meta-Photocycloaddition of trans-1,2-Dichloroethene to the Benzene Ring: Directed Cyclopropane Ring Formation in the Tricyclo[3.3.0.0^{2,8}]oct-3-ene Skeleton

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1,2-*trans*-Dichloroethene undergoes *meta*-photocycloaddition to benzonitrile, the toluonitriles, benzene, phenol, the cresols, fluorobenzene, chlorobenzene, trifluoromethylbenzene, and *m*-trifluoromethylbenzonitrile. The arene substituents selectively direct the positions of ethene attack, but in all cases the formation of the cyclopropane ring in the tricyclo[3.3.0.0^{2,8}]oct-3-ene skeleton is specifically controlled by the ethenyl chlorine to give exclusively the 6-*exo*-7-*endo*-dichloro adduct isomer.

The *meta*-photocycloaddition of ethenes to the benzene ring is a process 'which results in the greatest increase in molecular complexity of any general reaction'.[1] Since the first reports of the addition appeared in 1966[2,3] numerous accounts concerning the scope, limitations, and mechanistic features of the reaction have been published.[4] The regio- and stereo-selectivity of the addition can be rationalised and predicted by a mechanistic sequence involving a polarised bicyclo[3.2.1]-octenyl intermediate (1).[5,6] Theoretical calculations, however, predict that the S$_1$ arene becomes polarised on approach of the S$_0$ ethene[7] and further, kinetic data from the benzene–cyclopentene system are consistent with the reaction proceeding in one step, as outlined in Scheme 1, without the need for a discrete intermediate.[8] However, whether the cyclopropane ring in the adduct is formed simultaneously with, or subsequently to, bonding between the arene and ethene, the problem remains that this intramolecular cyclisation occurs in two ways [*i.e.*, *ab* and *ac* closures in (1)] and with substituted benzenes and/or unsymmetrically substituted ethenes this process leads to mixtures of *meta* cycloadduct isomers. In some systems thermal and/or photochemical interconversion of *meta* cycloadduct isomers can be accomplished by an ethenylcyclopropane–cyclopentene rearrangement,[9] but in our experience such conversions have limited applicability and are seldom quantitative due to the formation of polymeric material or other isomers arising from sigmatropic shifts.[10]

The potential of the *meta*-photocycloaddition as a key step in the synthesis of polyquinanes and related systems has been ably and elegantly demonstrated by Wender and co-workers.[1,11] If, however, the process is to be widely adopted for these and other applications,[12] then control has to be achieved over the direction of the closure giving the cyclopropane ring and hence over the resulting isomer formation in both the inter- and intra-molecular processes. Substituents on the 2-position of benzenoid compounds do induce some selectivity in the direction of ring closure[13] but in our preliminary accounts of the *meta*-photocycloaddition of *trans*-1,2-dichloroethene (TDCE) we described a possible method for specifically directing the cyclopropane formation.[14,15] We now present details of these studies and illustrate the scope and applicability of this novel method for controlling this feature of the *meta*-photocycloaddition reaction.
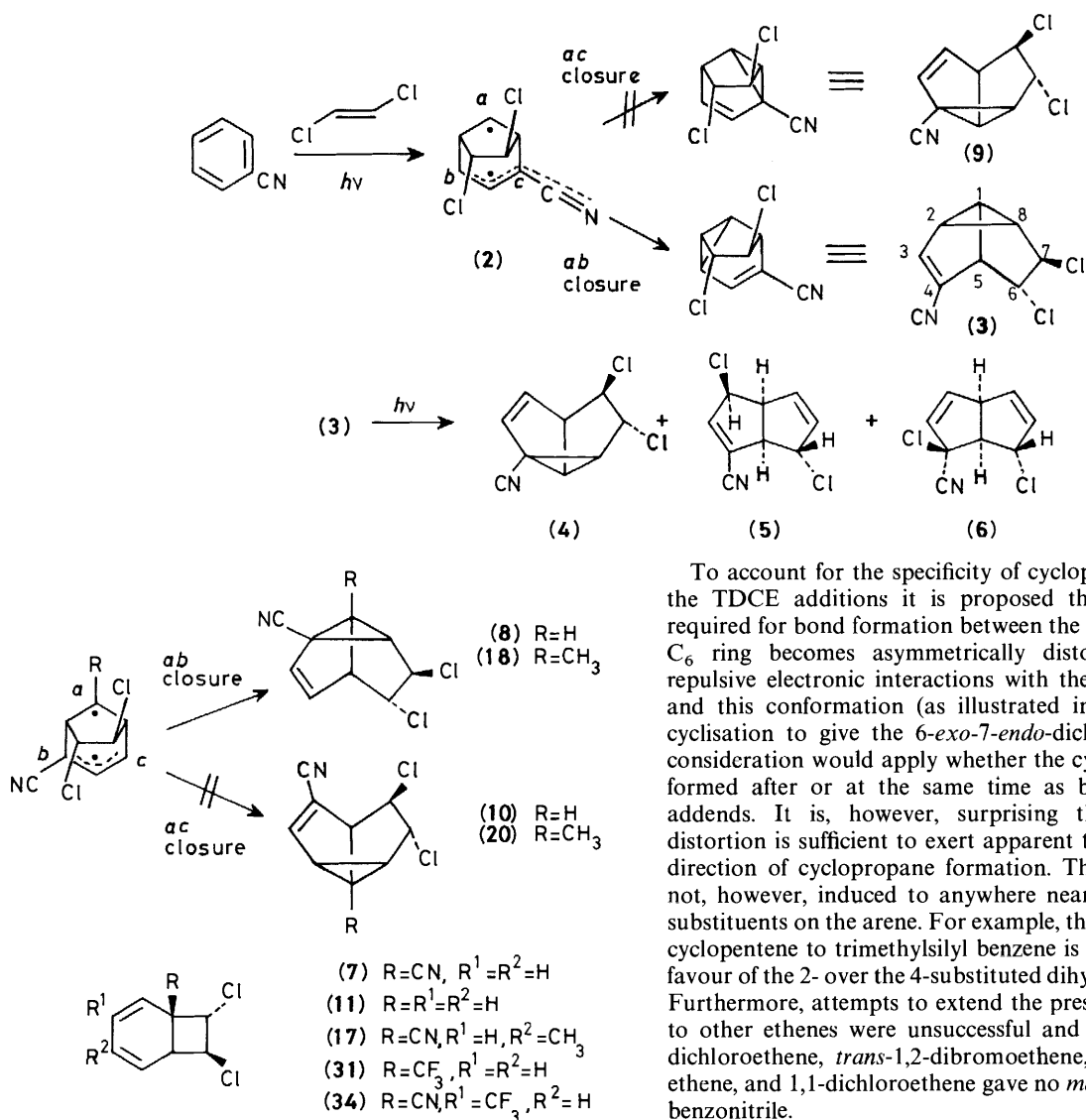
Results and Discussion

(*a*) *Photoaddition of TDCE to Benzonitrile.*—The objective of our studies with TDCE and substituted benzenes was to assess
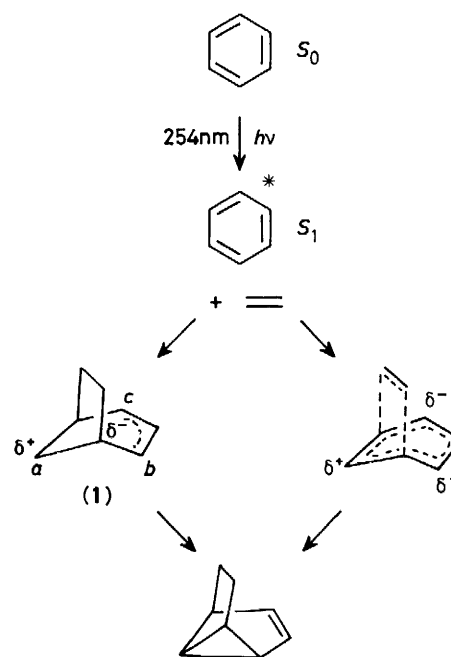
Scheme 1.

the possibility that steric and electronic effects of the addend substituents could be used to orient the ethene and arene preferentially in any precursor exciplex or other reaction intermediate and thereby to induce selectivity in the addition. Benzonitrile was initially used as the arene since it was considered that the nitrile function would delocalise the radical (or negative) centre in the proposed intermediate (2) and this would favour the cyclisation giving (3).[14] An earlier report of the photochemistry of the benzonitrile–TDCE system had only described formation of the *ortho* cycloadduct,[16] but this observation appeared surprising in view of the closely similar electron donor-electron acceptor properties of the addends which is a feature common for arene-ethene pairs preferentially undergoing the *meta* process.[6]

Indeed from 254 nm irradiation of either equivolume mixtures of the reactants or of 1.0M arene and 3.5M ethene in cyclohexane, methanol, or acetonitrile solution, the 4-cyano-6-*exo*-7-*endo*-dichloro dihydrosemibullvalene (3) was the major product. This adduct is, however, photolabile[17] and although it

ac closure ⫫ (9)

(2) *ab closure* (3)

(3) $\xrightarrow{h\nu}$ (4) + (5) + (6)

ab closure (8) R=H
(18) R=CH₃

ac closure (10) R=H
(20) R=CH₃

(7) R=CN, R¹=R²=H
(11) R=R¹=R²=H
(17) R=CN,R¹=H,R²=CH₃
(31) R=CF₃,R¹=R²=H
(34) R=CN,R¹=CF₃,R²=H

comprised *ca.* 95% of the product on short exposure, prolonged irradiation on a preparative scale reduced its proportion to *ca.* 60% of the isomer mixture. However, isolation of (3) was still easily achieved by crystallisation of the distilled reaction mixture and in this way gram quantities of this *meta* cycloadduct are readily available from 100 ml addend solutions irradiated for 16 h.

Three of the five 1:1 adduct isomers in the irradiation mixture following removal of (3) were shown to be derived from secondary photochemical processes of (3), involving ethenyl-cyclopropane–cyclopentene rearrangement and 1,3- and 1,5-chlorine shifts giving approximately equal amounts of (4), (5), and (6) respectively (10% total).[17] The two minor primary photoproducts were identified as the *ortho* cycloadduct (7) (15%) and the *meta* isomer (8) (15%). Significantly the adduct (8) has the same stereochemistry of the chlorine substituents as (3) and although these adducts must arise from different orientations of the addends, neither of the isomers (9) and (10) from the alternative modes of cyclopropane formation were detected. Thus the direction of the intramolecular cyclisation does not result from the delocalising effect of the nitrile substituent. Indeed Cornelisse and co-workers have shown that in the benzonitrile–cyclopentene system the 2,4-cycloaddition leads to a small selectivity favouring the 2- over the 4-cyano substituted dihydrosemibullvalene skeleton.[18]
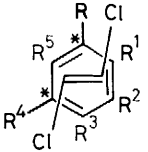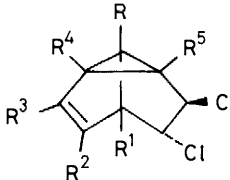
To account for the specificity of cyclopropane formation in the TDCE additions it is proposed that at the proximity required for bond formation between the ethene and arene, the C₆ ring becomes asymmetrically distorted by steric and repulsive electronic interactions with the *endo* chlorine atom and this conformation (as illustrated in Scheme 2) favours cyclisation to give the 6-*exo*-7-*endo*-dichloro adduct.[17] This consideration would apply whether the cyclopropane ring was formed after or at the same time as bonding between the addends. It is, however, surprising that the asymmetric distortion is sufficient to exert apparent total control over the direction of cyclopropane formation. This type of control is not, however, induced to anywhere near the same extent by substituents on the arene. For example, the *endo* 2,4-addition of cyclopentene to trimethylsilyl benzene is only 57% selective in favour of the 2- over the 4-substituted dihydrosemibullvalene.[19] Furthermore, attempts to extend the present substituent effect to other ethenes were unsuccessful and in particular *cis*-1,2-dichloroethene, *trans*-1,2-dibromoethene, *trans* 1,2-di-t-butyl-ethene, and 1,1-dichloroethene gave no *meta* cycloadducts with benzonitrile.

C₆H₆+TDCE $\xrightarrow{h\nu}$ *ab closure* (12)
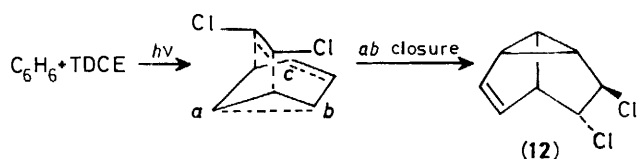
Scheme 2.

We next examined the reactions of a variety of TDCE-substituted benzene systems in order to assess how widely applicable the *endo* C–Cl controlling effect was in the *meta*-photocycloaddition reaction. Firstly, however, a reinvestigation of the TDCE–benzene system was necessary so that the effect with no directing aryl substituent could be determined: earlier work on 1,2-dichloroethenes had been largely concerned with the *cis* isomer and also primary photochemical adducts had not been detected.[20] The reaction of TDCE with benzene proceeded approximately ten times faster than that of the *cis* isomer, and gave β-chlorostyrenes and tetrachlorocyclobutanes (together 30%) and two 1:1 adducts in a ratio of 1:2.5. The minor isomer was isolated as its adduct with *N*-phenylmaleimide and was, therefore, assigned the *ortho* cycloadduct structure (11). The major product was separated by preparative h.p.l.c. and identified as the 6-*exo*-7-*endo*-dichloro *meta* cycloadduct (12): hence specific control over isomer formation is again exerted by

Table 1. Photoaddition of TDCE to toluonitriles[a]

Arene	Addend orientation		Adduct(s)
m-Toluonitrile	R = CH₃, R² = CN, other R's = H	⟶	(13)[b] R = CH₃, R² = CN, other R's = H
p-Toluonitrile	R² = CN, R⁵ = CH₃, other R's = H	⟶	(14)[b] R² = CN, R⁵ = CH₃, other R's = H
	R¹ = CH₃, R⁴ = CN, other R's = H	⟶	(15)[b] R¹ = CH₃, R⁴ = CN, other R's = H. Ratio (14):(15) = 1:1
o-Toluonitrile	R² = CN, R³ = CH₃, other R's = H	⟶	(16)[c] R² = CN, R³ = CH₃, other R's = H

[a] Efficiency of product formation essentially unaffected by solvent polarity. [b] Essentially sole product(s) at short irradiation times. [c] Comprises ca. 40% of the reaction mixture.
* Carbon atoms of the arene between which cyclopropane formation occurs exclusively.

the endo C–Cl bond. Alkyl and alkoxy substituents on the benzene ring direct the meta-cycloaddition of ethenes principally to the 2,6-positions, although in the former series the 3,5-addition becomes relatively more favoured as the bulk of the substituent increases.[13,21] However, irradiation of such arenes with TDCE gave complex mixtures, generally in low yields. Analysis of the crude unseparated products by ¹H n.m.r. spectroscopy indicated the presence of both β-chlorostyrenes and 6-exo-7-endo-dichloro meta cycloadducts but isolation of the products with analytically acceptable purities was not achieved. To determine if alkyl groups would undermine the highly selective addition of this ethene to benzonitrile, the TDCE–toluonitrile systems were studied. The resulting meta photocycloadducts and their addend precursor orientations are given in Table 1. The charge stabilising effect of the methyl (+ ve) and cyano (− ve) groups on the polarised arene[8] or in the polarised intermediate[22] reinforce one another for the addition to m-toluonitrile and only one adduct (13) results. With p-toluonitrile the nitrile substituent, as expected,[22] controls the positions of ethene attack and the two adducts arise from 2,4-addition, albeit involving different addend orientations. Nonetheless, the cyclopropane ring formation has again been specifically directed by the endo C–Cl bond. Prolonged irradiation of both systems produced more complex mixtures comprising the primary adducts and their photorearranged isomers. For example the ortho cycloadduct (17), the minor primary meta cycloadduct (18) and the secondary photoisomer (19) were isolated from the m-toluonitrile–TDCE system. As with the less favoured addition to benzonitrile giving (8), the formation of the 2-cyano compound (18) from m-toluonitrile is specific and none of the alternative ring closure product (20) was detected. The photoreactions of o-toluonitrile were not so clear-cut and even very short exposure times produced complex mixtures of which the 6-exo-7-endo-dichloro adduct (16), resulting from a nitrile-oriented addition and endo C–Cl directed cyclopropane formation, was the major component.

The photoaddition of TDCE was successfully accomplished with phenols, fluorobenzene, chlorobenzene and trifluorotoluenes and these results are summarised in Table 2. It may appear at first sight that the stereochemistry of the chlorine substituents in the products from the phenols differs from the exclusive 6-exo-7-endo relationship observed in the other

TDCE meta-photocycloadditions. The formation of these bicyclo[3.2.1]oct-2-en-8-ones is, however, readily accommodated by the mechanism shown in Scheme 3 involving acidolysis of the 1-hydroxy meta cycloadduct.[12] The only previous account of meta-photocycloaddition to a phenol describes the formation of a similar ketone to those described here from the irradiation of cyclopentene and phenol,[23] but in the present case this type of product is more likely to be observed rather than the meta cycloadduct as HCl is evolved during the reaction.

The 3,5- and 2,6-cycloaddition of TDCE to fluorobenzene reflects essentially one addend orientation. This regiochemistry of reaction can be rationalised by the inductive and mesomeric effects of the fluorine substituent stabilising the negative and positive charges respectively in a polarised intermediate, whether this is a bicyclo[3.2.1]octenyl species or the arene immediately prior to addition. The formation of (28) is noteworthy as it represents the first reported photocycloaddition to chlorobenzene. Previously, ethene insertion into the C–Cl bond and radical derived products had dominated the photochemistry of the chloroarene[24] and indeed in the present system ethene dimers, chlorobiphenyls and, in cyclohexane solution, solvent derived products comprise approximately 60% of the reaction mixture. It is, however, surprising from the expected interactions on approach of the addends and the electronic stabilising effects of the fluorine and chlorine substituents that fluorobenzene should yield equal amounts of 3,5- and 2,6-addition products whereas only the latter process is operating for the chloroarene. It would appear that at least in the meta-photocycloaddition reaction the electron-donating resonance effect of chlorine contributes more as a directing influence at some point along the reaction pathway than a combination of the electron-withdrawing effect of the halogen and the lower steric interactions in alternative orientations of the addends.

As in the case of fluorobenzene, the products from the reaction of TDCE and trifluoromethylbenzene indicate one general orientation of approach of the addends, and from this system both the 2,4- and 1,3-cycloadditions result giving (29) and (30) respectively. For trifluoromethylbenzonitrile, the directing influences of the two substituents reinforce one another and this feature promotes the 2,4-orientation of the addends and the formation of the 2,4-disubstituted dihydrosemibullvalenes (32) and (33).

(13)   (19)
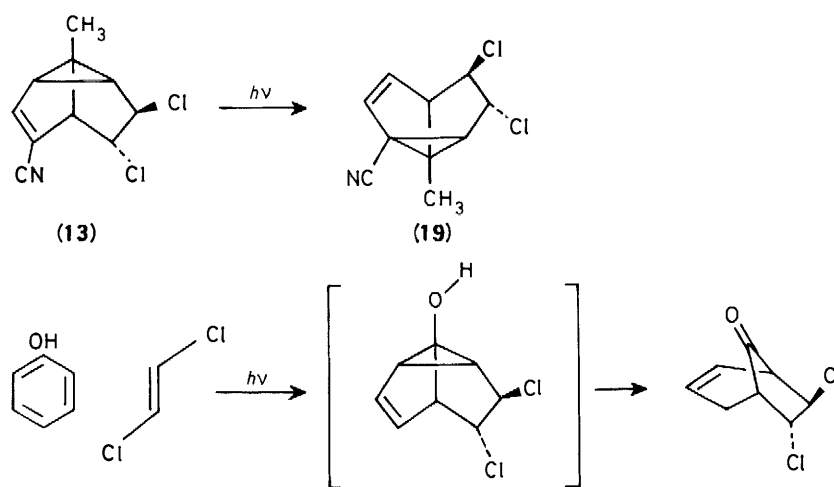
Scheme 3.

Table 2. Photoaddition of TDCE to phenols and halogenated arenes

Addend orientation   Adducts

Arene

Arene	Addend orientation	Adducts	
Phenol	R = OH, other R's = H →	(21) R's = H (70%)†	—
o-Cresol	R = OH, R^5 = CH$_3$, other R's = H →	(22) R^5 = CH$_3$, other R's = H	—
	R = OH, R^1 = CH$_3$, other R's = H →	(23) R^1 = CH$_3$, other R's = H (22):(23) = 1:2 (80%)†	—
m-Cresol	R = OH, R^4 = CH$_3$, other R's = H →	(24) R^4 = CH$_3$, other R's = H (50%)†	—
p-Cresol	R = OH, R^3 = CH$_3$, other R's = H →	(25) R^3 = CH$_3$, other R's = H (80%)†	
Fluorobenzene	R = F, other R's = H	→ (35) → (26) R^3 = F, other R's = H	
		→ (36) → (27) R = F, other R's = H (26):(27) = 1:1	
Chlorobenzene	R = Cl, other R's = H	→ (28) R = Cl, other R's = (50%)†	
Trifluoromethyl benzene	R^2 = CF$_3$, other R's = H	→ (38) → (29) R^2 = CF$_3$, other R's = H	
		→ (37) → (30) R^5 = CF$_3$, other R's = H (29):(30) = 3:1 + minor amounts of *ortho* cycloadducts (31)	
m-Trifluoromethyl- benzonitrile	R^2 = CF$_3$, R^4 = CN, other R's = H	→ (32) R^2 = CF$_3$, R^4 = CN, other R's = H	
	R^2 = CN, R^4 = CF$_3$, other R's = H	→ (33) R^2 = CN, R^4 = CF$_3$, other R's = H (32):(33) = 1:1.5 + minor amounts of *ortho* cycloadduct (34)	

* Carbon atoms of the arene between which cyclopropane formation occurs exclusively. † Percentage of product mixture.

(35)   (36)   (37)   (38)
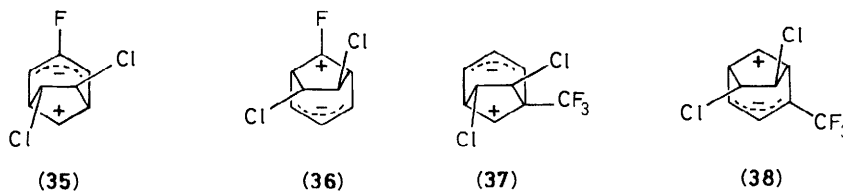
In all systems studied it is evident that the one feature which is constant in the TDCE addition is the specificity in the direction of formation of the three-membered ring in the *meta* cyclo-

adduct. Thus the data presented here show that despite the varying regiochemistries of the ethene addition which are induced by the arene substituents, specific control is gained over

the intramolecular cyclopropane ring formation by an *endo* C–Cl bond effect from the *trans*-1,2-dichloroethene addend. It remains to be seen if this feature can be used to control the addition and isomer formation of systems of synthetic interest. It is also worth noting that the *meta* cycloadducts reported here can be converted in good yield into either tetracyclo-[3.3.0.0^{2,8}0^{4,6}]octanes or semibullvalenes, depending on the nature and position of the substituent.[15]

Experimental

Preparative irradiations involved either equivolume mixtures of the addends or their solutions in cyclohexane in 50 × 1 cm silica tubes using two 60 cm 30W low pressure mercury arc lamps. Solvent effect studies (1.0M arene, 3.5M ethene) were performed in a 'merry-go-round' apparatus fitted with one 15W low pressure mercury arc lamp and holding eight 10 × 1 cm silica tubes. The solvents examined were cyclohexane, ethyl acetate, methyl cyanide or methanol, and 2,2,4,4,6,8,8-hepta-methylnonane was incorporated as the internal standard. Nitrogen degassing of solutions gave 'cleaner' reaction products but did not appreciably influence the reaction efficiency: periodic cleaning of the quartz irradiation tubes greatly increased the yields from preparative irradiations. No attempt was, however, made in this study to optimise product yields. The reactions were monitored by gas chromatography on a Hewlett–Packard 5790A instrument fitted with a flame ionisation detector and a 12m BPI (OVI equivalent) bonded phase capillary column. Isolation of the photoproducts involved removal of the reactants and solvent by rotary evaporation and distillation of the crude mixture at 0.05 mmHg pressure. Adducts (3) and (29) crystallised on storage of the distillate at −20 °C: other separations were achieved either by flash chromatography on Silica Woelm 32 63 or by preparative gas chromatography using a Perkin-Elmer F-21 instrument fitted with a 100 × 6 mm i.d. stainless steel column packed with 18% w/w Carbowax 20M or 20% Apiezon L on 60—80 mesh Chromosorb P. N.m.r. spectra were recorded in CDCl$_3$ solution, unless otherwise stated, on Perkin-Elmer R-34, Joel FX90Q, or Bruker WM250 instruments with TMS as internal reference. Infrared data were obtained using a Perkin-Elmer 1420 spectrophotometer. Elemental analyses were per-formed by the Chemistry Department, The City University, London, and accurate mass data were recorded on a V.G. Micromass 70-70 Spectrometer at the Physico-Chemical Measurement Unit (Harwell) and a Kratos MS80RF instru-ment at the Tate and Lyle Research Centre (Reading): the necessary purity of the sample for accurate mass data was assured in each case by capillary column gas chromatography and by t.l.c. (Camlab Polygram G/u.v. precoated sheets).

Details of the n.m.r. spectra of *meta* photocycloadducts of ethenes and arenes have been extensively published[25] and the present data are consistent with these assignments. Further, the 6-*exo*-7-*endo* dichloro structure of (3) was unambiguously established by X-ray crystallography:[14] the ^{1}H n.m.r. spectral features characteristic of this stereochemistry, and observed in the *meta* cycloadducts reported here, are that the *endo* 6-H appears as a broad singlet ($J_{6,5}$ 0.1, $J_{6,2}$ 1.0, and $J_{6,8}$ 0.01 Hz) and the *exo* 7-H as a double doublet ($J_{7,8}$ 8.0 and $J_{7,5}$ 2.5 Hz).

Photochemical Reactions

(a) *Benzonitrile and TDCE.*—Irradiation of an equivolume mixture (100 ml) of the addends in cyclohexane (200 ml) for 48 h with periodic cleaning of the quartz tubes gave, after vacuum distillation, an orange oil (6 g). The three primary photoadducts (3), (7), and (8) had respective g.c. retention times of 1.88, 1.00,

and 1.39. Adduct (3) crystallised (m.p. 103—104 °C) from the distilled mixture on storage at −20 °C or was separated by flash chromatography [20% diethyl ether in petrol (b.p. 60—80 °C)]. Isomers (7) and (8) were separated from the secondary photoproducts by preparative g.c. (Apiezon L). *Compound* (3), ^{1}H n.m.r. and infrared spectral data given in ref. 14, δ$_C$(22.5 MHz; C$_6$D$_6$) 149.6, 114.2, 73.5, 66.8, 60.2, 43.0, 37.7, and 34.9; λ$_{max}$.(iso-octane) 250 nm (ε$_{max}$. 5 400 l mol^{-1} cm^{-1}) (Found: C, 53.90; H, 3.65; and N, 6.90. C$_9$H$_7$Cl$_2$N requires C, 54.00; H, 3.55; and N, 7.00%). *Compound* (7), δ$_H$ 6.33 (3-H, dd, $J_{2,3}$ 9.5 and $J_{3,4}$ 6.0 Hz), 6.05 (4-H, dd, $J_{4,5}$ 9.5 Hz), 5.88 (5-H, dd and fine splitting, $J_{5,6}$ 6.0, $J_{3,5}$ 1.1, and $J_{2,5}$ 0.9 Hz), 5.70 (2-H, br d), 4.92 (8-H, d), 4.37 (7-H, overlapping dd, $J_{6,7} = J_{7,8}$ 8.5 Hz), and 3.40 (6-H, dd and fine splitting, $J_{6,8}$ 0.3 Hz); ν$_{max}$.(liquid film) 2 228, 1 615, and 825 cm^{-1} [Found: M^+, 198.9947 (20.5%) and 200.9918 (11.5%); calc. M, 198.9956 and 200.9926]. *Compound* (8), δ$_H$ 5.86 (3-H, d, $J_{3,4}$ 5.4 Hz), 5.61 (4-H, dd and fine splitting, $J_{4,5}$ 2.6 Hz), 4.86 (7-H, dd, $J_{5,7}$ 2.6 and $J_{7,8}$ 6.8 Hz), 4.13 (6-H, br s), 3.72 (1-H, overlapping dd, $J_{1,5}$ 7.0 and $J_{1,8}$ 7.0 Hz), 3.61 (5-H, m), and 3.01 (8-H, overlapping dd); ν$_{max}$.(liquid film), 2 236, 1 610, and 898 cm^{-1} [Found: M^+, 198.9951 (10.9%) and 200.9921 (7.2%); calc. M, 198.9956 and 200.9926].

(b) *Benzene and TDCE.*—Irradiation of an equivolume mixture (200 ml) of the addends for 20 h gave, on distillation, a yellow oil (3 g) which darkened on standing at room temperature. The *meta* cycloadduct (12) was isolated by preparative h.p.l.c., δ$_H$ 5.88 (3-H, dd and fine splitting, $J_{3,4}$ 5.4, $J_{2,3}$ 2.4, and $J_{1,3}$ 0.5 Hz), 5.40 (4-H, m, $J_{4,5}$ 2.4 and $J_{1,4}$ 0.7 Hz), 4.84 (7-H, dd, $J_{7,8}$ 6.4 Hz), 4.17 (6-H, br s), 3.38 (5-H, m, $J_{5,7}$ 2.4 Hz), 3.12 (1-H, four lines, $J_{1,2} = J_{1,5} = J_{1,8}$ = 7.0 Hz), 2.30 (8-H, m), and 2.09 (2-H, m, $J_{2,8}$ 8.0 Hz); ν$_{max}$.(liquid film) 1 620 and 940 cm^{-1} [Found: M^+, 173.9998 (11%); calc. M, 174.0002]. The ortho *cycloadduct* (11) was isolated as its Diels–Alder N-phenylmaleimide adduct by refluxing the photoproduct mixture (1.2 g) in diethyl ether (100 ml) in the presence of the dienophile (1.4 g) for 4 h. The 1:1:1 adduct (0.2 g) separated on cooling and was recrystallised from ethyl alcohol, m.p. 228—230 °C, δ$_H$ 7.55 (3 H, m, Ph), 7.23 (2 H, m, Ph), 6.49 (2 H, m), 4.85 (1 H, dd), 4.20 (1 H, br t), 3.32 (2 H, m), 3.14 (2 H, t, and 3.06 (2 H, m); ν$_{max}$.(Nujol mull) 1 714 cm^{-1} (Found: C, 61.63; H, 4.36; and N, 4.17%. C$_{18}$H$_{15}$NO$_2$Cl requires C, 62.08; H, 4.34; and N, 4.02%).

(c) *m-Toluonitrile and TDCE.*—A 48 h irradiation of an equivolume solution (300 ml) of the addends gave the distilled adduct mixture as an orange oil (5 g) comprising the four 1:1 adducts (13), (17), (18), and (19) in a respective ratio of *ca.* 4:1:7:3. Irradiation for 12 h gave a product (1.4 g), of which (13) was essentially the sole component; (13) recrystallised from 10% diethyl ether in pentane, m.p. 132—133 °C, δ$_H$ 6.84 (3-H, d, $J_{2,3}$ 2.75 Hz), 4.95 (7-H, dd, $J_{7,8}$ 6.5 and $J_{5,7}$ 2.5 Hz), 4.44 (6-H, br s), 3.39 (5-H, d), 2.47 (8-H, dd), 2.09 (2-H, dd, $J_{2,8}$ 8.0 Hz), and 1.64 (3 H, s, CH$_3$); δ$_C$(22.5 MHz) 151.4, 115.2, 112.9, 73.1, 67.0, 64.3, 53.9, 43.2, 40.0, and 19.0; ν$_{max}$.(Nujol mull) 2 217, 1 601, and 898 cm^{-1} (Found: C, 56.12; H, 4.19; and N, 6.60%. C$_{10}$H$_9$NCl$_2$ requires C, 56.10; H, 4.25; and N, 6.55%). Isolation of (17), (18), and (19) with purities >99% was achieved by preparative g.c. (20% SE30). *Compound* (17), δ$_H$(300 MHz) 6.21 (3-H, dd, $J_{3,4}$ 9.65 Hz), 5.74 (2-H, d, $J_{2,3}$ 6.0 Hz), 5.54 (4-H, d), 4.88 (8-H, d), 4.28 (7-H, overlapping dd, $J_{7,8}$ 8.0 and $J_{6,7}$ 8.15 Hz), 3.20 (6-H, d), and 1.90 (3 H, s, CH$_3$); ν$_{max}$.(liquid film) 2 240, 1 612, and 817 cm^{-1} [Found: M^+, 213.0104 (18.4%) and 215.0077 (11.8%); calc. M, 213.0112 and 215.0083]. *Compound* (18) δ$_H$(300 MHz) 5.86 (3-H, d, $J_{3,4}$ 5.6 Hz), 5.60 (4-H, dd, $J_{4,5}$ 2.5 Hz), 4.97 (7-H, dd, $J_{7,8}$ 6.8 Hz), 4.14 (6-H, br s), 3.33 (5-H, overlapping dd, $J_{5,7}$ 2.7 Hz), 2.74 (8-H, d), and 1.54 (3 H, s, CH$_3$); ν$_{max}$.(liquid film) 2 240, 1 612, and 817 cm^{-1} [Found: M^+,

213.0104 (16.4%) and 215.0072 (10.2%); calc. M, 213.0012 and 215.0083]. *Compound* (**19**) δ_H(300 MHz) 5.89 (4-H, dd, $J_{4,5}$ 2.5 Hz), 5.80 (3-H, d, $J_{3,4}$ 5.7 Hz), 4.29 (6-H, dd, $J_{6,7}$ 8.0 Hz), 3.81 (7-H, d), 3.29 (5-H, dd, $J_{5,6}$ 5.4 Hz), 2.42 (8-H, s), and 1.50 (3 H, s, CH_3); $\nu_{max.}$(liquid film) 2 238, 1 610, and 917 cm^{-1} [Found: M^+, 213.0106 (10.2%) and 215.0076 (6.4%); calc. M, 213.0012 and 215.0083].

(*d*) p-*Toluonitrile and TDCE.*—A 16 h irradiation of *p*-toluonitrile (30 g) and TDCE (50 ml) in cyclohexane (250 ml) gave, on distillation, a mixture (7.5 g) of the 1:1 adducts (**14**) and (**15**) in a 1:1 ratio. Prolonged irradiation gave a complex mixture of 1:1 adduct isomers. Flash chromatography [5% diethyl ether in petrol (b.p. 30—40 °C)] separated (**14**) and (**15**) in >98% purity. *Compound* (**14**) δ_H 6.80 (3-H, d, $J_{2,3}$ 2.5 Hz), 4.67 (7-H, d, $J_{5,7}$ 2.7 Hz), 4.37 (6-H, br s), 3.63 (5-H, dd), 3.19 (1-H, overlapping dd, $J_{1,2}$ 6.0 and $J_{1,5}$ 5.8 Hz), 2.12 (2-H, m), and 1.45 (3 H, s, CH_3); δ_C(22.5 MHz), 151.4, 115.1, 113.0, 72.3, 72.0, 60.5, 49.3, 46.7, 41.9, and 20.7; $\nu_{max.}$(liquid film) 2 220, 1 607, and 921 cm^{-1} [Found: M^+, 213.0109 (15.1%) and 215.0090 (10.6%); calc. M, 213.0112 and 215.0083]. *Compound* (**15**) δ_H 5.89 (3-H, d, $J_{3,4}$ 5.5 Hz), 5.47 (4-H, d), 4.91 (7-H, d, $J_{7,8}$ 6.4 Hz), 4.06 (6-H, br s), 3.22 (1-H, d, $J_{1,8}$ 6.8 Hz), 2.96 (8-H, overlapping dd), and 1.42 (3 H, s, CH_3); δ_C 137.7, 127.7, 118.6, 77.2, 65.4, 62.3, 50.8, 44.2, 30.4, and 20.1; $\nu_{max.}$(liquid film) 2 240, 1 612, and 892 cm^{-1} [Found: M^+, 213.0089 (1.8%) and 215.0075 (1.0%); calc. M, 213.0112 and 215.0083].

(*e*) o-*Toluonitrile and TDCE.*—A 12 h irradiation of a 25% v/v solution (50 ml) of *o*-toluonitrile in TDCE gave a mixture (1 g) of eight 1:1 adducts (m/z 213—215) in a ratio of 3.7:2.9:1.4:2.5:0.8:2.0:1.8:5.9, in order of increasing g.c. retention time. Isolation of the *major isomer* (**16**) was achieved by preparative g.c. (Apiezon L); δ_H 4.81 (7-H, dd, $J_{7,8}$ 5.6 and $J_{5,7}$ 2.4 Hz), 4.17 (6-H, br s), 4.08 (5-H, dd, $J_{1,5}$ 7.0 Hz), 3.18 (1-H, dd, $J_{1,2} = J_{1,8} = 7.0$ Hz), 2.60 (8-H, m, $J_{2,8}$ 7.8 Hz), 2.06 (3 H, s, CH_3), and 2.02 (2-H, m); $\nu_{max.}$(liquid film) 2 214, 1 599, and 870 cm^{-1} [Found: M^+, 213.0106 (14.8%) and 215.0077 (5.0%); calc. M, 213.0112 and 215.0083].

(*f*) *Phenols with TDCE.*—Phenol and the cresols were irradiated as 10 or 20% w/v solutions in TDCE. HCl was evolved and the solutions rapidly became dark orange or purple on exposure. Irradiation times were limited to a maximum of 18 h and from 150 ml solutions, on distillation mixtures were obtained as pale yellow oils (0.5—0.8 g). Longer exposure times were possible for 1.0M arene and 3.5M TDCE solutions in cyclohexane and for phenol this led to an increase in adduct yield of 50%. The major 1:1 adducts were isolated by prep. g.c. (20% Apiezon L) as colourless oils. *Compound* (**21**) $\delta_H(C_6D_6)$ 5.32 (2-H, m, $J_{2,3}$ 8.8 and $J_{2,4}$ 2.0 Hz), 5.04 (3-H, m, $J_{3,4}$ 2.6 and $J_{3,4'}$ 3.8 Hz), 4.02 (7-H, br overlapping dd), 3.89 (6-H, dd, $J_{6,7}$ 5.0 and $J_{5,6}$ 1.0 Hz), 2.43 (1-H, m, $J_{1,2}$ 6.0, $J_{1,7}$ 5.4 and $J_{1,3}$ 2.5 Hz), 2.32 (5-H, m), 2.28 (4-H, m, $J_{4,4'}$ 18.0 and $J_{4,5}$ 2.0 Hz), and 1.86 (4'-H, m, $J_{4',5}$ 2.0 Hz); δ_C(62.77 MHz) 208.4, 129.2, 127.2, 69.4, 66.4, 56.4, 52.3, and 41.9; $\nu_{max.}$(liquid film) 1 770, 1 606, and 806 cm^{-1} [Found: M^+, 189.9945 (28.3%) and 191.9931 (16.4%); calc. M, 189.9949 and 191.9920]. *Compound* (**22**) δ_H 5.69 (3-H, m, $J_{3,4}$ 2.8 and $J_{3,4'}$ 3.2 Hz), 5.47 (2-H, dd, $J_{2,3}$ 9.0 and $J_{2,4}$ 2.4 Hz), 4.27 (6-H, dd, $J_{6,7}$ 5.8 and $J_{5,6}$ 1.3 Hz), 4.09 (7-H, d), 2.94 (4-H, m), 2.89 (5-H, 6 lines, $J_{4,5} = J_{4',5} = 3.0$ Hz), 2.81 (4'-H, overlapping dd), and 1.20 (3 H, s, CH_3); $\nu_{max.}$(liquid film) 1 765 cm^{-1} [Found: M^+, 204.0099 (4.8%) and 206.0069 (3.1%); calc. M, 204.0106 and 206.0076]. *Compound* (**23**) δ_H 5.84 (2-H, m, $J_{2,3}$ 9.0 Hz), 5.76 (3-H, m, $J_{3,4} = J_{3,4'} = 3.0$ Hz), 4.38 (6-H and 7-H, br s), 3.00 (1-H overlapping dd, $J_{1,7}$ 5.8 and $J_{1,2}$ 6.0 Hz), 2.74 (4-H and 4'-H, dd, $J_{4,4'}$ 1.5 Hz), and 1.19 (3 H, s, CH_3); $\nu_{max.}$(liquid film) 1 767 cm^{-1} [Found: M^+, 204.0101 (34.9%) and

206.0068 (22.3%); calc. M, 204.0106 and 206.0076]. *Compound* (**24**) δ_H 5.46 (3-H, m), 4.53 (7-H, overlapping dd, $J_{1,7} = J_{6,7}$ 5.5 Hz), 4.26 (6-H, d), 2.94 (4-H, m, $J_{4,4'}$ 17.5 Hz), 2.80 (5-H, dd, $J_{5,6}$ 5.8 and $J_{4,5}$ 2.0 Hz), 2.76 (4'-H, m), 2.70 (1-H, m), and 1.88 (3-H, d, J_{3,CH_3} 2.0 Hz); $\nu_{max.}$(liquid film) 1 768 cm^{-1} [Found: M^+, 204.0012 (13.3%) and 206.0086 (10.5%); calc. M, 204.0106 and 206.0076]. *Compound* (**25**) δ_H 5.53 (2-H, m, $J_{1,2}$ 7.0 and $J_{2,4}$ 2.2 Hz), 4.44 (7-H, overlapping dd, $J_{1,7} = J_{6,7} = 5.0$ Hz), 4.26 (6-H, d, $J_{5,6}$ 5.4 Hz), 2.98 (4-H, m, $J_{4,4'}$ 17.0 and $J_{4,5}$ 3.5 Hz), 2.88 (1-H, m), 2.73 (4'-H, m, $J_{2,4}$ 2.0 Hz), 2.65 (5-H, m), and 1.72 (3 H, d, CH_3); $\nu_{max.}$(liquid film) 1 770 cm^{-1} [Found: M^+, 204.0099 (20%) and 206.0062 (14.1%); calc. M, 204.0106 and 206.0076].

(*g*) *Fluorobenzene and TDCE.* Irradiation of an equivolume solution (50 ml) of the addends for 18 h gave a dark brown solution with evolution of HF. Rotary evaporation followed by vacuum distillation gave a 1:1 adduct mixture as a colourless oil (0.85 g) which darkened rapidly at room temperature. Analysis of the oil by g.c. showed four components at injection block temperatures of >200 °C but at 120 °C only the two adducts (**26**) and (**27**) were evident: these were separated by prep. g.c. (20% Apiezon L injection temperature 120 °C). *Compound* (**26**) δ_H 4.88 (7-H, dd, $J_{7,8}$ 6.0 and $J_{5,7}$ 2.2 Hz), 4.61 (4-H, m), 4.18 (6-H, br s), 3.25 (5-H, m), 3.17 (1-H, overlapping ddd, $J_{1,2} = J_{1,5} = J_{1,8} = 6.0$ Hz), 2.40 (8-H, dd), and 1.99 (2-H, overlapping dd, $J_{2,8}$ 6.8 and $J_{2,4}$ 0.6 Hz); δ_F(84.3 MHz) -113.2 relative to CFCl$_3$; $\nu_{max.}$(liquid film) 1 606, 1 161, and 826 cm^{-1} [Found: M^+, 191.9900 (6.1%) and 193.9872 (4.1%); calc. M, 191.9908 and 193.9878]. *Compound* (**27**) δ_H 5.86 (3-H, m, $J_{3,4}$ 6.0 and $J_{2,3}$ 2.5 Hz), 5.57 (4-H, m, $J_{4,5}$ 2.5 and $J_{2,4}$ 0.7 Hz), 4.85 (7-H, dd, $J_{7,8}$ 6.0 Hz), 4.22 (6-H, d, $^4J_{6,F}$ 3.8 Hz), 3.73 (5-H, m, $J_{5,7}$ 2.5 Hz), 2.96 (8-H, m), and 2.75 (2-H, m, $J_{2,8}$ 9.0, $^3J_{2,F} = ^3J_{5,F} = ^3J_{8,F} = 14$ Hz); δ_F(84.3 MHz) -184 relative to CFCl$_3$; $\nu_{max.}$(liquid film) 1 610, 1 131, and 830 cm^{-1} [Found: M^+, 191.9902 (5.6%) and 193.9874 (3.7%); calc. M, 191.9908 and 193.9878].

(*h*) *Chlorobenzene and TDCE.*—Irradiation of an equivolume mixture (50 ml) of the addends for 18 h gave a pale yellow solution. Combination of the crude product mixture from three irradiations and vacuum distillation gave a pale yellow oil (4.2 g) which comprised ethene dimers (50%) and the 1:1 adduct (**28**) (50%). Irradiation of the addends (50 ml each) in cyclohexane (150 ml) gave a complex mixture of the ethene dimers, (**28**), chlorobiphenyls and solvent derived products. *Compound* (**28**) was isolated by flash chromatography (n-pentane) as a colourless oil, δ_H 5.86 (3-H, dd, $J_{3,4}$ 5.8 and $J_{2,3}$ 2.6 Hz), 5.53 (4-H, m, $J_{4,5}$ 2.4 Hz), 4.90 (7-H, dd, $J_{7,8}$ 6.2 Hz), 4.20 (6-H, br s), 3.57 (5-H, overlapping dd, $J_{5,7}$ 2.2 Hz), 2.74 (8-H, dd), and 2.50 (2-H, dd and fine splitting, $J_{2,8}$ 8.5 and $J_{2,4}$ 1.1 Hz); $\nu_{max.}$(liquid film) 1 610 and 816 cm^{-1} [Found: M^+, 207.9608 (3.2%), 209.9595 (2.8%), and 211.9537 (1.0%); calc. M, 207.9613, 209.9537, and 211.9553].

(*i*) *Trifluoromethyltoluene and TDCE.*—A solution of tri-fluorotoluene (50 ml) and TDCE (50 ml) in cyclohexane (200 ml) was irradiated for 48 h. Vacuum distillation gave a mixture (8.6 g) comprising three 1:1 adducts in a ratio of 1:3:9 (relative g.c. retention times of 1.0:1.5:2.25). On storage of the mixture at -25 °C the oil partly crystallised and the *major adduct* (**29**) was filtered off and recrystallised from 5% diethyl ether in petrol (b.p. 30—40 °C), m.p. 42—43 °C, δ_H 6.44 (3-H, m, $J_{2,3}$ 2.6 and $^4J_{HF}$ 2.0 Hz), 4.90 (7-H, dd, $J_{7,8}$ 6.5 and $J_{5,7}$ 2.75 Hz), 4.45 (6-H, br s), 3.54 (5-H, m), 3.40 (1-H, 4 lines $J_{1,2} = J_{1,5} = J_{1,8} = 6.0$ Hz), 2.55 (8-H, m, $J_{2,8}$ 8.0 Hz), and 2.20 (2-H, m); δ_C 138.7 (q, J_{CF} 5.35 Hz), 131.8 (q, J_{CF} 33.2 Hz), 121.8 (q, J_{CF} 269 Hz), 73.6, 67.1, 57.1, 44.6, 37.2, and 33.1; δ_F(84.3 MHz) -63.7 relative to CFCl$_3$; $\nu_{max.}$(liquid film) 1 653 and 885 cm^{-1} (Found: C, 44.55; H,

2.95%; $C_9H_7F_3Cl_2$ requires C, 44.45; H, 2.90%). The minor products, the *ortho* cycloadduct (31) and the other *meta* cycloadduct (30) were isolated following removal of (29) by prep. g.c. (20% Apiezon L) as colourless oils: purity >99%. Compound (30) δ_H 5.94 (3-H, dd, $J_{3,4}$ 5.6 and $J_{2,3}$ 2.4 Hz), 5.60 (4-H, dd and fine splitting, $J_{4,5}$ 2.5 Hz), 5.00 (7-H, d, $J_{5,7}$ 2.5 Hz), 4.19 (6-H, br s), 3.56 (5-H, m), 3.41 (1-H, overlapping dd, $J_{1,2} = J_{1,5} = 7.2$ Hz), and 2.68 (2-H, dd); δ_F(84.3 MHz) −68.8 relative to $CFCl_3$; v_{max}(liquid film) 1 610, 1 165, and 1 145 cm⁻¹ [Found: M^+, 241.9881 (3%) and 243.9838 (1.2%); calc. M, 241.9876 and 243.9846]. Compound (31) δ_H 6.37 (3-H, dd and fine splitting, $J_{2,3}$ 9.8 and $J_{3,4}$ 5.5 Hz), 6.03 (4-H, dd, $J_{4,5}$ 9.5 Hz), 5.84 (5-H, dd and fine splitting, $J_{5,6}$ 6.0, $J_{3,5}$ 1.2, and $J_{2,5}$ 0.8 Hz), 5.71 (2-H, 6 lines), 4.77 (8-H, d), 4.29 (7-H, overlapping dd, $J_{6,7} = J_{7,8} = 8.0$ Hz), and 3.21 (6-H, dd, $J_{6,8}$ 0.4 Hz); δ_F (84.3 MHz) −67.6 relative to $CFCl_3$; v_{max}(liquid film) 1 600, 1 180, 1 168, and 1 135 cm⁻¹ [Found: M^+, 241.9868 (17%) and 243.9837 (11%); calc. M, 241.9876 and 243.9846].

(*j*) m-*Trifluoromethylbenzonitrile and TDCE.*—Solutions of the arene (22.5 g) in TDCE (50 ml) were irradiated for 18 h. The ratios of the three 1:1 adducts (32), (33), and (34) were 3.6:2.6:1 respectively, and essentially time invariant (respective relative retention times of 1.3, 1.5, and 1.0). Combined crude product from three irradiations gave, on vacuum distillation, a mixture of adducts as a yellow oil (1.25 g). The adducts were separated by prep. g.c. (20% Apiezon L) as colourless oils. Compound (32) δ_H 6.38 (3-H, q, $^4J_{HF}$ 1.8 Hz), 4.92 (7-H, dd, $J_{7,8}$ 6.4 and $J_{5,7}$ 2.6 Hz), 4.40 (6-H, br s), 3.97 (1-H, br overlapping dd, $J_{1,8}$ 6.8 and $J_{1,5}$ 6.6 Hz), 3.72 (5-H, m), and 3.21 (8-H, overlapping dd); v_{max}(liquid film) 2 250, 1 663, 1 165, and 1 125 cm⁻¹ [Found: M^+, 266.9824 (5.9%); calc. M, 266.9829]. Compound (33) δ_H 6.73 (3-H, s), 4.93 (7-H, dd), 4.40 (6-H, br s), 3.78 (5-H, dd, $J_{5,7}$ 2.4 Hz), 3.62 (1-H, dd, $J_{1,5} = J_{1,8} = 7.0$ Hz), and 3.12 (8-H, overlapping dd, $J_{7,8}$ 7.1 Hz); v_{max}(liquid film) 2 230, 1 618, 1 155, and 1 057 cm⁻¹ [Found: M^+, 266.9825 (9.4%); calc. M, 266.9829]. Compound (34) δ_H 6.22 (2-H and 3-H, m), 6.15 (4-H, m), 5.01 (8-H, d), 4.31 (7-H, overlapping dd, $J_{7,8}$ 8.0 Hz), and 3.50 (6-H, dd, $J_{6,7}$ 8.5 and $J_{5,6}$ 5.0 Hz); v_{max}(liquid film) 2 246, 1 677, 1 606, 1 180, and 1 135 cm⁻¹ [Found: M^+, 266.9821 (12%); calc. M, 266.9829].

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