Factors Affecting the Photoaddition Reactions of Diphenylmethane

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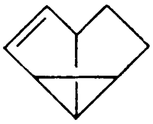
Diphenylmethane does not undergo photoaddition reactions which require initial excitation of the $S_0 \longrightarrow S_1$ transition of the arene. Reaction does, however, occur either by excitation within the charge-transfer absorption band of a ground-state complex between diphenylmethane and an addend (maleic anhydride) or by attack of a photoexcited addend (*N*-ethylmaleimide) onto the arene. It is considered that a mechanism for energy dissipation from S_1 diphenylmethane involves through-bond interaction between the phenyl groups.

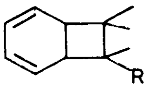
THE photochemistry of diphenylmethane has received little attention and published studies are essentially restricted to those of photoisomerisation,[1] cleavage reactions in the gas phase,[2] and its use as a hydrogen source for the reduction of photoexcited ketones.[3] Our interest in the photoreactions of this arene originated from a study of the trichromophoric systems $Ph_2CH(CH_2)_nNMe_2$ which were essentially photostable and, in particular, did not yield cyclisation products between a phenyl and the dimethylamino-moieties.[4] We suggest that this stability results, at least partly, by dissipation of the energy of the excited phenyl group by ' through-bond ' interaction with the other phenyl group: ' through-bond' interaction has recently been suggested to account for the arene fluorescence quenching of benzyl amines [5] and ethers.[6] In order to obtain further information on this aspect of arene photochemistry [7] we have investigated the intermolecular photoreactions of diphenylmethane with aliphatic amines and with ethylenes. Addends of the latter type were chosen such that (*a*) the arene, (*b*) the ethylene, or (*c*) a ground-state complex between the arene and ethylene was the initially excited species. Reactions of type (*a*) yield *meta* (1) and in certain cases *ortho* (2) cycloadducts from benzene [8] and its methyl and methoxy-derivatives [9–11] whereas those of types (*b*) and (*c*) lead exclusively to *ortho*-cycloaddition products.[7,12]

RESULTS AND DISCUSSION

Aliphatic amines undergo 1,2- and 1,4-acyclic addition to S_1 benzene and its simple derivatives *via* processes of electron and proton transfers and radical combinations to yield compounds of structures (3) and (4) respectively.[13,14] In some cases aniline derivatives also result,[13-15] and irradiation of these systems in aqueous acetonitrile results in Birch-type reduction of the arene as the major process again *via* an electron-transfer mechanism.[16] We have irradiated diphenylmethane with triethylamine and diethylamine in the absence and presence of methanol but in no case were amine–arene adducts analogous to those previously described detected. Further, irradiation of the arene–amine system under conditions which have previously been reported to yield the photoreduction products [16] gave no significant amounts of volatile products. These results may be taken to imply that electron transfer from the amine to the S_1 arene and the formation of the radical anion is not an efficient process since the corresponding species formed in the Birch reduction is seemingly readily protonated to yield (5).[17]

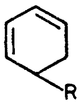


(1)

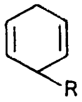


(2) R = H

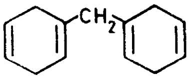
(6) R = CO_2Me



(3) R = $N(Alkyl)_2$ or NH(Alkyl)



(4) R = $N(Alkyl)_2$ or NH(Alkyl) or $-CH(Me)N(Alkyl)_2$

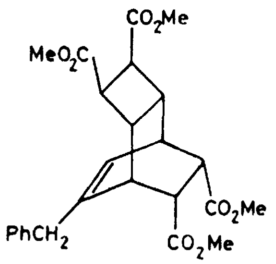


(5)

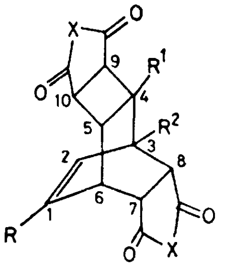
meta-Adducts of type (1) are formed from benzene and its simple derivatives in the presence of ethylenes such as cyclopentene and *cis*-cyclo-octene which have ionisation potentials closely similar to that of the arene,[7,8] In contrast excitation of benzene in the presence of methyl acrylate gives only a mixture of the *exo*- and *endo*-stereoisomers of the *ortho*-cycloadduct (6).[18] The former reaction is ' allowed ' as a concerted homopolar process from orbital symmetry considerations from the S_1 arene whereas the corresponding *ortho*-cycloaddition is ' allowed ' from the S_1 addend or a complex of the reactants, but is ' forbidden ' from S_1 benzene.[19] Such restrictions may be circumvented by the mixing of states and the intermediacy of exciplexes in product formation,[20] but there is little direct evidence on the involvement of such species in these reactions. In marked contrast to the above results, the 254 nm irradiation of diphenylmethane in the present of cyclopentene, *cis*-cyclo-octene, or methyl acrylate gave no detectable amounts of volatile products: variable amounts of polmeric materials were formed, particularly from the system involving the acrylate.

It is thus evident that in photoaddition reactions which originate from the S_1 state of the arene, diphenylmethane is inactive. This observation is consistent with the proposal that the molecule dissipates its excitation energy intramolecularly. Triplet-excited benzene and its alkyl derivatives undergo no photoaddition processes [7] but do sensitise photoreactions of alkenes.[21] Under the conditions of our experiments, formation of, and/or intermolecular energy transfer from, the triplet state of diphenylmethane appears to be a low efficiency reaction since only trace amounts (detected by g.l.c.) of the three cyclohexene photodimers, produced by triplet sensitisation,[8,21] were obtained from irradiation of diphenylmethane–cyclohexene mixtures. We do, however, note here that intramolecular reactions of triplet-state molecules which have the diphenylmethane moiety are known.[22]

If the lack of reaction of S_1 diphenylmethane is a result of interaction between the two phenyl groups, rather than the operation of some other (unknown) feature of the various systems, then ethylene photoaddition to diphenylmethane would be predicted to arise from (*a*) excitation of an ethylene–diphenylmethane complex which has a charge-transfer absorption of lower energy than the arene itself, and from (*b*) interaction with a photoexcited ethylene which has absorption at longer wavelength than the aromatic compound. Excitation of a ground-state complex of maleic anhydride with benzene or its alkyl derivatives is involved in the formation of the 2 : 1 photoadducts (7) and (8). Formation of a complex having charge-transfer absorption is a prerequisite for *ortho*-addition of this dienophile to arenes, but the observation of charge-transfer absorption does not necessarily mean that the photoreaction will occur.[12,23-27] Maleimide and certain of its *N*-substituted derivatives also yield 2 : 1 adducts [9] with benzenoid compounds [12,28] but in this case the reaction proceeds by way of excitation of the imide. Formation of maleimide–arene complexes are not essential for the photoreaction although they may be beneficial to the efficiency of the process.[29] Thus we have investigated the photoreactions of maleic anhydride and a maleimide with diphenylmethane.



(11)



(7) X = O, R = R^1 = R^2 = H
(8) X = O, R = R^1 and/or R^2 = Alkyl
(9) X = NH, N(Alkyl), or NCH_2Ph, R = R^1 = R^2 = H
(10) X = O, R = CH_2Ph, R^1 = R^2 = H
(12) X = O, R = Me, R^1 = R^2 = H
(13) X = O, R = R^1 = H, R^2 = Me
(14) X = NEt, R = CH_2Ph, R^1 = R^2 = H

Solutions of maleic anhydride in diphenylmethane exhibit a tail absorption beyond the arene out to *ca.* 355 nm. In this case it did not prove possible to determine the exact position of the wavelength maximum, but extrapolation from neat solutions of maleic anhydride in diphenylmethane suggested charge-transfer absorption in the 265—280 nm region as noted for other systems.[27] Irradiation within the charge-transfer absorption band of maleic anhydride and diphenylmethane (40 °C in Pyrex tubes) resulted in the formation of a single compound (h.p.l.c.) (m.p. 234—235 °C): this was deduced from spectral and analytical data (see Experimental section) to have the 2 : 1 adduct structure (10) reflecting initial 3,4-addition. The adduct was converted into the tetramethyl ester (11) (m.p. 106—107 °C) with MeOH–H^+. We assign an *exo*-3,4,*endo*-7,8-stereochemistry to this adduct by analogy with that proven for the maleic anhydride–benzene adduct (7).[30] Apart from obvious differences resultant of the benzyl group in (10) and (11) the i.r. and ^1H n.m.r. spectra of the two 2 : 1 adducts and of the two tetraesters derived therefrom were closely similar. The production of (10) is slow and from parallel experiments of maleic anhydride in diphenylmethane and in benzene we assess that the quantum yield for its formation is two orders of magnitude less than that reported for the 2 : 1 adduct (7).[25] Mechanistic differences between the sensitised and unsensitised photoaddition of maleic anhydride to benzenes have received comment.[12,24,26,31] For example with toluene as arene, the ratio of the 2 : 1 adducts (12) and (13) is respectively 1 : 1 in the presence of benzophenone and 4 : 1 in its absence.[26] The present addition was found to be photosensitised by benzophenone approximately three fold but again only the 2 : 1 adduct (10) was formed. Further, although the preferred positions of the photoaddition of maleic anhydride to methyl benzenes are markedly influenced by the temperature of the irradiated solution,[26] this variation was not observed for the reaction with diphenylmethane. Even at 125 °C, or in quartz apparatus, only the single isomer (10) was formed. This specificity of attack of maleic anhydride onto diphenylmethane may result from a preferred *exo*-3,4-orientation of the reactants in the complex and this is dictated by the bulky benzyl group.

The absorption spectra of solutions of *N*-ethylmaleimide in diphenylmethane were essentially additive of the components at wavelengths longer than 285 nm and no direct evidence for charge-transfer absorption of a complex was obtained. The longest wavelength absorption of *N*-ethylmaleimide in hydrocarbon solution is centred at 294 nm and tails to *ca.* 340 nm. Hence, the excited species is the addend, *N*-ethylmaleimide, on irradiation of its diphenylmethane solutions behind a Pyrex filter. Such a procedure gave a single product (m.p. 230—233 °C) at 38 °C. The structure of the product was deduced from spectroscopic and analytical data to be that of the 2 : 1 adduct (14): only this isomer was obtained at 125 °C although at the higher temperature large amounts of polymeric material were also produced. It is interesting to note here that whereas in the present reaction the addition is again specifically 3,4 onto the diphenylmethane, exclusive excitation within the charge-transfer absorption band of solutions of maleimide in anisole leads to the three possible modes of *ortho*-cycloaddition to the aromatic ring.[32]

Thus we have shown that the diphenylmethane chromophore does not enter into photoaddition reactions which require excitation of the arene, in which cases the system is essentially photostable: a possible reason for this is that the excitation energy is lost by interaction of the two phenyl groups *via* the intervening CH_2. On the other hand complexation of diphenylmethane with an addend such that the lowest energy transition of the system is that of charge-transfer absorption by the complex, results, on excitation within this band, in photochemical addition. Similarly diphenylmethane is also prone to addition reactions with photoexcited addends.

EXPERIMENTAL

The irradiation experiments involving the amines, cyclopentene, *cis*-cyclo-octene, methyl acrylate, and cyclohexene were carried out in quartz tubes using 15-W Hanovia low-pressure mercury-arc lamps. A 500-W Hanovia medium-pressure mercury-arc lamp was used for the photoadditions of maleic anhydride and *N*-ethylmaleimide to diphenylmethane. The amine solutions were degassed under nitrogen prior to irradiation and since the atmosphere has no observable effect on the efficiency of ethylene photoadditions to benzenoid compounds, the other experiments were conducted under air. The experiments were monitored by g.l.c. using OV17 and Apiezon L as the liquid phases for the reactions involving the amine and Carbowax 20M for those with the ethylenes. The involatile products from maleic anhydride and *N*-ethylmaleimide irradiations were examined by h.p.l.c. using a 25-cm Whatman Partisil PXS 10/25 column.

Irradiations of Diphenylmethane with Di- and Tri-ethylamine.—The equivolume solutions (10 ml) of the arene and each amine were irradiated for 24 h: in neither case was any product other than those derived solely from irradiation of the amine alone detected.[33] Incorporation of methanol [13] (equal volume with the arene and amine) into the irradiated solution had no observable effect.

The photoreduction of the arene was investigated under the conditions previously described.[16] Diphenylmethane (1 g), triethylamine (3 ml), water (2 ml), and acetonitrile (90 ml) solutions were degassed and irradiated in quartz tubes with (*a*) a 500-W medium-pressure mercury lamp, and (*b*) 15-W low-pressure mercury lamps. Only in the latter case and following 64 h irradiation was there any evidence for the formation of minor amounts ($\gg 0.01\%$ of the arene) of product: this was not further investigated.

Irradiations of Diphenylmethane with Cyclopentene, Cyclohexene, cis-*Cyclo-octene, and Methyl Acrylate.*—Equivolume solutions (10 ml) of each ethylene with the arene were irradiated for 24 h. Although in no case were photoaddition products detected, from the trace products of short retention time obtained from the experiment involving cyclohexene there were three components in the same ratio and with identical retention times under a variety of conditions as the three cyclohexene ($2\pi + 2\pi$) photodimers produced from benzene [8] or methyl acetoacetate [21a] photosensitised dimerisation.

2 : 1 *Photoaddition of Maleic Anhydride to Diphenylmethane.*—A solution of maleic anhydride (7.0 g recrystallised from diethyl ether) in diphenylmethane (50 ml freshly distilled) was irradiated at 40 °C in a Pyrex tube for 7 h. The starting materials were removed by vacuum distillation (0.1 mmHg) and the viscous amber residue was digested with diethyl ether (50 ml) and allowed to stand overnight. The insoluble white solid (70 mg) was filtered off and the minor amounts of polymeric material removed from the product by recrystallisation from acetone to give (10) (40 mg), m.p. 234—235 °C. The structure of (10) was deduced from the following analytical and spectroscopic data. Found: M^+ 364.095 2, $C_{21}H_{16}O_6$ requires 364.094 58, abundant ions at *m/e* 265, 237, 182, 168, and base ion at 167 m.u. The ^1H n.m.r. spectrum [100 MHz $(CD_3)_2CO$] had δ at 7.22 (5 H, s, phenyl H), 5.86 (1 H, d of m, *J* 2 and 7 Hz, =CH), 3.51 (2 H, d, *J* 2 Hz, CH_2Ph), 3.45—3.3 (2 H, m, H-3 and H-6), 3.1—2.75 (4 H, m, H-7, H-8, H-9, and H-10), and 2.7—2.5 p.p.m. (2 H, m, H-4 and H-5); $\nu_{max.}$ (Nujol mull) at 1 850m, 1 775s, 1 235m, 1 205m, 1 085s, 915s, and 695m cm^{-1}.

Irradiation of the above solution at 125 °C gave a very similar result but incorporation of benzophenone (9 g) gave an increased yield (1.1 g) of (10).

The Tetraester (11).—A mixture of compound (10) (0.54 g), concentrated sulphuric acid (4 drops), and methanol (50 ml) was heated under reflux for 1 h. The bulk of the methanol was removed and the resulting liquid diluted with diethyl ether (150 ml). The ethereal solution was washed with aqueous potassium carbonate and dried ($MgSO_4$) to give the crude ester (*ca.* 0.2 g) which was recrystallised from methanol (93 mg), m.p. 106—107 °C; Found: $M^+ =$ 456.177 77, $C_{25}H_{28}O_8$ requires 456.178 29, abundant ions at *m/e* of 397, 312, 168, and 91 m.u. The ^1H n.m.r. spectrum (60 MHz $CDCl_3$) had δ at 7.3 (5 H, s, phenyl-H), 5.9 (1 H, d, of m, *J* 2 and 7 Hz, =CH), 3.75—3.55 (14 H, s superimposed d, CO_2CH_3 and CH_2Ph), and 3.2—2.4 p.p.m. (8 H, series of overlapping m's, H-3 to H-10); $\nu_{max.}$ (Nujol), 1 740s, 1 730s, 1 500w, 1 320m, 1 285m, 1 260m, 1 250m, 1 230m, 1210m, 1 195m, 1 170m, 1 075w, 1 015w, 943w, 835w, 745w, and 705m cm^{-1}.

2 : 1 *Photoaddition of* N-*Ethylmalimide to Diphenylmethane.*—A solution of *N*-ethylmaleimide (7.0 g recrystallised from benzene) in diphenylmethane (50 ml freshly distilled) was irradiated at 38 °C for 7 h. The bulk of the starting materials was removed under reduced pressure (0.1 mmHg) and diethyl ether (50 ml) was added to the amber liquid residue which immediately produced a fine white solid. The solid (2.7 g) was filtered off, washed with diethyl ether, and recrystallised from acetone to give compound (14) (0.67 g), m.p. 230—233 °C. The acetone-soluble fraction was deduced from its spectroscopic properties to be polymeric. Irradiation of the above system at 125 °C produced

considerably more polymeric material than at 38 °C but the only adduct detected was (**14**): incorporation of 2,5-di-t-butylquinol (0.5 g) into the irradiations involving *N*-ethylmaleimide reduced the polymer formation to approximately half of that in its absence. Structure (**14**) was assigned on the basis of the following data. Found: M^+ 418.190 8, $C_{25}H_{26}N_2O_4$ requires 418.189 10, abundant ions at *m/e* 292, 250, 168, 126, and 91 m.u; the ^{1}H n.m.r. spectrum (220 MHz, $CDCl_3$) had δ at 7.4—7.15 (3 H, m, ArH), 7.15—7.05 (2 H, m, ArH), 5.75—5.60 (1 H, d of m, *J* 2 and 7 Hz, =CH), 3.6—3.3 (8 H, overlapping q and m's, CH_2Ph, 2-CH_2Me, H-3 and H-6), 2.8—2.5 (4 H, overlapping m's, H-7 to H-10), 2.2—2.1 (1 H, m, H-4 or H-5), 1.7—1.55 (1 H, m, H-5 or H-4), and 1.25—1.05 p.p.m. (6 H, two closely overlapping t's, CH_2CH_3); $\nu_{max.}$ (Nujol) at 1 765m, 1 695s, 1 500w, 1 340m, 1 225m, 1 135m, 745m, and 700m cm^{-1}.

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REFERENCES

[1] B. Brocklehurst, W. A. Gibbons, F. T. Lang, G. Porter, and M. I. Savadatti, *Trans. Faraday Soc.*, 1966, **62**, 1793.

[2] G. Porter and E. Strachan, *Trans. Faraday Soc.*, 1958, **54**, 1595; G. Porter and F. J. Wright, *Trans. Faraday Soc.*, 1955, **51**, 1469.

[3] See for example. K. Fukui and Y. Odaira, *Tetrahedron Letters*, 1969, 5255; K. Maruyama, T. Otsuki, H. Shindo, and T. Maruyama, *Bull. Chem. Soc. Japan*, 1971, **44**, 2000.

[4] D. Bryce-Smith, A. Gilbert, and G. Klunklin, *J.C.S. Chem. Comm.*, 1973, 330.

[5] R. S. Davidson and K. R. Trethewey, *J.C.S. Chem. Comm.*, 1976, 827.

[6] A. Gilbert and G. N. Taylor, *J.C.S. Perkin I*, 1980, 1761.

[7] For reviews of benzene photochemistry, see D. Bryce-Smith and A. Gilbert, *Tetrahedron*, 1976, **32**, 1309, and *Tetrahedron*, 1977, 3597.

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

[9] R. Srinivasan, *J. Amer. Chem. Soc.*, 1971, **93**, 3555; J. Cornelisse, V. Y. Merritt, and R. Srinivasan, *J. Amer. Chem. Soc.*, 1973, **95**, 6197; J. A. Ors and R. Srinivasan, *J. Org. Chem.*, 1977, **42**, 1321.

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

[11] W. M. Dadson, A. Gilbert, and P. Heath, *J.C.S. Perkin I*, 1980, 1314.

[12] D. Bryce-Smith, *Pure and Applied Chem.*, 1968, **16**, 47; *Pure and Applied Chem.*, 1973, **34**, 193.

[13] M. Bellas, D. Bryce-Smith, M. T. Clarke, A. Gilbert, G. Klunklin, S. Krestonosich, C. Manning, and S. Wilson, *J.C.S. Perkin I*, 1977, 2571.

[14] A. Gilbert and S. Krestonosich, *J.C.S. Perkin I*, 1980, 1393.

[15] J. A. Barltrop, N. J. Bunce, and A. Thomson, *J. Chem. Soc.* (*C*), 1967, 1142.

[16] J. A. Barltrop and R. J. Owers, *Chem. Comm.*, 1970, 1462; J. A. Barltrop, *Pure and Applied Chem.*, 1973, **33**, 179.

[17] D. N. Butler and R. Milburn, *Canad. J. Chem.*, 1972, **50**, 1249.

[18] R. J. Atkins, G. I. Fray, A. Gilbert, M. W. bin Samsudin, and G. N. Taylor, *J.C.S. Perkin I*, 1979, 3196.

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

[20] K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, 1971, **93**, 2073; W. Feree, J. B. Grutzner, and H. Morrison, *J. Amer. Chem. Soc.*, 1971, **93**, 5502.

[21] (*a*) R. G. Salomon, K. Folting, W. E. Streib, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1974, **96**, 1145; (*b*) P. J. Kropp and H. J. Krauss, *J. Amer. Chem. Soc.*, 1967, **89**, 5199; P. J. Kropp, *J. Amer. Chem. Soc.*, 1969, **92**, 5783.

[22] See for example, W. G. Dauben and W. A. Spitzer, *J. Amer. Chem. Soc.*, 1972, **92**, 5817, and R. W. Binkley, S-C. Chen, and D. G. Hehemann, *J. Org. Chem.*, 1975, **40**, 2406.

[23] D. Bryce-Smith and J. E. Lodge, *J. Chem. Soc.*, 1962, 2675.

[24] D. Bryce-Smith, R. R. Deshpande, and A. Gilbert, *Tetrahedron Letters*, 1975, 1627.

[25] W. H. Hardham and G. S. Hammond, *J. Amer. Chem. Soc.*, 1967, **89**, 3200.

[26] D. Bryce-Smith and A. Gilbert, *Chem. Comm.*, 1968, 19.

[27] D. Bryce-Smith, B. E. Connett, and A. Gilbert, *J. Chem. Soc.* (*C*), 1968, 816.

[28] D. Bryce-Smith and M. A. Hems, *Tetrahedron Letters*, 1966, 1895; J. S. Bradshaw, *Tetrahedron Letters*, 1966, 2039.

[29] C. E. Rees, Ph.D. Thesis, Reading University, 1973.

[30] D. Bryce-Smith, G. I. Fray, and B. Vickery, *J. Chem. Soc.* (*C*), 1967, 390.

[31] D. Bryce-Smith, R. R. Deshpande, A. Gilbert, and J. Grzonka, *Chem. Comm.*, 1970, 561.

[32] D. Bryce-Smith, A Gilbert, and B. Halton, *J.C.S. Perkin I*, 1978, 1172.

[33] L. T. Allan and G. A. Swan, *J. Chem. Soc.*, 1965, 4434 and 4822; K. G. Hancock and D. A. Dickinson, *J. Org. Chem.*, 1975, **40**, 969; *ibid.*, **39**, 331.