168. *Liquid-phase Photolysis. Part VIII.*[1] *Preparation of Adducts of Maleic Anhydride and Substituted Benzenes. Factors Governing Orientation and Reactivity in Photoaddition to Aromatic Rings.*

By D. Bryce-Smith and A. Gilbert.

Stable 2 : 1 photoadducts of maleic anhydride and toluene, t-butylbenzene, chlorobenzene, *o*- and *p*-xylene, biphenyl, and quinol have been prepared, and the rates of their formation relative to that of the maleic anhydride–benzene adduct have been measured approximately. All the substituents decreased the rate of formation of adducts. Benzonitrile, nitrobenzene, phenol, methyl benzoate, durene, hexamethylbenzene, naphthalene, and biphenylene did not form photoadducts with maleic anhydride; and of these, benzonitrile, nitrobenzene, methyl benzoate, and biphenylene did not form charge-transfer complexes. The initial photoaddition of maleic anhydride is 3,4- to biphenyl and 2,3- to quinol.

An orange 1 : 1 thermal adduct, different from that already known, has been isolated from solutions of quinol and maleic anhydride, and is formulated as a charge-transfer complex. It differs from quinhydrone in being more weakly hydrogen-bonded.

Structural and energy factors of importance in photoadditions to aromatic rings are discussed.

Benzene undergoes 1,2-photoaddition of maleic anhydride, and various acetylenes. In the case of maleic anhydride, the initial adduct reacts with a second molecule of the addendum:[2] the adducts of acetylenes isomerise to cyclo-octatetraenes.[3] Analogous sensitised additions of maleic anhydride to toluene, *o*-xylene, and chlorobenzene have been reported to occur: the structures of the products were assumed to be analogous to that of the benzene–maleic anhydride adduct.[2f] It has been shown in Part V that the unsensitised addition of maleic anhydride to benzene involves the photoexcitation of a charge-transfer complex rather than individual molecules of the reactants, and singlet rather than triplet excited species.[2d] The corresponding benzophenone-sensitised addition proceeds via triplet intermediates,[2d] and probably occurs via a triplet excited benzene–maleic anhydride charge-transfer complex formed by energy transfer from triplet benzophenone.[2d,4] The present work has been largely concerned with the orientation of 1,2-photoaddition of maleic anhydride to some substituted benzenes, and with the role of charge-transfer complexes in the formation of the adducts isolated.

Irradiation of a solution of maleic anhydride and biphenyl in cyclohexane at 35° gave a colourless 2 : 1 adduct, m. p. 280° (decomp.). The rate of formation of this adduct was increased almost threefold in the presence of benzophenone as sensitiser. It gave a tetramethyl ester, m. p. 148°. At 300° under nitrogen the adduct dissociated to biphenyl and maleic anhydride. Like the benzene–maleic anhydride adduct, it was attacked only slowly by potassium permanganate and bromine in carbon tetrachloride. The infrared spectrum closely resembled that of the benzene–maleic anhydride adduct:[2b] small additional peaks at 6·72 and 13·76 μ are attributed to a phenyl group. Depending on whether the initial addition of maleic anhydride to biphenyl is 1,2-, 2,3-, or 3,4- (and neglecting stereochemical aspects), the corresponding possible structures for the adduct may be written as in ciphers (I), (II), and (III). The ultraviolet spectrum ($\lambda_{max.}$ 247,

---

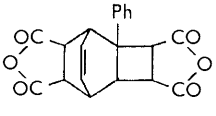
[1] Part VII, Bryce-Smith and Gilbert, *J.*, 1964, 2428.

[2] (*a*) Angus and Bryce-Smith, *Proc. Chem. Soc.*, 1959, 326; (*b*) *J.*, 1960, 4791; (*c*) Bryce-Smith, Gilbert, and Vickery, *Chem. and Ind.*, 1962, 2060; (*d*) Bryce-Smith and Lodge, *J.*, 1962, 2675; (*e*) Grovenstein, Rao, and Taylor, *J. Amer. Chem. Soc.*, 1961, **83**, 1705; (*f*) Schenck and Steinmetz, *Tetrahedron Letters*, 1960, No. 21, 1.

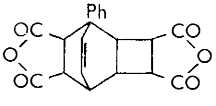
[3] (*a*) Bryce-Smith and Lodge, *Proc. Chem. Soc.*, 1961, 333; *J.*, 1963, 695; (*b*) Grovenstein and Rao, *Tetrahedron Letters*, 1961, No. 4, 148.

[4] Hammond and Hardham, *Proc. Chem. Soc.*, 1963, 63.

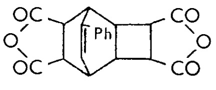
292 mμ; ε 13,500, 500) excluded structures (I) and (II) where the phenyl group is unconjugated with the ethylenic bond, and fully confirmed structure (III): cf. styrene ($\lambda_{max.}$ 247, 290 mμ; ε 13,500, 400).



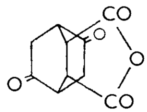
(I)



(II)

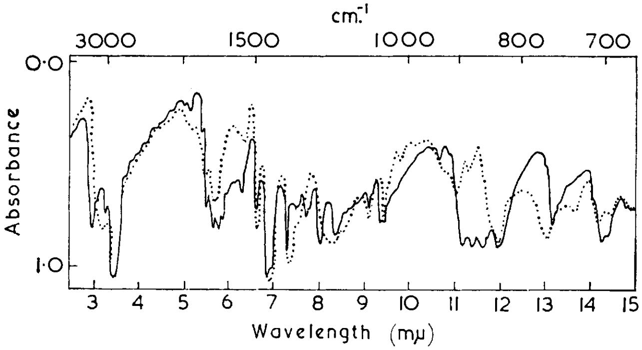


(III)



(IV)

Cookson and Wariyar prepared a 1 : 1 thermal adduct of maleic anhydride and quinol, and showed it to have structure (IV).[5] We have prepared a further 1 : 1 adduct, and also a 2 : 1 photochemical adduct. The new 1 : 1 adduct was obtained by very slow evaporation of an ethereal solution of maleic anhydride and quinol at *ca.* 15°. It formed large orange crystals which could easily be obtained free from crystals of the original components by hand picking, and analysis showed it to be a 1 : 1 adduct when the maleic anhydride and quinol were used in equimolecular proportions and also when either was in two-fold excess. At 40—43° in an open tube, it dissociated cleanly to maleic anhydride and quinol without melting. This compound seems best formulated as a charge-transfer complex analogous to those of hydrocarbons such as benzene with maleic anhydride which are so far known only in solution.[6] The moderate stability of the present adduct may be considered to stem from the stronger donor character expected for quinol relative to benzene. The infrared spectrum of solutions of maleic anhydride in benzene showed no features absent from the individual spectra of the pure components on an instrument of moderate resolving power (Perkin-Elmer Infracord), so something close to "contact" charge-transfer is probably involved.[7] On the other hand, the infrared spectrum of the present 1 : 1 quinol–maleic anhydride adduct differed somewhat from that of a 1 : 1 mixture of the components, although the overall forms were broadly similar (see Figure). Possibly the most interesting difference between these spectra is seen in the region of O–H stretching, the somewhat broad peak at *ca.* 3200 cm.$^{-1}$ shown by the mixture (and also with pure quinol) being shifted in the adduct to *ca.* 3400 cm.$^{-1}$ where it is much sharper: cf. *ca.* 3600 cm.$^{-1}$ for free phenolic hydroxyl groups. Evidently, the formation of a complex with maleic anhydride markedly reduces the ability of quinol to form hydrogen bonds. The present complex is formally analogous to quinhydrone, maleic anhydride replacing *p*-benzoquinone, yet the O–H stretching frequency of quinhydrone (where of course there is strong intramolecular hydrogen bonding) is at *ca.* 3200



········ Equimolar mixture of quinol and maleic anhydride.

——— Orange quinol–maleic anhydride 1 : 1 complex (Nujol mulls).

---

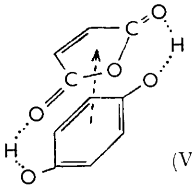
[5] Cookson and Wariyar, *Chem. and Ind.*, 1955, 915; *J.*, 1957, 327.

[6] Barb, *Trans. Faraday Soc.*, 1953, **49**, 143; Andrews and Keefer, *J. Amer. Chem. Soc.*, 1953, **75**, 3776.

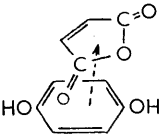
[7] Bryce-Smith and Vickery, unpublished work.

cm.$^{-1}$ as in quinol. The evidently reduced hydrogen-bonding in the 1 : 1 quinol–maleic anhydride complex does not result from crystal-lattice factors, for the infrared spectrum of a melt of equimolecular proportions of quinol and maleic anhydride at 65° in a closed system closely resembled that shown in the Figure for the crystalline 1 : 1 complex, and in particular exhibited the displacement of the O–H stretching frequency to *ca.* 3400 cm.$^{-1}$.* A reasonable model for the 1 : 1 complex (V) shows conditions highly favourable for intramolecular hydrogen-bonding. The rather low O–H stretching frequency in the complex may therefore result from a greater inter-ring separation than in quinhydrone (cf. ref. 8), or possibly from a skew orientation of the components (VI). The differences in the infrared spectra shown in the Figure slightly favour the second of the alternatives.

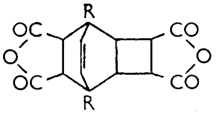
Irradiation of the present crystalline 1 : 1 quinol–maleic anhydride adduct in air led to no perceptible change when conducted below the dissociation temperature (*ca.* 40°). Irradiation of a melt of quinol and maleic anhydride at 70° through fused silica under air or nitrogen gave largely tarry matter; but when borosilicate glass was employed (this was opaque to radiation of wavelengths shorter than 290 mμ), small quantities of a 2 : 1 maleic anhydride–quinol adduct, m. p. 285° (decomp.), where obtained. The rate of formation was about trebled in the presence of benzophenone. At 300° under nitrogen this adduct reformed maleic anhydride and a trace of quinol, together with some tarry matter. The infrared spectrum was almost superimposable upon that of the benzene–maleic anhydride adduct [2b] except for an additional strong peak at *ca.* 3200 cm.$^{-1}$, indicative of the hydroxyl group. In particular, the absence of any significant peak in the 1700 cm.$^{-1}$ region indicated the absence of unconjugated ketonic carbonyl groups. This implies structure (VIIa) for the adduct which would result from initial 2,3-addition of maleic anhydride to quinol followed, as in the case of benzene, by 1,4-addition of a second molecule of maleic anhydride. An initial 1,2-addition to quinol would have led to compound (VIII), which contains an unconjugated carbonyl group.



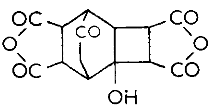
(V)



(VI)



(VIIa: R = OH)
(VIIb: R = Me)



(VIII)

Irradiation of a solution of maleic anhydride in *p*-xylene in the presence of a little benzophenone gave a 2 : 1 adduct, m. p. 340° (decomp.). Its infrared spectrum broadly resembled that of the benzene–maleic anhydride adduct. Maleic anhydride and t-butylbenzene likewise gave a 2 : 1 adduct, m. p. 265°.

Rates of the above and certain related addition reactions relative to the rate of addition of maleic anhydride to benzene are given in the Table, together with ultraviolet absorption data for any corresponding charge-transfer complexes.† The figures quoted were reproducible under the irradiation conditions employed. It can be seen that benzene underwent

---

* This also shows that the equilibrium in the melt at 65° favours the complex, although the crystalline complex itself dissociates at a temperature 20—25° lower than this in an open capillary.

† The relative rates listed in the Table refer to irradiation periods when the weights of adducts produced were checked to be a linear function of time. These periods were generally shorter than those given for the recommended preparative procedures in the Experimental section. Strictly, the relative rates should be corrected to a standard energy input since the total energy, as distinct from the quantal energy, which is in principle available for reaction, will tend to increase as $\lambda_{\max.}$ moves to longer wavelengths. Although some of the values for relative rates given in the Table may therefore tend slightly to underestimate the deactivating effects of the substituents, the general conclusions based on them are unaffected.

[8] Lord and Merrifield, *J. Chem. Phys.*, 1953, **10**, 166; Pimentel and Sederholm, *ibid.*, 1956, **24**, 639; Nakamoto, Margoshes, and Rundle, *J. Amer. Chem. Soc.*, 1955, **77**, 6480; Huggins and Pimental, *J. Phys. Chem.*, 1956, **60**, 1615.

Relative rates of 2 : 1 photoaddition of maleic anhydride to some aromatic compounds at 30°, unsensitised, and sensitised by benzophenone.

	Unsensitised	Sensitised	$\lambda_{\max.}$ (mμ) charge-transfer complex
Benzene	0·38	(1·0)	278 mμ
Toluene	0·12	0·5	284
t-Butylbenzene	0	0·25	290
Chlorobenzene	0	0·25	305
Biphenyl *	0·05	0·12	295
Phenol †	0 ¶	0 ¶	330
Benzonitrile	0	0	No complex
Nitrobenzene	0	0	No complex
Methyl benzoate	0	0	No complex
Acetophenone	0	0	No complex
o-Xylene	0	0·15	288
p-Xylene	0	0·08	290
Quinol ‡	0·02	0·07	335
Durene §	0	0	360
Hexamethylbenzene §	0	0	408
Biphenylene §	0	0	No complex ¶
Naphthalene §	0	0	298

* In cyclohexane. † At 50°. ‡ At 70°. § In cyclohexane at 30° and in melts at 80°. ¶ But see text.

addition more readily than any other aromatic compound as yet examined (cf. ref. 9). Those aromatic compounds containing electron-withdrawing groups did not add maleic anhydride except in the one case (chlorobenzene) where a charge-transfer complex was formed. Among those compounds forming charge-transfer complexes, increasing substitution hindered photoaddition: t-butylbenzene added less readily than toluene. Only phenol is apparently anomalous; although it formed a charge-transfer complex with maleic anhydride, irradiation of a liquid mixture of these gave an intractable mixture of products, seemingly polymeric. Any small quantities of a 2 : 1 adduct might well have escaped detection.

These observations suggest that addition of maleic anhydride to substituted benzenes involves photoexcitation of charge-transfer complexes, as is known to be the case with the addition to benzene itself; [2d] but the existence of such complexes is evidently not the only prerequisite for addition to occur. The slower addition to t-butylbenzene and the xylenes than to toluene, the slower addition to *p*- than to *o*-xylene, and the failure of durene and hexamethylbenzene to undergo any detectable addition, suggest that the steric effect of substituents is also an important factor. This is further borne out by the observed 3,4-addition to biphenyl and the 2,3-addition to quinol, reaction occurring at the least hindered positions. It is true that the lower rates of addition to the substituted benzenes show a partial correlation with the lower quantal energies at $\lambda_{\max.}$ for photoexcitation of the corresponding charge-transfer complexes; but comparison of the cases of t-butylbenzene and *p*-xylene in particular indicates that the availability of unsubstituted ring positions dominates the energy factor in this series of additions.

It must now be considered whether the addition of the first or the second molecule of maleic anhydride is rate-determining. The initial 1 : 1 adducts have not yet been isolated.* Apparently, 1,4-addition of a second molecule of maleic anhydride occurs very rapidly under the conditions so far employed (even irradiation of maleic anhydride and benzene at −8° gives only the normal 2 : 1 adduct),[11] Hammond and Hardham have reported that the quantum yield in the benzophenone-photosensitised formation of the 2 : 1 maleic anhydride–benzene adduct shows only a slight dependence on the concentration of maleic anhydride.[4] They inferred that dissociation of the intermediate 1 : 1 adduct competes

---

* A very stable dibenz-derivative has been obtained by addition of maleic anhydride to the 9,10-positions of phenanthrene.[10]

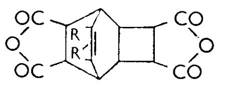
[9] Bryce-Smith, Gilbert, and Vickery, *Chem. and Ind.*, 1962, 2060.

[10] Bryce-Smith and Vickery, *Chem. and Ind.*, 1961, 429.

[11] Bryce-Smith and Lodge, unpublished work.

only weakly with addition of a second molecule of maleic anhydride. The smallness of the concentration effect implies that the addition of the first rather than the second molecule of maleic anhydride is largely rate-determining under their conditions. Although this conclusion does not automatically extend to the formation of the present series of adducts of substituted benzenes, the general effect of at least those electron-donating substituents shown in the Table can reasonably be assigned either to hindrance of the initial stage of 1,2-addition, or to promotion of the corresponding retrogression (possibly to both), since such substituents in 1,3-dienes have been shown, in cases relevant to the present work, to accelerate 1,4-addition of maleic anhydride.[12]

If the conclusion that the orientation of 1,2-addition of maleic anhydride to a substituted benzene tends to be such as to minimise interaction with the substituent applies to the cases of toluene, t-butylbenzene, and chlorobenzene, structures (IX), (X), and (XI) are indicated for the corresponding adducts: likewise, ciphers (XII) and (VII*b*) show the probable structures for the adducts of *o*- [2f] and *p*-xylene.



	R	R′
(IX:	H	Me)
(X:	H	Bu^t)
(XI:	H	Cl)
(XII:	Me	Me)

In view of the clearly recognisable formation of charge-transfer complexes by benzene and naphthalene (and indeed all other aromatic hydrocarbons as yet examined, even cyclohexene [13]), it is interesting that no such complex is formed between biphenylene and maleic anhydride. The only evidence for slight interaction lay in a 5-mμ bathochromic shift of the maleic anhydride absorption maximum normally found at 208 mμ. Evidently, any tendency towards bond-localisation in biphenylene does not favour its interaction with maleic anhydride. The unexpected lack of photoaddition of naphthalene to maleic anhydride [14] may indicate the structural difficulty of stabilising an initial 1 : 1 adduct (possibly in a high vibrational state) by addition of a second molecule of maleic anhydride, or collisional deactivation of an excited singlet naphthalene–maleic anhydride charge-transfer complex ($\lambda_{max.}$ 298 mμ) by naphthalene ($\lambda_{max.}$ 314 mμ).

Two, possibly three, mechanisms of unsensitised addition to aromatic rings can now be recognised. Firstly, addition of maleic anhydride to benzene occurs via photoactivation of a charge-transfer complex,[2d] and those aromatic compounds which do not form such complexes form no photoadducts with maleic anhydride. Nevertheless, the formation of a charge-transfer complex does not in itself mean that a stable photoadduct will be produced with maleic anhydride. As reported above, increasing substitution in benzene by alkyl groups, while not preventing the formation of charge-transfer complexes, tends to hinder photoaddition of maleic anhydride, possibly as a result of increasing steric compressions in the transition states for 1,2-addition. Dimethyl maleate does not form a charge-transfer complex with benzene, so it is not surprising that no photoadduct is formed. *p*-Benzoquinone, however, while forming a charge-transfer complex with benzene ($\lambda_{max.}$ 278 mμ, as for the benzene–maleic anhydride complex), does not form a photoadduct, and indeed inhibits the addition of maleic anhydride to benzene: yet no structural barrier to addition of *p*-benzoquinone is apparent. This seeming anomaly can be understood from the fact that the energy of the first excited singlet state of *p*-benzoquinone lies 39·4 kcal. below that of its charge-transfer complex with benzene. Quenching of the excited complex by energy transfer to unexcited uncomplexed *p*-benzoquinone can therefore provide an explanation both for the absence of a photoadduct and for the inhibition of addition of maleic anhydride to benzene. That benzene does not add to tetracyanoethylene

---

[12] Sauer, Lang, and Mielert, *Angew. Chem.* (*Internat. Edn.*), 1962, **1**, 268; Craig, Shipman, and Fowler, *J. Amer. Chem. Soc.*, 1961, **83**, 2885.

[13] Barltrop and Robson, *Tetrahedron Letters*, 1963, No. 9, 597.

[14] Stenberg and Perkins, *J. Org. Chem.*, 1962, **27**, 4111.

($\lambda_{max.}$ 320 mμ) on irradiation [15] must be explained differently, since the energy of the first excited singlet state of the latter lies 17·1 kcal. above that of the corresponding charge-transfer complex ($\lambda_{max.}$ 395 mμ). The energy of the first excited singlet state of maleic anhydride lies 34·3 kcal. above that of its singlet charge-transfer complex with benzene so the question of singlet–singlet quenching of the excited complex does not arise. The lack of parallel photochemical behaviour between maleic anhydride, *p*-benzoquinone, and tetracyanoethylene emphasises that relative reactivities based on reactions in the ground electronic states cannot be assumed to apply to reactions in excited electronic states.

A second mechanism of photoaddition to benzene is found with acetylenes. It was shown in Part VI that this does not occur via charge-transfer complexes.[3a] The nature of the excited intermediates in such reactions is currently being studied.

A third mechanism of photoaddition to benzenes may operate for olefins with electron-donating groups. The ability of benzonitrile to add such compounds as mono-olefins, vinyl acetate, and ethyl vinyl ether [16] contrasts with its failure to add maleic anhydride (see Table). We are investigating the possibility that the additions to benzonitrile involve exchange of the usual roles of donor and acceptor, as is the case with certain thermal 1,4-additions to dienes with electron-withdrawing substituents.[17]

EXPERIMENTAL

The ultraviolet source in all experiments was a Hanovia S-500 medium-pressure mercury arc lamp. The irradiation apparatus used was the water-cooled form of that previously described, unless otherwise indicated.[18]

2 : 1 *Photoadduct of Maleic Anhydride and Biphenyl.*—A solution of maleic anhydride (7 g.) and biphenyl (10 g.) in spectroscopically pure cyclohexane (180 ml.) was irradiated at 30° for 12 hr. under a slow stream of nitrogen. The 2 : 1 *adduct* of maleic anhydride and biphenyl (50 mg.), m. p. 280° (decomp.), precipitated, and was recrystallised from acetone (Found: C, 68·7; H, 4·15. $C_{20}H_{14}O_6$ requires C, 68·55; H, 4·0%). The rate of formation of the adduct was almost trebled when benzophenone (2 g.) was present in the above irradiated solution. The *tetramethyl ester*, m. p. 148°, was obtained in the normal way by the use of methanol and a trace of sulphuric acid (Found: C, 65·55; H, 6·0. $C_{24}H_{26}O_8$ requires C, 65·15; H, 5·9%). The infrared spectrum of the adduct had principal maxima at 1850m, 1764s, 1480w, 1225s, 1200m, 1075s, 1065m, 960w, 920s, 820m, 789w, 762s, 729m, and 700m cm.$^{-1}$.

Pyrolysis of the 2 : 1 *Photoadduct of Maleic Anhydride and Biphenyl.*—The adduct in a nitrogen-flushed Pyrex tube was plunged into a Wood's-metal bath at 300°. Maleic anhydride (m. p., mixed m. p.) and biphenyl (m. p., mixed m. p.) sublimed on to the cooler parts of the tube, leaving a small tarry residue.

Orange Crystalline 1 : 1 *Adduct of Maleic Anhydride and Quinol.*—A solution of maleic anhydride (5 g.) and quinol (5 g.) in ether (50 ml.) was allowed to evaporate slowly. The large orange crystals of a 1 : 1 *adduct* of maleic anhydride and quinol were easily separated from the starting materials by hand picking (Found: C, 57·2; H, 3·9. $C_{10}H_8O_5$ requires C, 57·7; H, 3·85%). The adduct dissociated to the starting materials without melting at 40—43° in an open capillary tube. Its infrared spectrum is recorded in the main text.

2 : 1 *Photochemical Adduct of Maleic Anhydride and Quinol.*—A melt of maleic anhydride (30 g.), quinol (30 g.), and benzophenone (7 g.) was irradiated for 36 hr. in a Pyrex flask above the ultraviolet lamp at such a distance as to keep the temperature of the melt at 70°. After solidification, the irradiated mixture was digested with diethyl ether, and the colourless 2 : 1 *adduct* (70 mg.), m. p. 285° (decomp.), was filtered off and recrystallised from acetone (Found: C, 55·1; H, 3·4. $C_{14}H_{10}O_8$ requires C, 54·9; H, 3·25%). Its infrared spectrum had principal maxima at 3330s, 1852m, 1763s, 1255m, 1230m, 1200m, 1080s, 1055m, 955m, 920s, 894w, 820w, 795w, 760m, 714m, and 694m cm.$^{-1}$.

Pyrolysis of the 2 : 1 *Photoadduct of Maleic Anhydride and Quinol.*—The adduct in a nitrogen-flushed Pyrex tube was plunged into a Wood's-metal bath at 300°. Maleic anhydride (m. p.,

---

[15] Bryce-Smith and Fray, unpublished work.
[16] Atkinson, Ayer, Büchi, and Robb, *J. Amer. Chem. Soc.*, 1963, **85**, 2257.
[17] Sauer and Wiest, *Angew. Chem.* (*Internat. Edn.*), 1962, **1**, 269.
[18] Blair, Bryce-Smith, and Pengilly, *J.*, 1959, 3174.

mixed m. p.) and a trace of quinol (m. p., mixed m. p.) sublimed into the cooler parts of the tube to leave a tarry residue.

2 : 1 *Photoadduct of Maleic Anhydride and* p-*Xylene*.—A solution of maleic anhydride (7 g.) and benzophenone (2 g.) in *p*-xylene (180 ml.) was irradiated for 12 hr. at 30° under a stream of nitrogen. The 2 : 1 *adduct* (0·10 g.), m. p. 340° (decomp.), was precipitated (Found: C, 63·95; H, 4·75. $C_{16}H_{14}O_6$ requires C, 63·55; H, 4·65%). The tetramethyl ester, m. p. 145°, was obtained by the use of methanol and a trace of sulphuric acid (Found: C, 61·0; H, 6·45 $C_{20}H_{26}O_8$ requires C, 60·9; H, 6·6%). The infrared spectrum of the adduct had principal maxima at 1854m, 1765s, 1230s, 1200m, 1100w, 1080s, 1050m, 960m, 948w, 915s, 850w, 820m, and 695m cm.$^{-1}$.

2 : 1 *Photoadduct of Maleic Anhydride and t-Butylbenzene*.—A solution of maleic anhydride (7 g.) and benzophenone (2 g.) and t-butylbenzene (180 ml.) was irradiated at 30° for 12 hr. under a slow stream of nitrogen. The 2 : 1 *adduct* (0·30 g.), m. p. 265°, was precipitated (Found: C, 65·6; H, 5·0. $C_{18}H_{18}O_6$ requires C, 65·45; H, 5·45%). The infrared spectrum had principal maxima at 1855m, 1764s, 1228s, 1200m, 1080s, 1070s, 953w, 915s, 812m, 785w, and 688m cm.$^{-1}$.

The 2 : 1 photoadducts of maleic anhydride and benzene, toluene, *o*-xylene, and chlorobenzene were prepared by irradiation of a solution of maleic anhydride (7 g.) and benzophenone (2 g.) in the aromatic compound (180 ml.) for 12 hr. at 30°. The properties of the products agreed with those previously reported.[2a,b,f]

For the experiments referred to in the Table, 2 g. of benzophenone and 7 g. of maleic anhydride were used in the presence of a large excess of the aromatic compound.

Nitrobenzene, benzonitrile, methyl benzoate, and acetophenone gave no photoadducts when they (180 ml.) were irradiated with maleic anhydride (7 g.) and benzophenone (2 g.) for 12 hr. at 30° under a slow stream of nitrogen. With acetophenone, uncrystallisable and apparently polymeric material (0·5 g.), m. p. 160° (decomp.), was formed (Found: C, 55·3; H, 5·7%; cf. ref. 2*c*). The omission of benzophenone led to similar results.

Biphenylene, naphthalene, durene, hexamethylbenzene, and phenol gave no photoadducts with maleic anhydride either by irradiation of solutions in cyclohexane or by irradiation of molten mixtures with or without benzophenone as sensitiser.

The spectra of charge-transfer complexes were obtained in chloroform solutions.

We thank Dr. J. W. McOmie for a specimen of biphenylene, the D.S.I.R. for a maintenance grant (to A. G.), and Esso Research Ltd. for laboratory facilities.

CHEMISTRY DEPARTMENT, THE UNIVERSITY, READING. [*Received, March 24th*, 1964.]