The Meta Photocycloaddition of Arenes to Alkenes

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Contents

I. Introduction

"The aromatic nucleus, known for its rigidity in the ground state, becomes an extremely flexible and extrovert acrobat when being doped with a light quantum!" This, slightly anthropomorphic, description of electronically excited benzene was given in 1967 by Egbert Havinga in an article[1] with his co-workers on the nucleophilic photosubstitution reactions of benzene derivatives. No less than 10 references were used to support this statement. They concern the photoisomerization of benzene to fulvene,[2] the formation of tri-*tert*-butyl(Dewar benzene) from tri-*tert*-butylbenzene,[3] the photochemical interconversion of the *o*-, *m*-, and *p*-xylenes[4] and the di-*tert*-butylbenzenes,[5] the phototransposition of carbon atoms in the benzene ring,[6] the photochemical addition of benzene to alcohols[7] and acids,[8] the ortho and meta photocycloaddition of benzene to alkenes and the para addition to 1,3-dienes,[9] the formation of benzvalene from excited benzene,[10] and the interesting suggestion that a Möbius-type structure might be a common intermediate in the various photoreactions of the benzene nucleus.[11]

In this review we will be primarily concerned with the meta photocycloaddition of photoexcited benzene and derivatives of benzene to alkenes. This remarkable reaction, which has no counterpart in thermal chemistry, has inspired physical organic chemists, synthetic organic chemists, and theoretical chemists during a period of more than 25 years. Yet, its mechanism, in particular the stereochemical aspects, is still only partly understood. There are beautiful examples of the synthetic use of the intramolecular meta photocycloaddition, but the synthetic potential of the intermolecular variant has by no means been fully exploited. The theoretical description of the process is beginning to get shape, but, again especially with regard to the stereochemical aspects, it is far from complete. The simplest examples of the meta photocycloaddition are depicted in Scheme 1.

These systems, benzene plus ethene[12] and 5-phenylpent-1-ene,[13] do actually undergo the meta photocycloaddition, but they are not the ones used by the discoverers of the reaction. At this point, they serve to illustrate the types of skeletons that can be obtained by this process. In the intermolecular reaction between benzene and open-chain alkenes a tricyclic molecule is formed while in the intramolecular reaction the monocyclic starting material is converted into several tetracyclic products.

Jan Cornelisse was born in 1937 in Leiden, The Netherlands. He studied chemistry at Leiden University and obtained his Ph.D. degree in 1965 under the supervision of Prof. Egbert Havinga. In 1973 he became a lecturer and in 1980 a professor of organic chemistry at Leiden. In 1972/1973 the author worked for one year at the Thomas J. Watson Research Center of IBM at Yorktown Heights, NY, with Dr. Srinivasan on the meta photocycloaddition of arenes to alkenes. During the years 1965–1980 at Leiden his research was concentrated on photosubstitution reactions of aromatic compounds. Since 1980 his main research themes have been the meta photocycloaddition of arenes and the chemistry of polycyclic aromatic compounds, the latter in collaboration with his colleague Professor Johan Lugtenburg. Prof. Cornelisse is Chairman of the Department of Chemistry at Leiden University and Chairman of the Havinga Foundation.

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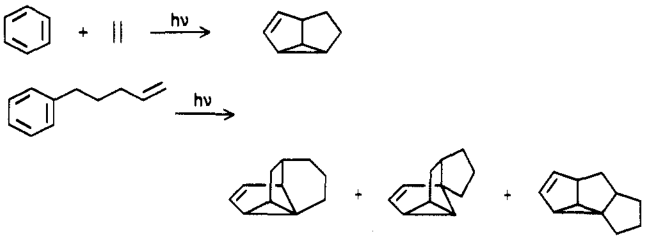
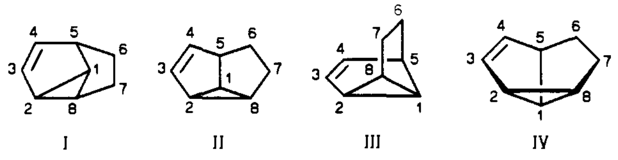
Scheme 1. Intermolecular and Intramolecular Meta Photocycloaddition



Scheme 2. Various Representations of Tricyclo[3.3.0.0^{2,8}]oct-3-ene, the Meta Photocycloadduct of Benzene and Ethene



Among the various aspects of the reaction that will be discussed in this review are the nature of the reactive excited state, the possible occurrence of intermediates along the reaction pathway, the theoretical description of the meta photocycloaddition, the influence of substituents on the benzene ring and the regiochemical aspects of the reaction, the influence of substituents on the alkene and the stereochemical aspects of the reaction, and synthetic applications of the meta photocycloaddition.

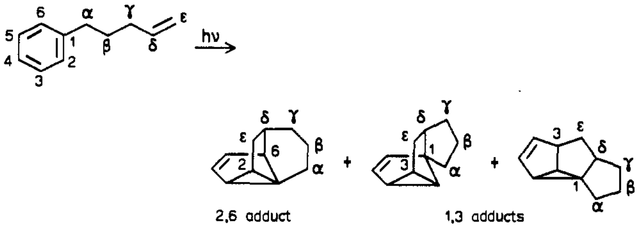
II. Pictorial Representation of the Adducts; Nomenclature

A variety of drawings have been used in the literature to represent the structure of the new carbon skeleton that is formed upon intermolecular meta addition of excited benzene to an alkene. Diagrams I–IV (Scheme 2) are the ones most commonly encountered; the numbering is according to IUPAC rules.

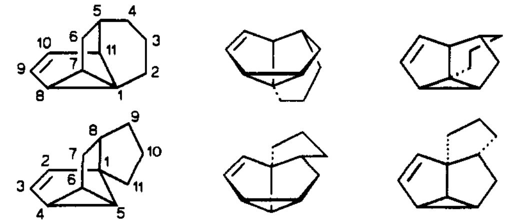
Diagram I shows most clearly that the addition has occurred at two carbon atoms (C_5 and C_8) which are in the meta position in the original benzene ring. Diagram II nicely shows the symmetry of the σ-framework of the adduct, which is a dihydrosemibullvalene. Diagram III is frequently used when stereochemical factors are discussed, because it shows how the alkene has approached the benzene ring, and diagram IV is often employed for substituted adducts because all carbon atoms are conveniently located at the periphery. Diagrams III and IV each represent one of the enantiomeric forms of the adduct, but it should be understood that in almost all cases the starting materials are either achiral substances or racemic mixtures, resulting in racemic mixtures of the adducts.

In many early papers on the meta photocycloaddition the process is named 1,3 addition, as opposed to 1,2 (ortho) and 1,4 (para) addition. This may lead to confusion when substituted benzenes are used. We will therefore consistently use the term "meta photocycloaddition" to indicate the reaction type while in indicating the positions of addition we will use the numbers of the carbon atoms of the benzene ring. For example, the major mode of meta cycloaddition of toluene to an alkene is 2,6, whereas benzonitrile, next to undergoing ortho cycloaddition, adds predominantly 2,4. Occasionally we will use the designations ortho, meta, para, and ipso to indicate the positions of addition with respect to a substituent, i.e. ortho,ortho (2,6), ortho,para (2,4), meta,meta (3,5) and ipso,meta (1,3). The same numbering system will be used for intramolecular additions. 5-Phenylpent-1-ene for example yields one 2,6 adduct and two 1,3 adducts; the numbers again refer to the benzene carbon atoms involved in the addition. It is also convenient to have indicators for the carbon atoms of the side chain and we will use the Greek letters α, β, γ, δ, and ϵ (Scheme 3).

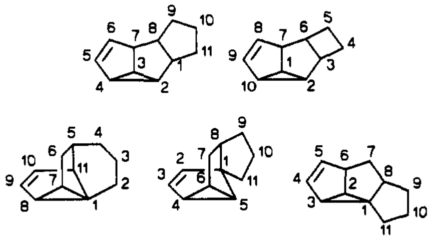
Scheme 3. Identification of Carbon Atoms in the Intramolecular Meta Photocycloaddition



Scheme 4. Various Representations of Tetracyclo[5.4.0.0^{1,8}.0^{5,11}]undec-9-ene (Top Row) and of Tetracyclo[6.3.0.0^{1,5}.0^{4,6}]undec-2-ene (Bottom Row)



Scheme 5. Tetracyclo[6.3.0.0^{2,4}.0^{3,7}]undec-5-ene, Tetracyclo[5.3.0.0^{2,10}.0^{3,6}]dec-8-ene, Tetracyclo[5.4.0.0^{1,8}.0^{5,11}]undec-9-ene, Tetracyclo[6.3.0.0^{1,5}.0^{4,6}]undec-2-ene, and Tetracyclo[6.3.0.0^{1,3}.0^{2,6}]undec-4-ene

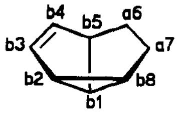


As in the case of the intermolecular addition, various ways are used in the literature to represent intramolecular photocycloadducts. Some examples are given in Scheme 4.

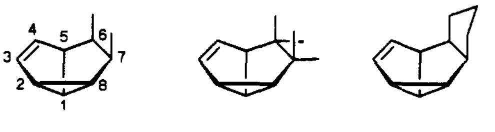
It is frequently desirable to indicate in the text the carbon atoms originating from the benzene ring and those from the alkene. In comparing substitution patterns of adducts the use of IUPAC numbering is rather inconvenient. Scheme 5 shows the intermolecular adducts derived from benzene with the alkenes cyclopentene and cyclobutene and the intramolecular adducts from 5-phenylpent-1-ene. These adducts differ in their numbering from each other and from the benzene–ethene adduct shown in Scheme 2.

For purposes of comparison we will use the numbering of the benzene–ethene adduct to indicate the carbon atoms of the basic skeleton and if this numbering differs

Scheme 6. Numbering of the Basic Skeleton of Meta Photocycloadducts



Scheme 7. Products of Meta Photocycloaddition of Benzene to *cis*-But-2-ene, 2,3-Dimethylbut-2-ene, and Cyclopentene



from that of the adduct under discussion the numbers will be preceded by a (from alkene) and b (from benzene) (Scheme 6).

III. The Discovery of the Meta Photocycloaddition

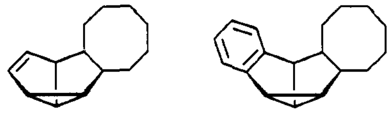
A. Intermolecular Meta Photocycloaddition

In 1966 Wilzbach and Kaplan[14] reported (manuscript received by the *Journal of the American Chemical Society* on Feb 4, 1966) that upon irradiation of solutions (ca. 10%) of *cis*-but-2-ene, cyclopentene, and 2,3-dimethylbut-2-ene in benzene, at room temperature under nitrogen, with light of 253.7 nm, 1:1 adducts of alkene and benzene are formed. The adducts could be separated from other hydrocarbon products by gas chromatography. They were found to have one double bond (for the butene adduct: IR $\bar{\nu} = 1602$ cm^{-1}; NMR two olefinic protons at 5.48 and 5.58 ppm, $J =$ ca. 5.5 Hz). It was deduced that the double bond must be part of a vinylcyclopropane chromophore and that the butene and dimethylbutene adducts were tricyclic and the cyclopentene adduct tetracyclic. Analysis of the NMR spectra, in which the six protons derived from benzene all are nonequivalent, revealed that the adducts were derivatives of tricyclo[3.3.0.0^{2,8}]oct-3-ene (Scheme 7).

It was noted that in the butene adduct strong coupling exists between protons 5 and 6 ($J = 5$ Hz) and between protons 7 and 8 ($J = 6$ Hz). This important observation made it possible to determine the configuration of the methyl groups as 6-endo,7-endo. In many later investigations the presence of coupling between H-5 and exo-H-6 and the absence of coupling between H-5 and endo-H-6 has been used to establish the structure of meta photocycloadducts. Evidently the cis configuration of the alkene has been retained during the addition, a phenomenon which is now known to be characteristic of the meta photocycloaddition.

Also in 1966, Bryce-Smith, Gilbert, and Orger[15] reported (manuscript received by the *Journal of the Chemical Society, Chemical Communications*, June 6, 1966) that irradiation at room temperature or in the solid phase at −60 °C of an equimolar mixture of benzene and *cis*-cyclooctene with radiation of wavelength 235–285 nm led to a mixture of 1:1 adducts from which the main component (ca. 85%) was readily obtained pure by treatment of the mixture with methanolic mercuric acetate. On the basis of physical and chemical evidence the adduct was identified as tetracyclo[6.6.0.0^{2,4}.0^{3,7}]tetradec-5-ene (Scheme 8).

Scheme 8. Products of Meta Photocycloaddition of Benzene and Naphthalene to *cis*-Cyclooctene



The stereochemical structure of the adduct was not determined. But-1-ene, oct-1-ene, cyclohexene, cycloocta-1,5-diene, and ethyl vinyl ether were also found to undergo photoaddition to benzene, yielding 1:1 adducts analogous to that from cyclooctene. Naphthalene was also irradiated in the presence of cyclooctene and the major of two 1:1 photoadducts was 5,6-benzotetracyclo[6.6.0.0^{2,4}.0^{3,7}]tetradec-5-ene (Scheme 8).

Thus the meta photocycloaddition of benzene to alkenes was discovered independently and almost simultaneously by Wilzbach and Kaplan[14] and by Bryce-Smith, Gilbert, and Orger[15] in 1966. Interestingly, both articles contain remarks about previous observations and reports regarding the newly discovered process. The communication by Wilzbach and Kaplan contains a note added in proof in which it is stated that the photochemical addition of benzene to cyclobutene, described by Srinivasan and Hill[16] (October 1965), also leads to a second product which is similar in structure to the adducts formed from but-2-ene and cyclopentene with benzene. In the communication by Bryce-Smith, Gilbert, and Orger it is mentioned that the formation of 1:1, monoolefinic, nonaromatic adducts between olefins and benzene is part of the subject matter of a British Patent Application (September 1965).

B. Intramolecular Meta Photocycloaddition

Instead of treating the first reported case of an intramolecular meta photocycloaddition as just another example of photoaddition, we prefer to mention it here, in the section on the discovery of the meta photocycloaddition, firstly because this intramolecular variant was discovered at a very early stage, secondly because it seems to have been unanticipated, and thirdly because it forms the basis of some very important synthetic applications.

Morrison and Ferree[17] reported in 1969 that photolysis of *cis*-6-phenylhex-2-ene leads to the formation of internal cycloadducts. A solution of this compound in cyclopentane was irradiated with light from a Vycor-enclosed, low-pressure mercury lamp. The authors had expected that excitation of the phenyl group would be followed by intersystem crossing and triplet energy transfer to the alkene, leading to cis,trans isomerization. Cis,trans isomerization did indeed occur, but the major product appeared to be a mixture of isomers resulting from intramolecular meta photocycloaddition of the alkene to the aromatic ring. On the basis of NMR (60 MHz!) chemical shifts and decoupling data, four possible structures of the adducts were suggested. In a later report, Ferree, Grutzner, and Morrison[18] showed that *cis*-6-phenylhex-2-ene yields two 1,3 adducts, *exo*-7-methyltetracyclo[6.3.0.0^{1,3}.0^{2,6}]undec-4-ene and *exo*-7-methyltetracyclo[6.3.0.0^{1,5}.0^{4,6}]undec-2-ene, while

Table 1. Meta Photocycloaddition of Benzene to Various Alkenes

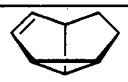
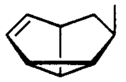
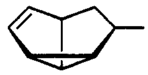
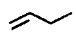
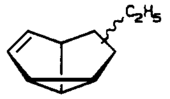
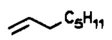
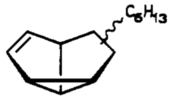
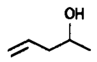
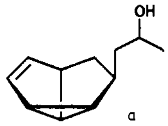
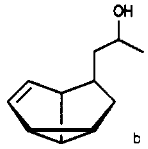
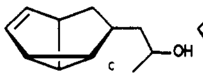
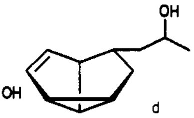
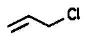
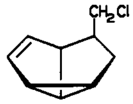
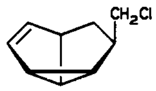
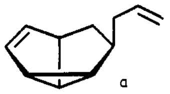
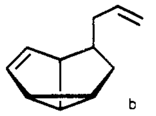
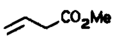
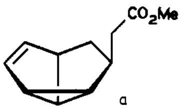
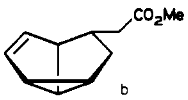
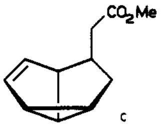
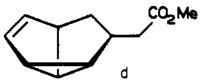
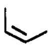
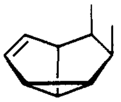
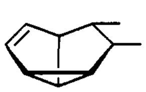
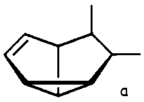
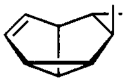
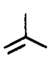
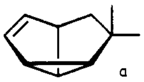
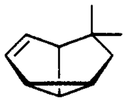
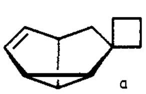
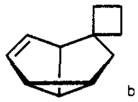
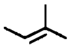
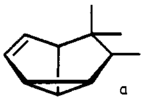
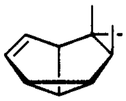
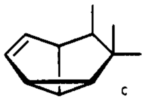
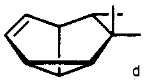
	alkene	meta adducts	remarks	ref(s)
1			φ = 0.11 [50 bar (~12 mol/L) ethene + 1 M benzene in dichloromethane]; φ_{others} = 0.08; major side products: ortho adduct + 1,3,5-cyclooctatriene	12
2		 	φ = 0.1 (14 bar propene + 1 M benzene in cyclohexane); no side products of low molecular weight	12
3		 	1:1 adducts analogous to those from benzene and cyclooctene	15
4	 	 	1:1 adducts analogous to those from benzene and cyclooctene	15
5	 	 a  b  c  d 	a:(b + c + d) = 14:8; the three components in the mixture of b, c, and d are present in the ratio 1:1:6, but it is not known which is which (30/50 v/v pentenol/benzene)	19, 20, 21
6	 	  	experimental details unpublished	20
7		 a  b	a:b = 8:5 (10% diene in benzene); φ_{meta} = 0.08 (1.0 M benzene + 1.75 M diene in isooctane); φ_{others} = 0.006; no ortho addition	22
8	 	 a  b  c  d 	a:(b + c + d) = 7:3; the three components in the mixture of b, c, and d are present in the ratio 1:4:6, but it is not known which is which (equivolume solution of benzene and ester)	21
9		 	φ_{meta} = 0.04 (10% alkene in benzene, ref 14); endo is major product (refs 23 and 25); ortho:para:meta = 6:1:40 (10% benzene in alkene, -15 °C, ref 24)	14, 23-25
10		 a  b	minor adduct, a; major adduct, b; φ_{meta} = 0.33; φ_{ortho} = 0.1; φ_{para} = 0.01 - 0.02 (benzene in neat alkene)	23-25
11		 a  b	a:b = 5:4; 10% of the product mixture is an "ene" product, 3-(2-methyl-2-propenyl)cyclohexa-1,4-diene (5% v/v alkene in benzene); with isopentane as diluent the ratio a:b increases to 1.6:1.	26, 27
12		 a  b	a:b = 1:1; combined yield, 5% (25% alkene in benzene)	28
13		 a  b  c  d	a:b:c:d = 1:1:1:1; also ortho addition and formation of "ene" products, 3-(1,2-dimethyl-2-propenyl)- and 3-(1,1-dimethyl-2-propenyl)cyclohexa-1,4-diene (10% alkene in benzene); φ_{meta} = 0.18; φ_{ortho} = 0.05; φ_{ene} = 0.07 (1.1 M benzene + 3.5 M alkene in isooctane)	26

Table 1 (Continued)

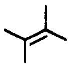
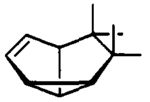
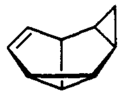
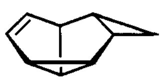
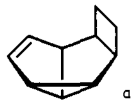
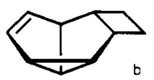
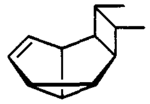
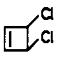
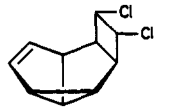
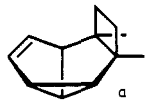
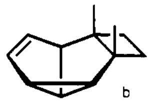
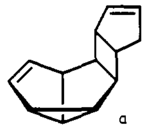
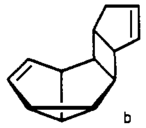
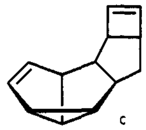
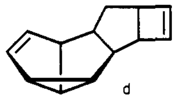
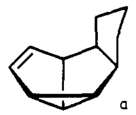
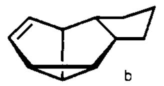
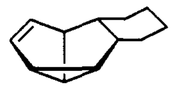
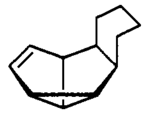
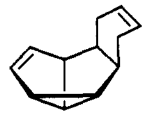
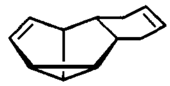
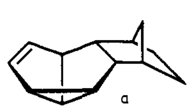
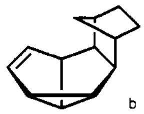
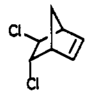
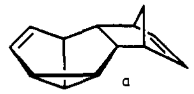
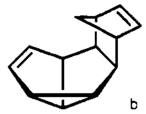
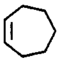
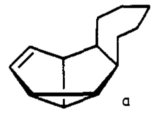
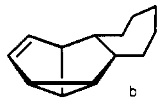
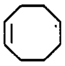
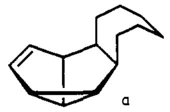
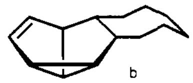
alkene	meta adducts	remarks	ref(s)
14 		$\varphi_{ortho} = 0.25$; $\varphi_{meta} = 0.03$; $\varphi_{ene} = 0.03$ (1.1 M benzene + 3.5 M alkene in isooctane); the "ene" product is 3-(1,1,2-trimethyl-2-propenyl)cyclohexa-1,4-diene	14, 26, 29–31
15 	 	no ortho or para addition; three 1:1 adducts, exo-meta, endo-meta, and a rearrangement product from endo-meta (5% alkene in benzene); proportions are time variant	26
16 	 a  b	the endo-meta adduct is the major product; the second major product is the para adduct; exo–meta (b) is a minor product; $\varphi_a = 0.81$; $\varphi_{para} = 0.09$ (0.9 M benzene + 0.88 M cyclobutene in isooctane)	26, 32, 33
17 		principal side product is para adduct; meta:para = 4:1 (20% alkene in benzene)	34
18 		yield 31–36% (1.45 M alkene in benzene)	35–37
19 	 a  b	a:b = 3:1; $\varphi = 0.10$ (1 M alkene + benzene in cyclohexane)	38
20 	 a  b	major product (yield 30%) is mixture of a and b; minor product (15%) is mixture of c and d; stereochemistry of c and d (endo or exo) not determined (15% alkene in benzene)	34
	 c  d		
21 	 a  b	$\varphi_a = 0.17$; $\varphi_b = 0.02$; $\varphi_{dimers} = 0.06$ (1.1 M benzene + 3.5 M alkene in isooctane, ref 30); $\varphi_a = [\text{alkene}] \times [2.59 + [2.38 \times [\text{alkene}]]]^{-1}$ with 4.5×10^{-2} M benzene in cyclohexane (ref 41); a:b = 88:12 (ref 40)	14, 30, 39–41
22 	 	low yields of three alkene dimers; low yields of three 1:1 adducts, tentatively assigned as exo-meta, endo-meta, and para in the ratio 1.0:1.8:0.6 (10% v/v benzene in cyclohexene)	15, 20, 26, 30
23 	 	three dimers of cyclohexadiene + three 1:1 adducts, endo-meta, exo-meta, and para (20% v/v alkene in benzene); in cyclohexane the ratio of the three adducts is 1:1:1	22
24 	 a  b	$\varphi_a = 0.27$; $\varphi_b = 0.05$ (8 M norbornene in benzene); other products are dimers of norbornene	42
25 	 a  b	after dechlorination a:b = 2:1 (15% benzene in alkene); stereochemistry was not determined; structures were assigned on the basis of the similarity of the NMR spectra with those of the adducts from norbornene	20, 21
26 	 a  b	$\varphi_a = 0.16$; $\varphi_b = 0.11$; $\varphi_{others} = 0.01, 0.01$ (1.1 M benzene + 3.5 M alkene in isooctane); the other products are probably dimers of cycloheptene	26, 30, 43
27 	 a  b	$\varphi_a = 0.31$; $\varphi_b = 0.07$; $\varphi_{ortho} = 0.09$ (1.1 M benzene + 3.5 M alkene in isooctane)	15, 30, 44, 45

Table 1 (Continued)

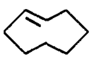
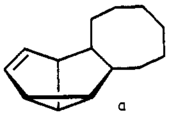
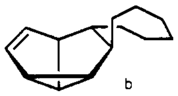
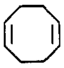
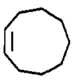
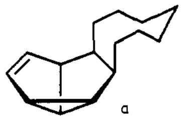
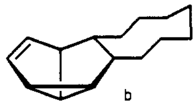
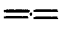
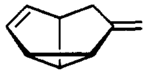
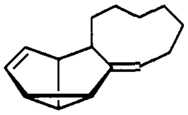
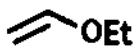
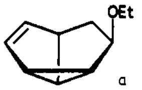
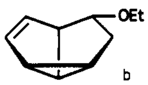
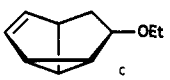
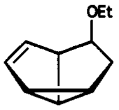
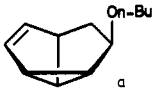
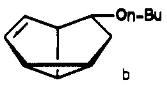
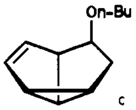
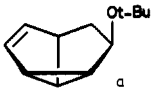
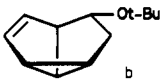
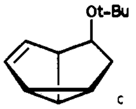
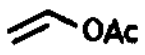
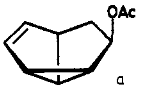
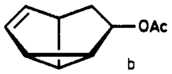
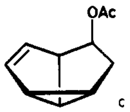
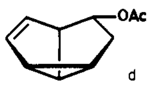
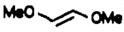
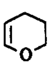
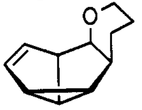
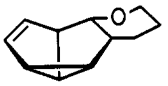
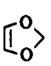
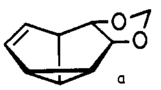
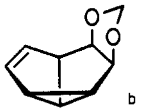
alkene	meta adducts	remarks	ref(s)
28 	 a  b	φ_a = 0.14; φ_b = 0.14; φ_{ortho} = 0.37 (1.1 M benzene + 3.5 M alkene in isooctane)	26, 30, 43, 44
29 	meta adducts are reported to be formed; structures are unpublished	1:1 adducts analogous to those from benzene and cyclooctene	15
30 	 a  b	φ_a = 0.13; φ_b = 0.02; φ_{others} = 0.02 (1.1 M benzene + 3.5 M alkene in isooctane); the other products are 1:1 adducts of unknown structure	26, 30, 43
31 		four adducts, ratio 2:12:6:1 (5% v/v allene in benzene); the para adduct (4π + 2π) is the major product; the meta adduct is the second most abundant product	22, 44, 46
32 		the major product is the para adduct (4π + 2π); para:meta = 6:1; no ortho cycloaddition (10% v/v alkene in benzene)	22, 46
33 	 a  b  c  d	the exo-ortho adduct is the major product; φ_{ortho} = 0.3; φ_a = 0.075; φ_b = 0.05; φ_c = 0.008 (estimated); φ_d = 0.03 (1.1 M benzene + 3.5 M vinyl ether in isooctane)	15, 30, 47–50
34 	 a  b  c	ortho:meta = 2.7:1, ortho adduct is exo; a:b:c = 1.25:1.1:1.0	48–50
35 	 a  b  c	a:b:c = 1:1:0.5; ortho adduct is also formed	50
36 	 a  b  c  d	a:b:c:d = 20:1:1:6 (equivolume mixture of benzene and vinyl acetate); the endo ortho adduct is also formed; φ_{meta} = 0.22; φ_{ortho} = 0.03 (1.1 M benzene + 3.5 M vinyl acetate in isooctane)	19, 27, 43, 51, 52
37 	meta adducts are formed; structures unpublished	φ_{ortho} = 0.04; φ_{meta} = 0.03 (1.1 M benzene + 3.5 M alkene in isooctane)	30
38 	meta adducts are formed as mixture of regio- and stereoisomers	ortho:meta = 7.5:1; endo-ortho > exo-ortho (equivolume mixture of addends)	43, 48, 50
39 	 	the meta adducts and the para adduct are only minor products; exo-ortho is the major adduct (95%); φ_{ortho} = 0.7; $\varphi_{meta + para}$ < 0.01 (1.1 M benzene + 3.5 M alkene in isooctane)	48–50, 53
40 	 a  b	φ_a = 0.31; φ_b = 0.07; $\varphi_{exo\text{-}ortho}$ = 0.21; φ_{para} = 0.04 (1 M dioxole in benzene)	48, 54–56

Table 1 (Continued)

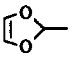
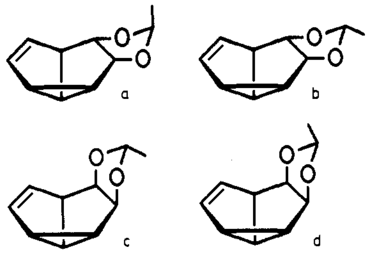
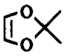
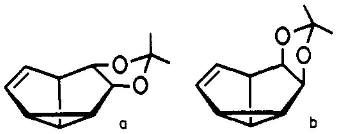
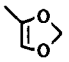
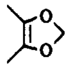
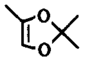
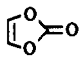
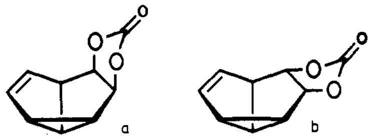
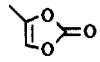
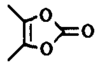
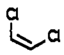
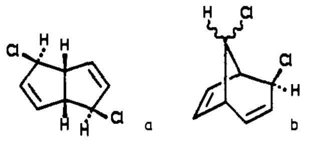
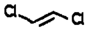
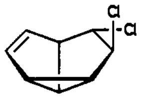
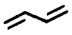
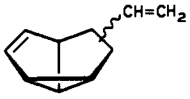
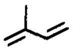
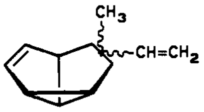
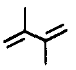
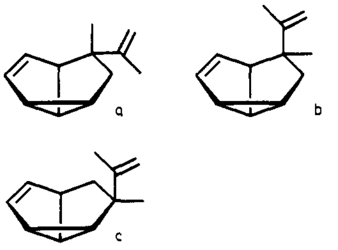
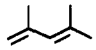
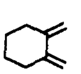
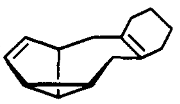
alkene	meta adducts	remarks	ref(s)
41 		reaction mixture contains meta adducts (40%), two exo-ortho adducts (40%) and a para adduct (16%); $\varphi_{\mathrm{tot}} = 0.5$ (1 M dioxole in benzene, ref 54); ratio of meta adducts is a:b:c:d = 56:31:11:2 (1.3 M benzene + 0.4 M dioxole in cyclohexane)	48, 54, 57
42 		a:b = 96:4; the major product is the exo-ortho adduct; $\varphi_{\mathrm{ortho}} = 0.39$; $\varphi_{\mathrm{meta}} = 0.12$; $\varphi_{\mathrm{para}} < 0.005$ (1 M dioxole in benzene)	54–56, 58
43 	meta adducts are reported to be formed; structures are unpublished	ortho:meta = >4:1	59
44 	meta adducts are reported to be formed; structures are unpublished	ortho:meta = >9:1	59
45 	meta adducts are reported to be formed; structures are unpublished	ortho:meta = >9:1	59
46 		a:b = 5:1; meta:para = 6:1 (1.0 M alkene in benzene)	20, 60
47 	meta adducts are reported to be formed; structures are unpublished		59
48 	meta adducts are reported to be formed; structures are unpublished		59
49 		three fractions of products A:B:C = 6:1:3; A, *cis*- and *trans*-β-chlorostyrenes; B, alkene dimers; C, 1:1 adducts a and b from acid-catalyzed rearrangement of para or meta adduct (1:4 v/v olefin in benzene)	61
50 		β-chlorostyrenes + tetrachlorocyclobutanes (together 30%) + two 1:1 adducts in a ratio of 1:2.5; the minor adduct is ortho and the major adduct is meta; it is thermally unstable and undergoes 1,3 and 1,5 Cl shifts	61–63
51 		meta adducts (mixture of isomers) constitute 17% of product mixture; the major photoprocess is para addition ($4\pi + 4\pi$) (benzene:butadiene = 10:1)	64
52 		meta adducts (mixture of isomers) constitute 32% of product mixture; para addition ($4\pi + 4\pi$) is the major other photoprocess (benzene:isoprene = 10:1)	65
53 		a, b, and c are the major meta adducts; a para adduct ($4\pi + 4\pi$) is the fourth major adduct; substitution products are formed in minor amounts (0.24 mol diene in 1.2 mol benzene)	66
54 	mixture of meta adducts	37% para adduct ($4\pi + 4\pi$); 21% meta adducts; 42% nonvolatile material (0.24 mol diene in 1.2 mol benzene)	66
55 		the major product is the para adduct ($4\pi + 4\pi$); the meta adduct is the minor product; meta:para = 1:2 (10% v/v diene in benzene)	22, 67

Table 1 (Continued)

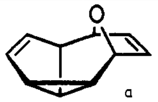
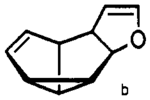
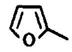
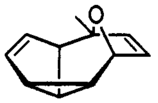
alkene	meta adducts	remarks	ref(s)
56 	 	4-(2-furanyl)bicyclo[3.1.0]hex-2-ene (6%); meta adduct a (30%); meta adduct b (3%); a cage compound formed by intramolecular [2 + 2] cycloaddition of the para $(4\pi + 4\pi)$ adduct (11%) and the ortho adduct; the proportions strongly depend on the reaction conditions (10–20% benzene in furan)	68–72
57 		meta adduct (52%) + a cage compound formed by intramolecular [2 + 2] cycloaddition of the para $(4\pi + 4\pi)$ adduct (22%) (equimolar amounts of methylfuran and benzene)	72

Table 2. Meta Photocycloaddition of Monosubstituted Benzenes to Various Alkenes

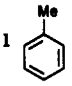
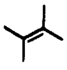
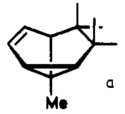
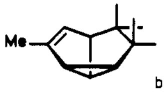
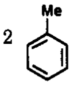
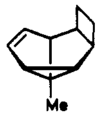
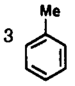
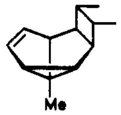
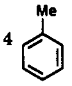
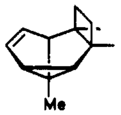
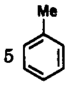
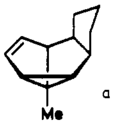
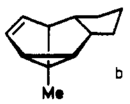
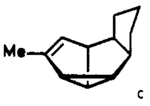
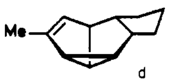
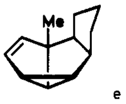
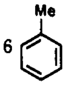
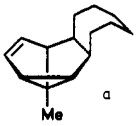
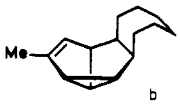
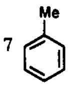
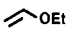
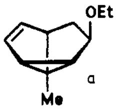
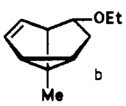
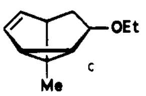
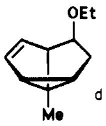
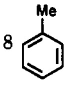
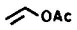
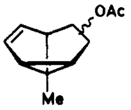
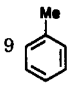
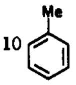
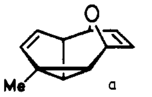
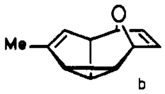
arene	alkene	adducts	remarks	ref(s)
1 		 	a:b = 1:1	73
2 			φ = 0.12 (1.4 M toluene + 0.9 M cyclobutene in cyclohexane)	74, 75
3 			φ = 0.11 (toluene + 1 M alkene in cyclohexane)	38
4 			φ = 0.02 (toluene + 1 M alkene in cyclohexane)	38
5 		    	φ_a = 0.21 (toluene + 1 M cyclopentene in cyclohexane, ref 38); a:b:c:d:e = 88:2:5:1:4 (0.5 M toluene + 1.5 M cyclopentene in cyclohexane, ref 40)	38, 40, 76
6 		 	relative efficiency of formation: a, 1.30; b, 0.03 (benzene = 1) (1 M toluene + 3.5 M cyclooctene in cyclohexane)	77, 78
7 		   	ortho:meta = 1:4.5; all four meta adducts are formed; 7-endo (a) comprises 40% of the product mixture; there are two ortho adducts (equivolume mixture of toluene and alkene)	47, 79
8 			mixture of meta adducts, little selectivity; minor amount of ortho adduct (equimolar amounts of toluene and vinyl acetate)	27, 51, 80
9 		meta adducts are reported to be formed; structures have not been published	similar results as with toluene and ethyl vinyl ether	47
10 		 	a, 41%; b, 26%; para adduct, 25%; cage compound formed by intramolecular [2 + 2] addition of the para adduct: 8% (1:4 w/w toluene/furan)	68, 72

Table 2 (Continued)

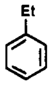
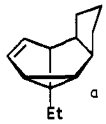
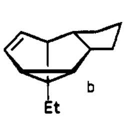
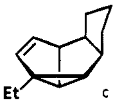
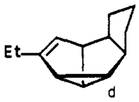
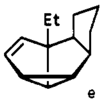
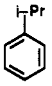
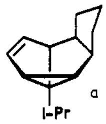
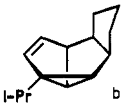
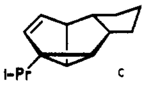
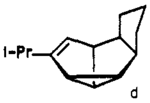
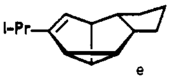
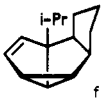
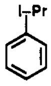
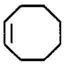
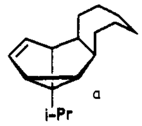
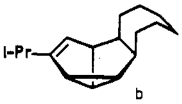
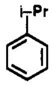
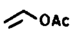
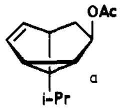
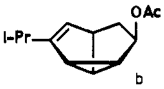
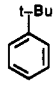
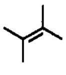
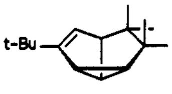
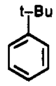
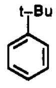
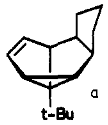
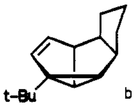
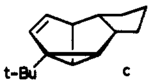
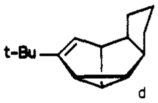
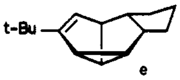
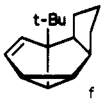
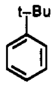
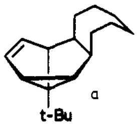
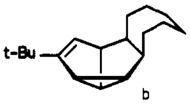
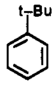
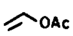
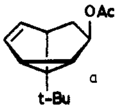
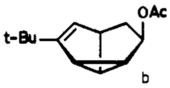
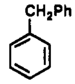
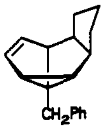
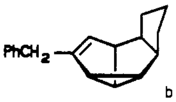
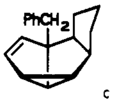
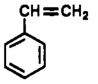
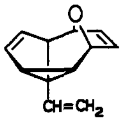
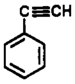
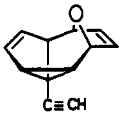
arene	alkene	adducts	remarks	ref(s)
11 		 a  b  c  d  e	a:b:c:d:e = 85:1:1:9:4 (0.5 M ethylbenzene + 1.5 M cyclopentene in cyclohexane)	40
12 		 a  b  c  d  e  f	a:b:c:d:e:f = 53:3:15:21:3:5 (0.5 M isopropylbenzene + 1.5 M cyclopentene in cyclohexane)	40
13 		 a  b	relative efficiency of formation: a: 0.4; b: 0.2 (benzene = 1) (1 M isopropylbenzene + 3.5 M cyclooctene in cyclohexane)	78, 80, 81
14 		 a  b	a:b = 4:1; >80% of the adduct mixture has the acetate group endo at C-7 (equimolar mixture of isopropylbenzene and vinyl acetate)	80
15 			only one isomer	73
16 		more than one meta adduct; structures have not been published	φ = 0.05 (1.0 M *tert*-butylbenzene + 0.9 M cyclobutene in cyclohexane)	75
17 		 a  b  c  d  e  f	a:b:c:d:e:f = 34:8:2:45:6:5 (0.5 M *tert*-butylbenzene + 1.5 M cyclopentene in cyclohexane)	40
18 		 a  b	relative efficiency of formation: a, 0.18; b, 0.26 (benzene = 1) (1 M *tert*-butylbenzene + 3.5 M cyclooctene in cyclohexane)	73, 78, 80, 81
19 		 a  b	a:b = 3:1; >80% of the adduct mixture has the acetate group endo at C-7 (equimolar mixture of *tert*-butylbenzene and vinyl acetate)	80
20 		 a  b  c	a:b:c = 76:15:8 (1.5 M diphenylmethane + 1.5 M cyclopentene in cyclohexane)	40
21 			meta adduct + dimers of styrene + [2 + 2] adduct between vinyl group of styrene and furan; meta:dimers:[2 + 2] = 1:1.7:1.7 (5% v/v styrene in furan)	82, 83
22 			meta adduct:arene dimers = 3:1 (5% v/v arene in furan)	82, 83

Table 2 (Continued)

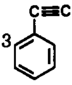
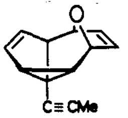
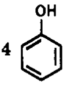
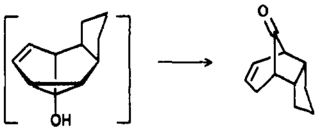
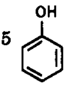
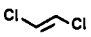
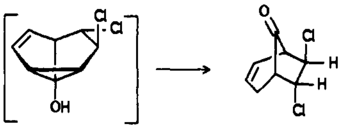
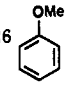
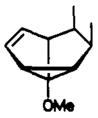
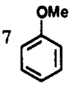
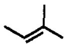
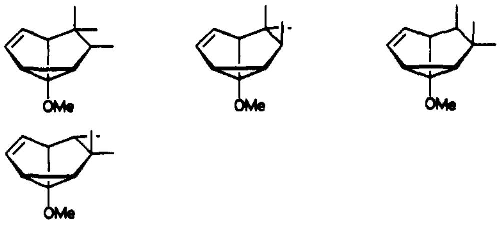
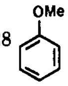
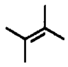
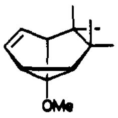
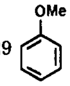
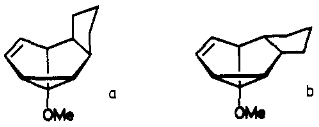
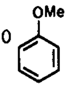
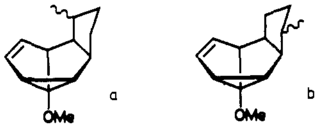
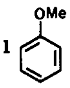
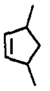
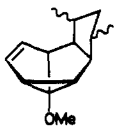
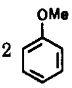
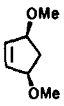
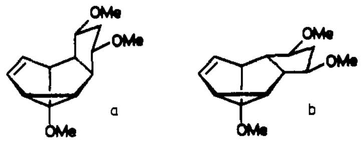
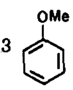
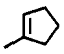
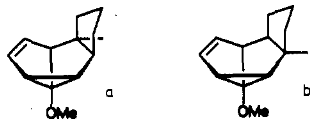
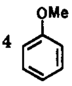
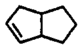
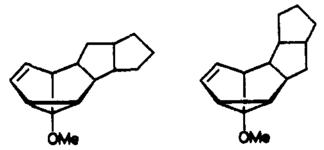
	arene	alkene	adducts	remarks	ref(s)
23				meta adduct:arene dimers = 5.7:1 (5% v/v arene in furan)	83
24				the meta adduct is supposed to undergo acid (phenol) catalyzed rearrangement under the reaction conditions	84
25				the rearranged adduct comprises 70% of the product mixture (10% or 20% w/v phenol in dichloroethene)	63, 85
26				yield, 22% (2 M anisole + 2 M alkene in cyclohexane); φ = 0.09 (anisole + 1 M alkene in cyclohexane)	86, 87
27				mixture of four meta adducts; no ortho adducts or "ene" products	79
28				the meta adduct is the major product (85%); dehydro dimers of the alkene are minor products	79
29				yield of a, 85% (2 M anisole + 2 M alkene in cyclohexane); φ_a = 0.17 (anisole + 1 M cyclopentene in cyclohexane); a:b = 87:13	40, 84, 86–88
30				yield, 60% (2 M anisole + 2 M alkene in cyclohexane); φ = 0.11 (anisole + 1 M alkene in cyclohexane); a:b = 1:1	86, 87
31		 c : t = 3 : 2		yield, 24% (2 M anisole + 2 M alkene in cyclohexane); φ = 0.08 (anisole + 1 M alkene in cyclohexane)	87
32				a, 49%; b, 7% (2.2 M anisole + 0.05 M alkene in cyclohexane); a third product (9%) was not identified	89
33				yields: a, 35%; b, 30% (2 M anisole + 2 M alkene in cyclohexane); φ = 0.02 (anisole + 1 M alkene in cyclohexane)	86, 87
34				yield, 64% (2 M anisole + 2 M alkene in cyclohexane); φ = 0.08 (anisole + 1 M alkene in cyclohexane); the two adducts are formed in the ratio of 3:2; stereochemistry not determined	86, 87

Table 2 (Continued)

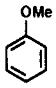
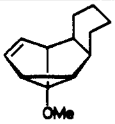
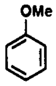
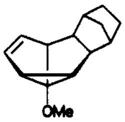
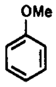
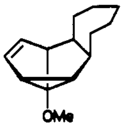
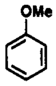
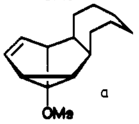
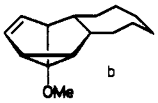
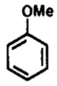
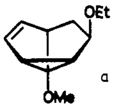
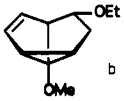
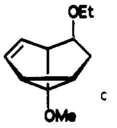
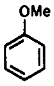
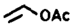
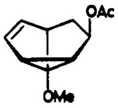
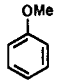
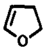
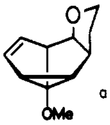
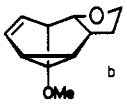
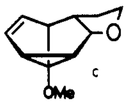
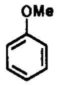
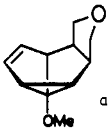
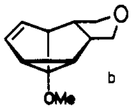
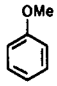
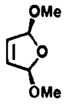
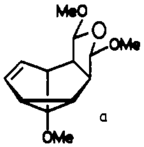
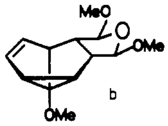
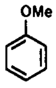
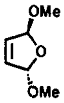
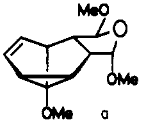
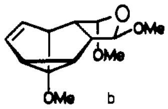
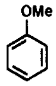
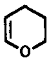
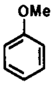
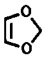
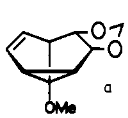
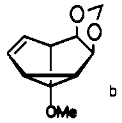
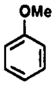
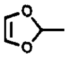
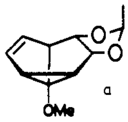
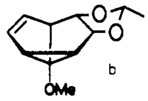
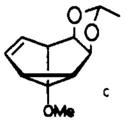
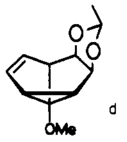
arene	alkene	adducts	remarks	ref(s)
35 			yield, 20% (2 M anisole + 2 M cyclohexene in cyclohexane); φ = 0.02 (anisole + 2 M cyclohexene in cyclohexane)	86, 87
36 			yield, 60% (one 1:1 adduct) (2 M anisole + 2 M norbornene in cyclohexane); φ = 0.05 (anisole + 1 M norbornene in cyclohexane); stereochemistry not determined	86, 87
37 			yield, 62% (2 M anisole + 2 M cycloheptene in cyclohexane); φ = 0.21 (anisole + 1 M cycloheptene in cyclohexane)	86, 87
38 		 	two components in the ratio 7:1, yield of a, 30%; the minor component is presumably exo (1:3 v/v anisole/cyclooctene)	77
39 		  	a:b:c = 1.5:2:1 (1 M anisole in ethyl vinyl ether)	47, 79, 90
40 		 and others	90% 2,6 addition; the 7-regioisomers constitute 50% of the mixture (equimolar amounts of anisole and vinyl acetate)	27, 51
41 		  	a:b:c = 3:2:1 (1 M anisole + 3.5 M alkene in methanol)	90
42 		 	a:b = 16:1 (1 M anisole + 3.5 M alkene in methanol)	90
43 		 	a, 66%; b, 14% (1.5 M anisole + 0.4 M alkene in cyclohexane)	89
44 		 	a, 27%; b, 10%; furan dimer, 23%; unidentified, 11% (1.5 M anisole + 0.4 M alkene in cyclohexane)	89
45 		meta adducts are reported to be formed; structures have not been published	similar results as with ethyl vinyl ether	47
46 		 	a:b:ortho adduct = 46:22:32 (1 M anisole + 2 M dioxole in 1,4-dioxane); product ratios are time variant	90, 91
47 		   	a:b:c:d = 52:33:12:3 (1.3 M anisole + 0.4 M alkene in cyclohexane)	57

Table 2 (Continued)

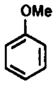
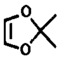
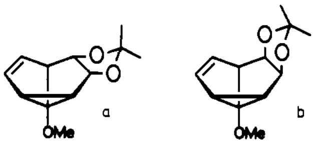
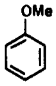
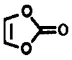
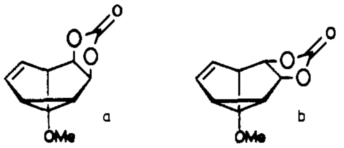
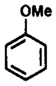
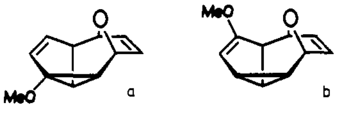
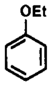
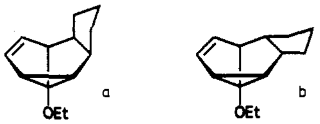
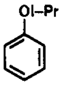
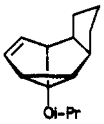
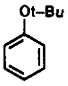
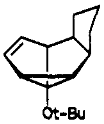
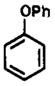
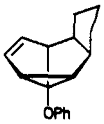
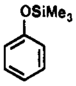
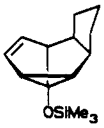
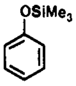
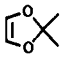
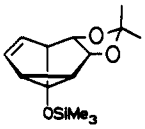
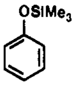
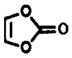
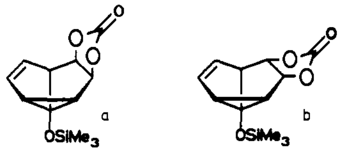
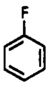
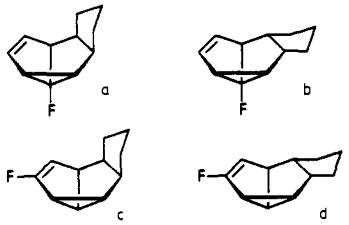
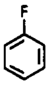
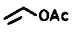
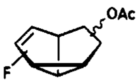
	arene	alkene	adducts	remarks	ref(s)
48				a:b:ortho adduct = 38:12:50 (1 M anisole + 2 M alkene in 1,4-dioxane); product ratios are time variant	91, 92
49				a:b = 2:1; also 16% ortho adduct (0.3 M anisole + 0.6 M alkene in 1,4-dioxane)	60, 92, 93
50				a:b:c = 55:38:7 (c is unidentified) (anisole in excess furan)	72
51				a:b = 96:4 (0.5 M arene + 1.5 M cyclopentene in cyclohexane)	40
52				only one isomer (0.5 M arene + 1.5 M cyclopentene in cyclohexane)	40
53				only one isomer (0.5 M arene + 1.5 M cyclopentene in cyclohexane)	40
54				only one isomer (0.5 M arene + 1.5 M cyclopentene in cyclohexane)	40
55				endo:exo = >9:1; + two side products (1.4:1) (<20%) + cyclopentene dimers (<10%) (0.3 M arene + 0.6 M alkene in cyclohexane)	92
56				endo:exo = <1:9.3 (endo undergoes rearrangement) + two side products (2:1) (<15%) + dimers (10%) (0.3 M arene + 0.6 M alkene in cyclohexane)	92
57				a:b = 1.3:1; part of a undergoes rearrangement; three further side products (<25%) + dimers (<10%) (0.3 M arene + 0.6 M alkene in 1,4-dioxane)	92
58				a:b:c:d = 2:32:55:11; also two para adducts and a substitution product (0.5 M arene + 1.5 M cyclopentene in cyclohexane)	76, 94–96
59				meta attack is nonselective; three positional isomers (equivolume solutions of fluorobenzene and vinyl acetate)	51

Table 2 (Continued)

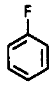
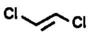
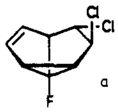
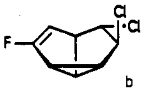
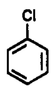
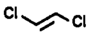
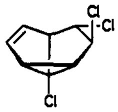
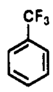
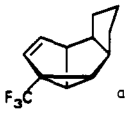
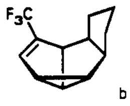
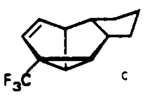
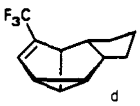
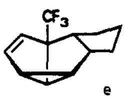
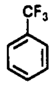
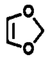
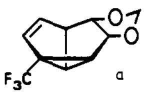
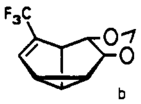
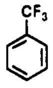
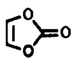
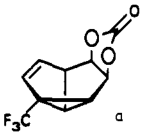
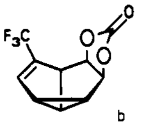
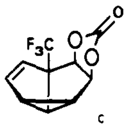
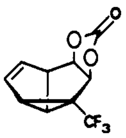
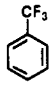
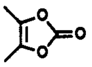
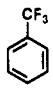
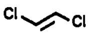
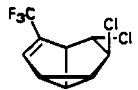
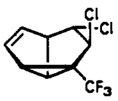
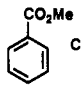
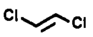
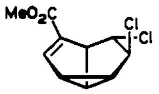
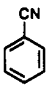
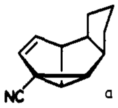
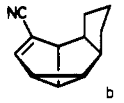
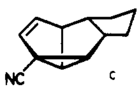
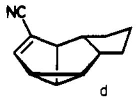
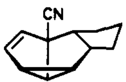
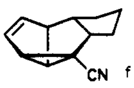
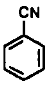
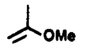
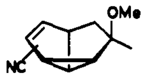
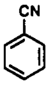
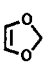
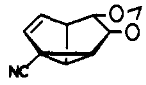
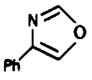
arene	alkene	adducts	remarks	ref(s)
60 		 a  b	a:b = 1:1 (equivolume mixture of fluorobenzene and dichloroethene)	63, 85
61 			meta adduct constitutes 50% of the product mixture; the other 50% are ethene dimers (equivolume mixture of chlorobenzene and dichloroethene)	63, 85
62 		 a  b  c  d  e	a:b:c:d:e = 41:27:8:10:14; <10% ortho adduct (0.3 M arene + 0.9 M cyclopentene in cyclohexane)	76, 97
63 		 a  b	a:b:ortho adduct:substitution product = 1.0:0.7:0.8:0.3 (1 M arene + 0.5 M alkene in 1,4-dioxane)	98, 99
64 		 a  b  c  d	a:b:c:d:para adduct = 1.0:0.6:0.7:0.5:0.1; also 20% unidentified products (1 M arene + 0.5 M alkene in 1,4-dioxane)	98, 99
65 		meta adducts are reported to be formed; structures have not been published	at least four products in low yield (1 M arene + 0.5 M alkene in 1,4-dioxane)	98, 99
66 		 a  b	a:b = 3:1; minor amount of ortho adduct (1/1/4 v/v/v arene/alkene/cyclohexane)	62, 63, 85
67 			other products (unidentifed) are also formed (equivolume mixture of reactants)	100
68 		 a  b  c  d  e  f	70% ortho addition; 30% meta addition; ratio of meta adducts, a:b:c:d:e:f = 36:22:16:23:2:1 (0.3 M benzonitrile + 0.9 M cyclopentene in cyclohexane)	97
69 			tentative structure of meta adduct; also ortho addition (1:10 benzonitrile:alkene)	101
70 		 	the oxazole is the major product; meta adduct is the minor product (0.2 M benzonitrile + 0.2–1.0 M dioxole in cyclohexane)	102

Table 2 (Continued)

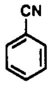
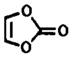
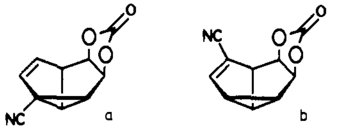
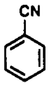
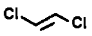
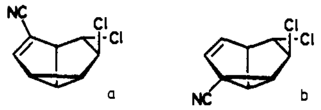
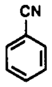
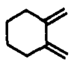
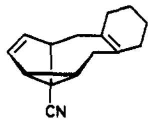
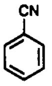
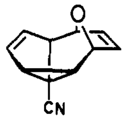
arene	alkene	adducts	remarks	ref(s)
71 			a:b = 45:55 (1 M benzonitrile + 3.5 M alkene in methanol)	93
72 			a, 60%; b, 15%; ortho adduct: 15%; a undergoes 1,3 and 1,5 Cl shifts (10%) (1/1/4 v/v/v arene/alkene/cyclohexane)	62, 63, 85, 100
73 			meta:para ($4\pi + 4\pi$) = 1:2.6	83
74 			single product (9/1 v/v arene/furan)	82, 83

Table 3. Meta Photocycloaddition of Di-, Tri-, and Hexasubstituted Benzenes to Various Alkenes

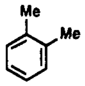
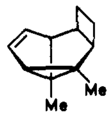
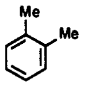
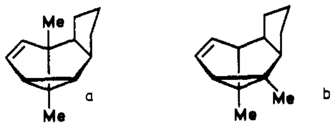
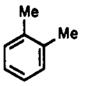
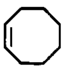
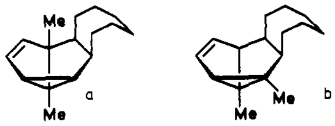
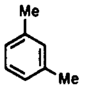
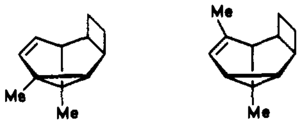
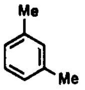
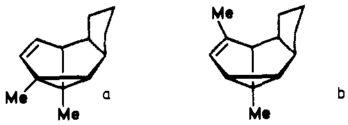
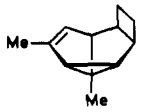
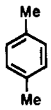
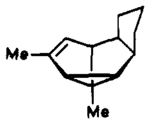
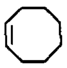
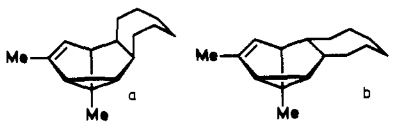
arene	alkene	adducts	remarks	ref(s)
1 			$\varphi = 0.05$ (1.2 M *o*-xylene + 0.9 M cyclobutene in cyclohexane)	74, 75
2 			$\varphi = 0.08$ (*o*-xylene + 1 M cyclopentene in cyclohexane); a:b = 3:1	38, 76
3 			a:b = 3:2; $\varphi \approx 0.3$ (1:3 v/v *o*-xylene/cyclooctene)	76
4 			$\varphi = 0.04$ (1.2 M *m*-xylene + 0.9 M cyclobutene in cyclohexane)	74, 75
5 			$\varphi = 0.05$ (*m*-xylene + 1 M cyclopentene in cyclohexane) a:b = 3:4	38, 76
6 			$\varphi = 0.14$ (1.2 M *p*-xylene + 0.9 M cyclobutene in cyclohexane)	74, 75
7 			$\varphi = 0.13$ (*p*-xylene + 1 M cyclopentene in cyclohexane)	38, 76
8 			a:b = 7:1, $\varphi \approx 0.3$ (1:3 v/v *p*-xylene/cyclooctene)	76

Table 3 (Continued)

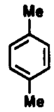
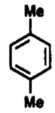
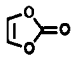
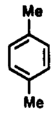
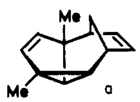
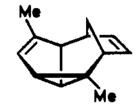
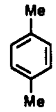
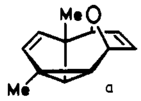
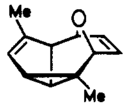
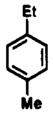
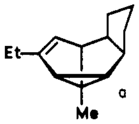
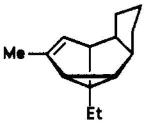
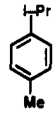
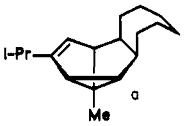
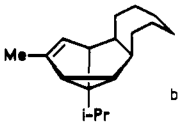
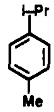
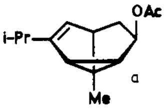
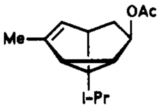
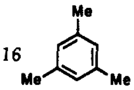
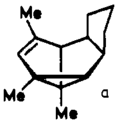
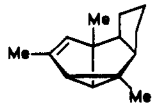
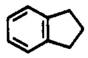
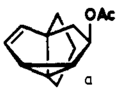
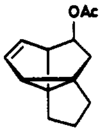
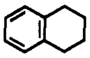
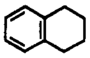
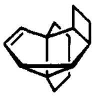
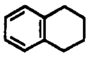
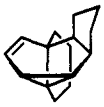
arene	alkene	adducts	remarks	ref(s)
9 		meta adducts are reported to be formed; structures have not been published	meta cycloadducts are the major volatile reaction products; 7-endo isomer constitutes ca. 60% of the meta adduct mixture; addition 2,6 with respect to one of the methyl groups	51
10 		meta adducts are reported to be formed; structures have not been published	the predominant products are meta cycloadducts	60
11 		 a  b	a, 58%; b, 31%; plus a third product of unknown structure (4:1 w/w *p*-xylene/cyclopentadiene)	68, 72
12 		 a  b	a, 25%; b, 32%; para adduct ($4\pi + 4\pi$), 2%; cage compound formed by intramolecular [2 + 2] cycloaddition of the para adduct, 22% (5:1 w/w *p*-xylene/furan)	72
13 		 a  b	a:b = 1.74:1.00 (1 M arene + 2.5 M cyclopentene in cyclohexane)	103
14 		 a  b	a:b = 5:1 (equimolar mixture of arene and cyclooctene, refs 80 and 81); one 1:1 adduct (a) with >95% selectivity (equimolar mixture of arene and cyclooctene, ref 78)	73, 78, 80, 81
15 		 a  b	a:b = 2:1; >80% of the mixture of meta adducts has the acetate group endo at C-7 (equimolar mixture of arene and vinyl acetate)	80
16 		 a  b	a:b = 2:1; φ = 0.015 (mesitylene + 1 M cyclopentene in cyclohexane)	38
17 		 a  b	yields: a, 21%; b, 2–3% (82 g of indan + 103 g of vinyl acetate in 100 mL of cyclohexane)	104
18 			(10% tetralin + 10% butene in cyclohexane)	105
19 			yield, 25% (10% tetralin + 10% cyclobutene in cyclohexane)	105
20 			φ = 0.011 (1.1 M tetralin + 1 M cyclopentene in cyclohexane)	105

Table 3 (Continued)

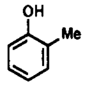
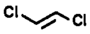
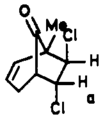
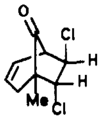
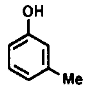
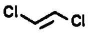
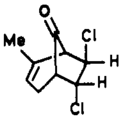
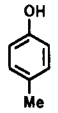
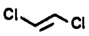
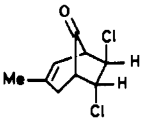
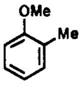
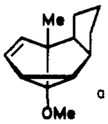
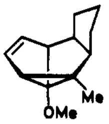
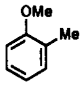
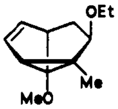
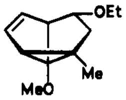
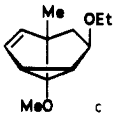
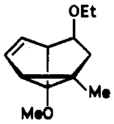
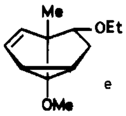
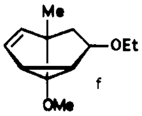
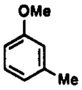
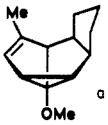
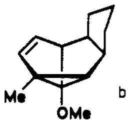
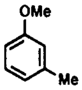
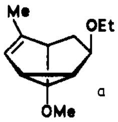
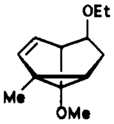
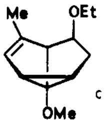
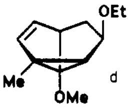
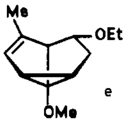
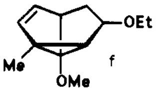
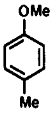
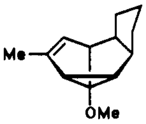
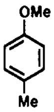
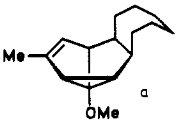
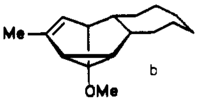
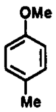
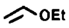
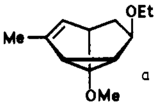
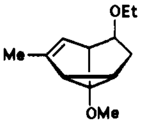
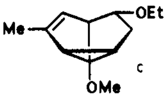
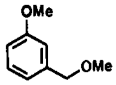
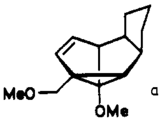
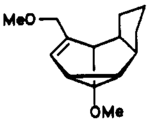
	arene	alkene	adducts	remarks	ref(s)
21			 a  b	a:b = 1:2; together 80% of the product mixture (10 or 20% w/v arene in dichloroethene); primary meta adduct undergoes rearrangement	63
22				the rearranged adduct constitutes 50% of the product mixture (10 or 20% w/v arene in dichloroethene)	63
23				the rearranged adduct constitutes 80% of the product mixture (10 or 20% w/v arene in dichloroethene)	63
24			 a  b	a:b = 2:1 (1 M arene + 3.5 M cyclopentene in cyclohexane)	106–108
25			 a  b  c  d  e  f	a:b:c:d:e:f = 1:1:4.5:2:1:0.5 (1 M arene in ethyl vinyl ether)	109, 110
26			 a  b	yields: a, 26%; b, 33% (2 M arene + 2 M cyclopentene in cyclohexane); $\varphi < 0.01$ (arene + 1 M cyclopentene in cyclohexane)	87
27			 a  b  c  d  e  f	a:b:c:d:e:f = 1.4:1.0:1.9:1.0:1.7:0.75 (1 M arene in ethyl vinyl ether)	109, 111
28				yield, 45% (2 M arene + 2 M cyclopentene in cyclohexane); $\varphi = 0.01$ (arene + 1 M cyclopentene in cyclohexane)	87
29			 a  b	a:b = 2:1 (equivolume mixture of arene and cyclopentene)	81
30			 a  b  c	a:b:c = 4.5:2:3.5 (1 M arene in ethyl vinyl ether)	109, 110
31			 a  b	a:b = 2:1 (cyclohexane)	107

Table 3 (Continued)

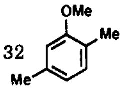
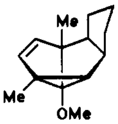
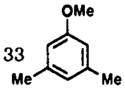
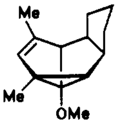
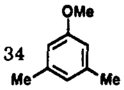
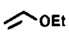
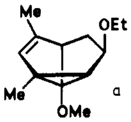
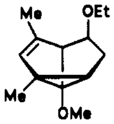
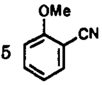
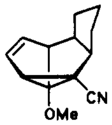
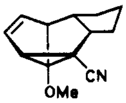
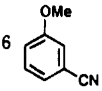
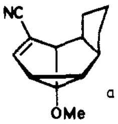
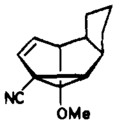
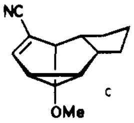
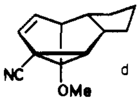
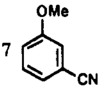
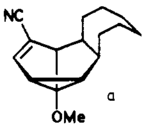
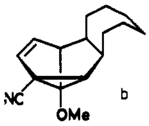
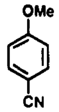
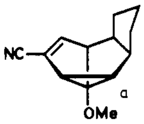
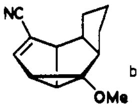
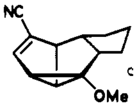
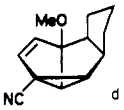
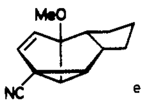
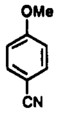
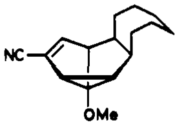
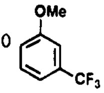
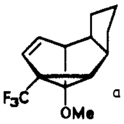
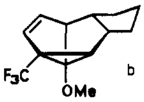
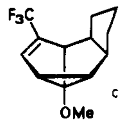
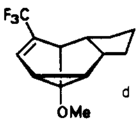
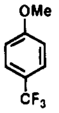
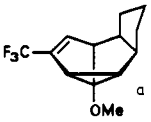
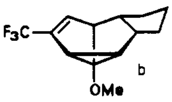
arene	alkene	adducts	remarks	ref(s)
32 			single adduct (cyclohexane)	107
33 			yield, 70% (0.1 M arene + 0.3 M cyclopentene in cyclohexane)	112
34 		 a  b	a, 30%; b, 30% (1 M arene in ethyl vinyl ether)	112
35 		 a  b	a:b = 1:1 (0.5 M arene + 1.5 M cyclopentene in cyclohexane); very slow reaction, meta adduct forms 5% of the product mixture	113
36 		 a  b  c  d	a:b:c:d = 67:13:13:7 (0.5 M arene + 1.5 M cyclopentene in cyclohexane)	113, 114
37 		 a  b	a:b = 1.0:1.4 (0.2 M arene in neat cyclooctene)	115
38 		 a  b  c  d  e	a:b:c:d:e = 45:20:10:15:10 (0.5 M arene + 1.5 M cyclopentene in cyclohexane)	113, 114
39 			meta adduct constitutes 65% of adduct mixture; ortho adducts are also formed (0.2 M arene in neat cyclooctene)	115, 116
40 		 a  b  c  d	a:b:c:d = 36:16:43:5 (0.5 M arene + 1.5 M cyclopentene in cyclohexane)	113
41 		 a  b	a:b = 78:22 (0.5 M arene + 1.5 M cyclopentene in cyclohexane)	113

Table 3 (Continued)

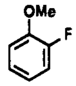
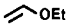
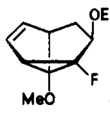
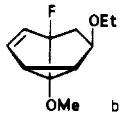
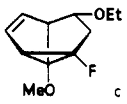
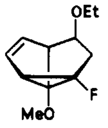
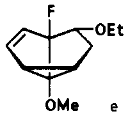
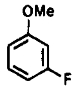
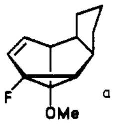
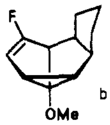
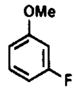
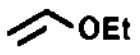
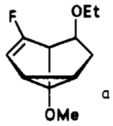
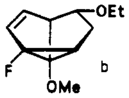
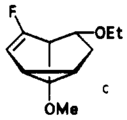
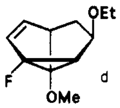
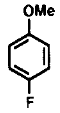
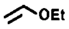
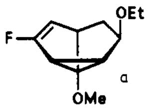
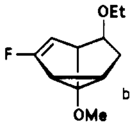
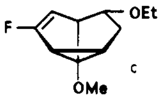
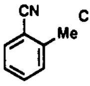
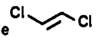
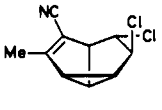
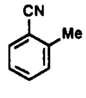
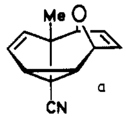
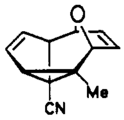
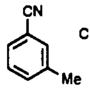
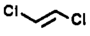
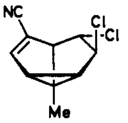
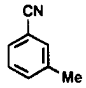
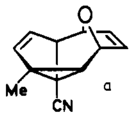
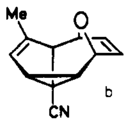
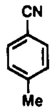
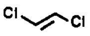
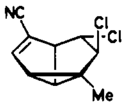
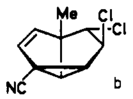
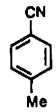
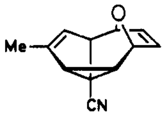
	arene	alkene	adducts	remarks	ref(s)
42			 a  b  c  d  e	a:b:c:d:e = 1:1.5:1:2:3 (1 M arene in ethyl vinyl ether)	109, 110
43			 a  b	a:b = 49:51 (0.5 M arene + 1.5 M cyclopentene in cyclohexane)	96
44			 a  b  c  d	a:b:c:d = 3.5:1:2:5 (1 M arene in ethyl vinyl ether)	109, 111
45			 a  b  c	a:b:c = 2:2.5:1 (1 M arene in ethyl vinyl ether)	109, 110
46				adduct comprises $\approx$40% of the reaction mixture; seven other 1:1 adducts are formed (25% v/v arene in dichloroethene)	63, 85
47			 a  b	a:b = 1.0:0.85 (equivolume mixture of arene and furan)	82, 83
48				essentially sole product at short irradiation times; at longer times rearrangement products and ortho adduct are formed (equivolume mixture of arene and alkene)	63, 85
49			 a  b	a:b = 1.0:2.8 (equivolume mixture of arene and furan)	82, 83
50			 a  b	a:b = 1:1; essentially sole products at short irradiation times (30 g of arene + 50 mL of dichloroethene in 250 mL of cyclohexane)	63, 85
51				sole product (40% v/v arene in furan)	82, 83

Table 3 (Continued)

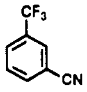
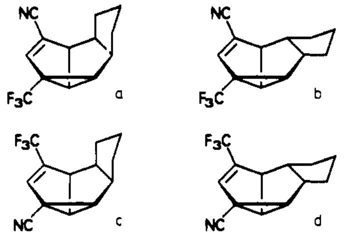
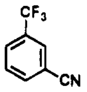
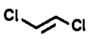
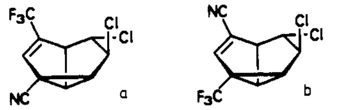
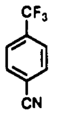
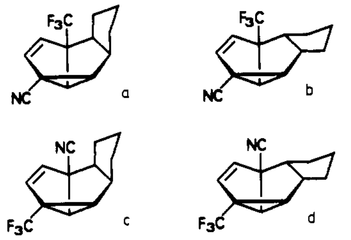
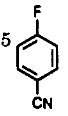
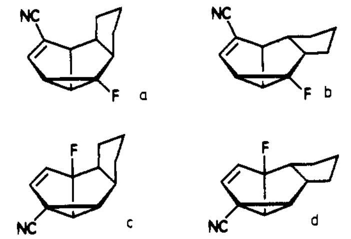
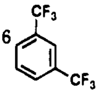
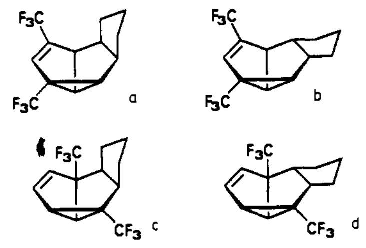
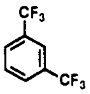
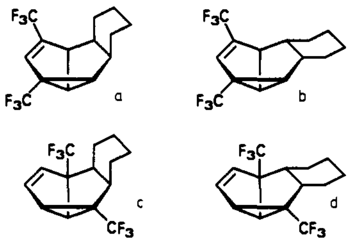
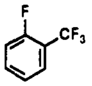
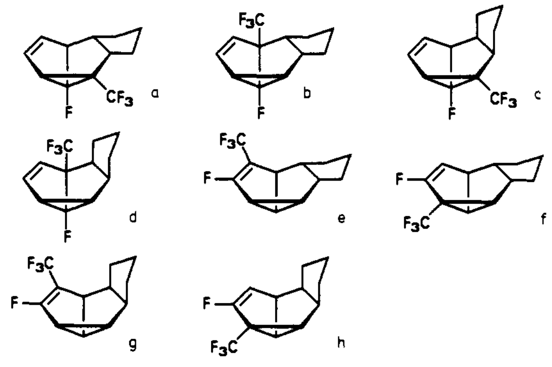
arene	alkene	adducts	remarks	ref(s)
52 			a, 6%; b, 3%; c, 7%; d, 13% of product mixture at 12% conversion; also 15 unidentified products of which 11 in 5% yield each (1 M arene + 1 M cyclopentene in cyclohexane)	117
53 			a:b = 1:1.5; plus minor amount of an ortho adduct (22.5 g of arene in 50 mL of dichloroethene)	63
54 			a, 28%; b, 18%; c, 5%; d, 4% of product mixture at 7% conversion; also 16 unidentified products of which two in yields of 14–16% (1 M arene + 1 M cyclopentene in cyclohexane)	117
55 			a:b:c:d = 41:17:30:12 (0.5 M arene + 1.5 M cyclopentene in cyclohexane)	96
56 			a, 16%; b, 41%; c, 9%; d, 6% of product mixture at 83% conversion; 28% of the unidentified products are 1:1 and 2:1 adducts (1 M arene + 1 M cyclopentene in cyclohexane)	117
57 			a, 19%; b, 47%; c, 13%; d, 3% of product mixture at 20% conversion; also nine unidentified products (1 M arene + 1 M cyclohexene in cyclohexane)	117
58 			a:b:c:d:e:f:g:h = 6:4:30:18:7:4:18:13 (0.5 M arene + 1.5 M cyclopentene in cyclohexane)	96

Table 3 (Continued)

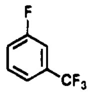
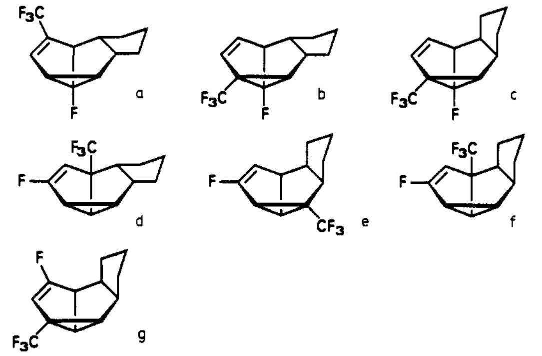
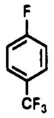
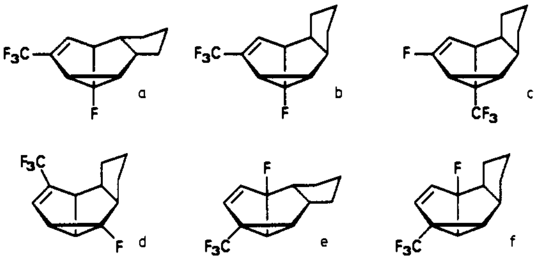
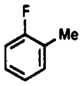
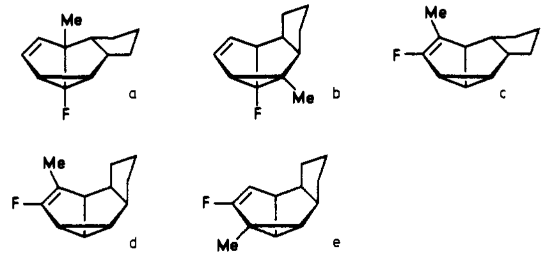
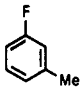
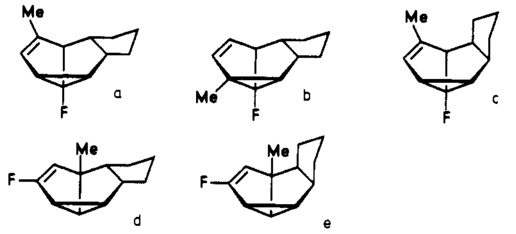
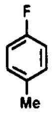
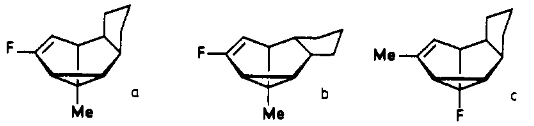
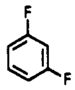
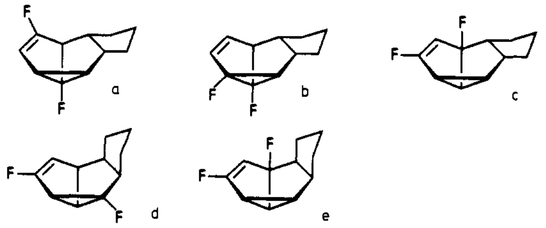
	arene	alkene	adducts	remarks	ref(s)
59				a:b:c:d:e:f:g = 10:3:20:1:34:10:22 (0.5 M arene + 1.5 M cyclopentene in cyclohexane)	96
60				a:b:c:d:e:f = 12:62:14:4:5:3 (0.5 M arene + 1.5 M cyclopentene in cyclohexane)	96
61				a:b:c:d:e = 40:12:19:12:17 (0.5 M arene + 1.5 M cyclopentene in cyclohexane)	96
62				a:b:c:d:e = 13:7:2:14:64 (0.5 M arene + 1.5 M cyclopentene in cyclohexane)	96
63				a is the major product (70% of the product mixture); b and c are minor products; fluorodimethylbiphenyls are also formed (5%) (1 M arene + 3.5 M cyclopentene in cyclohexane)	95
64				a:b:c:d:e = 4:6:21:29:40 (0.5 M arene + 1.5 M cyclopentene in cyclohexane)	118

Table 3 (Continued)

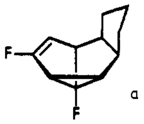
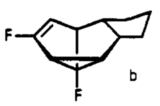
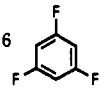
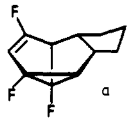
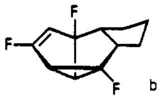
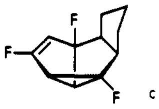
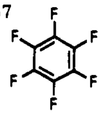
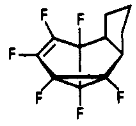
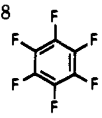
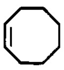
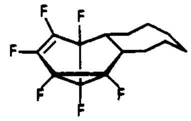
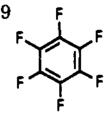
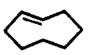
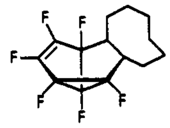
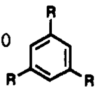
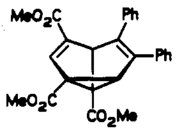
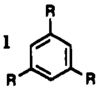
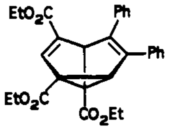
	arene	alkene	adducts	remarks	ref(s)
65			 a  b	a:b = 20:80 (0.5 M arene + 1.5 M cyclopentene in cyclohexane)	118
66			 a  b  c	a:b:c = 25:12:63 (0.5 M arene + 1.5 M cyclopentene in cyclohexane)	118
67				(0.5 M arene + 1.5 M cyclopentene in cyclohexane)	118, 119
68				five components A, B, C, D, and E in the ratio of 2:4:8:4:7; C is the exo-meta adduct; E is formed from C by 1,5 H-shift; A, B, and D contain the ortho adduct and products of its rearrangement(1:3 v/v arene/alkene)	31, 120
69				the meta adduct was not isolated, but a product resulting from 1,5 H-shift, constituting 50% of the product mixture was obtained (10:1 v/v arene/alkene)	31
70	 R = CO_2Me	$Ph-C\equiv C-Ph$		predominantly one 1:1 adduct in low yield (5%) (1:1 mixture of trimethyl ester and diphenylacetylene)	121
71	 R = CO_2Et	$Ph-C\equiv C-Ph$		yield 14.6% after hydration of the primary adduct; a secondary photoproduct is formed by *cis*-stilbene-type ring closure of the primary adduct (1:1 mixture of triethyl ester and diphenylacetylene)	121

Table 4. Meta Photocycloaddition of Benzene to Various Alkenes

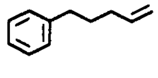
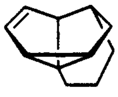
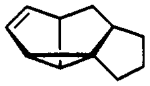
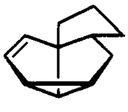
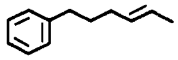
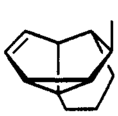
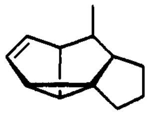
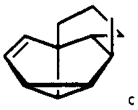
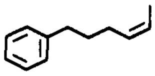
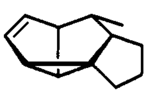
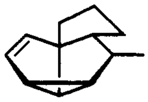
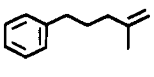
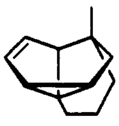
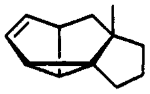
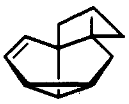
	starting material	adducts	remarks	ref(s)
1		 a  b  c	$\varphi_{dis} = 0.42$; $\varphi_a = 0.11$; $\varphi_b = 0.02$; $\varphi_c = 0.023$ (1% w/v in c-C_6H_{12}) a undergoes 1,5 H-shift on GLC	13, 122, 123
2		 a  b  c	a:(b + c) = 91:9 (ref 124); (0.01 M in cyclopentane, ref 18, or 1% w/v in cyclohexane, ref 124)	18, 124
3		 a  b	$\varphi_{tot} = 0.26$ (ref 18); a:b = 1:1 (0.06 M in cyclopentane, ref 18, or 1% w/v in cyclohexane, ref 124)	17, 18, 124
4		 a  b  c	$\varphi_{dis} = 0.35$; a:b:c = 1.65:1.65:1.00; $\varphi_{tot} = 0.65$ (1% w/v in c-C_6H_{12}); a undergoes 1,5 H-shift on GLC	123

Table 4 (Continued)

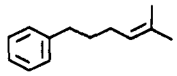
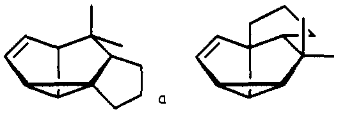
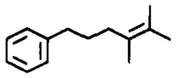
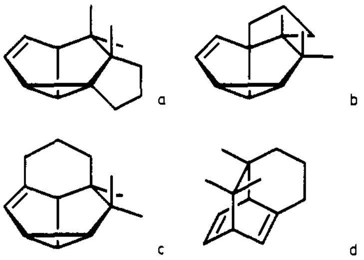
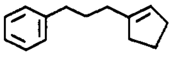
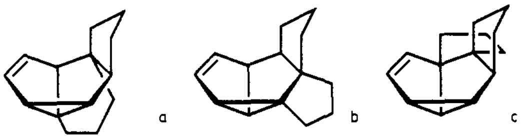
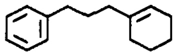
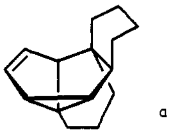
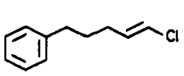
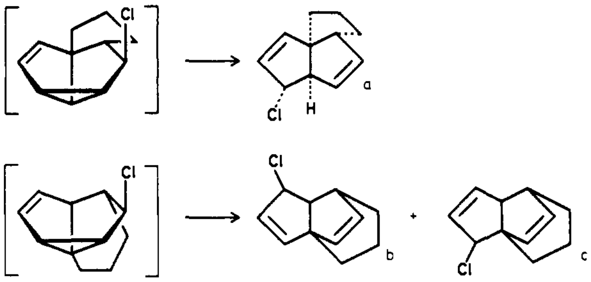
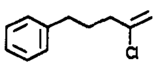
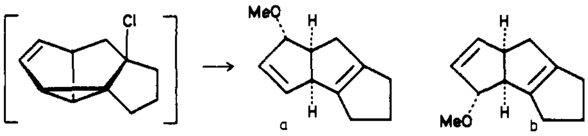
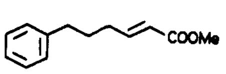
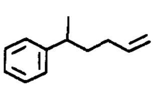
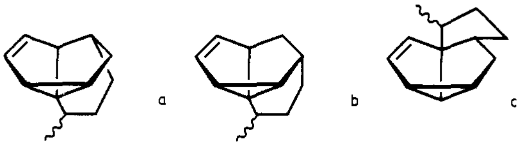
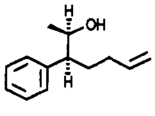
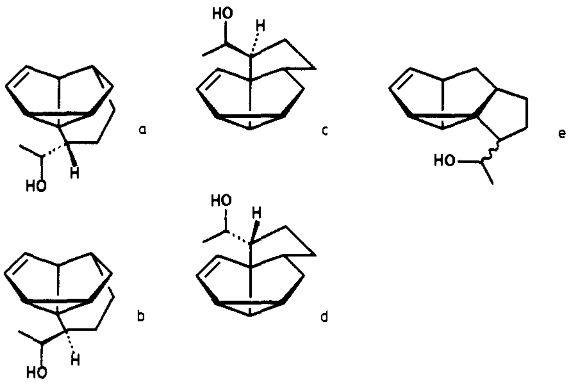
	starting material	adducts	remarks	ref(s)
5			a:b = 44:56 at 30% conversion (1% w/v in c-C_6H_{12}); ratio changes during irradiation	124
6			φ_{dis} = 0.075; a:b:c:d = 1.25:1.00:1.00:1.90 + two minor uncharacterized isomers; φ_{tot} = 0.03 (1% w/v in c-C_6H_{12})	123
7			φ_{tot} = 0.21; a:b:c = 1:1:0.5 (1% w/v in c-C_6H_{12})	78
8			φ_{dis} = 0.20; φ_a = 0.03; 9 other photoisomers; ratio, 1:2.8:1.25:1:8.5:6.5:4.5:20 (=a):4.5:2.5 (1% w/v in c-C_6H_{12})	78, 123
9			a:b:c = 4.3:1:1 (1% w/v in c-C_6H_{12}); primary adducts cannot be isolated; a and c arise by 1,3 Cl shift, b by 1,5 Cl-shift *Z*-isomer gives only *Z*-*E* isomerization	125
10			a:b = 1:4; plus two minor products (25% of total) from 2,6 addition; primary adduct not isolable; a and b from1,5 and 1,3 Cl-shift followed by solvolysis (methanol)	125
11		no meta photocycloaddition	only trans–cis interconversion	123
12			φ_{dis} = 0.40; a:b:c = 3.5:1.0:1.0 (plus 2 minor isomers, 0.7); φ_{tot} = 0.055 (1% w/v in c-C_6H_{12}); a undergoes 1,5 H-shift on GLC	123
13			a:b:c:d:e = 1:0.5:0.6:0.08:0.4 (0.03 M in hexane)	126

Table 4 (Continued)

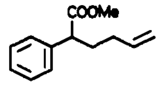
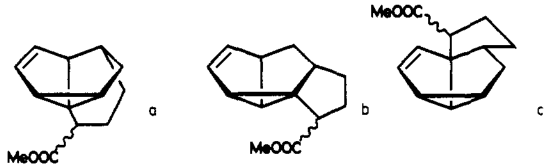
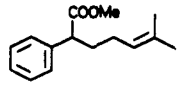
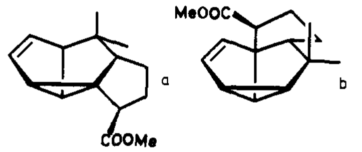
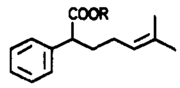
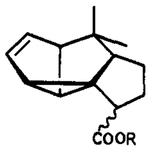
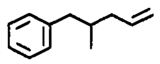
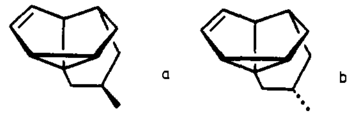
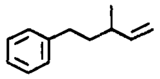
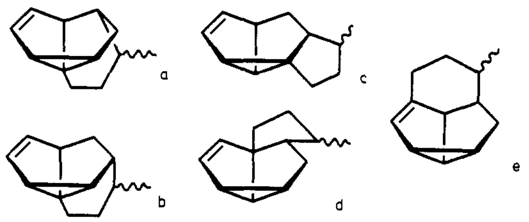
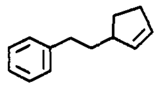
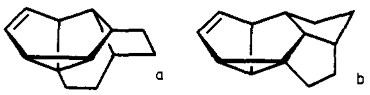
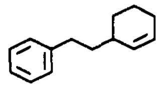
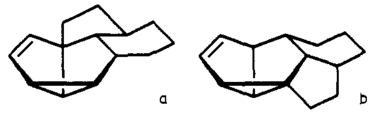
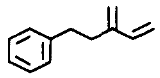
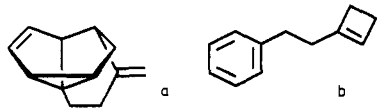
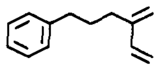
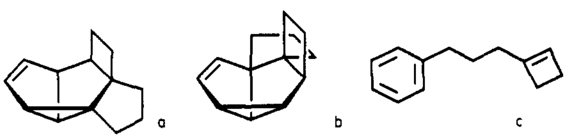
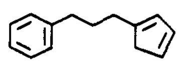
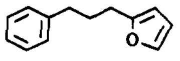
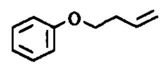
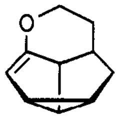
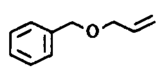
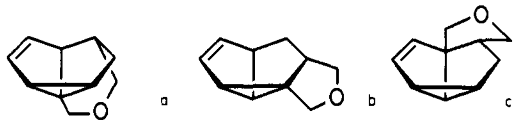
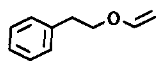
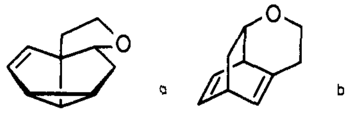
	starting material	adducts	remarks	ref(s)
14			of all three adducts both epimers are formed	127, 128
15			a, 16%, b, 12% (0.08 M in hexane)	127, 129
16	 R = menthyl		1:1 mixture of two chiral menthyl esters (*R* and *S*) was photolyzed in hexane; one reacts faster than the other	127
17			$\varphi_{dis} = 0.15$; a:b = 1.4:1.0; plus 3 minor isomers (0.8); $\varphi_{tot} = 0.035$ (1% w/v in c-C_6H_{12}); adducts undergo 1,5 H-shift on GLC	123
18			$\varphi_{dis} = 0.50$; a:b:c:d:e = 4.8:1.0:2.3:1.2:2.6; $\varphi_{tot} = 0.055$ (1% w/v in c-C_6H_{12}); a undergoes 1,5 H-shift on GLC; structure of b is tentative	123
19			$\varphi_{dis} = 0.30$; a:b = 9:1; $\varphi_{tot} = 0.12$ (1% w/v in c-C_6H_{12})	78, 123
20			$\varphi_{dis} = 0.20$; a:b = 1.35:1.00; $\varphi_{tot} = 0.15$ (1% w/v in c-C_6H_{12})	78, 123
21			$\varphi_a = 0.01$; $\varphi_b = 0.001$ (1% w/v in c-C_6H_{12})	130
22			$\varphi_a = 0.005$; $\varphi_b = 0.007$; $\varphi_c = 0.003$ (1% w/v in c-C_6H_{12}); c probably not precursor of a and b	130
23		no meta photocycloaddition	ill-defined polymeric material (1% w/v in c-C_6H_{12})	130
24		no meta photocycloaddition	essentially stable under reaction conditions (1% w/v in c-C_6H_{12})	130
25			very inefficient; excessive polymer formation (1% w/v in c-C_6H_{12})	13, 122
26			$\varphi_a = 0.017$; $\varphi_b = 0.03$; $\varphi_c = 0.02$ (1% w/v in c-C_6H_{12})	13, 122
27			$\varphi_a = 0.006$; $\varphi_b = 0.23$ (1, 5, or 10% w/v in c-C_6H_{12})	13, 122, 131

Table 4 (Continued)

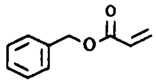
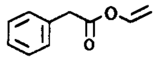
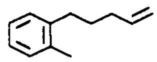
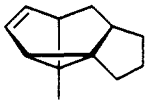
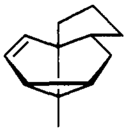
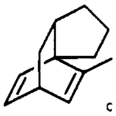
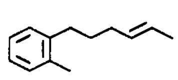
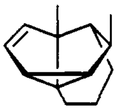
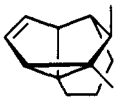
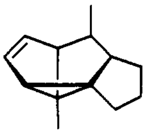
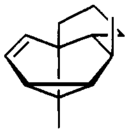
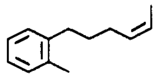
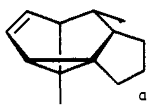
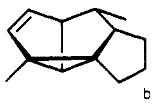
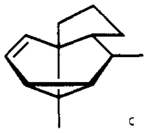
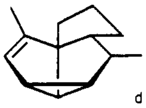
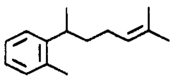
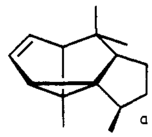
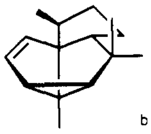
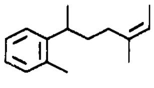
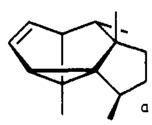
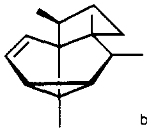
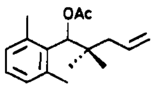
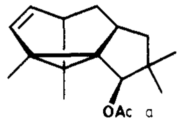
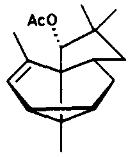
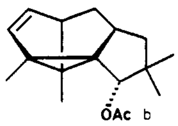
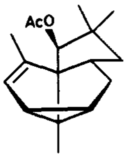
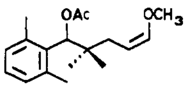
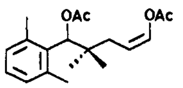
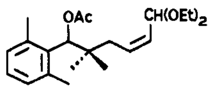
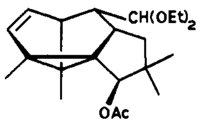
starting material	adducts	remarks	ref(s)
28 	no meta photocycloaddition	much polymer, dicyclohexyl, $PhCH_2OH$ (1% w/v in c-C_6H_{12}; some evidence of ortho addition)	123
29 	no meta photocycloaddition	traces of photoproducts, but largely photostable (1% w/v in c-C_6H_{12})	123
30 	 a  b  c	$\varphi_{dis} = 0.90$; a:b:c = 4.25:1.60:1.00; $\varphi_{tot} = 0.60$ (1% w/v in c-C_6H_{12})	123
31 	 a  b  c  d	a, 7%; b, 6%; c, 9%; d, 3%; plus products from *Z* isomer (7%) at 37% conversion (1% w/v in c-C_6H_{12})	132
32 	 a  b  c  d	a, 35%; b, 6%; c, 21%; d, 6% at 72% conversion (1% w/v in c-C_6H_{12})	132
33 	 a  b	a:b = 1:1; combined yield: 70% (pentane)	133
34 	 a  b	a:b = 1:1; combined yield; 72%; ratio changes during irradiation (0.075 M in c-C_6H_{12})	134
35 	 a  c  b  d	yields after deacetylation: a, 22–23%; b, 7%, c, 1%; d, 1% (cyclohexane)	135, 136
36 	little meta photocycloaddition	low yields of cyclized material (cyclohexane)	136
37 	little meta photocycloaddition	low yields of cyclized material (cyclohexane)	136
38 		yield, 15% (cyclohexane)	136

Table 4 (Continued)

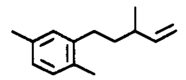
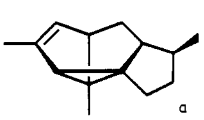
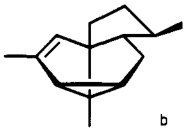
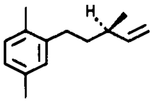
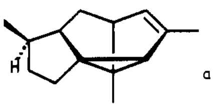
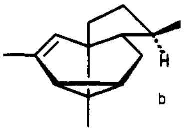
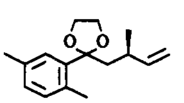
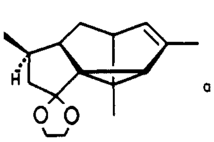
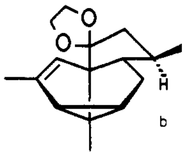
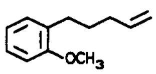
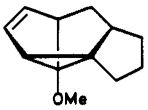
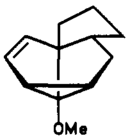
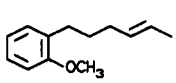
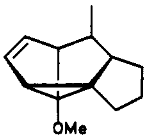
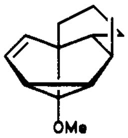
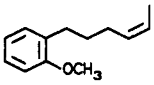
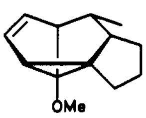
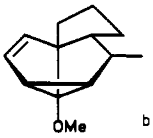
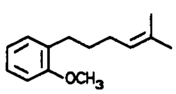
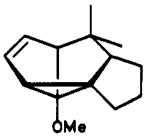
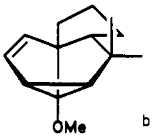
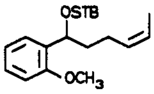
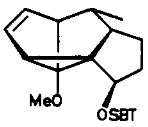
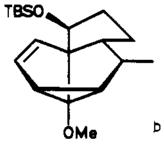
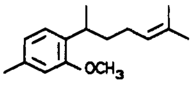
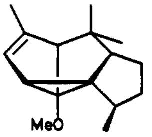
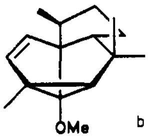
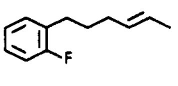
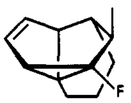
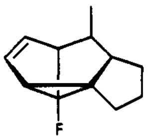
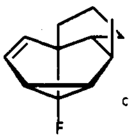
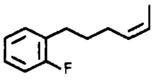
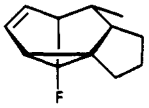
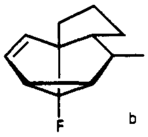
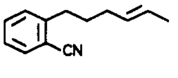
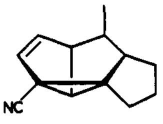
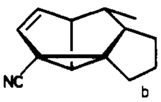
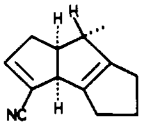
	starting material	adducts	remarks	ref(s)
39		 a  b	a:b = 1.88:1; 72% yield (cyclohexane)	137
40		 a  b	a:b = 2:1; 72% yield (cyclohexane); enantiomerically pure starting material and products	138
41		 a  b	a:b = 1.8:1; 42% yield (cyclohexane)	139
42		 a  b	φ_{dis} = 0.80; a:b = 4.65:5.60; plus 2 minor isomers (1.00); φ_{tot} = 0.5 (1% w/v in c-C_6H_{12})	123
43		 a  b	a:b = 31:18 (at 37% conversion, ratio changes during irradiation); plus adducts from *Z* isomer (1% w/v in c-C_6H_{12})	124
44		 a  b	a:b = 46:54 (1% w/v in c-C_6H_{12})	124
45		 a  b	a:b = 48:52 (at 36% conversion, ratio changes during irradiation) (1% w/v in c-C_6H_{12})	124
46		 a  b	a:b = 1:2.3; 63% yield (0.04 M in cyclohexane)	140
47		 a  b	a:b = 1:1; yield: 65% (~0.13 M in pentane)	141
48		 a  b  c	a, 10%; b, 28%; c, 9% at 78% conversion; also 17% 1,3 adduct from *Z* isomer (1% w/v in c-C_6H_{12})	132
49		 a  b	a, 35%; b, 19% at 72% conversion (1% w/v in c-C_6H_{12})	132
50		 a  b  c	a, 34%; b, 1%; c, 8% at 91% conversion (1% w/v in c-C_6H_{12}); c is formed by thermal 1,5 H-shift of 1,3 adduct b from *Z* isomer	132

Table 4 (Continued)

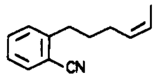
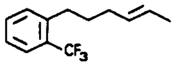
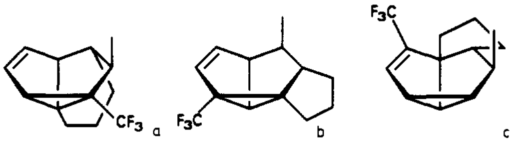
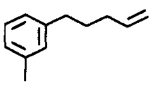
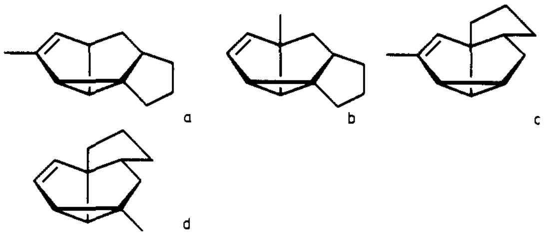
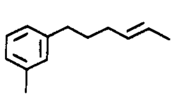
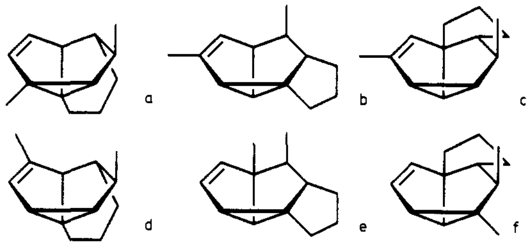
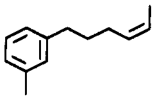
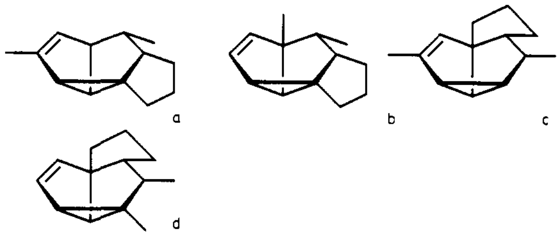
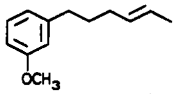
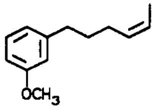
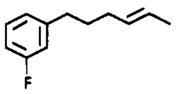
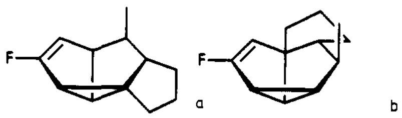
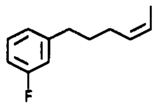
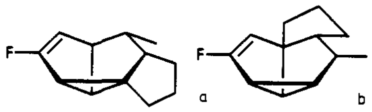
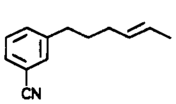
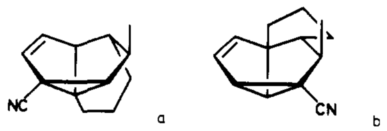
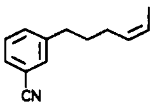
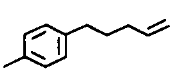
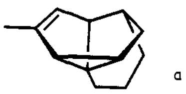
	starting material	adducts	remarks	ref(s)
51		no meta photocycloaddition	after 65% conversion (1% w/v in c-C_6H_{12}) no meta adducts detectable	132
52			a:b:c = 17:45:38; plus eight minor products (each <5%) (1% w/v in c-C_6H_{12})	124
53			φ_{dis} = 0.08; a:b:c:d = 1.00:3.70:10.00:3.25; four other isomers; φ_{tot} = 0.07 (1% w/v in c-C_6H_{12})	123
54			a, 24%; b, 11%; c, 6%; d, 12%; e, 3%; f, 1–2%; (plus products from *Z* isomer) at 69% conversion (0.6% w/v in c-C_6H_{12})	132
55			a, 29%; b, 9%; c, 25%; d, 4% at 72% conversion (1% w/v in c-C_6H_{12}); structures of b and d are tentative	132
56		no meta photocycloaddition	many photoproducts, only one isolable; probably an ortho or para adduct (1% w/v in c-C_6H_{12})	124
57		no meta photocycloaddition	*E* isomer plus four isolable products none of which is an ortho, meta, or para adduct (1% w/v in c-C_6H_{12})	124
58			a, 12%; b, 8%; plus 10% 1,3-adduct from *Z* isomer at 35% conversion (1% w/v in c-C_6H_{12})	132
59			a, 34%; b, 28% at 70% conversion (0.5% w/v in c-C_6H_{12})	132
60			a, 24%; b, 3% at 37% conversion (1% w/v in c-C_6H_{12})	132
61		no meta photocycloaddition	after 19% conversion (1% w/v in c-C_6H_{12}) no meta adducts detectable	132
62			φ_{dis} = 0.45; φ_a = 0.06; plus four other isomers (1% w/v in c-C_6H_{12}); product undergoes 1,5 H-shift on GLC	123

Table 4 (Continued)

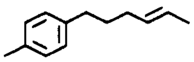
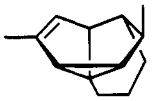
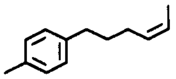
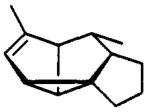
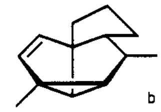
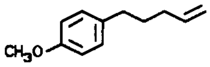
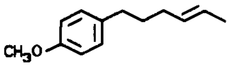
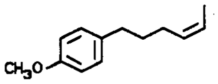
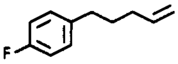
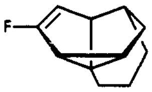
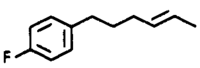
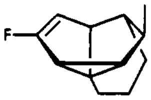
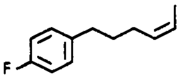
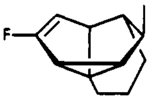
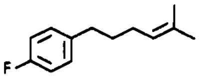
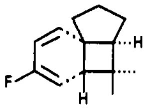
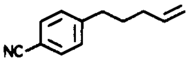
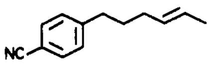
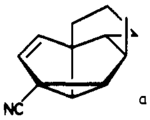
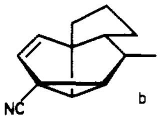
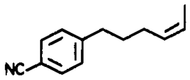
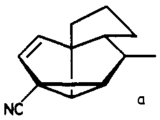
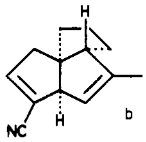
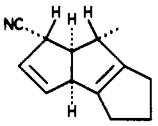
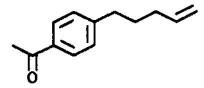
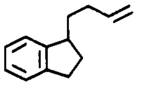
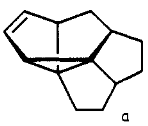
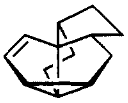
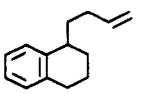
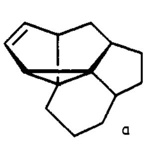
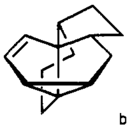
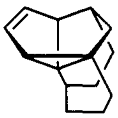
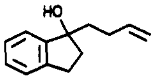
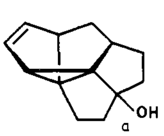
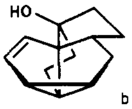
	starting material	adducts	remarks	ref(s)
63		 a	a, 16% at 19% conversion (1% w/v in c-C_6H_{12})	132
64		 a  b	a, 14%; b, 19%; plus 23% 2,6 adduct from *E* isomer at 70% conversion (1% w/v in c-C_6H_{12})	132
65		no meta photocycloaddition	no significant volatile products; varying amounts of polymeric material (1% w/v in c-C_6H_{12})	123
66		no meta photocycloaddition	*Z* isomer plus some minor products (<1%) which cannot be isolated (1% w/v in c-C_6H_{12})	124
67		no meta photocycloaddition	*E* isomer plus two minor products which are not ortho, meta, or para cycloadducts (1% w/v in c-C_6H_{12})	124
68		 a	yield > 95% (1% w/v in c-C_6H_{12})	95
69		 a	a, 33% at 34% conversion (1% w/v in c-C_6H_{12})	132
70		 a	a, 52% at 100% conversion (1% w/v in c-C_6H_{12}); no adducts from *Z* isomer	132
71		 a	a, 14% at 15% conversion (1% w/v in c-C_6H_{12})	132
72		no meta photocycloaddition	no significant volatile products; varying amounts of polymeric material (1% w/v in c-C_6H_{12})	123
73		 a  b	a, 35%; b (from Z isomer), 13% at 54% conversion (1% w/v in c-C_6H_{12})	132
74		 a  b  c	a, 44%; b, 3%; c, 2% at 63% conversion (1% w/v in c-C_6H_{12}); b and c are formed by thermal 1,5 H-shift	132
75		no meta photocycloaddition	no significant volatile products; varying amounts of polymeric material (1% w/v in c-C_6H_{12})	123
76		 a  b	$\varphi_{dis} = 0.7$; a:b = 1:1 (2% w/v in c-C_6H_{12})	142
77		 a  b  c	a:b:c = 3.7:1.0:1.5 (2% w/v in c-C_6H_{12}) structure of c is tentative	142
78		 a  b	a, 43%; b, 23% (0.03 M in *tert*-butyl methyl ether)	143

Table 4 (Continued)

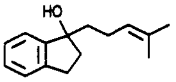
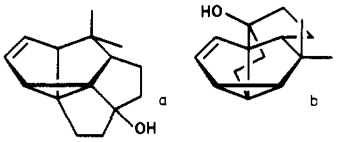
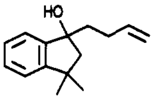
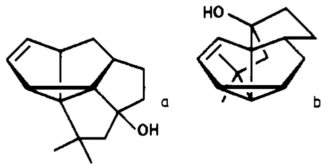
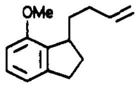
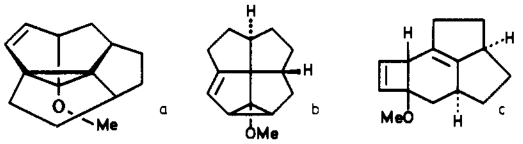
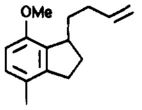
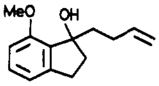
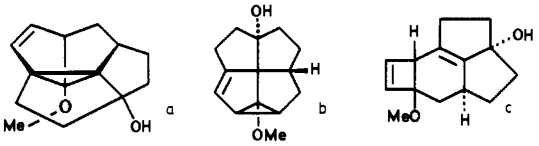
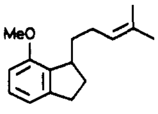
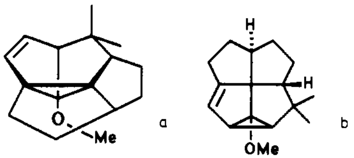
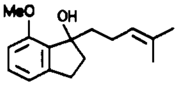
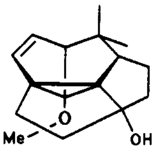
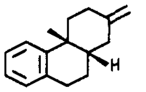
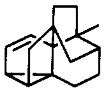
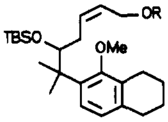
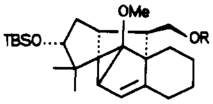
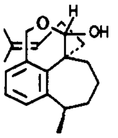
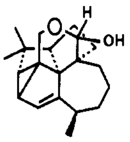
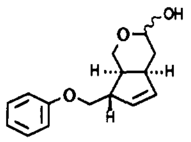
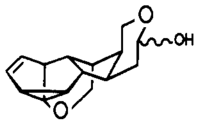
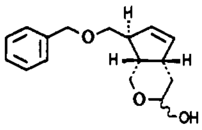
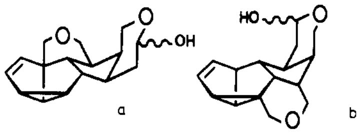
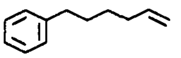
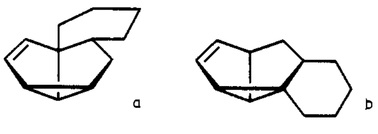
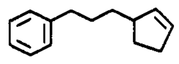
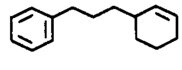
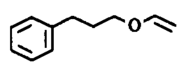
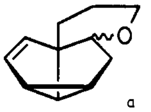
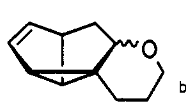
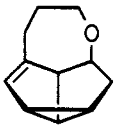
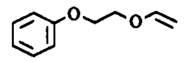
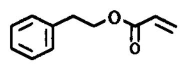
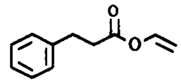
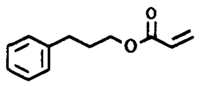
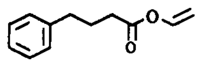
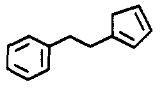
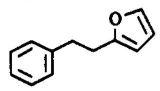
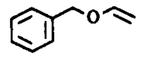
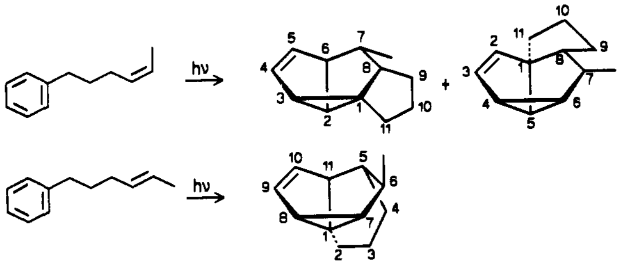
	starting material	adducts	remarks	ref(s)
79			a, 28%; b, 24% (0.025 M in *tert*-butyl methyl ether)	143
80			a, 30%; b, 12% (0.007 M in *tert*-butyl methyl ether)	143
81			a:b:c = 1.5:1:3.5 (0.05 M in *tert*-butyl methyl ether); adduct c is formed via initial ortho addition	143
82		no meta photocycloaddition	no monomeric products detected	142
83			a:b:c = 3–4:1:4–5 (0.013 M in *tert*-butyl methyl ether); adduct c is formed via initial ortho addition	143, 144
84			low yields: a, 3.3%; b, 7.7% (0.007 M in *tert*-butyl methyl ether)	143
85			low yield: 0.5% (0.016 M in *tert*-butyl methyl ether); major product (46%) is indene derivative formed by photodehydration	143
86			φ = 0.046 (0.02 M in hexane); a secondary photoproduct is formed from this adduct with high efficiency	145, 146
87	 R = H or Ac			128
88			yield, 51%	147
89			yield, 35%; solvent, ethanol	148
90			a:b = 2:3; combined yield; 42%; solvent, ethanol	148
91			a:b = 1:1; $\varphi_{tot} < 0.005$	43

Table 4 (Continued)

starting material	adducts	remarks	ref(s)
92 	no meta photocycloaddition	very low yield of one isomer, uncharacterized, $\varphi < 0.001$ (1% w/v in c-C_6H_{12})	123
93 	no meta photocycloaddition	very low yield of five isomers (7:1:1:3.5:5), uncharacterized, $\varphi < 0.001$ (1% w/v in c-C_6H_{12})	123
94 	 a  b  c	$\varphi_{dis} = 0.1$; $\varphi_a = 0.005$; $\varphi_b = 0.007$; $\varphi_c = 0.05$ (1% w/v in c-C_6H_{12})	13, 122
95 		very inefficient; excessive polymer formation (1% w/v in c-C_6H_{12})	13, 122
96 	no meta photocycloaddition	much polymer, dicyclohexyl, $PhCH_2CH_2OH$; some evidence for ortho addition (1% w/v in c-C_6H_{12})	123
97 	no meta photocycloaddition	traces of photoproducts, but largely photostable	123
98 	no meta photocycloaddition	much polymer, dicyclohexyl, $PhCH_2CH_2CH_2OH$; some evidence for ortho addition (1% w/v in c-C_6H_{12})	123
99 	no meta photocycloaddition	traces of photoproducts, but largely photostable (1% w/v in c-C_6H_{12})	123
100 	no meta photocycloaddition	ill-defined polymeric material (1% w/v in c-C_6H_{12})	130
101 	no meta photocycloaddition	ill-defined polymeric material (1% w/v in c-C_6H_{12})	130
102 	no meta photocycloaddition	almost quantitative yield of β-phenylpropionaldehyde (1% w/v in c-C_6H_{12})	13

Scheme 9. Intramolecular Meta Photocycloaddition of *cis*- and *trans*-6-Phenylhex-2-ene



trans-6-phenylhex-2-ene gives one 2,6 adduct, *endo*-6-methyltetracyclo[$5.4.0.0^{1,8}.0^{5,11}$]undec-9-ene (Scheme 9).

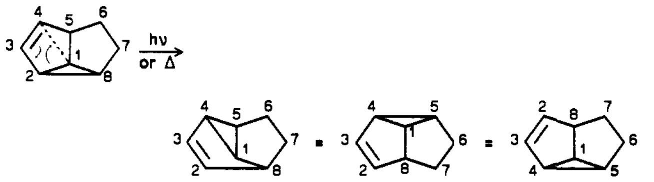
IV. Meta Photocycloadditions 1966–1992

The meta adducts that have been prepared, identified, and described during 26 years of research on meta photocycloaddition have been collected in Tables 1–4.

Table 1 contains the results of the irradiations of benzene in the presence of 57 alkenes and dienes; approximately 100 adducts have been reported. The column "remarks" provides information about quantum yields, product ratios, other products, and experimental conditions. In many cases meta photocycloaddition is not the only, sometimes not even the predominant, photoprocess. If the occurrence of ortho and/or para addition is specifically mentioned in the literature, this information is presented in the table. It should be borne in mind that ortho and para cycloadducts are rather labile, photochemically as well as thermally, and these products may therefore sometimes remain unnoticed, especially if irradiation times are long and GLC temperatures high. For the same reason, ortho:meta:para ratios should be treated with great caution. The same holds for ratios of meta adducts. When the alkene is asymmetrically substituted, two regioisomeric adducts may be formed, substituted at positions 6 or 7. Upon heating (e.g. on the GLC column) as well as upon irradiation (if degrees of conversion of starting material are high and products begin to absorb light) these adducts may undergo a vinylcyclopropane–cyclopentene rearrangement, which is degenerate in the unsubstituted adduct, but which converts one adduct into another if substituents are present[74] (Scheme 10). The carbon atoms in each of the pairs 2/4, 5/8, and 6/7 are interchanged.

Where known, the solvent and the concentrations of the reactants are given in the table. The ratio of adducts is often dependent on these experimental conditions, but systematic studies of solvent effects on product ratios have not been performed. In one instance, benzene and furan, it has even been reported[72] that the

Scheme 10. Vinylcyclopropane–Cyclopentene Rearrangement of a Meta Photocycloadduct



results of the irradiation under "British conditions" differ from those under "U.S. conditions".

Table 1 does not include those alkenes and dienes which fail to give the meta addition. Among these are maleic anhydride,[44,149] maleimide,[44,149] *N*-butyl-, *N*-phenyl-, *N*-benzyl-, *N*-*o*-tolyl-, *N*-*m*-tolyl-, *N*-*p*-tolyl-, *N*-*p*-anisyl-, *N*-*p*-*tert*-butylphenyl-, and *N*-(2,6-dimethylphenyl)maleimide,[44,149] methyl vinyl ketone,[30,49] methyl allyl ketone,[21] *N*,*N*-dimethylallylamine,[21] 1-amino-*N*,*N*-diethyl-2-methylpropene,[21] 1-amino-*N*,*N*-dimethylcyclopropene,[21] methyl vinyl sulfide,[21] acrylonitrile,[30,49,150,151] methacrylonitrile,[151] methyl acrylate,[49,151] methyl methacrylate,[49,151] 1,4-dioxene,[49,50] 1,1-dimethoxyethene,[50] *cis*-1,2-dimethoxyethene,[30] *cis*-1,2-di-*tert*-butylethene,[26,30] norbornadiene,[20,22] thiophene,[71] 2,5-dimethylfuran,[72] and 3-methylenecyclohexene.[22,67] No meta photocycloaddition to benzene was observed with the alkynes dimethyl 2-butynedioate,[20] methyl phenylpropynoate,[20] and cyclooctyne.[20] Many of the molecules mentioned above give ortho addition with benzene, but some do not add at all.

Tables 2–4 have been constructed in the same manner as Table 1 with the exception that Table 4 (intramolecular meta photocycloaddition) does contain molecules that fail, reportedly, to undergo the reaction.

Twenty monosubstituted benzenes and 32 alkenes and dienes in 74 different combinations have been irradiated, giving rise to ca. 150 meta adducts. These have been collected in Table 2. Substituents on the benzene ring appear to have a strong directing effect on the addition and arranging the monosubstituted benzenes and their adducts in a separate table is convenient for obtaining insight into the regiochemical consequences of the presence of the various substituents.

The higher substituted benzenes (44) are grouped in Table 3. The variety of alkenes (12) is noticeably less than in Tables 1 and 2; 71 combinations have successfully been tried, yielding ca. 175 meta adducts.

Intramolecular meta photocycloaddition is reviewed in Table 4. The reaction occurs with 76 of the 102 molecules that have been tried, yielding ca. 175 adducts. Meta addition is most successful with molecules having a chain of three atoms between arene and alkene. Entries 1–89 possess this structure, 90–97 have four, 98 and 99 five, and 100–102 two atoms between the chromophores. Entries 2–29 are molecules in which the benzene ring bears no substituents other than the side chain, 30–75 have one or more additional substituents on the benzene ring, arranged as much as possible in the order ortho, meta, para, and 76–88 have a saturated five-, six-, or seven-membered ring joined to the benzene ring.

V. Mechanism

A. Intermediates, Kinetic Aspects

1. The Reactive Excited State

In their report on the discovery of the meta photocycloaddition Bryce-Smith, Gilbert, and Orger[15] left open the question of the involvement of excited singlet or triplet state intermediate. They had found that benzophenone and acetone were ineffective as photosensitizers, but that rates of addition increased approximately 2-fold in the presence of β-propiolactone. No explanation for this effect has ever been offered.

Morikawa and Cvetanović[152] have studied the quenching of the excited singlet state of benzene ($^1B_{2u}$) by alkenes and dienes. They found that conjugated dienes are quite efficient quenchers of benzene fluorescence, much more efficient than alkenes and nonconjugated dienes. Trimethylethene and tetramethylethene show a distinct, although very small, intrinsic quenching efficiency. *cis*-But-2-ene is said to be a marginal case, having perhaps an extremely small quenching efficiency which, however, is not significantly different from zero. This observation has often been quoted as evidence against a direct interaction between $^1B_{2u}$ benzene and alkene as a primary step in the meta photocycloaddition. It should be realized, however, that these quenching experiments were carried out in the vapor phase. The observation by Morrison and Ferree[17] that a 0.8 M solution of *trans*-2-hexene reduces the fluorescence of toluene (4×10^{-3} M) by 22% has never drawn much attention.

Morrison and co-workers[17,18] in their study on the intramolecular photocycloaddition of the 6-phenylhex-2-enes found that benzene-sensitized photolysis of the cis isomer produced both cycloaddition and cis to trans isomerization at approximately equal rates. Sensitization with benzophenone or acetone produces no detectable cycloaddition but only cis to trans isomerization. These results do not provide information regarding the possible intermediacy of the triplet state of the aromatic moiety (E_T toluene = 83 kcal/mol; E_T benzophenone = 69 kcal/mol; E_T acetone = 79–82 kcal/mol), but they do indicate that the triplet state of the alkene is not involved in the cycloaddition. *cis*-Piperylene was found to quench inefficiently both cycloaddition and cis,trans isomerization: the Stern–Volmer slope for the former process is only 4.5 ± 1.3 M^{-1}. Internal quenching of arene fluorescence on the other hand is quite efficient. *cis*-6-Phenylhex-2-ene, *trans*-6-phenylhex-2-ene, and 5-phenylpent-1-ene have fluorescence intensities relative to toluene (=1.00) of 0.05, 0.04, and 0.05, whereas the relative fluorescence intensities of hexylbenzene, 5-phenylpent-2-ene and 6-phenylhex-2-yne are 0.90, 0.88 and, 0.72. Only the first three compounds undergo the meta addition and thus there seems to be a competition between arene fluorescence and interaction between arene and alkene leading to adduct. The effect of oxygen on the photochemistry of *cis*-6-phenylhex-2-ene is remarkable. Fluorescence is quenched by 42% in an oxygen-saturated solution; cycloaddition is quenched by 29%; and cis,trans isomerization is increased by a factor of 4. A similar phenomenon has been observed later in the study of the intermolecular reaction between benzene and cyclopentene.[153] Under conditions (4.5×10^{-2} M benzene + 0.3 M cyclopentene in cyclohexane) under which the fluorescence is reduced to 62% of its value in the absence of oxygen, the photochemical reaction is only reduced to 86%. The cause of this curious effect is still obscure.

Morikawa, Brownstein, and Cvetanović[23] have studied the effect of added oxygen and biacetyl on the photoreaction of benzene with *cis*-2-butene in the vapor phase. The results strongly suggest that the excited singlet benzene (or a derivative from it) and not the triplet $^3B_{1u}$ is involved in the formation of the photoadduct.

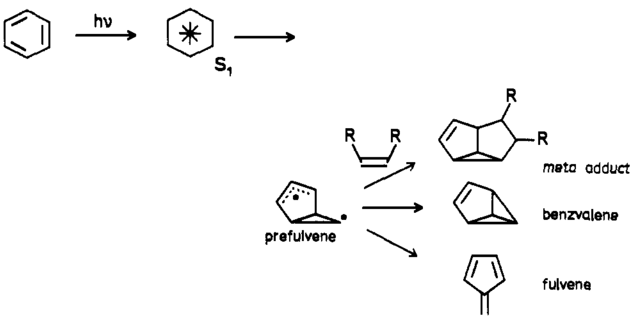
Mattay et al.[55] have investigated the effect of xenon on the photoaddition of benzene to 1,3-dioxole, 2-methyl-1,3-dioxole, 2,2-dimethyl-1,3-dioxole, and 1,4-dioxene in 1,4-dioxane. It was found that the presence of xenon causes a reduction of the quantum yields of ortho, meta, and para photocycloaddition to 30–70% of their values in argon-purged solutions. Xenon strongly accelerates singlet–triplet intersystem crossing and it was concluded that the photoaddition of benzene to the 1,3-dioxoles and to 1,4-dioxene involves exclusively the excited singlet state.

Osselton et al.[41] have determined the rate constant of the quenching of benzene fluorescence by cyclopentene in cyclohexane (8.3×10^7 L mol^{-1} s^{-1}) and the quantum yields of adduct formation at various concentrations of cyclopentene. The relation between quantum yield and cyclopentene (cp) concentration is: $\varphi = [\mathrm{cp}] \times (2.59 + 2.38 \times [\mathrm{cp}])^{-1}$. The measurements were performed in air-saturated solutions. The formation of the meta adduct via direct interaction between S_1 benzene and cyclopentene is in agreement with the observed kinetics. The rate constant of fluorescence quenching is the sum of physical quenching (back to ground state, $k_q = 4.82 \times 10^7$ L mol^{-1} s^{-1}) and chemical quenching (leading to adduct, $k_r = 3.48 \times 10^7$ L mol^{-1} s^{-1}). Under these circumstances (in air-saturated cyclohexane, with $\tau(S_1) = 11 \times 10^{-9}$ s) rather more than half of the S_1 benzene molecules undergoing interaction with cyclopentene revert to the ground state and rather less than half carry on to form the adduct. From the results of these measurements it cannot be concluded that interaction between S_1 of benzene and cyclopentene leads *directly* to the adduct. On kinetic grounds interaction leading to an intermediate en route to the adduct is equally feasible. A mechanism, however, in which an intermediate is irreversibly formed from the excited state, prior to interaction with the alkene, cannot be reconciled with the observed kinetics. This excludes the intermediacy of triplet states and of species such as benzvalene and the hypothetical diradical prefulvene.

From orbital-symmetry considerations, Bryce-Smith[154] had concluded, already in 1969, that interaction between $^1B_{2u}$ benzene and S_0 alkene, leading to a biradical with the bicyclo[3.2.1]octene skeleton, is symmetry allowed, whereas a similar reaction starting from $^3B_{1u}$ is symmetry forbidden.

On the basis of the above evidence it can be concluded that the meta photocycloaddition of arenes to alkenes proceeds from the first excited singlet state of the arene. It should be realized that such a conclusion is necessarily based on measurements performed with just a few, although probably fairly representative, substrates.

Scheme 11. The Hypothetical Prefulvene as an Intermediate in the Formation of the Meta Cycloadduct, Benzvalene, and Fulvene



2. Benzvalene

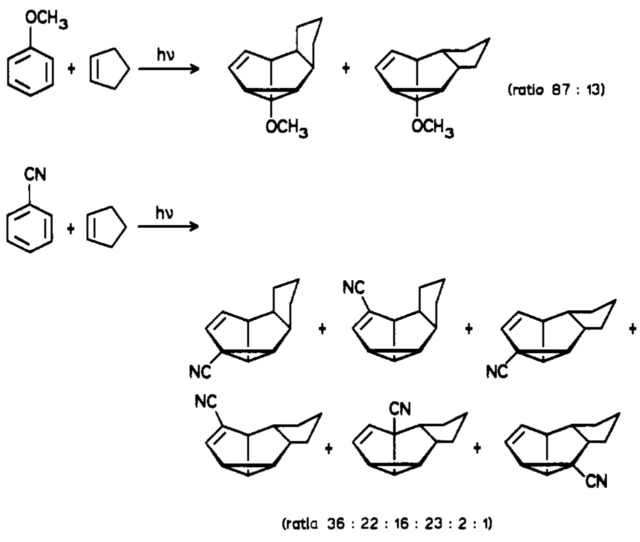
Wilzbach and Kaplan,[14] in their report on the discovery of the meta photocycloaddition, remarked that the adducts correspond to addition of an olefin across a cyclopropyl ring of benzvalene. In a later paper[155] they reported that the quantum yield of benzvalene formation from benzene in hexadecane is 0.05, while the quantum yield of adduct formation from benzene in cyclopentene amounts to 0.25. It was concluded that, unless the formation of benzvalene is markedly solvent dependent, the cycloaddition follows a different path.

3. Prefulvene

A biradical with the bicyclo[3.1.0]hex-2-ene skeleton was suggested to be a possible intermediate in a provisional mechanistic proposal made by Bryce-Smith et al.[15] in their first paper on the meta photocycloaddition. The singlet biradical was considered to be a tautomer of $^1B_{2u}$ benzene and a precursor of fulvene, benzvalene, and the meta cycloadduct[9] (Scheme 11); it was named prefulvene.[156]

The hypothetical prefulvene has never been detected, neither as an intermediate in valence isomerization of benzene, nor as precursor of the meta cycloadduct. Its intermediacy in the photoaddition would imply that of the three new σ-bonds that are formed during the process, the one closing the cyclopropane ring is formed first, while bonding to the alkene occurs at a later stage. It should be emphasized that Bryce-Smith, Gilbert, and their co-workers, who have advocated the prefulvene mechanism for many years, have considered the alternative mechanism, i.e. prior formation of the bonds with the alkene followed by closure of the cyclopropane ring, as a realistic possibility in all their papers since 1968. An orbital-symmetry analysis, published in 1969 by Bryce-Smith,[154] indicates that not only the transformation of $^1B_{2u}$ benzene into prefulvene is symmetry allowed but also the formation of the biradical that results from bonding of the termini of an alkene to meta positions of $^1B_{2u}$ benzene. The inability of alkenes effectively to quench the fluorescence of benzene in the gas phase[152] was considered[154] to favor the prefulvene mechanism, at least for gas-phase reactions. Of the other possible route it was said that it may be involved in liquid-phase reactions. Most studies on meta photocycloaddition have been performed with liquid solutions. Morikawa, Brownstein, and Cvetanović[23] have

Scheme 12. Regioselectivity in the Meta Photocycloaddition of Anisole and Benzonitrile to Cyclopentene



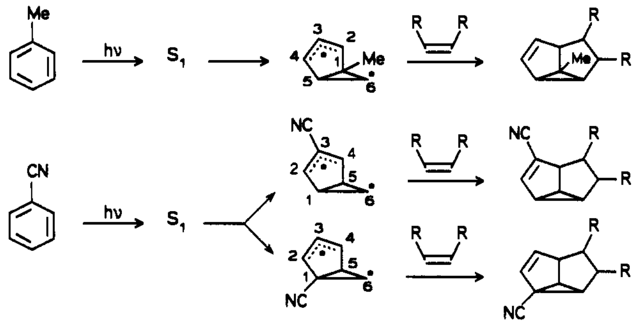
studied the kinetics of the cycloaddition of photoexcited benzene to 2-butene in the gas phase, and they have excluded the $^3B_{1u}$ state as an intermediate, but not a derivative from the $^1B_{2u}$ state such as the postulated prefulvene.

It can be seen from Table 2 that substituents on the benzene ring have a pronounced directing effect on the cycloaddition. Of the 20 substituents in the table, three (CH=CH$_2$, C≡CH, and C≡CMe) have only been used in a reaction with a diene and they will be dealt with later. The 17 other substituents can be divided into three groups: mesomerically electron-donating substituents (Me, Et, *i*-Pr, *t*-Bu, CH$_2$Ph, OH, OMe, OEt, *i*-PrO, *t*-BuO, OPh, OSiMe$_3$), electron-withdrawing groups (CF$_3$, CO$_2$Me, and CN), and two atoms that are inductively withdrawing and mesomerically donating (Cl and F). Inspection of the table reveals that the electron-donating substituents strongly favor position b1 in the adduct, they sometimes appear also at position b3 while b2, b4, b5, and b8 are the positions least favored (for numbering see Scheme 6). With the donor substituents OR (R = H, alkyl, or SiMe$_3$) the adduct substituted at b1 is formed exclusively (with alkenes).

With electron-withdrawing groups the situation is drastically different: when alkenes are used as addends the substituents CF$_3$, CO$_2$Me, and CN have a strong preference for positions b2 and b4; they are never found at b1. Two representative examples of the influence of donor and withdrawer effects are shown in Scheme 12.

During the years 1971 to 1985, when all this information about the effect of substituents became available, it became increasingly difficult to reconcile these effects with the prefulvene mechanism. The cases of toluene and benzonitrile will serve as examples. The methyl group strongly prefers position b1 in the adduct (Table 2, entries 1–8) and the cyano group is found predominantly at positions b2 and b4 (Table 2, entries 68–72).

Scheme 13. Formation of Meta Adducts via the Hypothetical Prefulvene Derivatives



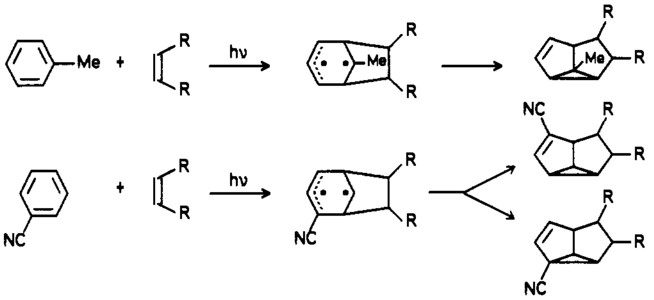
In Scheme 13 those methyl- and cyanoprefulvenes are drawn which would have to be intermediates if the addition were to start with closure of the cyclopropane ring. It is not clear why toluene would give only the 1-methylprefulvene and benzonitrile a mixture of 1- and 3-cyanoprefulvene, or if the other isomers would also be formed, why only these would react with the alkene. Also, it cannot be rationalized why 1-methylprefulvene would react only at positions 2 and 6 and 1-cyanoprefulvene only at positions 4 and 6. Similar arguments hold for the other monosubstituted benzenes and for the higher substituted benzenes. Prefulvene has also been written as a hybrid of a biradical and two zwitterionic forms[26] but this does not help in understanding the regioselectivities. The prefulvene hypothesis was abandoned in 1986.[157]

4. Bicyclo[3.2.1]octenyl Biradicals

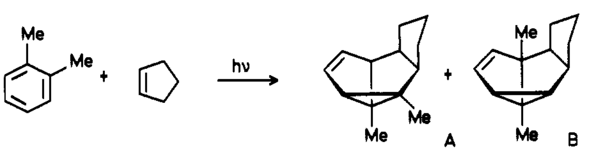
If, on the basis of the observed regioselectivities and on the basis of kinetic evidence, the meta addition cannot be rationalized via prior bond formation in the excited benzene molecule, one has to assume that the reaction starts with some kind of interaction between S$_1$ benzene and alkene. This interaction eventually leads to the formation of two σ-bonds, and the question then is: Are these bonds formed consecutively or simultaneously? This happens to be one aspect of the mechanism of the meta photocycloaddition about which there appears to be general consent. It was noted already at the time of the discovery that the stereochemistry of the alkene is retained during the process and this implies concerted formation of the two bonds. There are not many pairs of alkenes of which it can be said that *cis*-alkene gives cis adduct and trans gives trans. In fact, this is only true for but-2-ene (Table 1, entries 9 and 10) and cyclooctene (Table 1, entries 27 and 28, Table 3, entries 68 and 69). The primary meta adduct from *cis*-1,2-dichloroethene (Table 1, entry 49) has not been isolated and from its rearrangement products the original stereochemistry cannot be deduced. However, in all cases in which an alkene can exist in a cis and a trans configuration and in which one of the isomers has been used as the addend, the original stereochemistry is retained in the adduct.

If the interaction between excited benzene and ground-state alkene leads to the formation of a biradical in the early stages of the reaction, the same problem arises as in the case of the hypothetical prefulvene discussed above: how do we explain the directing effects of electron-releasing and electron-withdrawing substituents? As can be seen from Scheme 14, the bicyclo[3.2.1]octenyl biradicals that might be intermediates in the formation of methyl- and cyano-substituted adducts have their substituents at positions at which they can exert a stabilizing influence.

Scheme 14. Meta Photocycloaddition via the Bicyclo[3.2.1]octenyl Biradical



Scheme 15. Two Meta Photocycloadducts from o-Xylene and Cyclopentene



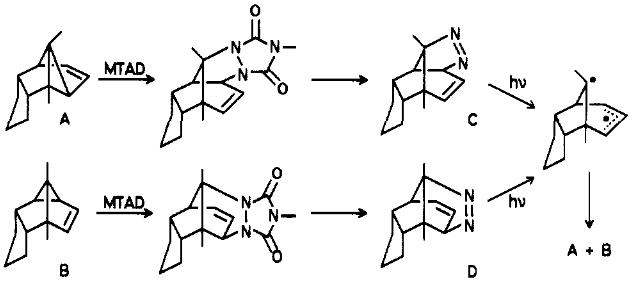
The possible intermediacy of such biradicals has been discussed by Bryce-Smith,[154] by Gilbert and co-workers,[27,79,81,123] and by Sheridan and co-workers.[77,158,159,160] This mechanistic proposal, however, does not give a rationale for the difference in regioselectivity of electronegative and electropositive substituents. Contrary to the case of prefulvene, this is not sufficient reason to reject it. The biradicals may be present during a certain stage of the reaction and then undergo the closure of the cyclopropane ring, but their formation may be preceded by an interaction between the excited benzene and the alkene during which the regioselectivity is determined, e.g. in an excited complex. In view of the difference in behavior between electron-withdrawing and electron-releasing substituents a certain degree of polarization at this stage of the reaction is likely, an aspect that will be discussed later.

An important discovery was made by Reedich and Sheridan[159] who succeeded in preparing molecules from which, by photochemical expulsion of nitrogen, the bicyclo[3.2.1]octenyl biradicals are formed. These radicals do indeed undergo the cyclopropane ring closure and, more importantly, if asymmetrically substituted molecules are used from which two different meta adducts can be formed, these products are formed in exactly the same ratio as the products in the meta photocycloaddition. Reedich and Sheridan have used the adducts from *o*- and *m*-xylene for their studies and the case of *o*-xylene will be shown here as an example. Irradiation of this compound in the presence of cyclopentene (1 mM each in cyclohexane) gives two adducts A and B in the ratio of 1:1.36 ± 0.02 (Scheme 15).

These adducts react with 3-methyltriazoline-2,4-dione (MTAD)[158,159] (Scheme 16), and upon hydrolysis and oxidation, the corresponding azo compounds C and D are formed. Elimination of nitrogen by photolysis leads to the same biradical which can then close in two ways and yield the compounds A and B. Irradiation of C in cyclohexane at 254 nm yields A and B in a ratio of 1:1.34, and irradiation of D gives the same products in a ratio of 1:1.32. Similar results are obtained upon triplet-sensitized (Michler's ketone) photolysis of C and D.[159]

The two meta photocycloadducts from *m*-xylene and cyclopentene are formed in a ratio of 1:1.0 ± 0.1 and also in this case the denitrogenations of the azo compounds prepared from these adducts afford the products in a ratio that is identical, within experimental error, to that obtained in the photoaddition.

Scheme 16. Generation of the Bicyclo[3.2.1]octenyl Biradical



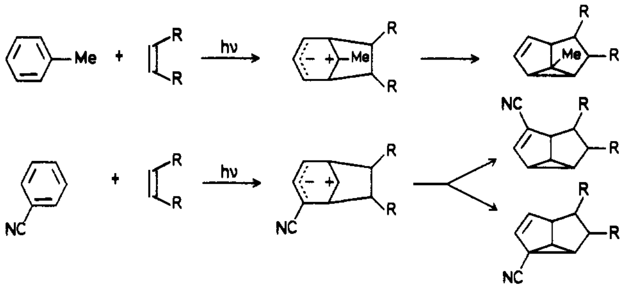
Thermal elimination of nitrogen from azo compounds C and D (Scheme 16) proceeds mainly via concerted $[\sigma^2s + \sigma^2s + \pi^2s]$ cycloreversion, the biradical is not formed and product ratios obtained from C and D differ from each other and from those in the photoaddition. Product ratios obtained by photolysis at 350 nm are somewhat different for C and D (1:1.10 and 1:1.77, respectively); it is only at 254 nm and in the triplet-sensitized reaction that the ratios match exactly.

These results provide evidence for the involvement of bicyclo[3.2.1]octenyl biradicals in meta photocycloadditions, and they thereby imply that closure of the cyclopropane ring is the final event during the process. It is not known, however, whether the biradicals, in the photochemical decomposition of the azo compounds as well as in the meta photocycloaddition, are intermediates in the true sense. So much has been speculated about various kinds of "intermediates" occurring during the meta cycloaddition that it is relevant at this point to recall the definition of "intermediate" as given by Lowry and Richardson:[161] "An *intermediate* is any chemical structure occurring during a reaction (necessarily having two or more elementary steps) that exists at a minimum of energy (i.e., for which any distortion raises the energy) and has a lifetime longer than the period of typical molecular vibrations (on the order of 10^{-13} to 10^{-14} s)". The biradical structures discussed above are very likely to play a role in the nitrogen eliminations as well as in the photocycloaddition and in view of the close similarity of product ratios both types of reaction probably involve the same species, but it may not be concluded that the meta photocycloaddition proceeds stepwise, via biradical intermediates in energy minima. The possibility should be left open that the biradical structures have a fleeting existence on a descending energy path, in the photochemical decomposition of the azo compounds as well as in the meta photocycloaddition.

5. Zwitterions

It was noted above that the biradical mechanism (Scheme 14) does not account for the difference in regioselectivity between electron-withdrawing and electron-releasing substituents. In the discussion on the prefulvene mechanism it was said that writing prefulvene as a hybrid of a biradical and two zwitterionic forms does not help much in understanding regioselectivity. The bicyclo[3.2.1]octenyl structure has also

Scheme 17. Meta Photocycloaddition via a Bicyclo[3.2.1]octenyl Zwitterion



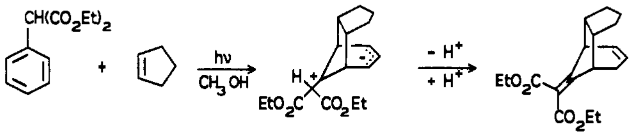
been written as such a hybrid[26,157] and in this case the zwitterionic form with the tertiary carbocation center and the allyl anion is in perfect agreement with the substituent effects as can be seen in Scheme 17.[90,97]

Interestingly, this zwitterionic form was first proposed by Bryce-Smith and Gilbert and their co-workers[26] in 1980, several years before the first meta photocycloaddition of a benzene derivative with an electron-accepting substituent was published.[100] In the latter publication, concerning the addition of benzonitrile to 1,2-dichloroethene, Gilbert and co-workers did comment on the fact that the addition takes place at the positions ortho and para to the substituent, a phenomenon that had not been observed before, but they interpreted their result in terms of the biradical, not mentioning the zwitterion proposed 3 years earlier. Jans et al.,[90] in their publication on the addition of anisole to various enol ethers, mentioned the zwitterion or the biradical as possible intermediates, while Osselton and Cornelisse,[97] describing the cycloaddition of benzonitrile and α,α,α-trifluorotoluene to cyclopentene, preferred the zwitterionic structure in rationalizing their results. At the same time, however, they admitted to have found no evidence for the existence of a discrete zwitterionic intermediate and they modified their mechanistic proposal by saying that the reaction should proceed with a certain degree of charge separation, the negative charge residing on the allylic moiety of the six-membered ring.

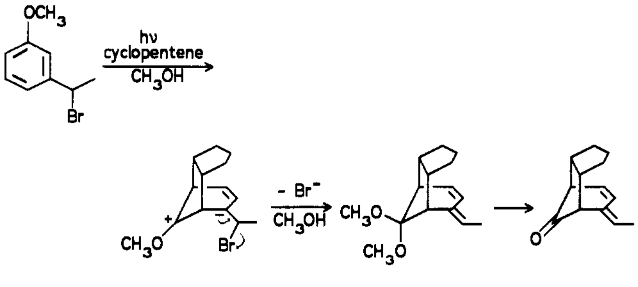
During the years 1985–1990 the zwitterion was repeatedly invoked in publications by Gilbert and his co-workers,[142,162] Mattay and his co-workers[91] and Cornelisse and his co-workers,[57,91,95,103,142] but at the same time these investigators realized that a discrete zwitterionic species with fully formed bonds between benzene and alkene may not be a realistic proposal. The species has also been represented with δ^+ and δ^- signs instead of full charges[89,113,163] and as a biradical with polar character;[62,82,115] it was also referred to as a dipolar intermediate which for convenience was represented as a zwitterion.[92,117] In other publications[63,93,96,164] the dipolar species was drawn with dotted lines between benzene and alkene, implying polarization of the benzene electron cloud before complete formation of the new σ-bonds.

Various attempts have been made to intercept the proposed zwitterionic structure.[97,113] Diethyl phenylmalonate has been irradiated in methanol in the presence of cyclopentene (Scheme 18). The zwitterion might lose its acidic proton instead of undergoing ring closure; protonation of the allylic anion moiety then would lead to a tricyclic adduct. No such adduct was isolated however.

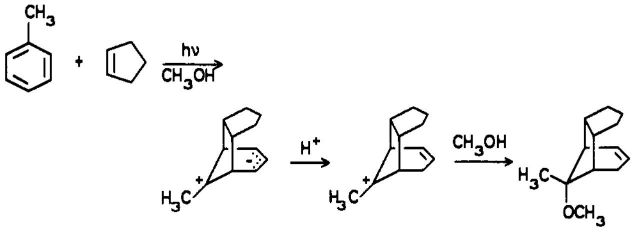
Scheme 18. Attempt To Prepare a Tricyclic Adduct from Diethyl Phenylmalonate and Cyclopentene



Scheme 19. Attempt To Prevent the Ring Closure of the Proposed Zwitterion



Scheme 20. Attempt To Trap the Zwitterionic Intermediate in Acidic Methanol



3-(1-Bromoethyl)anisole was irradiated in methanol in the presence of cyclopentene. The authors hoped that a bromide ion would be expelled from the allylic substituent (Scheme 19). A diene would result which, upon reaction with the solvent, would yield a ketal and eventually a ketone. No product containing a diene moiety was found.

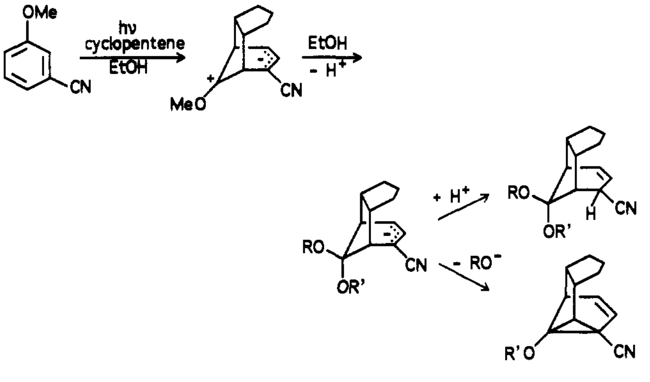
Toluene and cyclopentene were irradiated in acidified methanol in an attempt to protonate the allyl anionic part of the zwitterion. Reaction with the solvent would then lead to a tricyclic product (Scheme 20). No such product was detected.

m-Cyanoanisole was irradiated in ethanol in the presence of cyclopentene. This arene was chosen because a zwitterion formed from it would be well-stabilized and it would perhaps react with ethanol to form a mixed ketal. This ketal would either react with a proton from the solvent or lose the alcohol to undergo ring closure to a meta adduct (Scheme 21). This reaction was attempted in both acidic and basic solutions but no trace of either the ketal or the alkoxy-exchanged adduct was found.

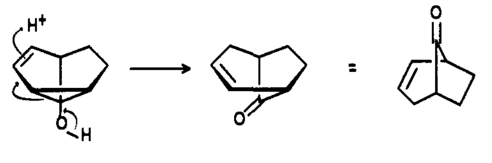
The proof of the existence of an intermediate was also attempted by irradiating *m*-cyanoanisole with cyclopentene in the presence of DCl in tetrahydrofuran. A hydrogen/deuterium exchange in the negatively charged allylic moiety would result in deuterium incorporation into the meta adduct. No trace of a tricyclic intercepted intermediate was found and the isolated meta adduct did not contain deuterium.

Thus, all attempts to trap the supposed zwitterionic intermediate were in vain. It should be realized that such species should have a very short lifetime and that they may not be easily trapped except by a very rapid intramolecular process.

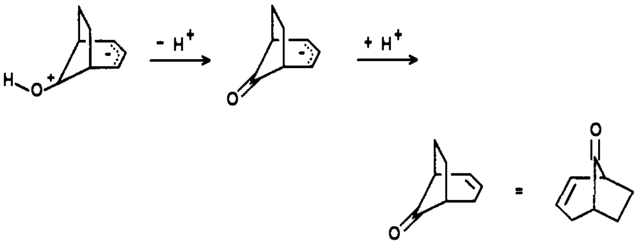
Scheme 21. Possible Trapping of a Zwitterionic Intermediate



Scheme 22. Formation of Tricyclic Ketone from 1-Hydroxy-Substituted Meta Adduct



Scheme 23. Possible Formation of Tricyclic Ketone from a Zwitterionic Intermediate



The results obtained with phenol and the cresols (Table 2, entries 24 and 25; Table 3, entries 21–23) are intriguing. The photoadditions to cyclopentene and 1,2-dichloroethene produce ketones. It is assumed[63,84,85] that meta adducts with the hydroxy group at position b1 are the primary products, but these have never been detected. The ketones are proposed to be formed by protonation at position b4, followed by opening of the cyclopropane ring, creation of a new double bond, and loss of a proton from the hydroxy group (Scheme 22).

Irradiations of arenes in the presence of 1,2-dichloroethene are reported[63,85] to produce HCl. This may be the source of the protons of which only a catalytic quantity is required. In the case of phenol and cyclopentene the former compound must be the proton source. In view of the zwitterion hypothesis the possibility has been considered[90] that the cyclopropane ring never closes in these cases, but that the zwitterionic intermediate loses a proton from the OH group, giving rise to a species with a keto group and an allylic anion moiety which would subsequently become protonated (Scheme 23).

It would be worthwhile to try to establish the mechanism of ketone formation under the irradiation conditions because this might provide a clue to the mechanism of photoaddition.

For the time being, we have to conclude that no experimental evidence has been obtained for the occurrence of zwitterionic intermediates, but that the regioselectivity observed in the photoaddition of substituted benzenes to alkenes can best be rationalized[93,164] by a certain degree of polarization of the excited benzene ring during the interaction with the alkene.

6. Exciplexes

The possibility of an exciplex as an intermediate in the meta photocycloaddition was already mentioned by Morrison and Ferree[17] in their first paper on the intramolecular reaction of 6-phenylhex-2-ene. After discussing the prefulvene mechanism, they proposed as an alternative possibility an intermediate complex of the excited phenyl group and alkene ("exciplex"); such a complex might either go on to give the product or dissociate to the ground state. The authors thanked Wilzbach and Kaplan for suggesting this possibility. Wilzbach and Kaplan, in their later communication[24] on the photoaddition of benzene to but-2-ene, referred to Morrison and Ferree[17] and remarked that the formation of such benzene–alkene exciplexes had been previously suggested, but not yet proven.

The 6-phenylhex-2-ene structure was compared by Morrison and co-workers[18] to molecules of the type $Ar(CH_2)_nAr$ which for $n = 3$ show strongly reduced phenyl monomer fluorescence and characteristic long-wavelength emission attributable to an intramolecular excimer.[165] No long-wavelength emission was observed from the 6-phenylhex-2-enes, but the arene fluorescence is quenched considerably by the alkene. From this and from the fact that quenching of the photoreaction by *cis*-piperylene and oxygen is about one-half as efficient as fluorescence quenching, the authors concluded that a short-lived, unquenchable, precursor to cycloaddition was involved and that this precursor was likely to be an exciplex.[18,166]

An exciplex was also considered to be an intermediate by Srinivasan and co-workers,[38,39,86,87] but no experimental evidence corroborating its involvement was presented. It was suggested[87] that benzene in its $^1B_{2u}$ state reversibly forms an open sandwichtype exciplex in which first the bonds between the 1 and 3 positions of benzene with the alkene are formed; the last bond to close in the formation of the cycloadduct is the bond forming the cyclopropane ring.

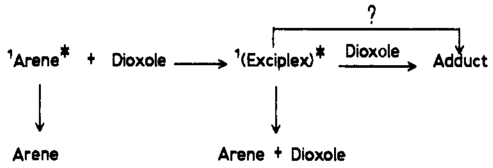
In 1977 Scharf and Mattay[58] reported the formation of ortho and meta photocycloadducts from benzene and 2,2-dimethyl-1,3-dioxole, and one year later Leismann and Mattay[167] found that this system, as well as the combinations benzene + 2-methyl-1,3-dioxole, benzene + 1,3-dioxole, benzene + 1,4-dioxene, and benzene + 1,2-bis[(trimethylsilyl)oxy]ethene, show exciplex emission in acetonitrile, but not in cyclohexane. It was concluded that these systems give rise to "weak exciplexes" because the wavelength of maximum emission (ca. 400 nm) and the magnitude of the Stern–Volmer constant for quenching of the benzene emission show little dependence on the ionization potential of the alkene. The exciplexes are supposed to have dipole–dipole rather than charge-transfer stabilization.[168] The alkenes which give emitting exciplexes with benzene quench its fluorescence at nearly diffusion-controlled rates. For 1,4-dioxene, 2,2-dimethyl-1,3-dioxole, 2-methyl-1,3-dioxole, and 1,3-dioxole the quenching rate constants are 35.0×10^8, 81.9×10^8, 82.5×10^8, and 87.3×10^8 L mol^{-1} s^{-1}, respectively.[55] For comparison, the quenching rate constants of cyclopentene, cyclohexene, and vinylene carbonate were also determined and their values were found to be much smaller: 1.2×10^8, 1.5×10^8, and 3.1×10^8 L mol^{-1} s^{-1}, respectively. Interestingly, the electron-rich alkenes with which exciplex emission was observed give considerable yields of ortho adducts next to meta adducts (1,4-dioxene gives only ortho addition), whereas for the other compounds no ortho addition has been reported.

A kinetic scheme was proposed[55] with the fluorescent exciplex as precursor of the photoadducts. Quantum yields of adduct formation, exciplex emission, and benzene fluorescence were measured as a function of alkene concentration. The kinetic data fit the proposed reaction scheme. The authors have also attempted to prove the intermediacy of the exciplex in the photoaddition by adding a quencher to the system benzene + 2,2-dimethyl-1,3-dioxole in acetonitrile. They found that triethylamine quenches the exciplex emission with a Stern–Volmer constant ($K_{SV} = 11.6 \pm 0.4$ L mol^{-1}) which is nearly identical to that for quenching of the 1,3 photoaddition ($K_{SV} = 11.7 \pm 1.5$ L mol^{-1}). The latter value, however, was not measured in acetonitrile because in that solvent the quantum yield of product formation is rather low; the value measured in dioxane was used, corrected for the difference in viscosity. Triethylamine quenches not only the fluorescence of the exciplex and the product formation, but also the fluorescence of benzene. In dioxane the value of $k_q\tau$ was 86.6 L mol^{-1} and the equality of the Stern–Volmer constants for quenching of exciplex emission and quenching of photoaddition may not be used as evidence in favor of the intermediacy of an exciplex. If exciplex and photoadduct are formed competitively instead of consecutively, Stern–Volmer constants for quenching of exciplex emission and product formation will also be equal if their common precursor (i.e. S_1 benzene) is quenched.

Leismann, Scharf and Mattay[169] have recognized this problem in their publication of 1984 in which they describe a very thorough and detailed investigation of the kinetics of formation and deactivation of exciplexes of S_1 benzene or toluene and 1,3-dioxole, 2,2-dimethyl-1,3-dioxole and 2,2,4-trimethyl-1,3-dioxole. The evolution in time of monomer and exciplex fluorescence after excitation using a nanosecond flash lamp was analyzed, and again it was concluded that the formation of exciplexes is diffusion controlled; their decay proceeds mainly (≥90%) via radiationless routes. The polar solvent acetonitrile enhances radiationless deactivation, possibly by promoting radical ion formation. Because decay of benzene fluorescence is essentially monoexponential, dissociation of the exciplex into S_1 benzene and dioxole is negligible.

In experiments with continuous irradiation Stern–Volmer constants were determined for the quenching of benzene fluorescence by the dioxoles, for the generation of exciplex fluorescence and for adduct formation. The first two values were found to be identical within experimental error and equal to the values obtained from the flash experiments. The Stern–Volmer constants calculated from adduct formation were, however, much smaller than expected on the basis of the exciplex scheme, and it was concluded that the exciplex hypothesis had to be improved. The authors did this by introducing an additional reaction step in which the exciplex meets a second molecule of dioxole. Collision leads to quenching of the exciplex with formation of either ground-state reactants or photoadduct. The role of the second olefinic partner was presumed to be catalytic. Donation of charge to the cationic site of the exciplex may weaken the solvent stabilization of exciplex and zwitterionic species and thus reduce the solvent-induced quenching of adduct formation. A mechanism involving product formation by direct collapse of the exciplex could not be excluded. Scheme 24 summarizes the mechanistic proposal.

Scheme 24. A Reaction Scheme Which Fits the Kinetic Data Obtained for the Photoreaction of Benzene and Toluene with Dioxoles[169]



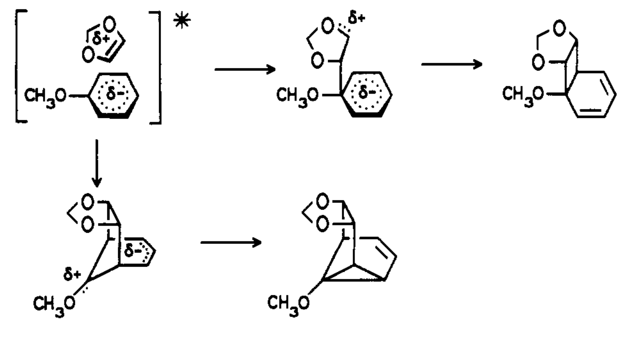
In cyclohexane no exciplex emission is observed. Leismann et al.[169] have measured the quantum yields of meta and ortho adduct formation from benzene and 2,2-dimethyl-1,3-dioxole in cyclohexane at various concentrations of the alkene in the absence and in the presence of triethylamine (TEA). In plots of $\varphi_{\mathrm{meta}}^{-1}$ versus [dioxole]$^{-1}$ the presence of TEA not only changes the slope, but also the intercept. This indicates that TEA quenches a species which is formed from S_1 benzene and dioxole and which is a precursor of the meta adduct. In the plots of $\varphi_{\mathrm{ortho}}^{-1}$ versus [dioxole]$^{-1}$ the slope is different in the presence of TEA but the intercept is the same as in its absence and the mechanism must be different from that of meta addition.

Although the authors have clearly shown that their kinetic results agree with a mechanism involving an exciplex as reaction intermediate, they have not explicitly stated that the data are incompatible with a scheme in which exciplex formation and adduct formation are competing instead of consecutive processes.

The enediol ethers are exceptional in the sense that they are the only alkenes with which exciplex formation and decay can be studied in conjunction with photoaddition. The dioxoles give two types of photoadducts with benzene: ortho and meta photocycloadducts. Mattay et al.[91,99,163] have pictured the exciplex as a common precursor to both types. The exciplex is supposed to possess a certain degree of charge transfer from the dioxole to the arene. Formation of the ortho adduct is thought to proceed stepwise as shown in Scheme 25 for anisole and 1,3-dioxole.[163] Another route leads to the meta adduct via a zwitterionic structure (or a polarized biradical). The dipolar character of the six-membered ring is supposed to be already present in the exciplex and it is at this stage that the regioselectivity is determined.

Although the relative orientations of the two addends must be different for ortho and meta addition, it is conceivable that both processes should proceed via the same exciplex. One may speculate that the exciplex does not have one favorite rigid geometry, but that it is in a double-minimum energy well on the excited state

Scheme 25. Exciplex as a Common Intermediate in the Formation of Ortho and Meta Adducts



potential-energy surface, with the minima separated by a small barrier.

In the case of anisole and 1,3-dioxole two ortho adducts are formed,[91] exo and endo, in a ratio of 7:1. Since the ortho adduct is proposed to arise via stepwise addition, formation of both stereoisomers can be accounted for if one assumes that rotation around the first-formed bond is possible. The predominance of exo-ortho over endo-ortho is ascribed to repulsion between the lone pairs on the oxygen atoms and the negative charge residing in the six-membered ring.[163] A similar explanation had been given earlier by Jans et al.[90] for the preponderance of exo-meta with respect to endo-meta in the addition of anisole to 1,3-dioxole. However, the amount of endo-meta adduct is certainly not to be neglected, exo:endo = 46:22,[91] and the question arises whether or not the exciplex mechanism can also accommodate the formation of these two stereoisomers. One would have to assume that the alkene in the exciplex is capable of moving around rather freely over the arene. This may be in agreement with the observation mentioned earlier that the complex is best described as a "weak exciplex", held together by dipole–dipole interaction or by slight electrostatic attraction, but it renders the rationalization of the regioselectivity more difficult. The alternative would be the existence of more than one exciplex (ortho and meta, exo and endo) and this might be at least partially in accordance with the results of the quenching experiments with triethylamine in cyclohexane by Leismann et al.[169] from which it was concluded that the ortho adduct may be formed directly (from the excited state of benzene) or via a short-lived intermediate other than the one involved in meta addition. The situation becomes even more complicated in the case of 2-methyl-1,3-dioxole (Table 1, entry 41) which with benzene gives two exo-ortho adducts, two exo-meta adducts and two endo-meta adducts. In each of these pairs, one isomer is formed via approach with the methyl group pointing toward the benzene ring, and the other with the methyl group away from benzene. The involvement of at least two different exciplexes seems inevitable, if exciplexes are intermediates. Exciplex emission has been observed with this system,[55,167,168] but there is no evidence concerning dual exciplexes.

Stereochemical aspects related to exciplex formation were studied by Mattay et al.[89] who irradiated anisole in the presence of *cis*- and *trans*-2,5-dihydro-2,5-dimethoxyfuran and *cis*-1,4-dimethoxycyclopent-2-ene (Table 2, entries 32, 43, and 44). No products were found with an endo configuration of both the five-membered ring and a methoxy group. The authors assume that if an exciplex is intermediate during the reaction, its formation is preceded by interaction between excited benzene and alkene, leading to polarization of the benzene electron cloud in the transition state or in an encounter complex. They conclude their discussion with the remark that although the existence of an exciplex is not conclusively proven in most cases of meta photocycloaddition, the assumption of an exciplex-like arrangement of the reactants as a necessary step is the best model to predict the stereochemistry of the adducts.

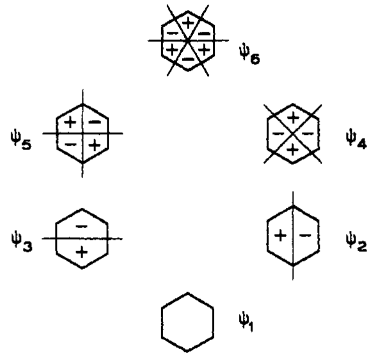
Finally, we should add that in a few cases a broad structureless emission, possibly attributable to exciplexes has been observed. This has been reported for 2,3-dimethyl-6-phenylhex-2-ene,[123] 5-(*p*-tolyl)pent-1-ene[123] and 2-(3-phenylpropyl)furan,[130] but a possible relation between exciplex and product formation was not investigated. In phenethyl vinyl ether,[13,131] like in many phenyl–ethenyl[13,122,123] and phenyl–dienyl[130] nonconjugated bichromophoric systems, the fluorescence is quenched 10-fold with respect to the analogue with a saturated side chain, but no long-wavelength emission was detected at temperatures down to −50 °C. Ethyl vinyl ether and 2,3-dihydropyran quench arene (benzene, toluene, anisole) fluorescence only weakly ($k_q\tau$ values in the range 1–15 L mol^{-1}), and no evidence for exciplex emission was found.[47,50,79] The same applies to *n*-butyl vinyl ether and 2,3-dihydrofuran which photoadd to benzene but give no detectable exciplex emission.[50] Furan quenches benzonitrile fluorescence in isooctane solution with $k_q \cong 1.1 \times 10^{10}$ L mol^{-1} s^{-1}, but again emission attributable to an exciplex was not observed.[82] On the other hand benzonitrile and 2,5-dimethylfuran do form an emissive exciplex (λ_{max} 362 nm) but in this system specificity of the photoreaction is lost and a multicomponent product mixture is formed.[82]

B. Theory

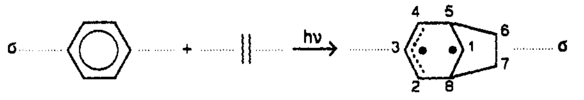
Orbital symmetry relationships for thermal and photochemical concerted cycloadditions (ortho, meta, and para) to the benzene ring were studied in 1969 by Bryce-Smith.[154] The cycloadditions of benzene to ethene and to *s-cis*- and *s-trans*-butadiene were analyzed, as well as the dimerization of benzene. The concerted meta cycloadditions of benzene to ethene and to *s-cis*-1,3-butadiene (in the 1,4 mode) were found to be allowed from $^1B_{2u}$ benzene and ground-state alkene or diene, both reactions leading to a biradical. A correlation diagram for the meta addition of benzene to ethene was derived.[20,44,170] The orbital symmetries of benzene are depicted in Scheme 26.

The wave function of the S_1 state of benzene, $^1B_{2u}$, has two components, one corresponding to excitation of an electron from ψ_3 to ψ_5 and the other to excitation from ψ_2 to ψ_4. The $^1B_{2u}$ state is represented as $\psi_3\psi_5 - \psi_2\psi_4$. During the transition from benzene + ethene to the biradical a plane of symmetry is retained, as shown in Scheme 27. The orbital correlation diagram is shown in Scheme 28. The orbitals of benzene, ethene and the biradical are classified as symmetric (S) or antisymmetric (A) with respect to the plane of symmetry and in the construction of this correlation diagram crossing of correlations between orbitals of like symmetry has been avoided. It can be seen that the combination of

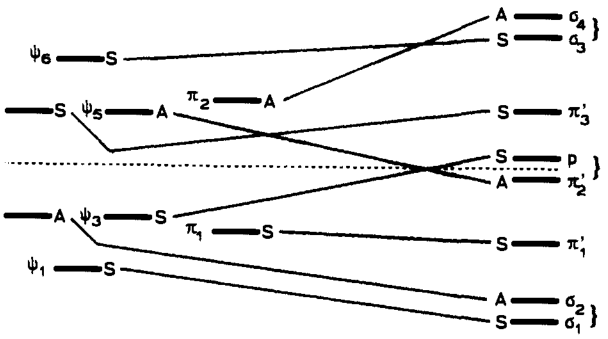
Scheme 26. Orbital Symmetries of Benzene



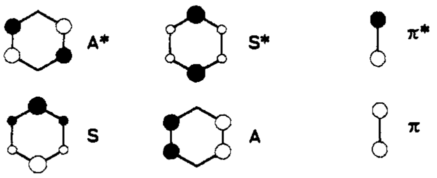
Scheme 27. A Plane of Symmetry (σ) Is Retained during the Transition from Benzene and Ethene to the Bicyclo[3.2.1]octenyl Biradical



Scheme 28. Orbital Correlation Diagram for Meta Cycloaddition of Benzene to Ethene



Scheme 29. Frontier Molecular Orbitals of Benzene and Ethene



ground-state ethene with the configuration $\psi_3\psi_5$ of benzene correlates with the ground state of the biradical.

In 1982 Houk[171] gave a qualitative rationalization of the selectivities in ortho, meta, and para cycloadditions of singlet excited benzene to alkenes, based on frontier orbital overlap considerations. The HOMO's and LUMO's of benzene were labeled S, A, S*, and A* according to their symmetries with respect to a plane perpendicular to the benzene ring and passing through the position of attachment of a substituent (the bottom carbon). These orbitals are shown, together with the π and π^* orbitals of ethene, in Scheme 29.

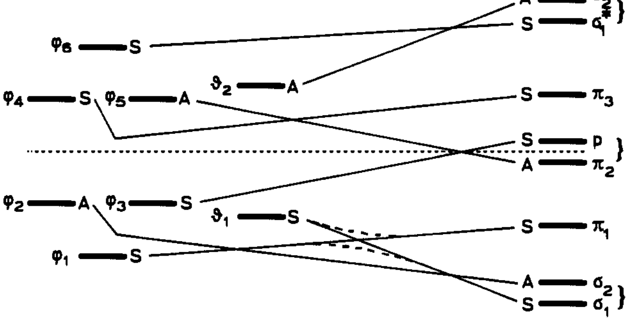
The lowest singlet state of benzene is described as SA*–AS*. In the ortho approach of benzene and ethene, stabilization may be achieved by interaction of A with π or of A* with π^*. The interactions between S and π^* and between S* and π will be less significant. In the meta approach, S interacts with π and A* with π^*. The other possibilities, S* with π and A with π^* will be much weaker. In the para approach, π does not interact with filled orbitals but only with S* and π^* interacts only with S; this reaction is photochemically forbidden. The S → A* configuration stabilizes the meta complex more than the ortho and the A → S* configuration stabilizes the ortho complex only. The ortho cycloaddition is favored by overlap factors. Houk has performed calculations with the STO-3G basis set of the ground-state orbital changes upon complexation of ethene with ground-state benzene in the various modes of cycloaddition. The changes in the frontier orbitals upon ortho approach are greater than in the meta mode, reflecting the greater orbital overlap. The A → S* in the ortho approach is highly stabilized owing to mixing of A with the lower-lying π of ethene. In the meta mode, the S → A* configuration is highly stabilized and although the overlap is less than in the ortho mode, the raising of the S orbital and the simultaneous lowering of A* causes more stabilization than for ortho. The result of these considerations is that the predicted stabilization of the ortho and meta complexes is essentially identical, in agreement with experimental results.[12]

From numerous examples in Table 2 it can be seen that a donor substituent on the benzene ring promotes meta addition at the positions 2 and 6, ortho to the substituent. The HOMO of the substituted benzene is derived from S and is increased in energy. The ortho and para coefficients are increased in magnitude at the expense of the ipso and meta coefficients. The orbital A*, which is also involved in interaction with the alkene, is essentially unchanged. The regioselectivity is caused by the increased size of the ortho coefficients relative to the meta in the S orbital.

Van der Hart, Mulder, and Cornelisse[172] treated the system consisting of ethene and benzene as a supermolecule. The ground-state energy and the optimized ground-state geometry of this supermolecule were calculated for various values of the bond distance (R) between the ethene and the benzene part in the meta addition mode using MNDO. For each optimized ground-state geometry the excitation energy from the ground state to the first excited state was calculated using CNDO/S with configuration interaction between the 60 lowest-energy one-electron excitations. The energy of the first excited state was obtained by adding the excitation energy to the MNDO calculated ground-state energy for each geometry.

The lowest excited state of benzene can be described by two open-shell configurations: $\psi_2\psi_4$ and $\psi_3\psi_5$. These open-shell configurations are indeed the main configurations in the first excited-state wave function in the CNDO/S calculations for large R. When the ethene approaches the benzene molecule one configuration, i.e. the one correlating with the open shell $\psi_3\psi_5$ configuration of excited benzene, becomes dominant. This is in perfect agreement with the MO correlation diagram of Bryce-Smith and Gilbert shown in Scheme 28. The configuration unmixing in the excited state of benzene is responsible for a considerable dipole moment in the early stage of the reaction. This charge redistribution in which positive charge is created at the carbon atom between the positions of addition and negative charge in the "allylic part" of the system, is in accordance with the regioselectivity of the meta photocycloaddition. The dipole moment disappears as the

Scheme 30. Intended Correlation Diagram for the Meta Photocycloaddition of Benzene to Ethene



reaction proceeds, the biradical itself has no polarity.

After passing a small barrier, the energy of the excited state is lowered by the approaching ethene. The crossing point between the energy surfaces for the antisymmetric and symmetric states is a true funnel. For reasons of symmetry the closure of the three-membered ring is not expected to take place as long as the system is in the excited state. Ring closure would lower the symmetry and introduce mixing with the ground state, pushing the excited state up to higher energy. Through the point of intersection, the system enters the potential surface of the ground state and slides down into a large potential well with at least three local minima. Two of these are connected to the ring closure and the third corresponds to the biradical. A large energy difference of 22.9 kcal mol^{-1} is calculated between the biradical and the final addition product, and the energy barrier which separates them is small (7.5 kcal mol^{-1}). This may be the reason why the biradical has never been intercepted. If the system proceeds directly to the product, without entering the biradical minimum, the reaction can be described as concerted but not synchronous. Further investigations into the origin of the regioselectivity of the meta photocycloaddition of benzene to alkenes and dienes were reported in 1991 by Van der Hart et al.[173] The correlation diagram given by these authors again concerns an interaction between benzene and alkene leading to a biradical with conservation of a plane of symmetry. The correlation diagram differs from the one given earlier (Scheme 28) in that the intended correlations between MO's are drawn. The correlation lines connect orbitals with maximum overlap and almost the same position of nodes (Scheme 30).

One avoided crossing (indicated by broken lines) is observed between MO's which are involved in the addition process. Both orbitals remain doubly occupied during the addition and no appreciable energy barrier is expected.

The electronic states of the separate addends can be described by zero-order wave functions. If the reactants approach each other and orbitals begin to overlap, the first-order interactions can be described with these zero-order wave functions. Van der Hart et al. define the following zero-order wave functions: $\Phi(B^*E)$ is the wave function of the locally excited complex between benzene and ethene, $\Phi(B^-E^+)$ and $\Phi(B^+E^-)$ are the wave functions of the charge-transfer configurations, and $\Phi(BE^*)$ is the wave function of the other locally excited configuration. Because the first excited state of benzene is a composite of two configurations, the wave function of (B^*E) has to be written as $\Phi(B^*E) = 2^{-1/2}\{\Phi_1 - \Phi_2\}$. The benzene orbitals are designated φ and the alkene orbitals ϑ.

The five wave functions are as follows:

$$\Phi_1 = 2^{-1/2}\{|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_4\varphi_3\bar{\varphi}_3\vartheta_1\bar{\vartheta}_1| + |\varphi_1\bar{\varphi}_1\varphi_4\bar{\varphi}_2\varphi_3\bar{\varphi}_3\vartheta_1\bar{\vartheta}_1|\}$$

$$\Phi_2 = 2^{-1/2}\{|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_5\vartheta_1\bar{\vartheta}_1| + |\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_5\bar{\varphi}_3\vartheta_1\bar{\vartheta}_1|\}$$

$$\Phi_3 = \Phi(B^-E^+) = 2^{-1/2}\{|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\vartheta_1\bar{\varphi}_5| + |\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\varphi_5\bar{\vartheta}_1|\}$$

$$\Phi_4 = \Phi(B^+E^-) = 2^{-1/2}\{|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\vartheta}_2\vartheta_1\bar{\vartheta}_1| + |\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\vartheta_2\bar{\varphi}_3\vartheta_1\bar{\vartheta}_1|\}$$

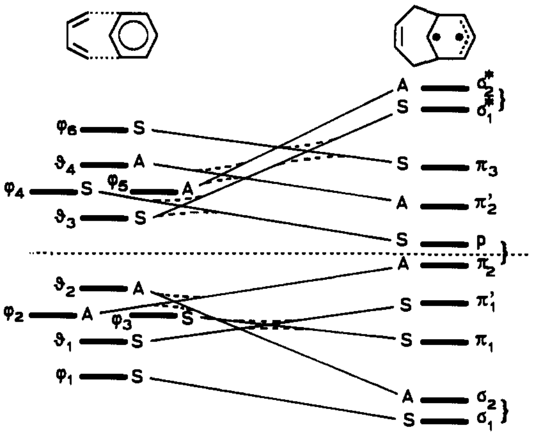
$$\Phi_5 = \Phi(BE^*) = 2^{-1/2}\{|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\vartheta_1\bar{\vartheta}_2| + |\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\vartheta_2\bar{\vartheta}_1|\}$$

Study of the interactions of these wave functions reveals that in the early stage of the addition process the wave functions of the charge-transfer configurations Φ_3 and Φ_4 mix with Φ_2, i.e. that part of the locally excited molecular state B*E which corresponds to the biradical state. This interaction lowers the energy and favors the addition process. The uniform electron density pattern in the benzene nucleus is changed by the interaction, and from the form of the orbitals φ_3 and φ_5, it can be seen that the contribution from B^-E^+ increases the electron density at atoms C-2, C-4, C-5, and C-8 (see Scheme 27 for the numbering), whereas under the influence of the charge-transfer configuration B^+E^-, the electron density is lowered more strongly at atoms C-1 and C-3 than at the other benzene carbon atoms. The configuration interaction thus leads to a partially polarized molecular complex and on this basis the regioselectivity of the meta photocycloaddition can be rationalized. Because this treatment, using the wave functions of benzene, is only valid for weak electron-donating and electron-withdrawing substituents, Van der Hart et al.[173] also studied the interactions of the MO's of the benzyl anion and the benzyl cation with those of ethene. Again the results are in agreement with the observed effects of substituents such as OCH_3, CN, and CF_3.

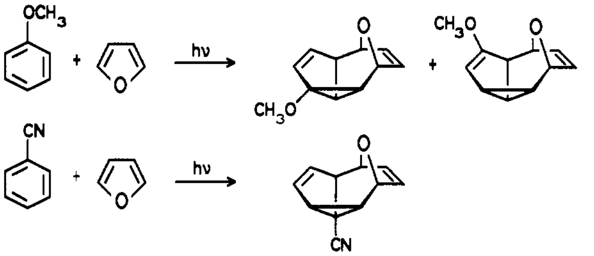
An extremely interesting result was obtained from a similar study of the interaction between benzene and 1,3-butadiene. The correlation diagram for this system is shown in Scheme 31.

Again a natural correlation method is used; the orbitals in benzene and diene are designated φ and ϑ, respectively, and π and π' are used for the orbitals in the ethylenic and allylic parts of the biradical. It can be seen from the correlation diagram that in the meta photocycloaddition of benzene to a diene it is the $\varphi_2\varphi_4$ configuration that correlates with the biradical state. In a similar way as for the alkene the zero-order wave functions of the locally excited complexes $\Phi(B^*D)$ and $\Phi(BD^*)$ (D = diene), and the charge-transfer configurations $\Phi(B^-D^+)$ and $\Phi(B^+D^-)$ were determined and their overlap considered. This analysis also shows that the electron configuration $\varphi_2\varphi_4$ of (B*D) is involved in the interaction. The important consequence is that during the interaction with the diene the electron

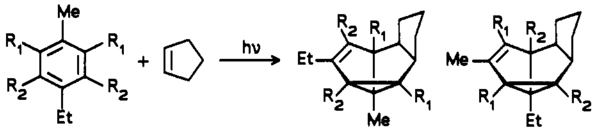
Scheme 31. Intended Correlation Diagram for the Meta Photocycloaddition of Benzene to 1,3-Butadiene



Scheme 32. Regioselectivity in the Meta Photocycloadditions of Anisole and Benzonitrile to Furan



Scheme 33. Determination of Isotope Effect by Intramolecular Competition



	ratio	k_H/k_D
$R_1 = R_2 = H$	1.74:1.00	
$R_1 = D; R_2 = H$	1.84:1.00	0.94 ± 0.01
$R_1 = H; R_2 = D$	1.61:1.00	0.93 ± 0.01

density at atoms C-1 and C-3 is increased (for numbering see Scheme 27) and that it is diminished at the atoms C-2, C-4, C-5, and C-8. This implies that the polarization of the benzene electron cloud in the interaction with the diene will be in the opposite direction as that in the case of an alkene and therefore the regioselectivity will be reversed. Gratifyingly, this is exactly what has been observed, although at the time of the discovery of the meta photocycloaddition to dienes this curious effect was not understood. Examples of the photoaddition of substituted benzenes to dienes are to be found in Tables 2 (entries 10, 21, 22, 23, 50, 73, and 74) and 3 (entries 11, 12, 47, 49, and 51). In Scheme 32 the reactions of anisole and benzonitrile with furan are shown; these results should be compared with those in Scheme 12.

Most of these reactions were performed with furan and there may be reason for some concern because furan also possesses the characteristics of an aromatic compound and its behavior might not be typical of a diene. Fortunately, 1,2-bis(methylene)cyclohexane and cyclopentadiene have also been used as addends and in their reactions with benzonitrile and *p*-xylene the same regioselectivity is observed as in the additions to furan.

C. Isotope Effects and Partial Rate Factors

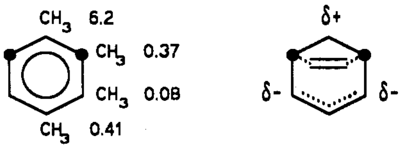
De Vaal et al.[103,164,174] have measured deuterium isotope effects on the meta photocycloaddition of several alkylbenzenes to cyclopentene. Such effects were measured in intermolecular competition experiments using mixtures of labeled and unlabeled isomers, for example toluene and 2,6-dideuteriotoluene, and in intramolecular competition experiments in which the alkene is given the choice to add at labeled or unlabeled positions in one molecule, for example 2,6- or 3,5-dideuterio-4-ethyltoluene. The results obtained from intermolecular competition experiments have revealed a novel effect, because the isotope effects were found to be concentration dependent. De Vaal et al.[174] have shown that this phenomenon is caused by formation and dissociation of arene excimers. If a deuterated and an undeuterated arene form an excimer, this species may dissociate into an excited- and a ground-state molecule. The concentration-dependent isotope effect is ascribed to a preference for dissociation into an excited unlabeled arene and a ground-state labeled arene, which boils down to excitation transfer from labeled to unlabeled compound via an exciplex (or mixed excimer). If corrections for this effect are applied, an isotope effect $k_H/k_D = 0.93$ is found for meta addition of cyclopentene to toluene compared to 2,6-dideuteriotoluene. No isotope effect was observed in the addition to 3,5-dideuteriotoluene where the D atoms are not at the positions of addition. This leads to the conclusion that the addition step is rate determining.

Complications resulting from interactions between labeled and unlabeled arenes can be avoided by performing intramolecular competition experiments in which the alkene has the choice to add to labelled or to unlabelled positions in the same molecule. An example of such an experiment is shown in Scheme 33.

The inverse isotope effect is in agreement with the change in hybridization from sp^2 to sp^3 of the carbon atoms undergoing the addition. 2-Deuterio-*p*-xylene and cyclopentene yield four different mono-deuterio-substituted adducts, which all have the methyl groups at positions b1 and b3. The isotope effect was determined by means of deuterium NMR and found to be $k_H/k_D = 0.97$. It was concluded[164] that the value of $k_H/k_D = 0.93$ for two D atoms agrees with that of 0.97 for one D atom. An isotope effect was also found by comparing CH_3-substituted molecules with CD_3-substituted analogues: $k_H/k_D = 1.06$. The effect is in agreement with hyperconjugative stabilization of the positive charge which is developed during the first stage of the addition at the carbon atom bearing the methyl group.

If there is a deuterium atom at one of the sites of addition and a hydrogen atom at the other, no isotope effect on the closure of the three-membered ring is found: the ratio of the two adducts, one with D at b5 and the other with D at b8 is unity. This is considered to be evidence for the (almost) complete formation of the bonds between alkene and arene prior to closure of the three-membered ring. If, however, there is a deuterium at one of the termini of the allylic moiety in the biradicaloid structure, a normal isotope effect $k_H/$

Scheme 34. Partial Rate Factors of the Methyl Group for Addition of Methylbenzenes to Cyclopentene



$k_D \approx 1.2$ is found. Apparently ring closure to the carbon atom bearing hydrogen is preferred, which is surprising because this carbon atom goes from sp^2 to sp^3. In this particular case the carbon atom becomes a bridgehead in a tricyclic system with a three- and two five-membered rings, and De Vaal et al.[164] argue that one has to calculate the difference in vibrational freedom of the C–H bond in the intermediate and in the product. Such calculations have not been published yet.

By comparing the quantum yields of the photoaddition of toluene, the three xylenes, the three trimethylbenzenes, the three tetramethylbenzenes, and pentamethylbenzene to cyclopentene with that of benzene, De Vaal et al.[40,175] have determined partial rate factors for the effect of a methyl group on the various modes of addition. With respect to a methyl group at a certain position on the arene, four modes are possible: ortho,ortho; meta,ipso; ortho,para; and meta,meta. From *m*-xylene and cyclopentene for instance, adducts are formed by addition ortho,ortho with respect to one of the methyl groups; this addition then takes place ortho,para with respect to the other. By comparing the quantum yield with that of toluene, the effect of a methyl group on ortho,para addition can be determined. From many combinations of methylbenzenes the authors have obtained a best-fitting set of four partial rate factors. To this end, the quantum yields had to be corrected for a statistical factor, for quenching of the arene by oxygen and by cyclopentene, for excimer formation of the arene and for the lifetime of the excited state. The four partial rate factors are given in Scheme 34. For addition at the carbon atoms indicated by black dots, the effects of a methyl group at each of four different positions are indicated. It can be seen that the values are in agreement with a mechanism in which the alkene has, in some type of complex, interaction with two meta positions of the excited benzene ring, thereby inducing positive charge at one carbon atom and negative charge in an allylic part. The methyl group has its largest activating effect when it is at the positive position (ortho,ortho addition) and its largest deactivating effect when it is at a position bearing negative charge (ortho,para addition).

D. Regioselectivity, Stereoselectivity

Much about the regioselectivity induced by substituents on the benzene ring in the intermolecular addition to alkenes has been said in previous sections. Donor substituents prefer position b1 in the adduct and acceptors positions b2 and b4 (see Scheme 12). This is in agreement with the charge distribution in the intermediate complex shown in Scheme 34. In the reaction with dienes the selectivity is reversed (see Scheme 32). Arenes with an ethenyl or ethynyl substituent have not been reported to undergo addition to alkenes, but there are three examples of addition to furan. In the adducts, the substituents $CH{=}CH_2$, $C{\equiv}CH$, and $C{\equiv}CMe$ (Table 2, entries 21–23) appear at the same position as CN (Table 2, entry 74), and they apparently behave as electron-withdrawing groups through their inductive effect. The halogens are interesting because they are inductively withdrawing and mesomerically donating. Fluorobenzene in its reaction with cyclopentene and with *trans*-1,2-dichloroethene (Table 2, entries 58 and 60) gives adducts with F at b1 and at b3.

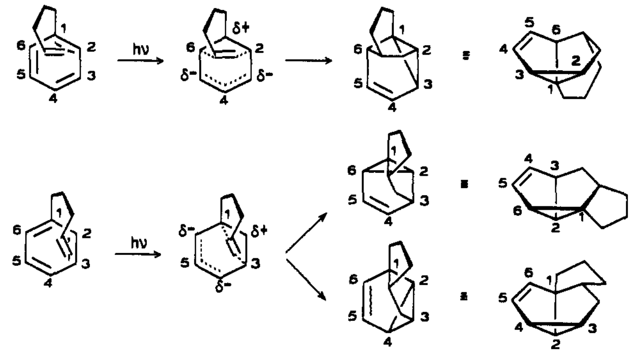
Fluorine is able to stabilize a positive charge at the adjacent carbon atom through resonance, and it stabilizes inductively a negative charge at the carbon next to the one to which it is attached (compare the effect of a CF_3 group). The latter effect causes fluorine to appear at the center position of the allylic moiety in the polarized intermediate and from thence at b3 in the adduct. Only one photoaddition with chlorobenzene has been reported (Table 2, entry 61), and chlorine evidently behaves as an electron-donating group.

Much has also been learned from studies of the photoadditions of the higher-substituted benzenes, but now that the regioselectivities can be rationalized, the results shown in Table 3 seem unexceptional and require only brief comment as far as the effects of the benzene substituents on the mode of attack are concerned. Mesitylene (entry 16) forms an interesting case because the adduct in which one of the methyl groups is at its preferred position (b1) has the other two at unfavored sites (see Scheme 34). This causes the quantum yield to be low and formation of a second adduct arising from a polarized intermediate with all methyl groups at relatively neutral positions is competitive. The case of the phenols (entries 21–23), from which the primary adducts cannot be isolated, has been treated in the section on zwitterions. Methoxy has a stronger directing effect than alkyl and the OCH_3 group invariably ends up at position b1 in adducts derived from alkyl-substituted anisoles (entries 24–34). The cyano group competes with methoxy and from *p*-cyanoanisole (entry 38) a considerable amount of the adduct with CN at b2 or b4 is formed, in addition to adduct with OCH_3 at b1. The directing effect of methoxy is stronger than that of CF_3 (entries 40 and 41) and stronger than that of fluorine (entries 42–45). Cyano overwhelms the influence of methyl (entries 46–51). If CF_3 and CN are in competition (entry 54), cyano wins (46% of the adduct mixture) but CF_3 is not completely overruled (9%). Many adducts are formed from fluoro-substituted α,α,α-trifluorotoluenes (entries 58–60), and F and CF_3 compete for their favorite places. In the fluorotoluenes (entries 61–63), the fluorine atom has the stronger directing effect.

Regioselectivity is also observed in the intramolecular photocycloaddition. Before discussing this, we want to reiterate that there are principally two modes of addition available to 5-phenylpent-1-ene and its derivatives: 2,6 addition and 1,3 addition. (2,4 addition has been observed in only a few cases: Table 4, entries 6, 18, 25, and 94.) These two possibilities are depicted in Scheme 35.

The numbers of the carbon atoms of the benzene ring have been retained in the adducts, making it easier to follow their course. In principle, two modes of closure of the three-membered ring are possible in the 2,6

Scheme 35. The Two Principal Modes of Intramolecular Meta Photocycloaddition



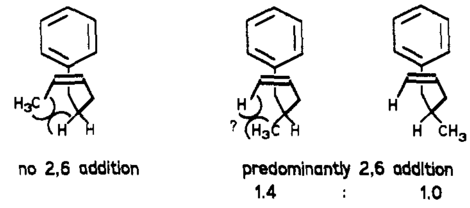
addition and in the 1,3 addition. In practice, only closure of the 1,3 bond takes place in the 2,6 addition. The adduct formed by closure of the 1,5 bond is severely strained and that may be the reason why it is very rarely observed. There are only two reports of its occurrence (Table 4, entries 12 and 18), and one of the assignments is tentative.

The constraint imposed by the tether connecting the arene and the alkene limits the possibilities for substituents on the arene ring to exert their directing influence. Furthermore, the presence of substituents on the side chain also affects the regiochemical course of the reaction.

The parent molecule, 5-phenylpent-1-ene, undergoes 2,6 as well as 1,3 addition in a ratio (quantum yields) of 72:28 (Table 4, entry 1). Investigations by Neijenesch et al.[124,132] on many ring-substituted derivatives of 6-phenylhex-2-ene have provided firm evidence in favor of a mechanism involving a polarized structure analogous to that proposed for the intermolecular reaction. Such polarized structures have been drawn in Scheme 35 and it can be seen that the alkyl chain stabilizes the positive charge in the 2,6 mode, whereas no stabilization is present in the 1,3 mode. However, a methyl group in the cis configuration on the terminal atom of the double bond drastically changes the regioselectivity: only 1,3 addition is observed from *cis*-6-phenylhex-2-ene (Table 4, entry 3 and Scheme 9). The complete absence of 2,6 addition in this molecule has been ascribed[128,141] to steric hindrance between the *cis*-methyl group and one of the hydrogen atoms at the β-carbon of the side chain; this steric effect must be stronger than the electronic effect. The trans isomer undergoes mainly (91%) 2,6 addition (Table 4, entry 2).

Methyl groups at other positions of the side chain also affect the ratio 2,6:1,3. Gilbert and co-workers[123] have investigated derivatives of 5-phenylpent-1-ene with methyl groups at the α-, β-, and γ-position (for numbering see Scheme 3). The α- and γ-isomers (Table 4, entries 12 and 18) undergo 2,6- as well as 1,3-addition. From the β-isomer (Table 4, entry 17), however, only 2,6-adducts have been obtained. One would be inclined to think that if the failure of *cis*-6-phenylhex-2-ene to undergo 2,6-addition is due to steric hindrance between *cis*-CH_3 and β-H, similar hindrance between *cis*-H and β-CH_3 would prevent 2,6-addition of β-methyl-5-phenylpent-1-ene. Of course the hindrance could be avoided in a conformation with the methyl group directed away from the olefinic hydrogen but the diastereomer arising from this conformation happens to be the minor product (ratio 1.4:1.0). An illustration of this curious phenomenon is given in Scheme 36.

Scheme 36. Contrasting Behavior of *cis*-6-Phenylhex-2-ene and 4-Methyl-5-phenylpent-1-ene



The polarized structure (Scheme 35) proposed to be operative in the 2,6-addition has inspired Neijenesch et al.[132] to try to stimulate the *cis*-methyl isomer to undergo this mode of addition, by placing substituents at appropriate positions. This was tried with a cyano group at position 3 (δ^-) as well as with a fluorine atom at C-4 or C-6 (next to δ^-), but it was to no avail. The 2-fluoro compound (Table 4, entry 49) underwent only 1,3 addition, the 3-cyano compound (Table 4, entry 61) did not give meta photoadducts at all, and the 4-fluoro analogue (Table 4, entry 70) gave a high yield of the 2,6 adduct, but only after the starting material had isomerized to trans! When this escape route was blocked by using the dimethyl derivative (Table 4, entry 71) the compound underwent only ortho addition.

A notable exception to the rule that a cis substituent on the alkene prevents 2,6 addition is seen in Table 4, entry 19. Here, the alkene is part of a five-membered ring which also includes the γ-carbon atom of the side chain. Apparently, this molecule can adopt a conformation, suitable for 2,6 addition, which is not attainable for open-chain cis-substituted compounds. Moreover, the cis substituent is CH_2 rather than CH_3 as in the other cases. The ratio 2,6:1,3 is reported[78,123] to be 9:1.

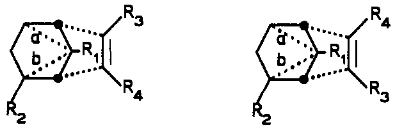
It is nevertheless possible to direct the intramolecular meta photocycloaddition by employing substituent effects in cases where steric factors are less important. Just a few examples will be given; many others can be seen in Table 4. If the symmetry of the arene moiety is further reduced by placing a substituent at position 2 or 3 (see Scheme 35), 1,3 and 1,5 addition are no longer equivalent. Compounds with a methoxy group at C-2 (Table 4, entries 43–47) undergo solely 1,3 addition, but 2-trifluoromethyl-substituted *trans*-6-phenylhex-2-ene (Table 4, entry 52) gives two products resulting from 1,5 addition, a small amount of 2,6 adduct, and no 1,3 adducts. This is in perfect agreement with the proposed polarization of the excited benzene ring. Likewise, the 3-fluoro-substituted 6-phenylhex-2-enes (Table 4, entries 58 and 59) yield only products resulting from 1,5 attack. Thus, whereas the unsubstituted *trans*-6-phenylhex-2-ene gives more than 90% 2,6 addition, the presence of a methoxy group at position 2 or a fluorine atom at position 3 completely suppresses this mode and only 1,3 (or 1,5) addition takes place. The regioselectivity rules derived for the intermolecular meta photocycloaddition thus apply equally well to the intramolecular process, albeit that in some cases they are overruled by steric effects.

Wender and his co-workers[128,133–141,147,176,177] have used the meta photocycloaddition as a key step in the synthesis of natural products. They have mostly been interested in the adducts formed by 1,3 attack and they have clearly chosen their starting materials in such a way that the substituents controlled the regio- and stereochemistry of the addition and appeared at the desired positions in the photoadducts. The starting materials in entries 33, 34, 38, 46, 47, and 88 of Table 4 all have a cis substituent at the terminal position of the alkene, and this excludes 2,6 addition, as has been pointed out above. Entry 38 has two ortho methyl groups, which renders 1,3 and 1,5 addition degenerate. This is not the case with the other five, and with these compounds the addition consistently takes place in the 1,3 mode, across the donor substituent on the arene ring (alkyl or methoxy). In entry 88 there are two different alkyl substituents; the addition mode actually observed is indicated in the table; the alternative is probably prohibited by steric factors. Entry 35 does not have a directing cis-olefinic substituent and there are no electronic factors opposing 2,6 addition, but steric effects may play a role in this instance. The two methyl groups at the β-carbon atom of the side chain as well as the two methyl groups at positions 2 and 6 are probably responsible. Although 1,3 addition is statistically favored, the yield is rather low. Wender et al.[135] invoke steric factors in rationalizing this, but 1,3 addition across one of the *o*-methyl groups causes the other one to appear at a negatively charged position in the polarized complex, and this may be an additional or alternative reason for the inefficiency. The same effect may play a role in the behavior of entries 39–41. These molecules, which also lack a cis-olefinic group, undergo 1,3 addition across a methyl group on the arene. This substituent stabilizes the polarized complex at the positive site. Addition in the 1,5 mode would place the methyl group at one of the negative positions and consequently this approach is discouraged.

Surprising results were obtained by Gilbert and Taylor[13,122,131] with compounds in which the tether between arene and alkene contains an oxygen atom, in the α, β, or γ position (Table 4, entries 25–27). 4-Phenoxybut-1-ene is photochemically quite unstable and it is reported to undergo a very inefficient 2,4 photocycloaddition, whereas one would have expected quite efficient 2,6 addition, by analogy with the intermolecular case of anisole with alkenes. Benzyl allyl ether behaves normally and it undergoes 2,6 as well as 1,3 addition. The 2,6:1,3 ratio (25:75), however, differs from that in the full-carbon analogue (Table 4, entry 1; 2,6:1,3 = 72:28). As can be seen from the quantum yields, this effect results mainly from a diminished efficiency of 2,6 addition, possibly caused by a decrease in electron-donor ability of the α-CH_2 group due to the neighboring oxygen atom. Phenethyl vinyl ether behaves enigmatically. There is no 2,6 addition, and 1,3 addition is very inefficient (only one of the two possible isomers is observed). The major product stems from para addition at positions 2 and 5. The intriguing effects of oxygen atoms in the side chain on the mode of addition remain to be clarified.

We now have to discuss other factors that are responsible for the formation of different regioisomers from a pair of addends. In the section on isotope effects and partial rate factors the four possible modes of attack (ortho,ortho; meta,ipso; ortho,para; and meta,meta) of an alkene on a monosubstituted benzene were mentioned. With an ortho or meta disubstituted benzene having unequal substituents there are six different modes of attack. We have discussed the directing effects of electron-donating and electron-withdrawing substituents on the various modes. Now, one has to realize that in principle each of these modes has two possibilities of closure of the three-membered ring and if the alkene has different substituents at either side of the double bond, it may approach the arene in two different ways. Thus, four different adducts can be formed from each of the six positional modes. For one of these modes, in a meta-disubstituted benzene derivative, this is illustrated in Scheme 37. Thus, 24 different regioisomers can be formed from one pair of addends, which is another illustration of the enormous complexity of the process. If one also considers stereochemistry, the actual number of isomers is 48, since each of the regioisomers has an endo and an exo diastereomer.

Scheme 37. There Are Six Different Pairs of Carbon Atoms to Which the Alkene Can Become Attached; One of the Six Pairs Is Indicated[a]



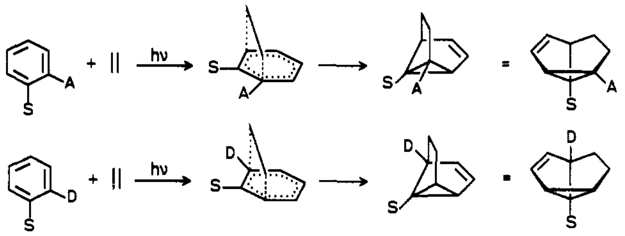
[a] From each of them four different regioisomeric adducts can be formed by two different directions of ring closure (a and b) and two orientations of the alkene.

We will first comment on the regioselectivity (or lack of it) related to the closure of the three-membered ring and the approach of the alkene. Subsequently, we will treat the subject of endo/exo stereochemistry, although it will not always be possible to rigorously separate the two aspects.

The effect of a benzene substituent on the cyclopropane ring closure might become apparent from those examples in which a monosubstituted benzene adds to a symmetrical alkene in an asymmetrical positional mode (i.e. ortho,para or ipso,meta) or in which a disubstituted benzene approaches a symmetrical alkene symmetrically with respect to one and asymmetrically with respect to the other substituent. The only examples in Table 2 from which conclusions might be drawn are entries 62, 63, 64, 68, and 71. (We will not consider the reactions with dienes because there are not sufficient examples.) These are all compounds with CN or CF_3. In Table 3 the pertinent examples are entries 36, 37, and 40. The only adducts which are formed in sufficient quantities to make comparisons meaningful are those with cyano or trifluoromethyl at positions b2 or b4. Inspection of the product ratios reveals that no significant specificity exists. In all cases both possibilities of cyclopropane ring closure are realized and there is no preference for closure to or away from the substituent. If the species would still have considerable dipolar character at the stage of ring closure, one would expect such preference to be induced by strong electron-withdrawing groups. Its absence is in agreement with calculations[172] from which it was concluded that the dipole moment disappears as the reaction proceeds.

Following this line of reasoning, it is of interest to consider substituents at the positions of addition. Such groups might play a role at the start of the addition process and they may affect the cyclopropane ring closure in an indirect fashion. Although the bonds between arene and alkene are supposed to be formed concertedly, bond formation need not be synchronous. The possibility has been discussed[96] that formation of one bond may precede that of the other, and this may generate a certain skewness in the intermediate species, causing preferential cyclopropane formation at one side, i.e. the side at which arene–alkene bond formation is further developed. We must search, therefore, for examples in which there are substituents at positions b5 or b8. In the addition of alkylbenzenes to cyclopentene the major products have the substituent at position b1. Although the percentages of other adducts are small, it may be significant that from toluene (Table 2, entry 5), ethylbenzene (Table 2, entry 11), isopropylbenzene (Table 2, entry 12), *tert*-butylbenzene (Table 2, entry 17), and diphenylmethane (Table 2, entry 20) adducts with the alkyl group at b5 have been found but those substituted at b8 are missing. The same happens to be true for α,α,α-trifluorotoluene (Table 2, entry 62), while benzonitrile (Table 2, entry 68) has b5:b8 = 2:1. It might appear therefore that the substituent, regardless of its nature, prefers position b5. The picture becomes different if one studies the pertinent examples from Table 3. These data may be more reliable because we no longer focus attention to minor products. In these disubstituted benzenes one substituent determines the principal mode(s) of attack and the other (the one we are interested in) has to follow suit. In the adducts from *o*-xylene (Table 3, entries 2 and 3) and from *o*-methylanisole (entry 24) the methyl group has a distinct preference for position b5. Of the two possible adducts from 2,5-dimethylanisole (entry 32) only the one with a methyl at b5 is found. The major product from *o*-fluorotoluene and cyclopentene (entry 61) has F at b1 and CH_3 at b5 and 78% of the products from *m*-fluorotoluene and cyclopentene have F at b3 and CH_3 at b5. On the other hand, only products with cyano at b8 are formed from *o*-cyanoanisole and cyclopentene while in the multitude of adducts from *o*- and *m*-fluoro-α,α,α-trifluorotoluene with cyclopentene (Table 3, entries 58 and 59) those with CF_3 at b8 are much more abundant than those with CF_3 at b5. One may conclude cautiously that donors prefer b5 and acceptors b8 and thus that cyclopropane ring closure occurs preferentially at the side of the acceptor. Osselton et al.[96] argue that if there is a certain degree of charge transfer between the addends, it will be from the cycloalkene to the excited benzene and an acceptor substituent at the site of addition will promote bond formation at the carbon to which it is attached. The substituted carbon will attain sp^3 character earlier than the other one and it will draw its neighbors closer together, thus causing the ring closure on its own side. The opposite will be true for donors at an arene carbon at which addition occurs. A pictorial illustration of the effect is given in Scheme 38.

Scheme 38. Effect of Donor and Acceptor Substituents on the Mode of Cyclopropane Ring Closure

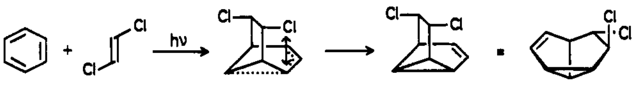


We now turn to the regiochemical effects induced by substituents on the alkene. From benzene and a monosubstituted alkene only two regioisomers can be formed. Inspection of Table 1 reveals that an alkyl substituent on the alkene has a preference for position 7 in the adduct (entries 2, 5, 7, and 8), and the same can be said of an alkoxy group (entries 33 and 34) and an acetate group (entry 36). A similar phenomenon is observed with the monosubstituted benzenes (Table 2, entries 7, 14, 19, and 40) and the disubstituted benzenes (Table 3, entries 9, 15, 17, 25, 30, and 44). There are a few cases in which there seems to be little preference (Table 1, entry 35; Table 2, entries 8 and 59; Table 3, entry 34) and a few others in which the 7-substituted adduct is not the major product but is still present in reasonable amounts (Table 2, entry 39; Table 3, entries 27, 42, and 45). On the whole, it would be safe to say that alkyl, alkoxy, and acetate have a certain preference for position 7, implying that these alkene substituents enhance cyclopropane closure at their side of the molecule. At this point it becomes necessary to include stereochemical aspects into the discussion because closer scrutiny of the tables reveals that the substituents at position 7 are predominantly in the endo configuration. In fact, exo substituents at this position are rarely observed, a phenomenon that seems to be especially pronounced in the case of the acetate group, as was noticed by Gilbert and bin Samsudin.[51]

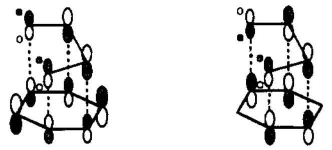
A very strong relationship between endo approach of an alkene substituent and cyclopropane ring formation was also found by Gilbert et al. In 1972, Bryce-Smith, Foulger, and Gilbert[61] discovered that benzene undergoes photoaddition to *trans*-1,2-dichloroethene (TDCE) but they detected only rearrangement products of the supposed meta adducts. Gilbert and co-workers[100] later reported the successful isolation and identification of adducts from benzonitrile and methyl benzoate with TDCE (Table 2, entries 67 and 72), and this was followed by their discovery[85] that the photoreaction of TDCE with benzonitrile, the three tolunitriles, α,α,α-trifluorotoluene, fluorobenzene, and chlorobenzene, gives substituted 6-*exo*-7-*endo*-dichlorotricyclo[3.3.0.0^{2,8}]oct-3-enes (Table 2, entries 60, 61, 66, and 72; Table 3, entries 46, 48, and 50). Only products are found in which the chlorine atom at position 7 is endo, and the results have been interpreted[62,63] in terms of an asymmetric distortion of the six-membered ring by steric and repulsive electronic interactions; the latter arise from the n electrons of the chlorine and the electrons of the allylic system whether this is anionic in character or neutral as in a biradical. Such distortion results in a conformation more favorable for cyclization at the side of the chlorine atom rather than at the opposite side (Scheme 39).

The preference of alkyl, alkoxy, and acetate groups to appear at the 7-endo position in the adduct may be related to the phenomenon observed with TDCE, although with these substituents the preference is less pronounced. It is perhaps significant that the major adduct from benzene and *trans*-but-2-ene has the same 6-exo-7-endo configuration as the sole product from

Scheme 39. Chlorine-Induced Asymmetric Distortion Leading to Specificity of Cyclopropane Ring Closure[62]



Scheme 40. Primary and Secondary Orbital Interactions in the Endo Addition of Benzene to a *cis*-Alkene



benzene and TDCE. Of course, with TDCE and *trans*-but-2-ene one alkene substituent has to be endo, but with the mono-substituted alkenes a problem still exists: if the substituent approaches in the endo direction, one can understand its directing effect on cyclopropane ring closure, but why would the substituent prefer endo attack at all, considering the supposed steric and repulsive interactions?

We have treated some characteristic regiochemical aspects of the meta photocycloaddition (in some cases related to stereochemical factors), and we have discussed several interpretations that have been proposed. Study of the addition products from the 202 inter- and the 102 intramolecular combinations of arenes and alkenes in the four tables certainly raises still other questions and reveals more intricacies but it is impossible in this context to treat them all.

Instead, we now turn to some stereochemical aspects of the reaction, in particular the question of endo versus exo stereochemistry. Wilzbach and Kaplan,[14] in their report on the discovery of the reaction, found that the major adduct of benzene and *cis*-but-2-ene has the endo configuration. This was confirmed by Morikawa et al.[23] and also by Srinivasan,[25] who identified the minor isomer as the exo adduct. From anisole (Table 2, entry 26) and tetralin (Table 3, entry 18) only the endo adducts have been found with *cis*-but-2-ene. The cyclic alkenes cyclobutene, *cis*-cyclooctene, and especially cyclopentene have been used very often in the meta photocycloaddition and they also display a strong preference for endo addition, as can be seen from numerous examples in Tables 1–3.

Srinivasan and co-workers[38] have postulated a sandwich structure for the complex of excited benzene and cyclobutene and they have suggested that endo orientation is preferred as a result of maximum overlap between the bonds of the two rings, without specifying which bonds were thought to be involved.

In his theoretical analysis Houk[171] concluded that secondary orbital interactions stabilize the endo complex and destabilize the exo complex. The orbital interactions playing a dominant role in the meta photocycloaddition are S-π and A*-π^* (see Scheme 29). In Scheme 40 the primary and secondary interactions leading to endo meta addition are indicated.

Photoreaction of *tert*-butylbenzene with *cis*-cyclooctene gives two meta adducts (Table 2, entry 18). The 2,6 endo adduct is the minor adduct, probably as a consequence of steric hindrance between the bulky *tert*-butyl group and the alkene. The 2,6 exo adduct is not observed; approach leading to this product would be even less favorable. Instead, the addends react in the 3,5 mode and the major product is formed by 3,5 endo addition, in spite of the fact that exo 3,5 approach would completely avoid steric interference between the alkene and the *tert*-butyl group. Bryce-Smith et al.[73] conclude that there must be additional bonding interaction between the alkene and S_1 *tert*-butylbenzene which occurs only in the endo orientation. They regard this secondary bonding intermolecular interaction between a CH_2 group and the aromatic ring as a weak type of hydrogen bonding between sp^3 and sp^2 carbon atoms, or more realistically as a form of "intermolecular hyperconjugation" involving a minor degree of electron donation from a group orbital of p-type symmetry on CH_2 into the lowest partly filled orbitals of the benzene ring.

There are some exceptions to the rule that cyclopentene prefers to give adducts with the endo configuration. More exo than endo is found with *m*-cyano-α,α,α-trifluorotoluene (Table 3, entry 52), *m*-bis(trifluoromethyl)benzene (Table 3, entry 56), *o*-fluorotoluene (Table 3, entry 61), and *p*-difluorobenzene (Table 3, entry 65). Relatively large percentages of exo (>30%) are found with α,α,α-trifluorotoluene (Table 2, entry 62), benzonitrile (Table 2, entry 68), *p*-cyano-α,α,α-trifluorotoluene (Table 3, entry 54), *m*-fluorotoluene (Table 3, entry 62), *m*-difluorobenzene (Table 3, entry 64), and 1,3,5-trifluorobenzene (Table 3, entry 66). Curiously, all these arenes bear electron-withdrawing substituents: CN, CF_3, and F. Fluorobenzene (Table 2, entry 58) shows a very intriguing, as yet unexplained effect. There are two adducts with F at position b1 and two with F at b3. The endo/exo ratio of the b1-substituted adducts is 2:32 and that of the b3-substituted adducts is 55:11. *o*- and *m*-Fluorotoluene (Table 3, entries 61 and 62) behave similarly: mainly exo when F is at b1, mainly endo when F is at b3. In the adducts from *p*-difluorobenzene, one F is at b1 and the other at b3; the endo/exo ratio is 20:80. Finally, 1,3,5-trifluorobenzene gives three adducts, one of which has F at b1 and it possesses the exo configuration. The origin of this curious effect of the fluorine atom and of the deviations from the "endo rule" with the electron-poor arenes remains to be elucidated.

The most notable exceptions to the preference for endo adduct formation, however, are found in the reactions of the 1,3-dioxoles (Table 1, entries 40–42; Table 2, entries 46–48, 56, 63, and 70). These cyclic enediol ethers are noted for their ability to give fluorescent exciplexes with benzene and for the fact that their meta photocycloaddition occurs mainly in the exo configuration. They also give relatively large amounts of other products, mainly ortho adducts. The dioxoles have been extensively investigated by Mattay et al.[54–58,91,92,98,99,102] and by Cornelisse et al.[57,90,91] With benzene, the endo/exo ratio is 18:82, with anisole 32:68 and from α,α,α-trifluorotoluene and benzonitrile only exo adducts have been found with 1,3-dioxole. It is perhaps significant that, although in all instances exo predominates over endo, the effect is strongest with electron-poor arenes and weakest with the electron-rich anisole. This is the same behavior as observed with cyclopentene.

A rationalization of the preference for exo adduct formation with the dioxoles was proposed by Jans et al.[90] and by Mattay et al.[56] These authors ascribed the reluctance of dioxoles to undergo endo addition to repulsion between the lone electron pairs on the oxygen atoms and the allylic part of the zwitterionic intermediate. However, next to this interaction which diminishes endo addition, there must be a factor which increases the efficiency of exo addition since the quantum yield of the latter process in the benzene/1,3-dioxole system is much higher (0.31 with 1 M 1,3-dioxole in benzene) than that of exo addition to cyclopentene (0.02); it is even higher than that of endo addition to cyclopentene (0.17 with 1.1 M benzene and 3.5 M alkene in isooctane). 2,3-Dihydrofuran, which has one oxygen atom and one CH_2 next to the double bond, has an endo/exo ratio of 50:50 with anisole (Table 2, entry 41) (addition does also take place with benzene but no quantitative data have been published) and with cyclopentene/anisole the ratio is 87:13. From 2,5-dihydrofuran and anisole the endo and exo adducts are formed in the ratio 94:6 (Table 2, entry 42).

Vinylene carbonate (Table 1, entry 46; Table 2, entries 49, 57, 64, and 71; Table 3, entry 10) has two oxygen atoms next to the double bond, and yet principally endo addition is observed. This alkene is less electron rich than 1,3-dioxole, and Mattay et al.[99] have suggested that there is less electron transfer from vinylene carbonate to excited benzene than from 1,3-dioxole. Consequently, there will be less electron repulsion between the oxygen lone pairs and the negatively charged moiety of the benzene ring in the excited complex. Alternatively, one might argue that the carbonyl group in vinylene carbonate reduces the electron density on oxygen, perhaps making it even slightly positive, and this would also result in preference for endo addition. The effect of benzene substituents on the endo/exo ratio is opposite to that found with 1,3-dioxole and with cyclopentene: with electron-withdrawing groups (CN, CF_3) 100% endo addition is found,[93,98,99] with donating substituents (OCH_3, $OSiMe_3$) there is 60–65% endo addition[92,93] and benzene[60] is intermediate with an endo/exo ratio of 83:17.

Finally, some further investigations concerning steric effects on the meta photocycloaddition should be mentioned. Gilbert and Heath[80] observed that in additions of isopropylbenzene and *tert*-butylbenzene to *cis*-cyclooctene considerable amounts of adducts with the substituent at position b3 are formed, next to b1-substituted adducts. These adducts arise by attack of the alkene at positions 3 and 5 of the arene, relative to the site of the substituent. With *tert*-butylbenzene the b3-substituted adduct is the major product and it was also established that it has the endo configuration (Table 2, entry 18). Bryce-Smith et al.[178] concluded from an examination of the effects of temperature and solvent polarity on the isomer ratios that the b1- and the b3-substituted isomers are derived from the same intermediate or from closely similar intermediates. As mentioned above, Bryce-Smith et al.[73] have based their concept of "intermolecular hyperconjugation" largely on the observation that 3,5 attack by *cis*-cyclooctene on *tert*-butylbenzene occurs endo rather than exo, in spite of larger steric hindrance.

De Vaal et al.[40] have measured quantum yields relative to benzene of the addition of various alkyl- and alkoxybenzenes to cyclopentene. The relative ratios of endo 2,6 and 3,5 attack (normalized to benzene = 1.00) to toluene, ethylbenzene, isopropylbenzene, and *tert*-butylbenzene were found to be 1.38:0.08; 0.78:0.08; 0.19:0.08; 0.06:0.08. From these figures they concluded that the efficiency of the 3,5 mode of attack does not increase, but that the 2,6 attack decreases in efficiency upon increase of the size of the substituent, thus making the larger groups appear to direct toward the other sterically less demanding mode of attack. The fact that the formation of the b3-substituted adduct is not deactivated sterically was explained by assuming that the addition is also possible from a situation in which the double bond of the alkene and the arene undergo interaction while the rest of the alkene ring is tilted away from the arene.

Similar results were obtained recently by Bryce-Smith, Gilbert, et al.[78] who determined the efficiency of meta photocycloaddition of toluene, isopropylbenzene, and *tert*-butylbenzene to *cis*-cyclooctene, again relative to benzene. The 2,6:3,5 ratios found are 1.30:0.03; 0.4:0.2; 0.18:0.26. (The datum for 3,5 addition to toluene should be regarded as qualitative.) Thus, the same trend is observed as that in the additions to cyclopentene.

Cyclohexene behaves anomalously in comparison with other cycloalkenes in its addition to arenes. The quantum yield of addition to benzene is about one-eighth of that of cyclopentene. This behavior has been studied by Bryce-Smith, Gilbert, et al.,[78] and the reluctance of cyclohexene to undergo the meta addition has been found to be caused by steric hindrance. The half-chair conformation of cyclohexene inevitably results in one of the β-methylene groups inhibiting the proximity required for bonding of the addends. Exo approach does not suffer from this effect and the quantum yields of exo addition of cyclohexene (0.01) and cyclopentene (0.025) to benzene are of the same order. The authors[78] have constructed molecules in which the arene and the cycloalkene are connected by a chain of CH_2 groups. In the molecules shown in entries 7 and 8 of Table 4 the alkene can add only in an endo orientation. Addition of the cyclopentene derivative is relatively efficient, whereas the addition of the cyclohexenyl compound occurs with a very low quantum yield and is evidently sterically inhibited. The molecules of entries 19 and 20 of Table 4 must have exo orientation in the addition, and both of them react quite efficiently and with similar quantum yields.

E. Ortho vs Meta Photocycloaddition

It was said in the introduction that this review is primarily concerned with the meta photocycloaddition of arenes to alkenes. In this section we will not dwell on the mechanism of the ortho addition, but only consider factors that are of importance in determining which type of reaction prevails for a given pair of addends.

It was observed by Bryce-Smith[44] that the so-called 1,4 "ene addition" and perhaps also the ortho cycloaddition are derived from an intermediate or intermediates having a degree of polar character, but that meta cycloaddition does not involve polarity factors to any significant extent.

In 1974 Bryce-Smith et al.[30] formulated a rule that has become famous for its predictive value: $\varphi_{\text{ortho}} > \varphi_{\text{meta}}$ when 9.6 eV < IP (alkene) < 8.65 eV. Ortho photoaddition is generally the preferred process with relatively powerful donor and acceptor alkenes while for alkenes of ionization potentials similar to that of benzene (9.24 eV) meta addition is preferred.[31]

Bryce-Smith et al.[26,157] have discussed some deviations from the rule and remarked that the range 8.65–9.6 eV may prove a little too restricted to cover all addends. Gilbert et al.[50] have discussed the possibility that it may be more meaningful to relate the relative efficiencies of the two processes (ortho and meta addition) with ionization potentials only within a series of structurally very similar ethenes. It has however been possible to predict successfully for many systems the preferred mode of ethene–benzene photocycloaddition.[27]

Houk[171] arrived at the same conclusion by deriving the Bryce-Smith/Gilbert generalization in a slightly different way, on the basis of a study of orbital interactions. He also finds that the ortho adduct is favored when the alkene is either a better donor or a better acceptor than benzene.

Mattay[59,163,179] has also derived a rule which makes it possible to predict the mode of reaction between an arene and an alkene if the donor and acceptor properties of the reactants are known. Not only the ortho and meta photocycloadditions are considered, but also electron-transfer reactions leading to substitution on the arene or on its side chain (e.g. CF_3) (or rather addition of the CF_3 group to the alkene) and additions to the CN group of benzonitrile. Mattay's rule is based on the Weller theory of electron transfer. He considers the free enthalpies of electron transfer according to the Rehm–Weller equation:

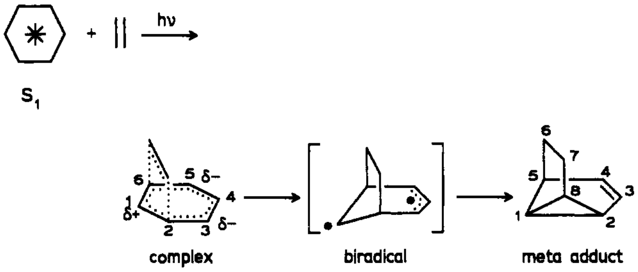
$$\Delta G = F[E_{1/2}^{\text{ox}}(\text{D}) - E_{1/2}^{\text{red}}(\text{A})] - \Delta E_{\text{excit}} + \frac{e^2 N}{4\pi\epsilon_0 a}\left[\frac{1}{\epsilon} - \frac{2}{37.5}\right]$$

in which $E_{1/2}^{\text{ox}}(\text{D})$ = oxidation potential of the donor; $E_{1/2}^{\text{red}}(\text{A})$ = reduction potential of the acceptor; ΔE_{excit} = excitation energy; F = 96 490 C; $e = 1.602 \times 10^{-19}$ C; $\epsilon_0 = 8.854 \times 10^{-12}$ Fm^{-1}; ϵ = dielectric constant of the solvent; ϵ of acetonitrile is 37.5; $N = 6.023 \times 10^{23}$ mol^{-1}; a = encounter distance, 7 Å; the energies are in eV.

For a given arene–alkene pair ΔG has to be calculated twice, in one calculation supposing that the arene is the donor, in the other that it is the acceptor. Then it can be decided what the direction of charge transfer will be.

Alkenes having poor electron-donor or poor electron-acceptor abilities preferentially yield meta cycloadducts in photoreactions with benzene; this is the case if $\Delta G > 1.4$–1.6 eV. All other alkenes undergo ortho cycloaddition. In photoreactions of alkenes with substituted benzenes similar correlations with the ΔG values exist. For example, in reactions of alkenes with benzonitrile the rule correctly predicts that electron transfer prevails if $\Delta G < 0$, addition of the alkene to the nitrile group occurs if $0 < \Delta G < 0.5$, ortho addition in the region $0.5 < \Delta G < \sim 1.7$ and meta addition if $\Delta G > \sim 1.7$ eV. The boundaries of the ΔG areas are not very sharp and in overlapping regions two types of reaction with one alkene are observed.

Scheme 41. Simplified Mechanism of the Meta Photocycloaddition of an Arene to an Alkene (The adduct has IUPAC numbering.)



F. Summary of Mechanistic Conclusions

When a benzene derivative and an alkene are brought together and irradiated, an addition may take place. If the reduction and oxidation potentials of the reactants are such that ΔG, calculated via the method developed by Mattay,[163,179] is larger than ~1.5 eV, the reaction is likely to be a meta photocycloaddition reaction. The olefinic carbon atoms become bonded to two carbon atoms of the benzene ring which are meta with respect to each other (carbons 2 and 6). At a later stage during the reaction a bond, creating a cyclopropane ring, is formed between arene carbon atom 1 and one of the carbon atoms 3 and 5; a double bond is formed between carbons 4 and 5 (or 3 and 4) and a derivative of tricyclo[3.3.0.0^{2,8}]oct-3-ene is created.

The reaction may be performed with a mixture of the neat addends, or with a solution of the arene and the alkene in an inert solvent. The concentrations have to be such that the arene absorbs (most of) the light, because the reaction starts from the first excited singlet state of the arene.

An interaction then takes place between HOMO's and LUMO's of the arene and HOMO (π) and LUMO (π^*) of the alkene. The formation of the two bonds between arene and alkene is concerted and alkene stereochemistry is always preserved. If a plane of symmetry is defined perpendicular to the arene ring and perpendicular to the central bond of the alkene, through carbon atoms 1 and 4, the arene orbitals may be labeled S (symmetric) and A (antisymmetric) with respect to that plane. The principal interaction leading to meta addition is S-π and A*-π^*. This interaction, during which one of the two configurations describing the first excited state of benzene becomes dominant over the other, leads to a polarization of the electron cloud of the benzene ring, causing the carbon between the positions of addition, carbon atom 1, to become slightly positively charged and carbon atoms 3 and 5, the termini of an allylic moiety, to acquire negative charge (Scheme 41).

This polarization causes the reaction to be regioselective with substituted arenes: donor substituents (e.g. alkyl, alkoxy) prefer position 1, whereas acceptor substituents (e.g. CN, CF_3) appear principally at positions 3 and 5 in the polarized complex (2 and 4 in the final adduct). Meta photocycloaddition may also occur between an *s-cis*-diene (at its positions 1 and 4) and an arene. In that case the principal orbital interaction leading to product is not with SA*, but with S*A with the result that the charges in the polarized complex are reversed. Consequently, the regioselectivity is also reversed.

There may be an energy barrier between S_1 benzene and the complex, but there are no known temperature effects on quantum yields or rate constants. Deuterium isotope effects are in agreement with bonding between arene and alkene being the primary event and they also support the supposed polarization. The molecular arrangement in which the two addends interact may conveniently be called a complex; it is on the excited-state surface, but it is not known whether it exists in an energy minimum (exciplex) or is on a descending energy pathway on the hypersurface. Emitting exciplexes have been observed with 1,3-dioxoles and benzene, but there is no rigorous proof that these exciplexes are intermediates on the reaction pathway leading to meta adducts.

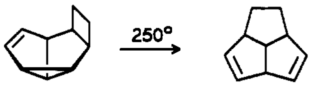
Cis-disubstituted alkenes (especially *cis*-cycloalkenes) preferentially yield adducts with the endo configuration as a result of secondary orbital interaction. The dioxoles, however, add predominantly exo, presumably owing to repulsion in the endo approach between lone pairs on the oxygen atoms and the negatively charged allylic moiety of the arene part of the complex. With monosubstituted alkenes, a preference for formation of the 7-endo isomer is often observed.

Cyclopropane ring closure occurs during the second stage of the reaction. The system passes through a funnel and reaches the ground-state surface. The polarization disappears, and a biradicaloid structure is supposed to be involved. It is unknown whether a biradical in an energy minimum is a true intermediate. If biradicals with the structure indicated in Scheme 41 are independently generated, they do yield meta adducts. No radicals, or any other intermediates, have ever been detected or intercepted while the photoaddition was in progress.

If position 3 (in the complex, Scheme 41) is substituted while position 5 is not, hardly any preference is observed for either of the two possible ways of ring closure, which seems to indicate that the biradicaloid structure is not polarized to an appreciable extent. Some preference has been found when one of the positions 2 or 6 is substituted. An acceptor substituent promotes cyclopropane ring formation on its side, possible owing to nonsynchronous formation of the arene–alkene bonds and an ensuing skewness of the complex; a donor substituent induces preferential ring formation on the opposite side.

Intramolecular meta photocycloaddition is observed when arene and alkene are connected by a chain of three atoms. In rare cases the process occurs when the connecting chain contains four atoms. The principal modes of addition are 2,6 and 1,3 with respect to the point of attachment (carbon 1) of the tether. When the arene contains an ortho or a meta substituent, there are two possibilities for 2,6 addition; 1,3 and 1,5 addition now lead to differently substituted adducts. Due to steric effects, only one mode of closure of the cyclopropane ring is realized in the 2,6 addition (at the open-ended side of the alkene), but 1,3 (and 1,5) addition gives two different adducts, one with three five-membered rings linearly fused, the other with an angular triquinane skeleton. A cis substituent on the alkene prohibits 2,6 addition. Substituents on the arene moiety have directing effects similar to those in the intermolecular addition. The mechanism of the intramolecular process is supposed to be similar to that of the intermolecular addition, but there are not many kinetic and spectroscopic data to support this.

Scheme 42. (2′-Vinylcyclopropyl)cyclobutane Rearrangement of the Endo Benzene–Cyclobutene Adduct



When a reaction displays distinct regio- and stereoselectivity and when the existence of discrete intermediates along the reaction pathway has not been rigorously proven, it is often mechanistically characterized as "concerted, but nonsynchronous" and for the time being this is also the best description of the mechanism of the meta photocycloaddition of arenes to alkenes.

VI. Thermal and Photochemical Reactions of Meta Adducts; Synthetic Applications

The meta photocycloaddition of benzene to an alkene leads to a new alkene. When the reaction proceeds and the concentration of the adduct increases, the possibility of addition of excited benzene to the primary adduct also increases; the formation of 2:1 benzene–cyclooctene adducts was mentioned already in 1966 by Bryce-Smith, Gilbert, and Orger.[15] It can be regarded as the second step in a phototelomerization of benzene and photopolymerization of benzene via successive meta photocycloaddition has indeed been reported by Bryce-Smith and Gilbert.[180]

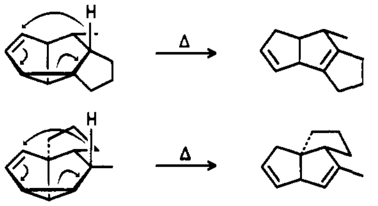
The major photoadduct of benzene to cyclobutene, the endo-meta adduct, has been shown by Srinivasan[32] to undergo a (2′-vinylcyclopropyl)cyclobutane rearrangement (a [1,5] sigmatropic rearrangement) upon pyrolysis in the vapor phase (~100 Torr) at about 250 °C (Scheme 42).

Meta adducts possessing similar structures, obtained from *o*- and *m*-xylene with cyclobutene[74] (Table 3, entries 1 and 4), from benzene and 3,4-dimethylcyclobutene[34] (Table 1, entry 17) and from benzene and bicyclo[3.2.0]hepta-2,6-diene[34] (Table 1, entry 20) undergo the same type of rearrangement. The reaction proceeds with retention of the stereochemistry of the migrating σ-bond.

A second product which is reported[32] to be formed upon pyrolysis of the endo benzene–cyclobutene adduct is the exo isomer. It is supposed to arise via homolysis of the bridge (a6-a7, for numbering see Scheme 6), followed by inversion and ring closure. Heating of the minor adduct (endo) from benzene and norbornene (Table 1, entry 24) to 280 °C for 20 min transformed it quantitatively into the major adduct (exo). The latter was found to be stable under these conditions.[42] The endo-meta adduct of benzene and cyclopentene (Table 1, entry 21) is likewise converted (80% yield) into the exo adduct.[39]

Morrison and co-workers[18] found support for their structural assignment of the 1,3 meta adducts formed from *cis*-6-phenylhex-2-ene in the observation that both adducts upon heating at temperatures above 330 °C undergo a sigmatropic [1,5] H-shift (Scheme 43).

Scheme 43. Sigmatropic [1,5] H-Shift of Intramolecular 1,3 Meta Photoadducts

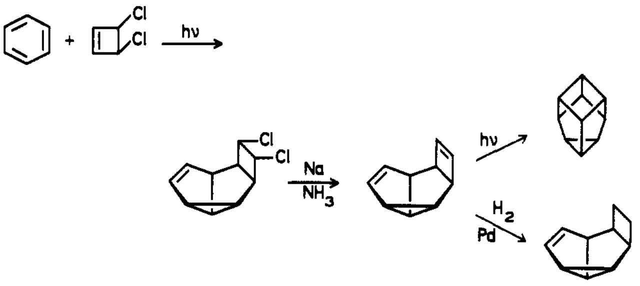


This rearrangement had been reported ealier[181] for the parent compound, tricyclo[3.3.0.0^{2,8}]oct-3-ene. The reaction obviously requires an endo H-atom at carbon atom a7 (numbering, see Scheme 6), and it has been used to distinguish between molecules possessing this structural feature and those that do not. The stereochemistry of the meta photoadducts from benzene and the but-2-enes was reinvestigated and established by Srinivasan[25] using this criterion. The same method was used to differentiate between the two isomers formed from benzene and methylenecyclobutane[28] (Table 1, entry 12). Studies by Bryce-Smith et al.[26] and by Gilbert et al.[79] have also proven it to be a very useful chemical means of structure elucidation, next to physical methods such as NMR. The 2,6 adducts formed via the intramolecular meta photocycloaddition seem to be especially prone to undergo the [1,5] H-shift, as inspection of the column "remarks" of Table 4 reveals. These molecules often undergo the reaction upon separation on the GLC column,[123] on analytical GLC as well as on preparative GLC with the result that only the rearranged 2,6 adducts are isolated. It is not clear whether the relative ease with which the 2,6 adducts undergo this type of rearrangement is due to instability, caused by internal ring strain, or to geometrical factors such as the distance between the hydrogen atom at a7 and carbon atom b4.

The [1,5] H-shift has been used to advantage by Wender et al.[134] in their synthesis of (±)-isocomene (Table 4, entry 34). Adduct **34b** undergoes the [1,5] H-shift upon thermolysis at 235–240 °C in toluene solution. The product, dehydroisocomene, was converted further into isocomene. Adduct **34a** does not possess an endo hydrogen atom at a7 and cannot undergo the rearrangement. However, the adduct is not useless, because upon heating it is transformed into adduct **34b** via the vinylcyclopropane–cyclopentene rearrangement mentioned earlier (Scheme 10). Wender et al.[134] therefore thermolyzed a mixture of the two adducts and obtained dehydroisocomene in 50–60% yield. They also demonstrated that the two adducts can be interconverted photochemically. This provides additional evidence for their stereochemical structure: they must have been formed via one mode of approach of alkene and arene, followed by the two possible ways of closure of the cyclopropane ring.

The possibility of interconversion of two meta adducts formed by different ways of cyclopropane ring closure, via a thermal vinylcyclopropane–cyclopentene rearrangement was noted already in 1971 by Srinivasan[74] in his study of the photoaddition of toluene and the xylenes to cyclobutene and subsequently in his report[25] on the stereochemistry of the meta photoadducts from benzene and the but-2-enes. Although this rearrangement is a well-known and well-studied reaction, its mechanism in the case of these types of molecules has not been investigated. The photochemical and the thermal interconversions of the adducts may well follow different paths and it is conceivable that one of them proceeds via biradicals. These biradicals will then result from scission of the bond b1–b2, and they may be identical to those generated by Reedich and Sheridan[159] (see the section on the proposed bicyclo[3.2.1]octenyl biradicals).

Scheme 44. Synthetic Use of the Meta Photoaddition of Benzene to *cis*-3,4-Dichlorocyclobutene



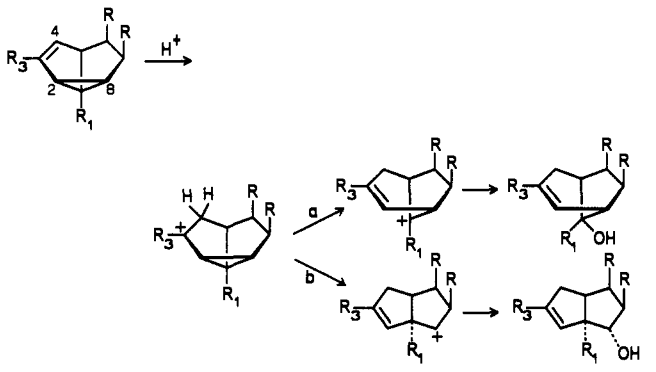
Photochemical interconversion and sometimes photoequilibration of 1,3 meta photoadducts was observed by Wender and his co-workers on various occasions[104,134,137-139] and used by them to establish the relationship of the adducts as vinylcyclopropane isomers.

The first comment on the preparative interest of the meta photocycloaddition was made by Bryce-Smith, Gilbert, and Orger[15] in their communication on the discovery of the reaction. They could prepare 30 g of the adduct of benzene and *cis*-cyclooctene by irradiation for 100 h with a 100-W medium-pressure mercury arc lamp. A further illustration was given by Bryce-Smith, Frost, and Gilbert[182] in their description of a versatile constant transmission photochemical reactor with a built-in wall scrubber. With this instrument they could produce the adduct at a rate of 2 g/h with one 500-W medium-pressure Hanovia lamp and maintain this rate of formation for more than 24 h. However, as recently as 1989, Fenton and Gilbert[162] remarked that with the notable exception of the elegant studies of Wender and co-workers principally with intramolecular systems, the general synthetic usefulness of the meta photocycloaddition remains essentially unexploited.

In recent reviews by Wender and his co-workers[128,177] the synthetic applications of the photocycloaddition or arenes to alkenes (not only meta) have been expertly and extensively described and it would be unwise to try to repeat what they have written and too early to update it. We will therefore restrain ourselves in this respect and comment only briefly on some aspects of the synthetic use of the reaction, principally those concerning transformation of the adducts.

Allred et al.[35,36] have prepared tetracyclo[5.3.0.0^{2,10}.0^{3,6}]deca-4,8-diene by meta photocycloaddition of benzene to *cis*-3,4-dichlorocyclobutene (Table 1, entry 18), followed by dechlorination with excess sodium in ammonia (Scheme 44). The stereochemistry of the chlorine atoms in the primary product was established later by Srinivasan and co-workers.[37] The tetracyclic diene could be photochemically converted into a new $(CH)_{10}$ isomer, hexacyclo[4.4.0.0^{2,4}.0^{3,9}.0^{5,8}.0^{7,10}]decane[35] and by reduction into tetracyclo[5.3.0.0^{2,10}.0^{3,6}]dec-8-ene.[36]

Scheme 45. Acidolysis of Meta Photocycloadducts[162,a]



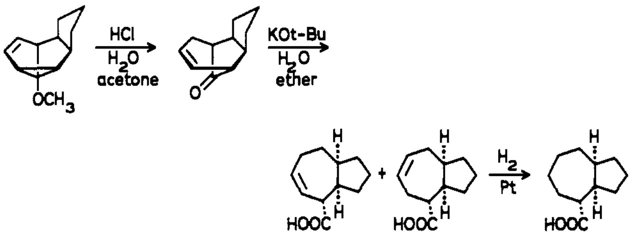
[a] (a) R_1 = alkyl, R_3 = H or alkyl; (b) R_1 = H, R_3 = H or alkyl.

The first photochemical synthesis of propellanes via meta photocycloaddition was described by Srinivasan and co-workers[105] (Table 3, entries 19 and 20) who added tetralin to cyclobutene and to cyclopentene and obtained molecules with the [4.3.3]propellane skeleton. Wender and Dreyer[104] used indan and vinyl acetate (Table 3, entry 17) and obtained a mixture of adducts of which the one with a [3.3.3]propellane structure was the most abundant.

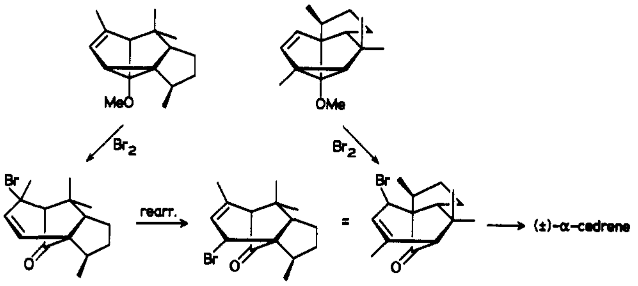
One of the attractive aspects of the meta photocycloaddition is the creation of molecules containing fused five-membered rings. In the intermolecular addition of an arene to a linear alkene, two five-membered rings are formed, while intermolecular reaction of a benzene derivative to cyclopentene as well as intramolecular addition of a derivative of 5-phenylpent-1-ene in the 1,3 mode leads to products with three five-membered rings. The primary adducts, however, also contain a three-membered ring and for most synthetic applications this ring has to be cleaved. This is usually accomplished by creating electron-deficiency at carbon atom 3 (Scheme 45), next to the cyclopropane ring, via attack (electrophilic or radical) at the double-bond position 4. Which of the two possibilities for ring opening then occurs (breaking of 1–2 or of 2–8), depends largely on the substituents present in the molecule. Opening of the bond 1–2 leads to a molecule with the bicyclo[3.2.1]octane skeleton, whereas the breaking of 2–8 creates a bicyclo[3.3.0]octane derivative. Fenton and Gilbert[162] have investigated the acidolysis of products resulting from the addition of various arenes to *cis*-cyclooctene. They have found that a substituent at position 1 results in specific breaking of bond 1–2, to produce a tertiary carbocation and thence the 8-hydroxybicyclo[3.2.1]oct-2-ene, whereas 2–8 cleavage and formation of the bicyclo[3.3.0]oct-2-ene skeleton requires a substituent at position 3 in the photoadduct (Scheme 45).

The 2,8 cleavage is selective to 75–90% but for examples in which both 3- and 1-substituents are present the latter controls the reaction and breaking of the 1,2 bond is the sole process. Acidolysis of the unsubstituted adduct from benzene and *cis*-cyclooctene ($R_1 = R_3 = H$; R–R = $-(CH_2)_6-$) gives a 1:1 mixture of alcohols resulting from both 1,2 and 2,8 opening of the cyclopropane ring. In contrast, the reaction of the corresponding benzene–cyclopentene adduct yields only the bicyclo[3.2.1]oct-2-ene skeleton.[84]

Scheme 46. Synthesis of a Perhydroazulene Derivative from the Anisole–Cyclopentene Adduct



Scheme 47. Opening of the Cyclopropane Ring by Bromine in a Synthesis of (±)-α-Cedrene[141]

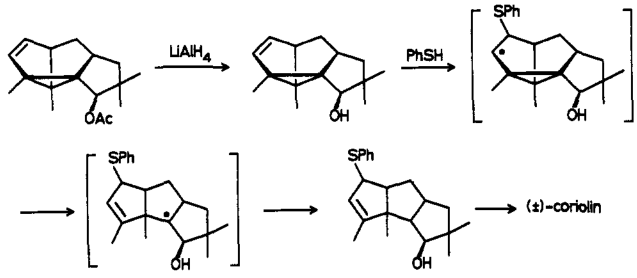


Srinivasan et al.[84] have used anisole as a reactant in the meta photocycloaddition. With cyclopentene one major product (Table 2, entry 29), the *endo*-1-methoxy-substituted adduct, was formed in 85% isolated yield. Refluxing this adduct with HCl in aqueous acetone gave a major product in 80% yield which could be identified as a derivative of bicyclo[3.2.1]oct-2-en-8-one. Obviously in this case the b1–b2 bond has broken, creating a methoxy-stabilized carbocation at b1. Reaction with water and subsequent hydrolysis then leads to the ketone. The synthetic utility of the reaction was demonstrated by converting the tricyclic ketone into a mixture of carboxylic acids which was then catalytically reduced to a perhydroazulene derivative (Scheme 46).

The scope of the meta photoaddition of anisole was widened considerably by Ors and Srinivasan[87] who showed that this molecule adds to a variety of alkenes (Table 2, entries 26, 29–31, and 33–37), producing adducts that can be converted into ketones analogous to the one shown in Scheme 46.

Intramolecular adducts with a methoxy group at position b1 were synthesized by Wender et al.[140,141] (Table 4, entries 47 and 46). In the reaction used for the synthesis of (±)-α-cedrene[141] the two 1,3 adducts (Table 4, entries 47a and 47b) were treated as a mixture with 4 M HCl/acetone (1:4) and two ketones, cedren-11-one and its Δ^9 isomer were obtained. The authors[141] discovered a more effective method for carrying out the conversion of both cycloadducts into a single product, cedren-11-one, by treating the mixture of photoadducts with bromine (1 equiv in CH_2Cl_2). The initial reaction is electrophilic attack of bromine at the double bond of the adducts at position b4 and this is followed by cleavage of the cyclopropane ring (b1–b2) and formation of the bromo ketone. The tertiary allylic bromide formed by attack of Br_2 at position b4 of adduct **47a** rearranges to the more stable secondary allylic bromide which is formed directly from **47b** (Scheme 47). Debromination with tri-*n*-butyltin hydride and Wolff–Kishner reduction of the carbonyl group provided (±)-α-cedrene. The same type of cleavage of the cyclopropane ring could be effected with mercuric

Scheme 48. Opening of the Cyclopropane Ring by the Thiophenoxy Radical in a Synthesis of (±)-Coriolin[136]



acetate.[140] Adducts **46a** and **46b** were treated with this reagent and essentially one hydroxy ketone was obtained which was further elaborated into the antileukemic agent (±)-rudmollin.

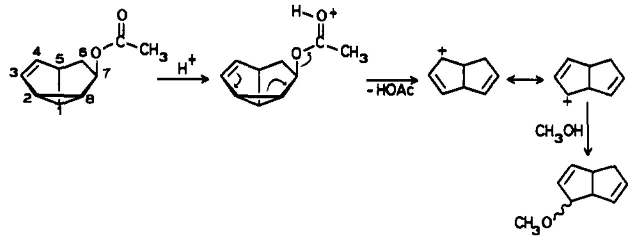
Wender et al. have also used radical-based methods for cleavage of the cyclopropane ring. In the examples to be mentioned the bond b2–b8 (for numbering, see Scheme 6) was cleaved, creating molecules with fused five-membered rings. Adduct **35a** (Table 4) was deacetylated with LiAlH$_4$ and the alcohol was heated with 1.0 equiv of thiophenol.[136] The thiophenoxy radical adds to carbon b4, creating a cyclopropylcarbinyl radical at b3. This species undergoes cleavage of the cyclopropane bond (b2–b8) more favorably aligned with this radical and a hydrogen atom is abstracted by the ensuing radical at b8 (Scheme 48). The thiophenoxy group was removed by reductive desulfurization and further transformation eventually led to (±)-coriolin.

In the syntheses of (±)-silphiperfol-6-ene, (±)-7*αH*-silphiperfol-5-ene and (±)-7*βH*-silphiperfol-5-ene[137] the radical derived from acetaldehyde was added to adduct **39b** (Table 4) at position b4 by irradiating a solution of the adduct in acetaldehyde. This method not only led to cleavage of the bond b2–b8 and migration of the double bond from b4–b3 to b3–b2, but also to the introduction of a desired carbon functionality at b4. Similar methods were used in the synthesis of (−)-retigeranic acid[138] (addition of the photogenerated formamide radical to adduct **40b** by irradiating this adduct in *t*-BuOH in the presence of acetone and formamide) and that of (±)-subergorgic acid[139] (addition of the free radical obtained from acetonitrile to adduct **41b** by refluxing an acetonitrile solution of benzoyl peroxide and the adduct). In both cases the b2–b8 bond was cleaved, possibly as a result of favorable orbital alignment.

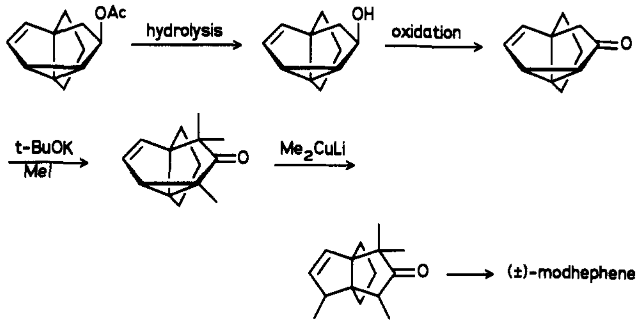
The photochemical meta addition of benzene to vinyl acetate was first described by Gilbert et al.[19] and the same authors later reported[51] that toluene, anisole, fluorobenzene, and *p*-xylene also yield meta adducts with this alkene. The major products are those having a 7-endo acetate group. In weakly acidic methanol the major benzene adduct (Table 1, entry 36) is transformed into 2-methoxybicyclo[3.3.0]octa-3,7-diene.[27] (Scheme 49).

Fenton and Gilbert[162] have investigated the effect of substituents (Me and OMe) at positions 1 and 3 of the adduct on the methanolysis. With R$_1$ = Me and R$_3$ = H the products are again formed by rupture of the bond 2-8, but now a mixture of 1-methyl-4-methoxybicyclo[3.3.0]octa-2,7-diene and 1-methyl-2-methoxybicyclo[3.3.0]octa-3,7-diene (ratio 3:1) is formed. When R$_1$ = OMe and R$_3$ = H, the reaction starts with protonation of the acetate group (not with protonation of the double bond) but now cleavage of the 1-8 bond accompanies elimination of acetic acid. The carbocation at C-1 reacts with methanol and a ketal is formed which slowly forms the ketone, bicyclo[3.2.1]octa-2,6-dien-8-one, under the reaction conditions. The third possibility for cyclopropane bond cleavage is of course breaking of the bond 1–2, and this does in fact take place when R$_3$ = Me (and R$_1$ is either Me or MeO). Now the protonation does take place at C-4 and the 1–2 bond opens, forming a carbocation at C-1 which reacts with MeOH. The product is a methyl ether (R$_1$ = Me) or a ketal (R$_1$ = OMe) and the acetate group stays in the molecule.

Scheme 49. Methanolysis of the Major Adduct from Benzene and Vinyl Acetate[27]



Scheme 50. Opening of the Cyclopropane Ring by Reaction of a Ketone with Me$_2$CuLi in a Synthesis of (±)-Modhephene[104]

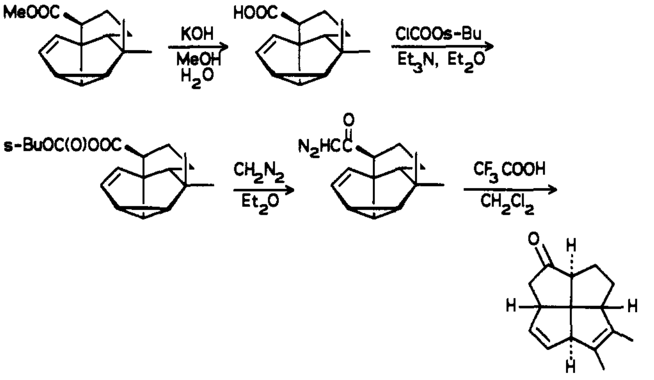


The benzene–vinyl acetate photoaddition has been used as the starting point in a synthesis of (±)-isoiridomyrmecin.[52] The major adduct (Table 1, entry 36a) was converted into the alcohol (LiAlH$_4$) which was then oxidized to the ketone (MnO$_2$). This was methylated (LDA, MeI, −78 °C) at position 6; the methyl group had the exo configuration as a result of attack at the convex face of the adduct. The desired opening of the bond 2–8 was accomplished by reaction with Me$_2$CuLi at −78 °C and subsequent trapping of the enolate; the methyl group is introduced at C-2 and the reaction is described as 1,5 addition.

A similar strategy was followed in the synthesis of (±)-modhephene.[104] Adduct **17a** (Table 3) was hydrolyzed, the alcohol oxidized and the ketone trimethylated at positions a6, a6, and b8 (for numbering, see Scheme 6) with *t*-BuOK and MeI. A fourth methyl group was introduced, at b2, by reaction with Me$_2$CuLi and during this reaction (1,5 addition) the cyclopropane ring opened (cleavage of the bond b2–b8) (Scheme 50). The resulting product was converted in a few steps into (±)-modhephene.

In the examples just mentioned a functionality adjacent to carbon b8 of the adduct (acetate or carbonyl group) assists in the process of cleaving the cyclopropane

Scheme 51. Synthesis of a [5.5.5.5]Fenestradienone via Meta Photocycloaddition



ring. This feature was also used in a synthesis of (±)-hirsutene.[135] The major intramolecular meta adduct (Table 4, entry 35a) contains an acetate group next to carbon b8. This was deacetylated with $LiAlH_4$, and the resulting alcohol was treated with 10-camphorsulfonic acid. Protonation of OH was followed by elimination of water, opening of the bond b2–b8, and loss of a proton from the methyl group at b2.

Wender and co-workers have also employed reductive cleavage of the cyclopropane bond b2–b8, with Li/NH_3, Et_2O, and EtOH in their synthesis of (±)-coriolin[136] (Table 4, entry 35; the major adduct a was first deacetylated, the alcohol oxidized and then the ketone was reductively cleaved), and with Li in CH_3NH_2 in their synthesis of (±)-silphinene[133] (see Table 4, entry 33, adduct b) and of (±)-laurenene[147] (see Table 4, entry 88).

Keese and co-workers[126] have used the intramolecular meta photocycloaddition as a possible synthetic route to [5.5.5.5]fenestranes. In an exploratory investigation, they have irradiated 3-phenylhept-6-en-2-ol and obtained five adducts, two by 2,6 addition and three by 1,3 addition (Table 4, entry 13). Adducts **13a**, **13c**, and **13e** were found to undergo the [1,5] sigmatropic H-shift upon heating (275 °C), leading to a diene. In the case of **13c**, treatment of the adduct with $HClO_4$ led to the same diene as the one obtained upon heating, via protonation at b4, cleavage of the bond b2–b8 and loss of a proton at a7. Interestingly, treatment of **13a** with $HClO_4$ did not lead to a diene but to an allylic alcohol, formed by hydration of the cyclopropane ring (H at b8, OH at b2).

Chiral selectivity in intramolecular arene–alkene photocycloaddition was also investigated by Keese and co-workers[127] in the course of their study on the preparation of fenestranes and they have irradiated compounds with a chiral ester substituent at position 6 of 2-methyl-6-phenylhex-2-ene (Table 4, entry 16). A 1:1 mixture of two chiral menthyl esters was photolyzed, and one of the diastereomers reacted faster than the other. Both produced the 1,3 adducts shown in the table with high chemical selectivity and moderate chiral induction.

The analogous methyl ester was irradiated by Mani and Keese[129] and two 1,3 adducts were obtained (Table 4, entry 15). The angular adduct could be transformed into an *all*-cis-[5.5.5.5]fenestradienone (Scheme 51); during the reaction a methyl group migrated.

Of the two 1,3 meta photocycloadducts formed in an intramolecular addition, the one with the angular structure already has three-quarters of the [5.5.5.5]-fenestrane skeleton. As can be seen from Scheme 35, the fourth ring should be built between the α-carbon atom of the side chain and carbon atom 6 of the benzene ring. Two extra carbon atoms are required to complete the fourth ring and in the experiment of Scheme 51 a two-carbon substituent was constructed at the appropriate position in the adduct. However, if the two-carbon bridge were already present in the starting material, the fenestrane could be constructed in one photochemical step, although it would still contain the three-membered ring. Evidently, the starting material required is an indan derivative and this approach has, partly successfully, been used by Keese and co-workers.[143,144] They first irradiated the 7-methoxyindan derivative shown in Table 4, entry 83. The major photoadduct, **83c**, is the result of an initial ortho cycloaddition which is followed by a sequence of reactions for which the authors have suggested a mechanism.[144] The other two adducts are formed by 1,3 addition across the methoxy group, followed by the two different modes of cyclopropane ring closure. The minor product (Table 4, adduct 83b) was heated in toluene at 242 °C for 5 min, but the expected [1,5] H-shift that would lead to a [5.5.5.5]fenestrane containing two double bonds, a methoxy, and a hydroxy group was not observed and another rearrangement had apparently taken place.

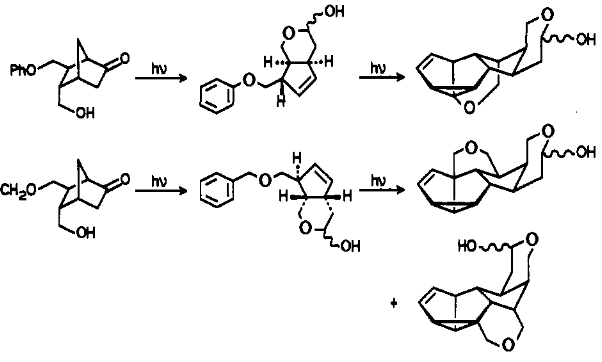
Later,[143] Keese and co-workers have studied the photoreactions of various other derivatives of 1-(but-3-enyl)indan. The 7-methoxy derivative gave the same type of products (Table 4, entry 81) as the 1-hydroxy-7-methoxy compound. The presence of two methyl groups at the terminal C atom of the double bond (Table 4, entries 84 and 85) suppressed the formation of the ortho adduct, but the yields of meta adducts were very low. A major change occurred when molecules lacking the 7-methoxy group were irradiated. Now the addition took place across carbon atom 3a of the indan skeleton, regardless of the presence or absence of methyl groups at the double bond or at C-3 (Table 4, entries 78–80). Thermolysis of adduct **81b** at 240 °C did not afford a [5.5.5.5]fenestrane derivative, but instead a vinylcyclopropane rearrangement took place, giving **81a**, and this molecule then underwent the [1,5] H-shift. Several other transformations of the adducts were studied, but no [5.5.5.5]fenestrane has yet been obtained via this route.

The 2,6 meta photocycloaddition of 3-methylene-5-phenylpent-1-ene reported by Ellis-Davies et al.[130] (Table 4, entry 21) may have a low quantum yield, but it provides an intramolecular meta cycloadduct with functionality on the bridging unit. With chemical conversions of more than 50% and selectivities of better than 90% the process is considered very attractive for synthetic purposes.

Very interesting results have recently been reported by De Keukeleire and He[148] (Table 4, entries 89 and 90). The lactols shown as starting materials in the table are actually the products of a Norrish type I reaction of aryl-substituted norbornan-2-ones. They undergo in situ the meta photocycloaddition in a so-called tandem reaction (Scheme 52).

Irradiation of the norbornanones at 300 nm in ethanol, followed by oxidation of the crude reaction mixture

Scheme 52. Norrish Type I Cleavage Followed by Intramolecular Meta Photocycloaddition in a Tandem Reaction[148]



with pyridinium dichromate gave the bicyclic lactones which upon further irradiation at 254 nm were converted into the meta adducts in their lactone form. Irradiation of the norbornanones at 254 nm in cyclohexane/ethyl acetate (5:1) followed by oxidation led to the same adducts, which had apparently been formed in situ from the photogenerated lactols.

The authors plan to use these addition reactions in the synthesis of naturally occurring bulleranes.

With the aim of developing a facile synthesis of gymnomitrol, a compound with the same carbon skeleton as the alcohol obtained upon acidolysis of the anisole–cyclopentene adduct but with several additional methyl groups, Hoye[107] has attempted to photoadd o-methylanisole to 1,2-dimethylcyclopentene but, probably owing to steric hindrance, no addition was observed. Cyclopentene itself does add to o-methylanisole and to other anisole derivatives investigated by Hoye[107] (Table 3, entries 31 and 32).

The addition of styrene, phenylacetylene, and benzonitrile to furan provides meta adducts (Table 2, entries 21, 22, and 74) in gram quantities,[82] and the authors state that this illustrates the potential of employing substituent-orienting factors in arene photocycloadditions to improve reaction selectivity to the point of synthetic usefulness.

When a benzene derivative adds to *trans*-1,2-dichloroethene, inevitably one of the chlorine atoms is in the endo position with respect to the benzene ring. It has been discovered by Gilbert et al.[62,63,85,100] that closure of the three-membered ring invariably occurs at the side of the endo chlorine atom with the result that 6-*exo*-7-*endo*-dichloro adducts are formed (Table 1, entry 50; Table 2, entries 25, 60, 61, 66, 67, and 72; Table 3, entries 21, 22, 23, 46, 48, 50, and 53). This interesting directing effect on the ring closure, which has been discussed in the section on regio- and stereoselectivity, has been employed by Cosstick and Gilbert[125] to selectively obtain either the angular or the linear triquinane skeleton in the intramolecular photocycloaddition. *trans*-1-Chloro-5-phenylpent-1-ene in the conformation required for 1,3 addition has its chlorine atom oriented in such a way that the directing effect leads to the angular adduct (Table 4, entry 9). In fact, not the adduct itself, but a product resulting from a 1,3 Cl shift was isolated, next to rearranged 2,6 adducts as minor products. 2-Chloro-5-phenylpent-1-ene undergoes the other type of ring closure upon 1,3 addition (Table 4, entry 10), which leads to a linear adduct. The reaction had to be performed in alcoholic solvents because in solvents such as cyclohexane or acetonitrile multicomponent mixtures were obtained and HCl was evolved. The adduct underwent spontaneous chlorine shifts followed by solvolysis. For synthetic applications it is of interest that it has been clearly demonstrated that it is possible to gain control over the direction of cyclopropane ring closure in meta adduct formation.

VII. Acknowledgments

I want to express my gratitude to the many people with whom I have collaborated in the field of meta photocycloaddition and from whom I have learned most of what I know about the subject. I am indebted to Dr. R. Srinivasan, who introduced me to this fascinating chemistry, and to Dr. Andrew Gilbert, a pioneer in the field of arene cycloadditions, and Dr. Jochen Mattay, with both of whom I have had fruitful collaboration and pleasant personal contacts over a number of years.

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