t, Me on C=CH)

obtained for the adducts of vinyl acetate with toluene, isopropylbenzene, t-butylbenzene, and *p*-methylcumene.

REFERENCES

[1] (a) K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.,* 1966, **88**, 2066; (b) D. Bryce-Smith, A. Gilbert, and B. H. Orger, *Chem. Comm.,* 1966, 512.

[2] D. Bryce-Smith and A. Gilbert, *Tetrahedron*, 1976, **32**, 1309; *Tetrahedron*, 1977, **33**, 2459, and references therein.

[3] K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, 1971, **93**, 2073.

[4] D. Bryce-Smith, B. Foulger, J. Forrester, A. Gilbert, B. H. Orger, and H. M. Tyrrell, *J.C.S. Perkin I*, 1980, 55.

[5] R. Srinivasan, *J. Amer. Chem. Soc.*, 1971, **93**, 3555.

[6] J. Cornelisse, V. Y. Merritt, and R. Srinivasan, *J. Amer. Chem. Soc.*, 1973, **95**, 6197.

[7] J. A. Ors and R. Srinivasan, *J. Org. Chem.*, 1977, **42**, 1321.

[8] H.-G. Heine and W. Hartmann, *Angew. Chem. Internat. Edn.*, 1975, **14**, 698.

[9] J. Mattay, H. Leismann, and H. D. Scharf, *Chem. Ber.*, 1979, **112**, 577.

[10] M. F. Mirbach, M. J. Mirbach, and A. Saus, *Tetrahedron Letters*, 1977, 959.

[11] A. Gilbert and M. W. bin Samsudin, *J.C.S. Perkin I*, 1980, 1118.

[12] D. Bryce-Smith, *Chem. Comm.*, 1969, 806.

[13] D. Bryce-Smith, *Pure Appl. Chem.*, 1973, **34**, 193.

[14] A. Gilbert in 'Photochemistry,' ed. D. Bryce-Smith, Specialist Periodical Report, vols. 1—10, The Chemical Society, London, 1970—1980.

[15] D. Bryce-Smith, A. Gilbert, B. H. Orger, and H. M. Tyrrell, *J.C.S. Chem. Comm.*, 1974, 334.

[16] A. Gilbert, G. N. Taylor, and M. W. bin Samsudin, *J.C.S. Perkin I*, 1980, 869.

[17] D. Bryce-Smith and H. C. Longuet-Higgins, *Chem. Comm.*, 1966, 593.

[18] A. Morikawa and R. J. Cvetanovic, *J. Chem. Phys.*, 1968, **49**, 1214.

[19] I. Haller, *J. Chem. Phys.*, 1967, **47**, 1117.

[20] D. Bryce-Smith, *Pure Appl. Chem.*, 1968, **16**, 47.

[21] W. Feree, J. B. Grutzner, and H. Morrison, *J. Amer. Chem. Soc.*, 1971, **93**, 5502.

[22] D. Bryce-Smith, W. M. Dadson, A. Gilbert, B. H. Orger, and H. M. Tyrrell, *Tetrahedron Letters*, 1978, 1093.

[23] See A. Gilbert and P. Heath, *Tetrahedron Letters*, 1979, 2831, for a preliminary communication of part of these results.

[24] B. H. Orger, Ph.D. Thesis, University of Reading, 1969.

[25] W. R. Roth and B. Peltzer, *Annalen*, 1965, **685**, 56; R. Srinivasan, *Tetrahedron Letters*, 1971, 4551.

[26] I. W. J. Still and T. S. Leong, *Tetrahedron Letters*, 1979, 1097.