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Photochemical 1,3 Addition of Benzene to Olefins. Orientational Specificity Induced by Methyl Substituents on Aromatic and Olefinic Rings

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Abstract: Photochemical addition of toluene and *o*-, *m*-, and *p*-xylenes to cyclopentene gave principally 1,3 adducts (3,7-*endo*-tetracyclo[6.3.0.$0^{2,11}$.$0^{3,7}$]undecene-9) in which a methyl group was oriented specifically in C-1 position. Addition of mesitylene to cyclopentene was exceptional in that both the 1,9,11- and 2,8,10-trimethyl derivatives were formed although the former predominated. From quantum yields for these additions, it was concluded that a methyl substituent on a benzene ring exercised a significant activation in the excited state on the ortho positions and possibly a deactivating effect on the meta positions. With increasing substitution of the aromatic ring with methyls, steric effects also came into play, the quantum yield for 1,3 addition for mesitylene being only ~0.1 of the value for benzene. Addition of benzene to 1,2-dimethylcyclobutene was as efficient as to cyclobutene. Addition of toluene to 1,2-dimethylcyclobutene was sixfold slower than to cyclobutene or *cis*-3,4-dimethylcyclobutene. At the same time, the orientational specificity was retained in all these additions. A model of the complex between the singlet excited benzene and olefins is proposed which takes into account the features of the 1,3 additions.

Although numerous examples of the photochemical 1,3 addition of benzene to olefins are known,[1-7] the factors which control the peculiar features of this reaction are largely unknown. Three of the most striking peculiarities follow. (i) 1,2, 1,3, and 1,4 additions all occur from the same (singlet) excited state of benzene but their relative importance is olefin dependent.[1c,5] 1,3 addition is the predominant process in linear and cyclic monoolefinic hydrocarbons. (ii) 1,3 addition is not directly related to the formation of benzvalene[1b,8] even though a diradical intermediate (I) may appear to serve as a common precursor. (iii) Mono- and dimethyl

I

substituted benzenes have been shown[9] to add (in the 1,3 mode) to cyclobutene with a high degree of orientational specificity.

Following an original suggestion by Morrison and Ferree,[6] Wilzbach and Kaplan[1c] have proposed that the addition reactions to olefins may proceed from a complex between the excited singlet benzene and the olefin. A detailed kinetic study[10] of the benzene–cyclopentene system lends support to this suggestion and offers a basis for explaining the peculiarities mentioned above.

In this work, the orientational specificity of the addition has been studied in order to establish its generality and its limitations and to explain it within the exciplex mechanism.

Results

The 1,3 photoadditions that were investigated fall into two general series. In one, the additions of methyl-substituted benzenes to cyclopentenes were studied both qualitatively and quantitatively. The second consisted of quantitative measurements on the addition of benzene and toluene to cyclobutene, 1,2-dimethylcyclobutene, and *cis*-3,4-dimethylcyclobutene.

Methylbenzenes–Cyclopentene. The methylbenzenes that were investigated are listed in Table I. In every instance one or more 1,3-addition products were isolated. Their mass spectra and analyses indicated that they were 1:1 adducts. Since spectroscopic data showed that they contained only one olefinic group per molecule, they should be tetracyclic. In their infrared spectra, the adducts had a weak absorption at 1595–1603 cm^{-1} (or at 1648–1650 cm^{-1} when a methyl substituent was present at the double bond) which showed the presence of a cyclopentene ring. In their ultraviolet spectra, the adducts had an absorption maximum or shoulder at

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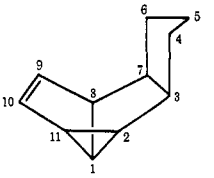
Table I. Properties of Tetracyclo[6.3.0.0^{2,11}.0^{3,7}]undec-9-enes



Aromatic hydrocarbon	Adduct	Mass spectrum parent peak *m/e*	Uv spectrum[a] λ_{max}, nm (ϵ)	Ir spectrum,[b] cm^{-1}	Nmr spectrum,[c] δ in ppm	Quantum[d] yield
Benzene	Unsubstituted	*e*	*e*	*e*	*e*	0.16
Toluene	1-Methyl	160	220 (2080)	3050, 3010, 2960, 1595, 1443, 1348, 970, 920, 911, 890, 868, 783, 758, 744	1.32–1.41 (8 H); 2.59 (d of q, H-8); 1.37 (s, CH_3); 2.90 (m, H-3); 3.55 (m, H-7); 5.51 (d of d, H-9); 5.62 (d of d, H-10)	0.21
p-Xylene	1,10-Dimethyl	174	222 (3740)	3050, 2970, 1648, 1443, 1376, 960, 893, 820–810	1.36 (s, CH_3(1)); 1.15–1.82 (8 H); 1.76 (d of d, CH_3(10)); 2.51 (d of q, H-8); 2.90 (m, H-3); 3.16 (m, H-7); 5.04 (s, H-9)	0.13
o-Xylene	(A) 1,8-Dimethyl	174	223 (2770)	3050, 3000, 2908, 1603, 1453, 1356, 968, 783, 758	1.28 (s, CH_3(1)); 1.04 (s, CH_3(8)); 1.08–1.89 (8 H); 2.85 (m, H-3 + H-7); 5.27 (d, H-9); 5.56 (d of d, H-10)	
	(B) 1,2-Dimethyl	174	225 (1870)	3050, 2950, 1595, 1446, 1382, 1343, 1313, 950, 912, 778, 760	1.08 (s, CH_3(2)); 1.11–1.89 (8 H); 1.28 (s, CH_3(1)); 2.62 (d of q, H-8); 2.67 (d of m, H-3); 3.10 (m, H-7); 5.51 (d of d, H-9); 5.60 (d of d, H-10)	0.08
m-Xylene	(A) 1,9-Dimethyl	174	225 sh (3550)	3050, 2975, 1648, 1448, 1375, 980–970, 902, 825	1.20–1.82 (8 H); 1.36 (s, CH_3(1)); 1.72 (m of d, CH_3(9)); 2.28 (d of d, H-8); 2.94 (m, H-3); 3.19 (m, H-7); 5.25 (s, H-10)	
	(B) 1,11-Dimethyl	174	230 sh (1690)	3100, 2990, 1600, 1450, 1380, 1353, 780, 760	1.11 (s, CH_3 (11)); 1.27 (s, CH_3(1)); 1.30–1.84 (8 H); 2.60 (d of t, H-8); 2.88 (m, H-3); 3.16 (m, H-7); 5.47 (m, H-9 + H-10)	0.05
1,3,5-Trimethylbenzene (mesitylene)	(A) 1,9,11-Trimethyl	188	241 (5440)	3050, 2990, 2900, 1649, 1450, 1378, 974, 910, 868, 826	1.05–1.82 (8 H); 1.05 (s, CH_3(11)); 1.25 (s, CH_3(1)); 1.73 (d of d, CH_3(9)); 2.31 (d, H-8); 2.98 (m, H-3); 3.16 (m, H-7); 5.10 (d, H-10)	
	(B) 2,8,10-Trimethyl	188	238 sh (2720)	3050, 2990, 2900, 1650, 1450, 1373, 1340, 847	1.06 (s, CH_3(8)); 1.12 (s, CH_3(2)); 1.23–1.82 (8 H); 1.74 (d, CH_3(10)); 2.12 (d, H-1); 2.68 (m, H-3); 2.83 (m, H-7); 4.85 (s, H-9)	0.015

[a] Solvent: *n*-pentane. [b] Liquid film. [c] Solvent CCl_4, TMS as internal reference, 220 MHz. [d] Solvent cyclohexane, 2537 Å, olefin concn 1 *M*. [e] See ref 10.

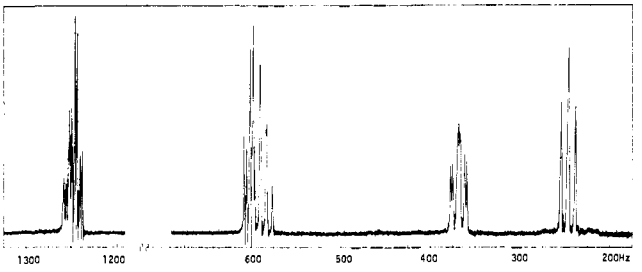
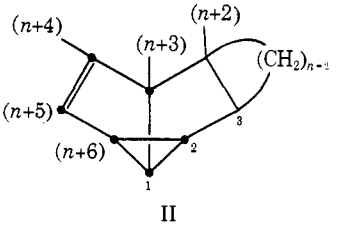


Figure 1. Proton magnetic resonance spectrum of benzene protons in typical endo 1,3 adduct: 220-MHz spectrum; frequencies downfield from TMS as internal reference; solvent, CCl_4.

220–241 nm[11] (ϵ_{max} ~2000) which indicated the presence of a vinylcyclopropane chromophore.

(11) The maximum appeared to shift to longer wavelengths when a methyl substituent was present at the double bond. But the simultaneous increase in end absorption tended to obscure the presence of a clear maximum.

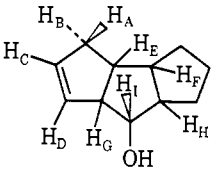
The proton magnetic resonance spectra of these adducts of 220 mHz provided conclusive evidence for their structures and particularly the positions of the methyl groups in them. In a typical spectrum of an endo 1,3 adduct, II (irrespective of the olefin) derived



II

from benzene, if the coupling to the protons in the olefin moiety is eliminated by deuteration, the six protons located on the benzene carbons (these are indicated in II by filled circles) fall in three pairs (Figure 1). The low field pair (H_{n+4} and H_{n+5}) falls at δ 5.5–6.0,

Table II. Nuclear Magnetic Resonance Data on Europium Complexes of Alcohols Derived from Methylbenzene Adducts



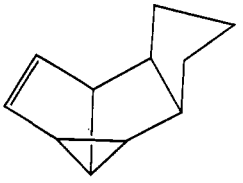
Va A-I = H
Vb G = CH_3; rest = H
Vc E = G = CH_3; rest = H
Vd C = G = CH_3; rest = H

Compd	Chemical shifts, δ ppm, of protons A-I in $Eu(DPM)_3$ complexes[a]									Chemical shifts of methyl substituents before ($\delta CdCl_3$) and after (δEu^{n-1}) complexing		
	H_A	H_B	H_C	H_D	H_E	H_F	H_G	H_H	H_I	$\delta CdCl_3$	δEu^{n-1}	ΔEu
Va	7.26	8.36	9.00	10.01	17.46	20.10	18.56	18.10	~30.3			
Vb	7.26	8.36	9.00	10.01	17.46	20.10		18.10	~30.3	1.38(G)	16.31	14.93
Vc	7.26	8.36	9.00	10.01		20.10		18.10	~30.3	1.38(G)	16.31	14.93
										1.80(E)	9.06	7.26
Vd	7.26	8.36		10.01	17.46	20.10		18.10	~30.3	1.38(G)	16.31	14.93
										2.08(C)	5.21	3.13

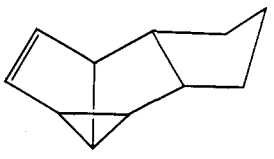
[a] Values extrapolated to a 1 : 1 complex, see ref 10 for details.

the downfield absorption always being due to $H_{(n+5)}$. They are coupled to each other (~6 Hz) and to the adjacent allylic protons (2 Hz). $H_{(n+5)}$ shows a more complex fine structure than $H_{(n+4)}$. Of the two midfield protons, H_1 occurs as a quartet, its coupling to H_2, $H_{(n+3)}$, and $H_{(n+6)}$ being approximately equal (7 Hz). $H_{(n+3)}$ is a doublet of doublets (J = 7 and 2 Hz). The chemical shifts of these protons relative to each other are variable, the difference changing in both magnitude and sign. The remaining protons fall between δ 1 and 2, always in the order shown. $H_{(n+6)}$ shows the more complex structure of the two.

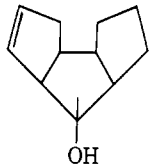
The position of a methyl group in the adduct (when a methylbenzene was used as the aromatic compound) was indicated by: (i) the absence of the corresponding proton absorption, (ii) the simplification of the adjacent proton absorptions, and (iii) the chemical shift of the methyl group. Since the mid- and high-field protons were frequently obscured by protons derived from the



III



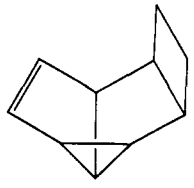
IV



V

olefin moiety, the redundancy in these three criteria was eliminated. The tabulated data on the nmr spectra (Table I) are self-explanatory.

In earlier work,[10] it had been shown that benzene added to cyclopentene to give more (4:1) of the endo (III) than the exo (IV) adduct, the stereochemistry referring to the juncture of the olefin. All of these adducts in Table I were similarly derived from endo addition *without exception*. The evidence in every instance rested on the chemical shifts and coupling of the nmr absorptions which differ quite significantly between the endo and the exo adducts.[10] Additional evidence for these assignments was obtained for the adducts from toluene, *o*-xylene, and *p*-xylene by the conversion of each adduct of ring structure III to its tricyclic alcohol derived from V. The nmr spectra of the latter, alone and when complexed with $Eu(DPM)_3$, were compared to the corresponding spectra of V (the alcohol derived from the benzene adduct III), the stereochemistry of which has been unequivocally established previously.[10] Double resonance studies further proved that in the alcohols derived from the alkyl-substituted adducts, the proton resonances had the same chemical shifts as in V. Table II is a summary of the chemical shifts of the various protons in V and its methyl derivatives when complexed (1:1) with the europium shift reagent.



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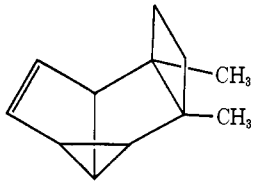
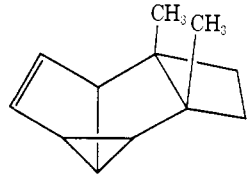


VII

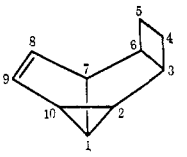


VIII

Benzene and Toluene. 1,2- and *cis*-3,4-Dimethylcyclobutene. The structures of the 1,3 adducts of benzene and toluene to cyclobutene and of benzene to *cis*-3,4-dimethylcyclobutene have been reported before.[5,9,10] The 1,3 adducts of benzene and toluene to 1,2-dimethylcyclobutene are of special interest from a mechanistic viewpoint. Therefore, their structures and stereochemistry were examined in detail.

The photoaddition of benzene to 1,2-dimethylcyclobutene gave principally two 1:1 adducts (Table III) in a ratio of 3:1. These were identified as 1,3 adducts from their infrared spectra (C=C stretching absorption at 1600 cm^{-1}), ultraviolet spectra ($\lambda^{max}_{pentane}$ 221–223 nm, ϵ_{max} ~3000), and nmr spectra. The proton spectra was considerably simplified by studying the adducts

Table III. Properties of Tetracyclo[5.3.0.0.^{2,10}.0^{3,6}]dec-8-enes

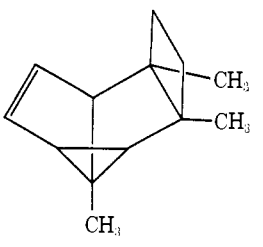


Aromatic hydrocarbon	Olefin	Adduct	Mass spectrum parent peak *m/e*	Uv spectrum[a] λ_{max}, nm (ϵ)	Ir spectrum,[b] cm^{-1}	Nmr spectrum,[c] δ in ppm	Quantum[d] yield
Benzene	1,2-Dimethylcyclobutene	3,6-Dimethyl (VII)	160	221 (3040)	3060 (m); 2960 (s); 2880 (m); 1600 (w); 805 (s); 780 (s); 755 (s); 708 (m)	0.93 (s, CH_3); 1.09 (s, CH_3); 1.29 (t, H-2, J = 7 Hz); 1.37–1.50 (3 H); 1.77 (t of d, H-10, J = 7 Hz, J = 2 Hz); 1.89 (1 H); 2.65 (q, H-1, J = 6 Hz); 2.72 (d of d, H-7, J = 6 Hz, J = 2 Hz); 5.66 (d of d, H-8, J = 5 Hz, J = 2 Hz); 5.71 (d of d, H-9, J = 5 Hz, J = 2 Hz)	
Benzene	1,2-Dimethylcyclobutene	3,6-Dimethyl[e] (VIII)	160	223 (2900)	3060 (m); 2960 (s); 1600 (w); 810 (m); 785 (m); 735 (s); 720 (m)	0.91 (s, CH_3); 0.96 (s, CH_3); 1.31–1.42 (2 H); 1.59, 1.62 (H-2 + H-10); 1.73 (2 H); 2.64 (q, H-1, J = 6 Hz); 2.72 (d of d, H-7, J = 6 Hz, J = 2 Hz); 5.45 (H-8 + H-9)	0.10
Toluene	1,2-Dimethylcyclobutene	1,3,6-Trimethyl (IX)	174	223 (5200)	3060 (m); 2930 (s); 2220 (s); 1600 (w); 895 (m); 815 (s); 755 (s)[f]	1.08 (d, H-2, J = 7 Hz); 1.39 (s, CH_3); 1.53 (d, H-10, J = 7 Hz); 2.44 (d, H-7, J = 2 Hz); 5.68 (H-8 + H-9)[f]	0.02
Toluene	3,4-Dimethylcyclobutene	1,4,5-Trimethyl (X)	174	235 sh (~1700)	3050 (m); 2940 (s); 1670 (m); 880 (s); 830 (m); 810 (w); 708 (s)	0.85 (d, CH_3, J = 7 Hz); 0.90 (d, CH_3, J = 7 Hz); 1.34 (t, H-2, J = 7 Hz); 1.36 (s, CH_3); 1.57 (d, H-10, J = 7 Hz); 1.70 (H-5); 2.35 (H-4); 2.60, 2.74 (H-3 + H-6); 2.82 (d of d, H-7, J = 7 Hz, J = ~1 Hz); 5.70 (H-8 + H-9)	0.11

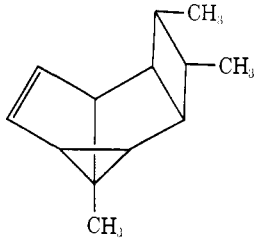
[a] Solvent: *n*-pentane. [b] Liquid film. [c] Solvent CCl_4, TMS as internal reference, 220 MHz. [d] Solvent cyclohexane, 2537 Å, olefin concn 1 *M*. [e] 3,6 exo. [f] These data refer to adduct prepared from fully deuterated olefin.

derived from benzene and 1,2-dimethylcyclobutene-d_{10}. It was observed that in the major adduct, the chemical shifts and couplings were nearly the same as the values in the principal 1,3 adduct of benzene to cyclobutene to which a endo stereochemistry (VI) has been assigned.[5,12] The major and minor adducts in the present instance would therefore be VII and VIII, respectively. It may be noted that in VII the chemical shift difference between the methyl groups is smaller than in VIII. This is presumably due to one methyl group in VIII which is nearly above the π electrons of the olefinic bond. Such an orientation is known to give rise to an upfield chemical shift in the proton resonance.[13]

The addition of toluene to 1,2-dimethylcyclobutene gave one major 1,3 adduct (mass spectral parent peak at 714; $\lambda^{max}_{pentane}$ 223, ϵ_{max} 5100; infrared absorption at 1600 cm^{-1}). The nmr spectrum of this compound resembled VII closely and indicated that the location of the methyl group derived from the toluene was at C_1. Its structure must be as in IX. These conclusions were confirmed by examining the nmr spectrum of the 1,3 adduct of toluene to 1,2-dimethylcyclobutene-d_{10}. A



IX



X

remarkable feature of this spectrum was the absorption due to the two olefinic protons which showed no separation even at 220 nHz.

The single adduct of toluene to *cis*-3,4-dimethylcyclobutene was identified to be a 1,3-addition product (X) on the basis of its spectral features which were typical of such adducts. The orientation of the vicinal methyl groups shown in this representation is based on earlier studies on the photoaddition of benzene to this olefin.[12]

Quantum Yields. At a fixed value of 1 *M* for the concentrations of the various olefins, the quantum yields for the 1,3 addition of methyl-substituted benzenes were determined (Tables I and II). The concentration of the aromatic compound was between 1.2 and 1.4 *M*. The dependence of these quantum

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(13) J. N. Shoolery and M. T. Rogers, *J. Amer. Chem. Soc.*, **80**, 5121 (1958).

yields on the concentration of the olefin was checked in the toluene–cyclopentene system. At olefin concentrations of 1.0, 4.5, and 9.1 *M*, the quantum yields were 0.21, 0.38, and 0.43 compared with values for benzene of 0.16, 0.28, and 0.30.[10] The ratio of the quantum yields ($\Phi_{toluene}/\Phi_{benzene}$) was seen to be nearly constant (1.31, 1.38, 1.41), which suggested that for a comparison of the quantum yields it was justifiable to use the values at an arbitrary (but constant) concentration of the olefin.

Discussion

The results obtained in this study on the photoaddition of methylbenzenes to cyclopentene show that the orientational specificity that was reported before[9] for methylbenzene–cyclobutene systems is not an isolated phenomenon. There is evidence that such specificity extends to linear olefins such as 2-butene as well.[14]

Two explanations have been proposed[9] to account for the preferential orientation of the methyl groups in the photoadducts. The first is the intermediacy of a highly symmetric species in which one methyl group will always be appropriately located in order to occupy the C-1 position in the products. The two likely candidates with such a high degree of symmetry are benzene itself[15] and prismane. It has already been pointed out[9] that this explanation will fail if 1,3 addition proceeds in a wholly random fashion.

A more attactive explanation is based on the possibility that a methyl substituent may possess a strong directive influence in the singlet excited state of the aromatic hydrocarbon. The two explanations are not mutually exclusive, because any directive influence due to a methyl group would effectively combine with the symmetry of an intermediate to lead to a limited number of adducts.

The quantum yields reported here lend quantitative support to the idea that a methyl group on the benzene ring has a definite activating effect on the ortho positions.[16] Thus benzene which has six equivalent modes of 1,3 addition to cyclopentene has a quantum yield (Table I) of 0.027/mode. Toluene which has only one mode of addition (*i.e.*, 2,6) to give the observed product has a quantum yield of 0.21/mode. In addition to this activating effect on the ortho positions, a methyl group must have some deactivating effect on the meta positions as well, because no adduct which corresponded to addition to the C-3 or C-5 positions was detected. If the quantum yield for any of these modes was the same as in benzene, *i.e.*, 0.027/mode (which would have been the case in the absence of any deactivation), the product would have amounted to $^1/_8$ of the ortho addition product and would have been detected. Qualitatively, the same pattern of ortho activation and meta deactivation can be inferred from the quantum yields for the addition of benzene and toluene to cyclobutene.

A consideration of the quantum yields for *p*-xylene shows that with increasing methyl substitution a complex interdependence between activation and deactivation due to the methyl groups prevails. *p*-Xylene has two pairs of positions (2,6; 3,5) ortho to a methyl group but meta to another. The quantum yields for 1,3 addition to cyclopentene and cyclobutene are 0.065 and 0.070/mode, respectively, which are in between the values for benzene and toluene.

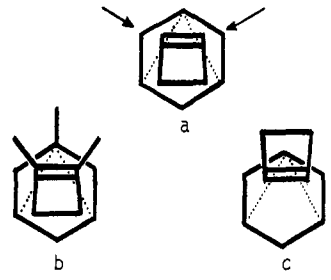

Figure 2. Model of complex for 1,3 addition: (a) endo addition of benzene to cyclobutene, (b) addition of toluene to 1,2-dimethylcyclobutene, (c) exo addition of benzene to cyclobutene.

An increase in the number of methyl substituents to three decreases the quantum yield for 1,3 addition. The orientational specificity is also reduced. Thus, mesitylene yields both of the possible 1,3 adducts to cyclopentene, the "favored" adduct (1,9,11-trimethyl) being only a factor 2 more important than the minor 2,8,10-trimethyl isomer. But it is noteworthy that the quantum yield for the addition is only 0.015 for both products together. A significant part of this decrease may be due to steric hindrance to the addition which is possibly another factor which adversely influences orientational specificity.

A striking example in which these effects can be sorted out is in the addition of benzene or toluene to 1,2-dimethylcyclobutene. Benzene gives two 1,3 adducts, VII and VIII, the sum of the quantum yields for the two being the same as for VI, the 1,3 adduct of benzene to cyclobutene. This indicates that dimethyl substitution at the double bond of a cyclic olefin does not offer any steric hindrance to addition. In contrast, the quantum yield for the addition of toluene to 1,2-dimethylcyclobutene is sixfold smaller than its quantum yield for the corresponding addition to cyclobutene. At the same time orientational specificity is maintained, the major product being IX in which the methyl group from the toluene moiety is at the C-1 position. The lowering in the quantum yield should therefore be attributed to the mutual steric hindrance offered between the three methyl groups, while the orientational specificity should be attributed to the directive effect of the methyl group on the aromatic ring. The deactivation that exists in the meta positions is illustrated by this example also, as adducts to other carbon positions in the toluene ring are not significant. As a control, the quantum yield for the addition of toluene to *cis*-3,4-dimethylcyclobutene was measured and found to be entirely "normal," *i.e.*, of the same magnitude as for cyclobutene. Therefore, it is the location of the two methyl groups on the olefinic bond that introduced the hindrance.

A model of the exciplex for these 1,3 additions which takes into account the observations reported here is as follows. The olefin and the excited singlet benzene form a sandwich structure (Figure 2) in which the π

(14) R. Srinivasan, C. S. Angadiyavar, V. Y. Merritt, and J. Cornelisse submitted for publication.

(15) The singlet (B_{2u}) state of benzene is believed to retain the hexagonal structure of its ground state: J. H. Callomon, T. M. Dunn, and I. M. Mills, *Phil. Trans. Roy. Soc. London, Ser. A*, **259**, 499 (1966).

(16) It is pertinent to note that the quantum yields for these reactions are indicative of the true reactivities of the aromatic compounds because their natural lifetimes in their singlet excited states are nearly the same (±7%): A. Reiser and L. J. Leyshan, *J. Chem. Phys.*, **56**, 1011 (1972).

electrons of the olefinic bond are exactly above a pair of carbons (1,3) of the aromatic ring. A small ring olefin gives almost exclusively the endo adduct[5] which suggests that maximum overlap between the bonds of the two rings (Figure 2a) is probably favored. With increasing ring size (which would make such an overlap less efficient) more and more of the exo isomer is also observed.[7,10] A linear olefin such as *cis*-2-butene gives endo as well as exo adducts.[1a,4,17] Bonding between the aromatic hydrocarbon and the olefin is concerted[1c] and is presumably followed by the puckering of the benzene nucleus and the closure of the cyclopropane along either of the dotted lines—invariably both such isomers are observed. When two methyl substituents are present at the double bond of the olefin, it is reasonable to expect that they offer little steric interaction. But when toluene is used instead of benzene, the methyl group lies between the olefinic methyl groups (Figure 2b) and, therefore, will cause considerable steric repulsion. To form an exo adduct, the olefinic ring will have to lie external to the aromatic ring. Such a position would not give as much overlap between the two rings as in the orientation shown in Figure 2c. Not only are exo adducts less favored than endo adducts when benzene is used, but exo adducts are undetectably small when the aromatic ring has a single methyl substituent on it. Similarly constituted exciplexes in which bonding is between an olefin and a pair of adjacent or opposite carbon atoms will serve to explain 1,2 and 1,4 additions from the same singlet excited state.[1c,5,6]

The most direct evidence for such an exciplex will undoubtedly be obtained from spectroscopic observations.[18] There is also need to understand the chemistry of the exciplex in terms of its stability as a function of the olefin and of the alkyl substituents on the benzene. Such studies are now in progress.

Experimental Section

Infrared spectra were determined on a Perkin-Elmer Infracord spectrophotometer. Mass spectra were recorded on a Hitachi Perkin-Elmer RMS-4 mass spectrometer. Ultraviolet spectra were measured on a Cary 14 spectrophotometer. Nuclear magnetic resonance spectra at 60, 90, and 220 MHz were run on a JEOL Co. Minimar, a Bruker HFX-10, and on a Varian HR-220 spectrometer, respectively. The last was operated by the Consortium at The Rockefeller University in New York. Microanalysis were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.

The three xylenes, mesitylene, and cyclopentene were obtained from Chemical Samples Co., Columbus, Ohio. Since they were found to be better than 99% pure, they were used as obtained. Toluene (Mallinckrodt) was used as supplied. Cyclobutene, 1,2-dimethylcyclobutene, and 1,2-dimethylcyclobutene-d_{10} were synthesized from the corresponding 1,3 dienes by photoisomerization.[19] Details of the synthesis of cyclobutene have been described.[20]

1,2-Dimethylcyclobutene. A solution of 2,3-dimethyl-1,3-butadiene (50 g, Chemical Samples Co., 99% purity) in ether (400 ml) was irradiated at 253.7 nm in a Rayonet type RS preparative reactor. During the long irradiation (60 days), the container did not have to be changed because there was very little polymer formation on the walls of the reaction vessel. At the end of the irradiation (as determined by the total disappearance of the starting material), the contents were distilled on a 18-in. spinning-band column. Following the removal of ether, 1,2-dimethylcyclobutene (28 g, 56%) of 99% purity distilled: bp 66–68°.[19] The residue consisted of dimers (8 g) and polymer (12 g).

2,3-Dimethyl-1,3-butadiene-d_{10} prepared from acetone-d_6[21] was used to prepare 1,2-dimethylcyclobutene-d_{10}.

Preparative scale irradiations were carried out in a Rayonet Type RS preparative photochemical reactor fitted with four RPR-208 modules (254 nm). The cylindrical quartz irradiation tubes measured 12 × 1 in. (o.d.) and their capacity was 100 ml of solution. Each tube was filled with cyclopentene (50 ml), an aromatic hydrocarbon (25 ml), and cyclohexane (25 ml) and sealed by means of a rubber serum cap, through which samples could be removed using a syringe. The reaction solutions were monitored by vpc (0.25 in. × 12 ft 10% UCON 550X, ~160°, He pressure 40 psi) at 24, 48, 60, and 72 hr, and the irradiations were terminated when the formation of adducts began to level off (usually ~60 hr). The photolysis solutions were distilled at reduced pressures to remove solvent and unreacted starting materials, in each case limiting the bath temperature to less than 80–85°. The residues were further distilled under high vacuum (~10 μ), condensing with liquid nitrogen to separate the product mixture from polymeric materials. The neat products were stored at −80° due to their tendency to polymerize.

The mixture of products, as a thick viscous yellow oil, was separated into pure components by means of preparative vpc (UCON 550X column, as above), using multiple 100 to 250 μl injections. The collection temperatures and retention times for the various adducts are as follows: toluene–cyclopentene 130°, 22 min; *p*-xylene–cyclopentene 150°, 16.3 min; *o*-xylene–cyclopentene 125°, 50.6 min (B), 58.1 min (A); *m*-xylene–cyclopentene 140°, 25.6 min (A), 21.2 min (B); mesitylene–cyclopentene 165°, 17.4 min (A), 14.0 min (B).

Due to losses of the cyclopentene during work-up, the data below indicate (1) amounts of crude residue (including dimeric material, polymer, and mixtures of exo and endo adducts) obtained from a single unrecycled 100-ml run, (2) actual isolated amounts of pure (vpc) separated adduct(s), and (3) the per cent isolated yield based on the initial amount of aromatic compound: toluene 5.8 g, 2.4 g, 11%; *p*-xylene 4.1, 1.7, 8%; *m*-xylene 2.1 g, 0.4 g (A), 0.3 g (B), 4%; *o*-xylene 2.6 g, 0.2 g (B), 0.6 g (A), 5%; mesitylene 1.3 g, 0.2 g (A) 0.1 g (B), 1%.

The spectral data (ir, nmr, uv, mass spectrum) for the adducts are shown in Table I. The combustion analyses are shown in Chart I.

Chart I

Aromatic hydrocarbon	Calcd	Found
Toluene	$C_{12}H_{16}$: C, 89.93; H, 10.07	C, 89.88; H, 10.09
p-Xylene	$C_{13}H_{18}$: C, 89.59; H, 10.41	C, 89.50; H, 10.50
o-Xylene (mixture of isomers)	$C_{13}H_{18}$: C, 89.59; H, 10.41	C, 89.63; H, 10.36
m-Xylene (mixture of isomers)	$C_{13}H_{18}$: C, 89.59; H, 10.41	C, 89.61; H, 10.39
Mesitylene (mixture of isomers)	$C_{14}H_{20}$: C, 89.29; H, 10.71	C, 89.33; H, 10.78

Hydrations of all of the 1,3 adducts were carried out in the manner described previously.[10] Typically, a sample of the vpc purified adduct (150 mg) was dissolved in 80% aqueous acetone (7 ml), acetone (2 ml), and concentrated HCl (0.35 ml). The mixture was refluxed overnight under a nitrogen atmosphere. The greenish solution was neutralized with 50% K_2CO_3 and extracted with CH_2Cl_2 (~25 ml). The extracts were dried over anhydrous sodium sulfate and filtered, and the solvent was removed on a rotary evaporator to give nearly quantitative (85–100%) yields of the crude alcohols. Analytical samples were obtained by vpc collection at ~155° using a 0.25 in. × 12 ft SE30 column.

syn-**Tricyclo[6.3.0.0^{3,7}]-1-methyl-2-hydroxyundec-9-ene (Vb):** mp 88.5–90° (hexane); ir (KBr pellet) 3360, 2950, 2890, 1635, 1445, 1375, 1303, 1278, 1260, 1175, 1110, 999, 992, 890, 777, and 690 cm^{-1}; mass spectrum parent peak *m/e* 178; nmr (60 MHz, $CDCl_3$, TMS) 85.4–6.0 (m, 2 H), 2.5–3.5 (m, 3 H), 2.1–2.4 (m, 2 H), 2.03 (s, 1 H), 1.50 (s, 3 H); 0.7–2.11 ppm (7 H).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.83; H, 10.13.

syn-**Tricyclo[6.3.0.0^{3,7}]-1,10-dimethyl-2-hydroxyundec-9-ene (Vd):** waxy semisolid (colorless); ir (neat melt) 3490, 2970, 2900, 1660, 1445, 1375, 1183, 1110, 1085, 920, and 841 cm^{-1}; mass spectrum

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parent peak $m/3$ 192; nmr (60 MHz, $CDCl_3$, TMS) 85.2–5.5 (d, 1 H, $J \sim 7.5$), 2.4–3.3 (m, 3 H), 1.96–2.21 (m, 2 H), 2.08 (s, 3 H), 1.38 (s, 3 H), 0.9–2.0 ppm (8 H).

Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.15; H, 10.41.

***syn*-Tricyclo[6.3.0.0^{3,7}]-1,8-dimethyl-2-hydroxyundec-9-ene (Vc):** ir (neat smear) 3500, 3040, 2965, 2900, 1648, 1447, 1373, 1093, 921, 780–90, 706 cm^{-1}; mass spectrum parent peak m/e 192; nmr (60 MHz, $CDCl_3$, TMS) δ 5.7–6.2 (m, 2 H), 1.80 (s, 3 H), 1.38 (s, 3 H), 1.4–3.6 (12 H).

Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.27; H, 10.50.

Additions of the cyclobutenes to the aromatic compounds were carried out in the same fashion as the addition of benzene to cyclobutene.[5] The spectral properties of the adducts are given in Table III. Combustion analysis are given in Chart II. Details of the equipment and the procedure used in the quantum yield measurements are given elsewhere.[5]

Chart II

Compd	Calcd	Found
VII + VIII	$C_{12}H_{16}$: C, 89.93; H, 10.07	C, 90.01; H, 10.01
IX	$C_{13}H_{18}$: C, 89.59; H, 10.41	C, 89.95; H, 10.30
X	$C_{13}H_{18}$: C, 89.59; H, 10.41	C, 89.20; H, 10.20

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Primary Processes in the Photochemistry of Phenylalanine and Derivatives in Aqueous Solution. Biphotonic Photoionization and Photodissociation Reactions

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Abstract: The photophysical and photochemical processes which phenylalanine and its derivatives phenylalanine amide and *N*-acetylphenylalanine undergo in aqueous solutions at 20° were investigated with the help of the fast reaction technique of flash photolysis. Only the first $^1A_{1g} \rightarrow {}^1B_{2u}$ transition of benzene was optically excited. The transient absorption spectra of the various intermediates observed were characterized and the decay kinetics of these species determined. Both the photodissociation process leading to the formation of the benzyl radical and the photoionization process leading to the hydrated electron e_{aq}^- were found to be strongly dependent on the state of ionization of the free end groups –COOH and $-NH_3^+$, and in particular to the amino group. At pH 5.9, reactions 1–3 are suggested. The dependence of the various processes with pH was obtained as typical "titration" curves which followed the pK_a of the ground state molecule. The addition of low concentrations of characteristic quenchers such as ethyl pyruvate and Ni^{2+} ions indicated that the excited state precursors of these processes must be relatively long lived, probably the triplet excited states. From the dependence upon light intensity, the photodissociation processes leading to the benzyl radical in neutral and acid solutions of phenylalanine, phenylalanine amide, and *N*-acetylphenylalanine were found to be biphotonic in water at 20°. The photoionization process was also found to be biphotonic in nature. In alkaline solutions (above the pK_a of the amino group) of phenylalanine and phenylalanine amide one quantum only was required to bring about the corresponding photodissociation reaction. The quenching experiments showed that a triplet state was also involved as the precursor in alkaline solutions. It is important to note that even though all the excitation is initially absorbed by the aromatic ring, the ejected electron in the photoionization process comes from the $-COO^-$ group, demonstrating the involvement of strong intramolecular interactions.

The protein macromolecules contain a large number of chromophoric groupings which are capable of interacting with light both in the free state and as part of the polymer. In most proteins the majority of quanta in the 250–300 nm region are absorbed by the aromatic amino acids tyrosine (Tyr), tryptophan (Trp), and phenylalanine (Phe).[2–5] On the basis of the observed sequence of the singlet excited state energies, it was proposed[6] that electronic energy transfer Phe → Tyr → Trp was feasible as a result of dipolar resonance coupling. Consequently, most of the previous studies have been devoted to tryptophan and to tyrosine since most proteins contain either Trp or Tyr (or both) in addition to Phe. However, destruction of phenylalanine occurs on uv irradiation in the free state[7] or when present in proteins.[8] Furthermore, it has recently been shown that the photodissociation and photoionization processes of tyrosine[9,10] and aromatic alkylcarboxylic

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