The Stereo- and Regio-specific Formation of 11-Oxatetracyclo[6.2.1.0²,⁴.0³,⁷]undeca-5,9-dienes by the Substituent-directed Photocycloaddition of Furan to the Benzene Ring

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Furan undergoes specific 2,5–2',6'(*meta*)-photocycloaddition to benzonitrile, the toluonitriles, phenylacetylene, and 1-phenylpropyne. 2-Phenylpropene yields exclusively a $[2_\pi + 2_\pi]$ cycloadduct with furan whereas both types of addition occur with styrene. In contrast, 1,4–2',5'(*para*)-photocycloaddition is the sole or principal reaction from 254 nm irradiation of isoprene, 2,3-dimethylbuta-1,3-diene, or 2,3-dimethoxybuta-1,3-diene with benzonitrile; only with the fixed *cis*-1,3-diene, 1,2-dimethylenecyclohexane, is the *meta*-cycloadduct formed in significant amounts. The control over the regio- and stereo-chemistries of the *meta*-cycloaddition is discussed in terms of substituent stabilization of the developing polarity in the electronically excited aromatic ring on approach of the addends and secondary orbital interactions.

The photochemical addition of 1,3-dienes to the benzene ring is notoriously unselective giving 1:1 adducts derived from 1,4-*para* and 1,4-*meta*-processes as well as 2:1 and 2:2 adducts and 1-phenylbuta-1,3-dienes.[1] The addition is appreciably more selective and favours the 1,4-*para*-reaction for diene addends which have a preferred *cisoid* conformation (2,4-dimethylpenta-1,3-diene)[2] and for those which are constrained in a *cis*-geometry (1,2-dimethylenecyclohexane).[3] This limited direction of the reaction is, however, lost for the addition of furan to benzene[4,5] and alkyl benzenes[5] and again multicomponent mixtures are obtained but in which the 2,5-*para*-cycloadduct is generally the major product.

Arene substituents such as methoxy, cyano, and trifluoromethyl exert powerful directing effects on the mode of photocycloaddition of ethenes to the benzene ring (*i.e. ortho versus meta*-process)[6,7] and on the regio- and stereo-chemistries of the reactions.[8,9] These features have given a clear insight into the mechanisms of these processes.[6–11] In particular, the regiochemistry of the *meta*-photocycloaddition reaction is rationalized by the substituents directing the orientation of the

addends, as shown in Scheme 1, to provide maximum stabilization of the charge centres developing in the six-membered ring on approach of the ethene.[11] This latter reaction feature is satisfying supported and the direction of polarity in the benzene ring confirmed by semi-empirical calculations.[12]

Our renewed interest in furan–benzene and diene–benzene systems was initially to assess the feasibility of increasing the selectivity of these additions by the introduction of electron-acceptor substituents in the arene; this would increase polar interactions with the electron-donor addends and thereby possibly align the molecules in one orientation preferentially. In the ground state, such interactions are expected to orient the furan and benzene ring as in (1) and if these were carried over


(1)

(3)
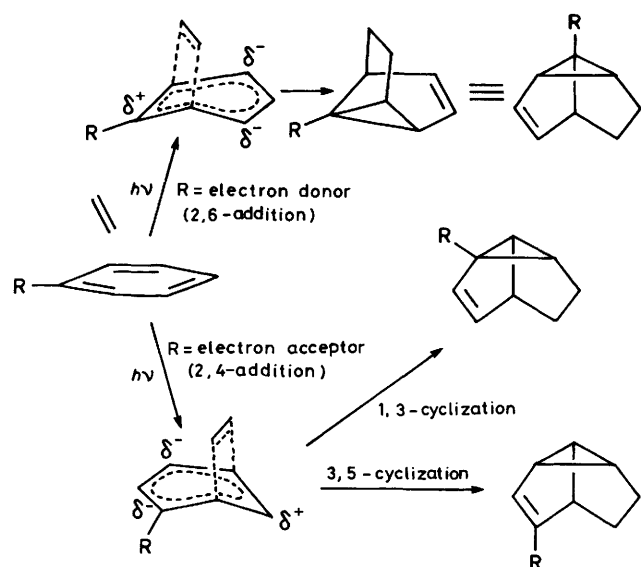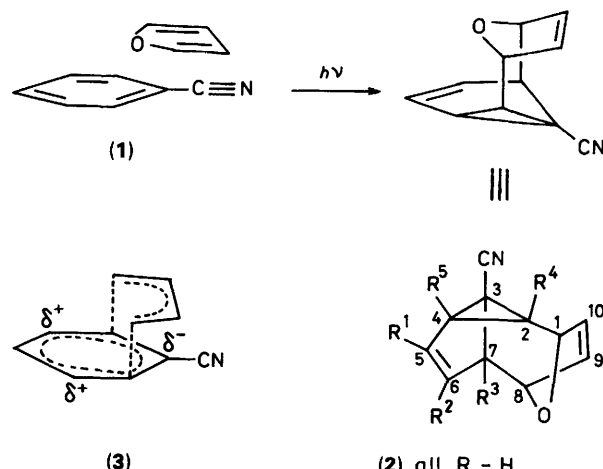
(2) all R = H
(4) R¹ = Me, other R = H
(5) R³ = Me, other R = H
(6) R⁴ = Me, other R = H
(7) R⁵ = Me, other R = H
(8) R² = Me, other R = H

Scheme 1.

to an intermediate excited state complex then subsequent addition may lead selectively to the 2,5-2',6'-cycloadduct (2) (*i.e. meta*-cycloaddition to the arene). It is, however, to be noted that this increase in the electron-donor–electron-acceptor relationship of the addends may, as in the photocycloaddition

of ethenes to the benzene ring, disfavour the *meta*-process.[7] Further, the *meta*-cycloaddition of ethenes having electron-withdrawing substituents occurs at the arene 2,4-positions (see Scheme 1) reflecting stabilization of the developing allyl anionic moiety in the six-membered ring.[10] The deduced orienting effects from ground-state polarity of the addends and the stabilization of developing charges in the six-membered ring thus appeared to be at variance with one another. This transpired not to be the case and in this paper we present the details of our preliminary report concerning the photo-cycloaddition of furan to benzenes[13] and consider the mechanism to account for the observed regio- and stereo-specificities in this reaction as well as assess the scope of using the arene substituents to direct the addition of 1,3-diene units to the benzene ring.

Results and Discussion

The photochemical reaction of furan and benzene yields the 1:1 adducts outlined in Scheme 2 in amounts dependent on

Scheme 2.
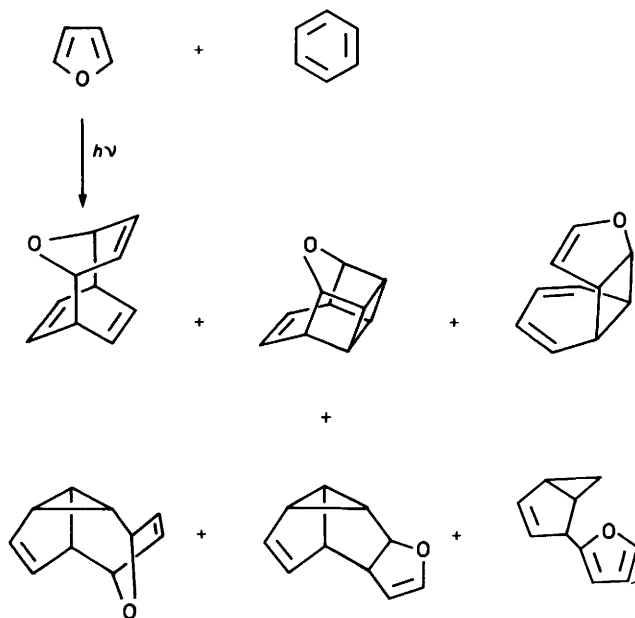
the reaction conditions and reflecting their variable photo-labilities.[4,5] In marked contrast, 254 nm irradition of mixtures of furan and benzonitrile gave the 1:1 adduct (2) as the sole product. Isolation of (2) (m.p. 63.5–64.5 °C) was readily achieved in gram quantities by flash chromatography of the vacuum-distilled product from 48 h irradiations (100 ml, of 9:1 v/v mixtures of the arene and furan respectively). The reaction product thus reflects a 2,5-2′,6′-cycloaddition of the furan to benzonitrile and the prior orientation of the addends as in (1). The formation of (2) is inconsistent with the direction of polarity developed in the aromatic ring on approach of an ethene; as shown in Scheme 1 this would lead to attack of the furan at the arene 2,4- and not the observed 2,6-positions. However, following our preliminary communication on the formation of (2),[13] Professor Mulder and Dr. van der Hart kindly informed us that from semiempirical calculations of photoadditions to the benzene ring it is concluded that the approach of a 1,3-diene moiety to the excited arene would lead, during the early stages of the reaction, to a developing polarity in the six-membered ring which is the reverse of that produced by the approach of an ethene.[14] The result of this polarity reversal is that, for an

Table 1. Photocycloaddition of furan to the toluonitriles.

Arene	Addend orientation	Adducts		Respective ratio of adducts
		(1, 3)[a]	(1, 5)[a]	
p-Toluonitrile R³ = Me, R¹ = R² = H (4)				
o-Toluonitrile R¹ = Me, R² = R³ = H(5)		(6)		1.0:0.85
m-Toluonitrile R² = Me, R¹ = R³ = H(7)		(8)		1.0:2.8

[a] Carbon atoms between which the cyclopropane ring formation occurs.

electron-withdrawing substituent on the arene to stabilize the developing negative charge during the 1,3-diene addition, it is required that the addends become oriented with the diene over the 2,6-positions of the benzene ring as in (3) (*cf.* Scheme 1 for ethene addition). Thus in the present reaction of furan and benzonitrile, the ground-state interaction (1) of the addends predicted from the reactant polarity is the same as that deduced in the excited state based on the substituent stabilization of developing charges in the aromatic ring. Furthermore, in the formation of (2) additional control to give the *exo*-specificity may be provided by the interaction of the lone pair on oxygen with the developing positive charge in the electronically excited arene. Thus for these addends there is total control over the mode and regio- and stereo-chemistries of the reaction and, in particular, the electron-donor–acceptor relationship of the addends does not inhibit the *meta*-addition and promote alternative pathways as in ethene additions to the benzene ring.[6,7]

  meta-Photocycloaddition to substituted benzenes can give rise to product isomers as a result of the two different ways that the cyclopropane ring can be formed during the reaction; this applies whether this intramolecular cyclization is simultaneous with or subsequent to the bonding between the addends.[11] For 2,6-addition to mono-substituted arenes, as in the present case, this feature simply yields enantiomers but for other regiochemistries of reaction or with 1,2- or 1,3-disubstituted benzenes, positional isomers of the adducts will result. In the case of ethene additions there is frequently little selectivity in this cyclization but as we have shown the process can be directed specifically by a chloro-substituent on the addend for both the inter-[15] and intra-[16] molecular *meta*-cycloadditions. A potentially more versatile effect to influence the direction of cyclopropane ring formation in *meta*-photocycloadditions originates from the electron-donor or electron-acceptor characteristics of the substituents on the arene 2-position.[17] In particular, during addition of ethenes to the arene 2,6-positions, a 2-methyl substituent shows a preference for promoting intramolecular cyclization between the 1,5- rather than the 1,3-positions (*ca.* 1:0.5 respectively).[18] In contrast, a methyl group at the 3- or 5-positions (*i.e.* positions to which the cyclization occurs) affects the adduct isomer ratio to only a small degree.[19] In order to assess these substituent influences on the present specific photocycloaddition, we examined the photoreactions of the furan–toluonitrile systems; these results are summarized in Table 1. The reactions of the toluonitriles were appreciably less efficient (*ca.* 5 ×) than the furan–benzonitrile system but again the additions are specifically at the 2,6-positions of the arene and the addition has exclusively *exo*-stereochemistry. Thus for the *para*-arene isomer only one product is formed and so there is no evidence that the stabilizing influence of the methyl group

Table 2. Photoproducts from irradiation of furan with benzenes having conjugative substituents.
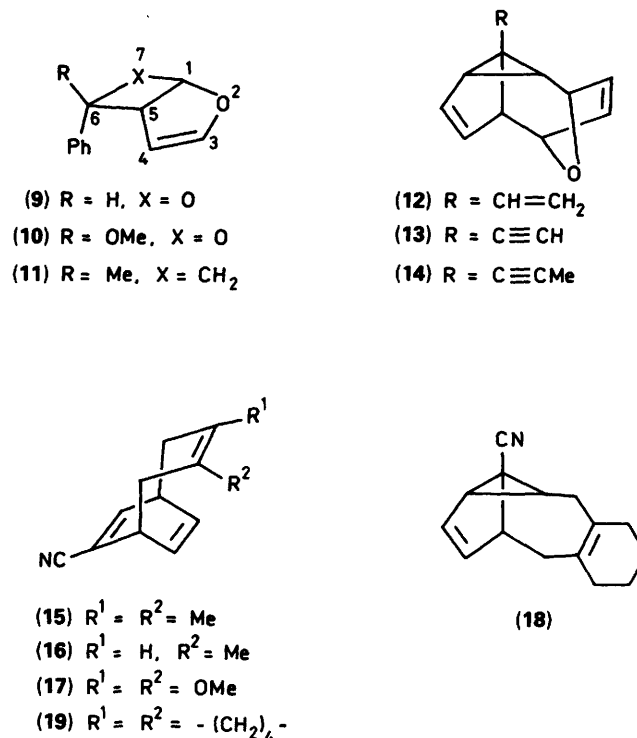
Arene	Photoproducts	Respective ratio
Benzaldehyde	Oxetane (9)	
Methyl benzoate	[Oxetane (10)] ⟶ Benzoylfuran	
2-Phenylpropene	Cyclobutane dimers, $[2_\pi + 2_\pi]$ adduct (11)	1:1.4
Styrene	Cyclobutane dimers, $[2_\pi + 2_\pi]$ adduct, *meta*-cycloadduct (12)	1:1.7:1.7
Phenylacetylene	*meta*-Cycloadduct (13), arene dimers	3:1
1-Phenylpropyne	*meta*-Cycloadduct (14), arene dimers	5.7:1

on the developing positive charge in the six-membered ring competes to any discernable degree with the corresponding effect of the cyano group on the negative charge and aligns the addends differently from the orientation in (3). Similarly for *o*-toluonitrile the cyano group is the dominant orienting substituent but the directing effect of the methyl group on the cyclopropane formation in the adduct is less than that observed for ethene *meta*-cycloadditions. In contrast, the methyl substituent of *m*-toluonitrile appears to have a marked influence on the direction of the intramolecular cyclization and closure between the 1,5-positions is greatly preferred. As noted above, substituents at this position have little influence on the direction of cyclopropane formation during the *meta*-cycloaddition of ethenes but in such cases the methyl group is substituted at the terminus of a developing allylic anionic moiety to which it would give little stabilization. Electron-withdrawing groups can, of course, stabilize this system and the addition of cyclopentene to benzonitrile or α,α,α-trifluorotoluene leads to 2,4-addition and a degree of preferential cyclization involving the 1,3-positions.[10] With the proposed reversal of polarity in the six-membered ring for the furan addition, the stabilizing influences of the substituents in *m*-toluonitrile reinforce one another and in this case the methyl group resides on a developing allylic cationic moiety. The observed preferred direction of cyclopropane ring formation reflects the slightly lower electron density at the 5- than the 3-position determined by simple Hückel MO calculations.[20]

We next examined what directing influence other conjugative substituents would have on the regiochemistry of the furan addition; these results are summarized in Table 2. Not surprisingly, the photoreaction of furan with aryl carbonyl compounds did not involve addition to the benzene ring but occurred exclusively at the arene substituent and although recent studies of the addition of furan to benzaldehyde only describe 1:2 cycloadducts,[21] in our hands the product was the 1:1 oxetane (9). We were not, however, able to detect the oxetane from furan and methyl benzoate. Instead 3-benzoylfuran was obtained, presumably by loss of methanol from the labile oxetane (10). It may have been expected that furan would photoreact similarly with the vinyl substituent of styrene and 2-phenylpropene. Indeed, irradiation of the latter arene in furan solution gave only two diphenylcyclobutanes (arene dimers) and the 1:1 adduct (11) in a respective ratio of 1:1:4. In a similar experiment, however, styrene yielded the *exo-meta*-cycloadduct (12) as well as the expected $[2_\pi + 2_\pi]$ adduct and arene dimers in a ratio of 1:1.7:1.7 respectively. It thus appears that the vinyl group is providing some small degree of influence over the orientation of the phenyl group and the furan to give a specific 2,6-*exo*-addition. This effect may originate from a secondary orbital interaction between the furan and arene substituent. Clearly the alignment of the addends in this case is not as well oriented for addition to the

benzene ring as that for benzonitrile since in the latter system no addition of the type observed for electron-donor ethenes[22] occurs to the cyano group. The lack of addition to the arene in 2-phenylpropene is then interpreted in terms of the methyl group twisting the π-system out of planarity and the interaction which does occur between the furan and the ethene moiety simply results in their $[2_\pi + 2_\pi]$ photocycloaddition.

If this is indeed the correct interpretation of the styrene and benzonitrile results it then appears that the successful secondary orbital interaction to orient that addends for 2,6-addition to the aromatic ring is only ideally achieved for π-bonded substituents whose axis bisects and passes through the plane of the aromatic ring. The obvious test of this proposal lies in the photoreactions of phenylacetylenes and furan. Furthermore, in contrast to the benzonitriles, in phenylacetylenes there will be little tendency for the addends to take up a preferred orientation in the excited state as a result of the substituent stabilizing the developing negative charge in the arene on approach of the furan. Phenyl-acetylenes are known to undergo photodimerization to yield 1-phenylazulenes and 1-phenylnaphthalenes.[23] This pathway was, however, minimized by irradiation of 5% v/v solutions of phenylacetylene or 1-phenylpropyne in furan; the only other photoproduct formed in each case was a 1:1 adduct in 75 and 85% of the total reaction yield respectively. Structures (13) and

(9) R = H, X = O
(10) R = OMe, X = O
(11) R = Me, X = CH₂

(12) R = CH=CH₂
(13) R = C≡CH
(14) R = C≡CMe

(15) R¹ = R² = Me
(16) R¹ = H, R² = Me
(17) R¹ = R² = OMe
(19) R¹ = R² = -(CH₂)₄-

(18)

(14) were assigned to the adducts from phenylacetylene and 1-phenylpropyne respectively and hence as for benzonitrile the addition is specifically at the 2,6-arene positions with *exo*-stereochemistry. Thus it is concluded that secondary orbital interactions between the arene substituent and furan are an important feature in controlling the mode and the stereochemistry of the addition process and where this directing effect is absent as in benzene and methylbenzenes then little selectivity is observed.

It was of interest to determine if such control would be observed in the additions of 1,3-dienes to the aromatic ring. The 1,3-dienes chosen for study with benzonitrile were 2,3-dimethyl-buta-1,3-diene, isoprene, and 2,3-dimethoxybuta-1,3-diene: these results are summarized in Table 3. The first of these

Table 3. Photocycloaddition of 1,3-dienes to benzonitrile.

1,3-Diene	Cycloadduct
2,3-Dimethylbuta-1,3-diene	1,4-*para*-Adduct (15)[24]
Isoprene	1,4-*para*-Adduct (16) + other 1:1 adducts
2,3-Dimethoxybuta-1,3-diene	1,4-*para*-Adduct (17) + other 1:1 adducts
1,2-Dimethylenecyclohexane	1,4-*meta*-Adduct (18) + 1,4-*para*-adduct (19) (respective ratio 1.0:2.6)

systems has been described by Japanese workers and reported to give the 1,4-2′,5′-cycloadduct (15).[24] This account has been frequently overlooked in reports of similar studies and in view of the implied specificity for the *para*-cycloaddition to the aromatic ring compared to our observation of an exclusive *meta*-reaction with furan, we reinvestigated this system. The sole 1:1 adduct does indeed have structure (15) and is formed in a 4:1 ratio with uncharacterized diene dimers (M^+ m/z 164). Crystals of the adduct, m.p. 73–74 °C, are conveniently obtained in gram quantities by storing the distilled product mixture from irradiations for 24 h of mixtures (50:50 v/v; 50 ml) of the addends. Such a $[2_\pi + 4_\pi]$ photoreaction is the most commonly observed process for 1,3-diene–arene reactions but is remarkable in the present case for the absence of competing addition processes. In contrast, each of the other two conformationally mobile dienes gave at least three 1:1 adducts although again the *para*-cycloadducts [*i.e.* (16) and (17)] were the major product constituting 55 and 80% respectively of the reaction mixture. Thus, although there has .been a change in the preferred mode of reaction in going from furan to 1,3-dienes, it is apparent that the arene substituent still has a marked controlling influence on the regiochemistry of the addition. Furthermore, in contrast to the major products from 1,3-diene–benzene systems[1,25] the present adducts all reflect involvement of the *cisoid* diene. We therefore examined the reaction of benzonitrile with a fixed *cis*-1,3-diene. 1,2-Dimethylenecyclohexane was chosen in preference to cyclopentadiene or cyclohexa-1,3-diene since these latter have a marked propensity for photodimerization. The *meta*- and the *para*-adduct isomers (18) and (19) were essentially the sole products of this irradiation and were formed in a respective ratio of 1.0:2.6. It is, therefore, evident that the cyano substituent does control the regiochemistry of each type of addition, but has little influence on the reaction mode selectivity and, as in the addition of this diene to benzene, the *para*-process is favoured.

It does, however, remain to be seen if the control of addend orientation and isomer formation observed in the present systems is widely applicable and can be exploited in other 1,3-diene–arene cases of synthetic interest.

Experimental

The photochemical procedures, analytical instrumentation, and methods of chromatographic separation, in the present study are the same as those described in reference 15. No attempt was made in this study to optimize product yields.

Photochemical Reactions.—(a) *Benzonitrile and furan.* For preparative purposes, benzonitrile (180 ml) and furan (20 ml) were irradiated (254 nm) for 48 h with periodic cleaning of the quartz tubes and gave, after vacuum distillation (130–140 °C; 0.05 mmHg) of the sole product, a pale yellow oil (3.8 g). Flash chromatography [10% diethyl ether in light petroleum (b.p.

30–40 °C)] of the oil to remove minor contaminants gave crystals, m.p. 63.5–64.5 °C (from pentane), of (2). The ^{1}H NMR and IR data of (2) are given in ref. 13; δ_C(22.5 MHz, CDCl$_3$) 136.6, 134.9, 129.7, 127.6, 125.4, 77.1, 76.7, 46.2, 44.0, 30.4, and 18.7 (Found: C, 77.1; H, 5.25; N, 8.1%. C$_{11}$H$_9$NO requires C, 77.15; H, 5.3; N, 8.2%).

(b) p-*Toluonitrile and furan.* A 40% v/v solution (100 ml) of *p*-toluonitrile in furan gave a pale orange oil (1.5 g) after vacuum distillation (140–150 °C; 0.05 mmHg) following irradiation for 40 h. The cycloadduct (4) was isolated and further purified (>99%) by flash chromatography [diethyl ether–light petroleum (b.p. 30–40 °C), 1:1]; δ_H(220 MHz, C$_6$D$_6$) 6.06 (10-H, ddd, $J_{9,10}$ 6.0, $J_{1,10}$ 1.6, $J_{8,10}$ 0.7 Hz), 5.77 (9-H, dd, $J_{8,9}$ 1.8 Hz), 4.69 (6-H, m, $J_{6,7}$ 2.2, $J_{2,6}$ 1.4, $J_{6,Me}$ 0.6 Hz), 4.59 (1-H, br overlapping dd), 3.99 (8-H, br overlapping dd, $J_{7,8}$ 2.2 Hz), 2.67 (7-H, m), 2.20 (4-H, br d, $J_{4,Me}$ 0.4, $J_{2,4}$ 7.8 Hz), 1.67 (3-H, br s, Me), and 0.91 (2-H, overlapping doublets, $J_{1,2}$ 1.6 Hz); ν_{max}(liquid film) 2 230s and 1 609w cm^{-1}, [Found: M^+, 185.0840 (2.8%). Calc. for C$_{12}$H$_{11}$NO: M, 185.0838].

(c) o-*Toluonitrile and furan.* Irradiation of an equivolume mixture (75 ml) of the addends for 48 h gave 1.0 g of a vacuum-distilled (140–150 °C; 0.01 mmHg) pale yellow oil. The two cycloadducts were separated and isolated in >98% purity by preparative GLC (20% Apiezon L + 2% KOH on 60–80 mesh Chromosorb P). Adduct (5) showed δ_H(220 MHz, CDCl$_3$) 6.59 (10-H, dd, $J_{9,10}$ 6.0 Hz), 6.32 (9-H, dd, $J_{8,9}$ 1.9 Hz), 5.86 (5-H, dd, $J_{5,6}$ 5.5, $J_{4,5}$ 2.8 Hz), 5.34 (6-H, dd, $J_{2,6}$ 1.6 Hz), 5.07 (1-H, overlapping dd, $J_{1,10}$ 1.5 Hz), 4.16 (8-H, d), 2.96 (4-H, dd, $J_{2,4}$ 8.0 Hz), 1.51 (2-H, overlapping doublets, $J_{1,2}$ 1.8 Hz), and 1.28 (3 H, s, Me); ν_{max}(liquid film), 2 227m and 1 670w cm^{-1} [Found: M^+, 185.0841 (22.5%)]. Adduct (6) had δ_H(220 MHz, CDCl$_3$) 6.63 (10-H, dd, $J_{9,10}$ 5.9, $J_{8,10}$ 0.6 Hz), 6.32 (9-H, dd, $J_{8,9}$ 2.0 Hz), 5.99 (5-H, dd, $J_{4,5}$ 2.7 Hz), 5.44 (6-H, dd, $J_{5,6}$ 5.6, $J_{6,7}$ 2.2 Hz), 4.88 (1-H, d, $J_{1,10}$ 1.6 Hz), 4.38 (8-H, overlapping doublets, $J_{7,8}$ 2.3 Hz), 3.28 (7-H, overlapping doublets), 2.51 (4-H, d), and 1.46 (3 H, s, Me); ν_{max}(liquid film) 2 226 m and 1 603 m cm^{-1} [Found: M^+, 185.0842 (17.9%)].

(d) m-*Toluonitrile and furan.* Following irradiation for 48 h of an equivolume mixture (100 ml) of the addends vacuum distillation gave a mixture of the adducts as a pale yellow oil (1.2 g). The two adducts were separated by preparative GLC (above conditions) in >99% purity. Adduct (7) had δ_H(220 MHz, CDCl$_3$) 6.53 (10-H, dd + fine splitting, $J_{9,10}$ 6.0, $J_{1,10}$ 1.5, $J_{8,10}$ 0.5 Hz), 6.27 (9-H, dd, $J_{8,9}$ 1.8 Hz), 5.81 (5-H, d, $J_{5,6}$ 5.5 Hz), 5.39 (6-H, dd, $J_{6,7}$ 2.3, $J_{2,6}$ 1.3 Hz), 5.03 (1-H, overlapping doublets, $J_{1,2}$ 1.8 Hz), 4.43 (8-H, br d), 3.20 (7-H, overlapping doublets, $J_{7,8}$ 2.4 Hz), 1.45 (3 H, s, Me), and 1.25 (2-H, overlapping doublets); ν_{max}(liquid film) 2 228m and 1 603 cm^{-1} [Found: M^+, 185.0835 (10.5%)]. Adduct (8) showed δ_H(220 MHz, CDCl$_3$) 6.57 (10-H, dd + fine splitting, $J_{9,10}$ 5.8, $J_{1,10}$ 1.6, $J_{8,10}$ 0.6 Hz), 6.32 (9-H, dd, $J_{8,9}$ 2.0 Hz), 5.53 (5-H, m, $J_{5,Me}$ 1.5, $J_{4,5}$ 2.6 Hz), 5.02 (1-H, overlapping doublets, $J_{1,2}$ 1.8 Hz), 4.59 (8-H, overlapping doublets, $J_{7,8}$ 2.5 Hz), 2.92 (7-H, br d, $J_{7,Me}$ 0.4 Hz), 2.83 (4-H, m, $J_{2,4}$ 7.8 Hz), 1.79 (3 H, dd, Me), and 1.42 (2-H, dd); ν_{max}(liquid film) 2 230 m and 1 605 cm^{-1} [Found: M^+, 185.0833 (15.8%)].

(e) *Benzaldehyde and furan.* Irradiation of a 20% v/v solution (10 ml) of benzaldehyde in furan for 48 h and vacuum distillation (50–60 °C; 0.1 mmHg) gave 6-phenyl-2,7-dioxabicyclo[3.2.0]hept-3-ene (9) (0.3 g) as an oil; flash chromatography [5% diethyl ether in light petroleum (b.p. 60–80 °C)] led to a purity of >99%; δ_H(220 MHz, CDCl$_3$) 7.42–7.30 (5 H, m, Ph), 6.62 (3-H, ddd, $J_{3,4}$ 2.9, $J_{3,5}$ 1.5 Hz), 6.47 (1-H, overlapping doublets, $J_{1,5}$ 4.4, $J_{1,3}$ = $J_{1,6}$ = 0.8 Hz), 5.51 (6-H, br d), 5.40 (4-H, overlapping doublets, $J_{4,5}$ 2.8 Hz), and 3.58 (5-H, m, $J_{5,6}$ 3.2 Hz); ν_{max}(liquid film) 1 600m, 1 050s, and 950s cm^{-1} [Found: M^+, 174.0682 (1.4%). Calc. for C$_{11}$H$_{10}$O$_2$: M, 174.0678].

(f) *Methyl benzoate and furan.* Irradiation of a 20% v/v solution (100 ml) of methyl benzoate in furan for 72 h gave 3-benzoylfuran (2.0 g) following vacuum distillation and flash chromatography.

(g) 2-*Phenylpropene and furan.* Irradiation for 48 h of a 5% v/v solution (150 ml) of 2-phenylpropene in furan gave, following vacuum distillation, 3.0 g of a mixture of a 1:1 adduct and dimers of the arene. The adduct (11) was separated from the mixture by preparative GLC (above conditions) with purity >99%, δ_H 7.47–7.28 (3 H, m, Ph), 7.20–7.11 (2 H, m, Ph), 6.17 (3-H, dd, $J_{3,4}$ 2.8, $J_{3,5}$ 1.5 Hz), 5.12 (1-H, overlapping dd + fine splitting, $J_{1,5} = J_{1,7} = 6.8$ Hz), 4.87 (4-H, overlapping dd, $J_{4,5}$ 2.8 Hz), 3.67 (5-H, m, $J_{5,7}$ 3.6 Hz), 2.73 (7-H′, br dd, $J_{1,7'}$ 5.2, $J_{5,7'}$ 1.2 Hz), 2.45 (7-H, 8 lines, $J_{7,7'}$ 12.4 Hz), and 1.48 (3 H, s, Me); δ_C(22.5 MHz, CDCl$_3$) 147.9, 146.2, 128.2, 128.0, 125.7, 125.4, 103.6, 75.6, 55.8, 45.5, 41.0, 33.2, and 21.8; ν_{max}(liquid film) 1 600 cm^{-1} [Found: M^+, 186.1307 (1.5%). Calc. for $C_{12}H_{12}O_2$: M, 186.1041].

(h) *Styrene and furan.* A 5% v/v solution (280 ml) of styrene in furan after irradiation for 96 h and vacuum distillation (110–120 °C; 0.5 mmHg) gave a pale oil (6.0 g) consisting of two 1:1 adducts and two dimers of styrene. The adducts were separated and isolated with purities >98% by preparative GLC (above conditions). Adduct (12) had δ_H(220 MHz, CDCl$_3$) 6.39 (10-H, d of 4 lines, $J_{9,10}$ 6.0, $J_{1,10}$ 1.52, $J_{8,10}$ 0.6 Hz), 6.03 (9-H, dd, $J_{8,9}$ 1.75 Hz), 5.97 (5-H, dd, $J_{5,6}$ 5.4, $J_{4,5}$ 2.6 Hz), 5.48 (–CH=, vinyl, dd, J_{trans} 17.0, J_{cis} 10.7 Hz), 5.41 (6-H, d of 4 lines, $J_{2,6}$ 1.4, $J_{6,7}$ 2.2 Hz), 5.02 (1-H, overlapping doublets, $J_{1,2}$ 1.8 Hz), 4.86 and 4.78 (=CH$_2$, double doublets, J_{gem} 1.12 Hz), 4.51 (8-H, overlapping doublets, $J_{7,8}$ 2.4 Hz), 3.15 (7-H, overlapping doublets), 2.93 (4-H, dd, $J_{2,4}$ 7.4 Hz), and 1.03 (7-H, 6 lines); δ_C(22.5 MHz, CDCl$_3$) 142.3, 136.1, 134.2, 129.3, 128.7, 110.3, 78.0, 77.5, 44.6, 41.3, 35.5, and 30.1; ν_{max} 1 624 and 1 593 cm^{-1} [Found: M^+, 172.0880 (6%). Calc. for $C_{12}H_{12}O$: M, 172.0885]. The [(2$_\pi$ + 2$_\pi$)] cycloadduct showed δ_H 7.34–7.12 (5 H, m, Ph), 6.32 (3-H, dd $J_{3,4}$ 2.8, $J_{3,5}$ 1.8 Hz), 4.99 (1-H, m, $J_{1,7}$ 6.8, $J_{1,7'}$ 5.2, $J_{1,5}$ 6.8 Hz), 4.76 (4-H, overlapping doublets, $J_{4,5}$ 2.8 Hz), 3.96 (5-H, m, $J_{5,6}$ 7.8, $J_{5,7}$ 3.6, $J_{5,7'}$ 1.2 Hz), 3.73 (6-H, 4 lines, $J_{6,7}$ 8.7, $J_{6,7'}$ 8.2 Hz), and 2.68 (7-H and 7-H′, m, $J_{7,7'}$ 9.8 Hz); ν_{max}(liquid film) 1 596 cm^{-1} [Found: M^+, 172.0894 (4%)].

(i) *Phenylacetylene and furan.* A 5% v/v solution (75 ml) of the acetylene in furan was irradiated for 20 h and gave a blue solution consisting of the adduct (13) and two dimers of the arene (1.25 g of vacuum-distilled oil). The adduct was isolated as a crystalline solid, m.p. 64–65 °C (from pentane), either by flash chromatography [20% diethyl ether in light petroleum (b.p. 60–80 °C] or preparative GLC (above conditions), δ_H(220 MHz, CDCl$_3$) 6.55 (10-H, d of 4 lines, $J_{9,10}$ 5.8, $J_{1,10}$ 1.56, $J_{8,10}$ 0.6 Hz), 6.21 (9-H, dd, $J_{8,9}$ 1.8 Hz), 5.97 (5-H, dd, $J_{4,5}$ 2.6, $J_{5,6}$ 5.6 Hz), 5.40 (6-H, d of 4 lines, $J_{2,6}$ 1.4, $J_{6,7}$ 2.2 Hz), 5.01 (1-H, overlapping doublets, $J_{1,2}$ 1.8 Hz), 4.46 (8-H, overlapping doublets, $J_{7,8}$ 2.4 Hz), 3.09 (7-H, overlapping doublets), 2.48 (4-H, dd, $J_{2,4}$ 7.6 Hz), 2.00 (–C≡C–H, s), and 1.23 (2-H, overlapping doublets); δ_C(22.5 MHz, CDCl$_3$), 136.5, 134.5, 130.0, 129.3, 128.5, 87.7, 77.7, 77.2, 48.6, 43.4, 31.3, and 22.3 [Found: M^+, 170.0737 (36.4%). Calc. for $C_{12}H_{10}O$: M, 170.0729].

(j) 1-*Phenylpropyne and furan.* A solution (200 ml) of the acetylene (10 g) in furan was irradiated for 72 h and gave a green-blue oil (1.0 g) following vacuum distillation. The oil consisted of the 1:1 adduct (14) and two dimers of the arene. The adduct was isolated in >98% purity by preparative GLC

δ_H(220 MHz, CDCl$_3$) 6.54 (10-H, m, $J_{9,10}$ 6.0, $J_{1,10}$ 1.6, $J_{8,10}$ 0.7 Hz), 6.20 (9-H, dd, $J_{8,9}$ 1.8 Hz), 5.99 (5-H, dd, $J_{4,5}$ 2.6, $J_{5,6}$ 5.4 Hz), 5.38 (6-H, ddd, $J_{2,6}$ 1.4, $J_{6,7}$ 2.2 Hz), 5.10 (1-H, dd, $J_{7,8}$ 2.0 Hz), 5.00 (8-H, br overlapping doublets, $J_{7,8}$ 2.2 Hz), 3.02 (7-H, overlapping doublets), 2.35 (4-H, dd, $J_{2,4}$ 7.4 Hz), 1.75 (3 H, s, Me), and 1.15 (2-H, overlapping doublets) (Found: M^+, 184.0894. Calc. for $C_{13}H_{12}O$: M, 184.0885).

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