932. *Liquid-phase Photolysis. Part IV.* A Stable Adduct of Benzene and Maleic Anhydride.*

By H. J. F. Angus and D. Bryce-Smith.

Ultraviolet irradiation of solutions of maleic anhydride in benzene gave a crystalline 2 : 1 adduct. From chemical and physical evidence, this is considered to be tricyclo[4,2,2,$0^{2,5}$]dec-7-ene-3,4,9,10-tetracarboxylic acid dianhydride.

The use of an unsubstituted aromatic hydrocarbon as the diene component in Diels–Alder reactions has hitherto been confined to anthracene and the more complex polycyclic hydrocarbons. Reaction between naphthalene and maleic anhydride has been only barely detected, even when carried out under forced conditions, and no property of an adduct has been described.[1] The presence of vinyl substituents greatly increases the reactivity of aromatic hydrocarbons towards dienophiles, and the reactions of maleic anhydride with styrenes (*e.g.*, isosafrole and 1,1-diphenylethylene) constitute the only previously known, unambiguous examples of Diels–Alder addition to an isolated benzene ring.[2] In these the aromatic ring contributes only one double bond of the buta-1,3-diene unit. Cookson and Wariyar's [3] and Takeda's [4] 1 : 1 adducts from maleic anhydride and quinols provide possible examples of addition to a benzene ring, but it is not excluded that addition occurs to the alicyclic 1,3-diene system in the monoketo-tautomer of the quinol. Kitahonoki [5] was unable to prepare an adduct from quinol dimethyl ether and maleic anhydride. Barb [6] and Andrews and Keefer [7] obtained spectroscopic evidence for the formation of apparently weak, 1 : 1 charge-transfer complexes between some aromatic compounds, including benzene, and maleic anhydride or benzoquinone, but no adduct was isolated (cf. Pfeiffer and Böttler [8]).

As previously reported,[9] we have found that benzene and maleic anhydride form a stable 1 : 2 adduct at 60° under the influence of ultraviolet radiation. With the relatively intense source employed, *ca.* 1 g. of the adduct was formed during an irradiation time of

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* Part III, *J.*, 1960, 2003.

[1] Kloetzel, Dayton, and Herzog, *J. Amer. Chem. Soc.*, 1950, **72**, 273.

[2] Wagner-Jauregg, *Annalen*, 1931, **491**, 1; Hudson and Robinson, *J.*, 1941, 715; Bruckner, *Ber.*, 1942, **75**, 2034; Bruckner and Kovacs, *J. Org. Chem.*, 1948, **13**, 641; 1949, **14**, 65; Bruckner, Kovacs, and Huhn, *ibid.*, 1951, **16**, 1481; Walling, Briggs, Wolfstirn, and Mayo, *J. Amer. Chem. Soc.*, 1948, **70**, 1537; Hukki, *Acta Chem. Scand.*, 1951, **5**, 31; Alder and Schmitz-Josten, *Annalen*, 1955, **595**, 1.

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

[4] Takeda, *Annalen*, 1957, **606**, 153.

[5] Kitahonoki, *J. Pharm. Soc. Japan*, 1959, **79**, 396.

[6] Barb, *Trans. Faraday Soc.*, 1953, **49**, 143.

[7] Andrews and Keefer, *J. Amer. Chem. Soc.*, 1953, **75**, 3776.

[8] Pfeiffer and Böttler, *Ber.*, 1918, **51**, 1819.

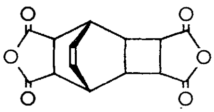
[9] Angus and Bryce-Smith, *Proc. Chem. Soc.*, 1959, 326.

18 hr. It was essential to keep the inner surface of the quartz cell optically clean by mechanical rubbing with glass wool, otherwise a brown resin was rapidly formed and reaction soon virtually ceased.

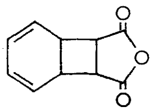
The adduct, $C_{14}H_{10}O_6$, had m. p. 350°, and was soluble in acetone, dimethylformamide, and dimethyl sulphoxide, but almost insoluble in benzene and ether. It was conveniently purified as the corresponding tetracarboxylic acid and had the calculated equivalent. Tetra-methyl and -ethyl esters were prepared. The former had a molecular weight very close to the expected value, and per-acid titration indicated the presence of one ethylenic bond. The anhydride decomposed at 360° *in vacuo* to give maleic anhydride and benzene as the only volatile, organic products. The benzene was completely free from fulvene, since this hydrocarbon is recognisable by its yellow colour at concentrations of only 0·01%.[10,11] Fulvene has been shown not to isomerise to benzene at 360°.[11]

Detailed stereochemical aspects are examined below, but it is considered that the new adduct is best formulated as tricyclo[4,2,2,$0^{2,5}$]dec-7-ene-3,4,9,10-tetracarboxylic acid dianhydride (I).

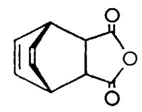
The nature of the initial radiation-induced step is uncertain. It may, on the one hand, involve a singlet–singlet transition of benzene to the first excited (B_{2u}) state, as discussed in Part III in connection with the photo-isomerisation to fulvene.[11] Alternatively, maleic anhydride may be the essential activated species. This second possibility is consistent with the observation that acetone apparently inhibited the isomerisation of benzene to fulvene, but was virtually without effect on the addition of maleic anhydride. Also, maleic anhydride, either alone or in hexane, was rapidly converted into an unidentifiable black material on irradiation, although this was not formed in benzene; but other explanations for both of these effects are possible. The reported formation of a charge-transfer complex between benzene and maleic anhydride is a further complication, particularly since the nature of the bonding involved, if any, remains unclarified.[6,7] Association of this type has been recognised by relatively high absorption between 270 and 350 mμ, not observed with benzene or maleic anhydride alone. Since the present ultraviolet source emitted strongly within this region, photoactivation of a charge-transfer complex could, in principle, precede the formation of an adduct having more conventional bonding; this possibility is also attractive from entropy considerations.* Whatever the true explanation may be, it seems most probable that the initial reaction is essentially a 1,2-addition, involving a photo-excited molecule, to give the adduct (II). Formation of (I) by the addition of a second molecule of maleic anhydride should be rapid and not require photo-activation.



(I)



(II)



(III)

In the formation of the isolated product (I) an initial 1,2-addition is considered to be more likely than the 1,4-type characteristic of conventional Diels–Alder reactions. Both (II) and (III), the 1,4-adduct, may be expected to dissociate readily into benzene and maleic anhydride, and only in the case of (II) could this be easily prevented by the addition of a second molecule of maleic anhydride. The suggested 1,2-addition has analogies in the photo-dimerisation of cinnamic acid to truxillic and truxinic acid, and of stilbene to tetraphenylcyclobutane.[12] If the initial addition were exclusively of the 1,4-type, two

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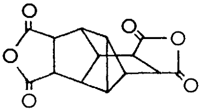
* *Added in Proof.*—Further work [21] has shown that this is the correct mechanism.

[10] Blair and Bryce-Smith, *Proc. Chem. Soc.*, 1957, 287.

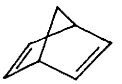
[11] Angus, Blair, and Bryce-Smith, *J.*, 1960, 2003.

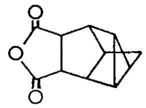
[12] Mustafa, *Chem. Rev.*, 1952, **51**, 1.

modes of addition to the 1,4-adduct (III) could be devised. First, (III) might undergo 1,2-addition to give (I), or some form of substitutive addition; but such an unusual process, to be reasonably rapid, would presumably require a further photo-activation stage: this is inherently improbable. Secondly, the adduct (III) might conceivably add maleic anhydride with rearrangement to give (IV); such a possibility is consistent with Ullmann's demonstration that bicyclo[2,2,1]hepta-2,5-diene (V) can add maleic anhydride to give (VI).[13] Since Ullmann's reaction required a high temperature and gave a low yield, the analogous reaction involving (III) appears unlikely to occur with the rapidity that would probably be necessary. Further, (IV) is saturated, in conflict with the present findings. It therefore seems unlikely that an initial 1,4-addition would be recognised by the eventual formation of stable products under the conditions we have used. This, however, in no way implies the absence of such an addition.



(IV)

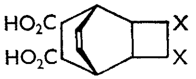

(V)



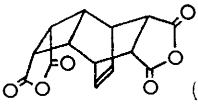
(VI)

Structure (I) for the benzene–maleic anhydride adduct is supported by considerable resemblances between the infrared spectrum of the corresponding tetracarboxylic acid and those of the acids (VII) derived from maleic anhydride adducts of some 7,8-disubstituted bicyclo[4,2,0]octa-2,4-dienes.* [14]

This is illustrated in the Figure for the acid derived from the adduct, m. p. 265°, of maleic anhydride and a 7,8-dichloro-derivative.



(VII)



(VIII)

(X = Cl or Br)

The absence of absorption maxima in the 1460 cm.$^{-1}$ region, which would arise from $\geqslant$CMe and $>$CH$_2$ deformation vibrations, provides further support for structure (I). Unfortunately, cyclobutanes cannot yet be unambiguously recognised from infrared spectra, but the adduct, its derivatives, and the acids (VII) show a moderately pronounced peak within the range 880—920 cm.$^{-1}$, in accordance with a tentative assignment.[15] The broad similarity illustrated in the Figure, particularly marked over the range 1100—4000 cm.$^{-1}$ and at 880 cm.$^{-1}$, seems to leave little doubt that closely related structures are involved.

The ultraviolet spectrum of the benzene–maleic anhydride adduct acid in water showed certain peculiarities. Maxima at 265 and *ca.* 205 mμ were observed, having $\varepsilon = 55$ and *ca.* 1000, respectively. These confirm the expected non-benzenoid character. On the other hand, the source of the low-intensity maximum at 265 mμ is not obvious from structure (I). Certain acids having a conjugated structure, *e.g.*, crotonic and oxalic acid, have a maximum of comparable intensity in this region,[16] although others, *e.g.*, maleic and itaconic acid and saturated carboxylic acids in general, show no well-defined maximum at wavelengths above 210 mμ. It is tempting in the present case to attribute this maximum to transannular interaction between –C=C– and –CO$_2$H (cf. Cookson and Wariyar [17]), and

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* These were kindly prepared by Mr. B. Vickery.

[13] Ullmann, *Chem. and Ind.*, 1958, 1173.

[14] Reppe, Schlichting, Klager, and Toepel, *Annalen*, 1948, **560**, 1.

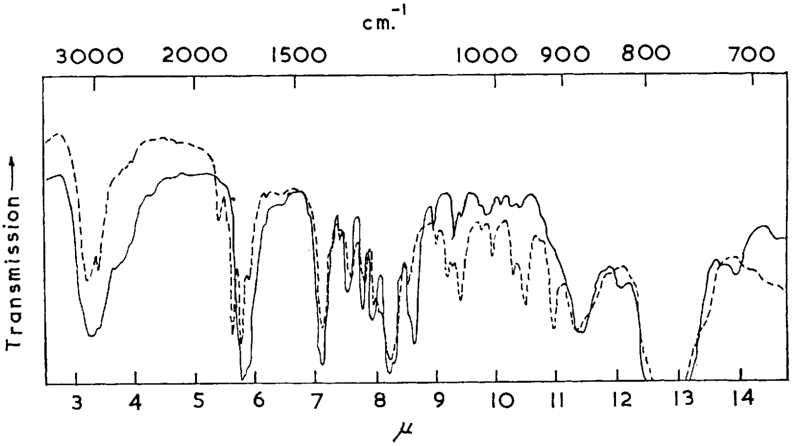
[15] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1958, pp. 13, 30, 31.

[16] Braude, *Ann. Reports*, 1945, **42**, 105.

[17] Cookson and Wariyar, *J.*, 1956, 2302.

this may also account for the maximum at 205 mμ, which has a magnitude between the values normally found with saturated and αβ-unsaturated carboxylic acids.

Stereochemistry of the Benzene–Maleic Anhydride Adduct.—Attempted fractionation gave no indication that the adduct was other than a single isomer. Considerations of group interactions, steric requirements, and the general *cis–endo* stereospecificity of Diels–Alder 1,4-addition suggest that structure (VIII) may best represent its configuration. Models indicate a rather close approach between the ethylenic bond (7,8) and the " cyclobutane " (2,3,4,5) anhydride ring. Any transannular interaction is likely to involve these features.



——— *Maleic anhydride–benzene adduct.*
– – – – *Maleic anhydride–*7,8-*dichlorobicyclo*[4,2,0]*octa*-2,4-*diene adduct.*

(*Free acids in carbon tetrachloride.*)

EXPERIMENTAL

Benzene was purified as described in Part III.[11] The photolysis apparatus (water-cooled form) has been described in Part I.[18]

Preparation of the Benzene–Maleic Anhydride Adduct.—The following describes a typical experiment. This was successfully repeated in experiments designed to build up a stock of the adduct.

A solution of maleic anhydride (5 g., 0·051 mole) in benzene (87 g., 1·1 mole) was irradiated at 55—60°, under nitrogen, for 18 hr., with stirring. The adduct formed a white deposit, m. p. 350° (decomp.),* on the cell walls, immediately above the liquid level, and less pure, pale-brown material was deposited on the glass wool. No fulvene was produced. Material insoluble in benzene was collected by filtration and removed from fragments of glass wool by dissolution in undried acetone. Evaporation of the acetone gave a pale-brown, solid residue, which was largely a mixture of the partly hydrolysed adduct and maleic anhydride. Two recrystallisations from water, with charcoal, gave the *acid* corresponding to the adduct (0·9 g., 11·5%) [Found: C, 54·1; H, 4·3%; equiv., 77·7. $C_{14}H_{14}O_8$ requires C, 54·2; H, 4·5%; equiv., 77·5 (calculated for a tetracarboxylic acid)]. With slow heating the acid was converted into the *anhydride*, m. p. 350° (decomp.), without melting (Found: C, 60·8; H, 3·6. $C_{14}H_{10}O_6$ requires C, 61·3; H, 3·6%), but with rapid heating it melted with frothing at *ca.* 280° (depending upon the rate), resolidified, and finally melted at 330—340° (decomp.). The anhydride was also prepared by heating the acid (0·05 g.) in acetic anhydride (15 ml.) under reflux for 2 hr., and was precipitated

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* This is believed to be more accurate than the m. p. 356° given in a preliminary communication.[9]

[18] Blair, Bryce-Smith, and Pengilly, *J.*, 1959, 3174.

by the addition of light petroleum (b. p. 40—60°). It was only sparingly soluble in dry hydrocarbons, ether, carbon tetrachloride, and cold ethanol, although traces of water in the solvents or in the air readily gave the acid; it was freely soluble in cold dimethylformamide and warm dimethyl sulphoxide. The ultraviolet spectrum of the acid in water had peaks at *ca.* 205 mμ ($\varepsilon \sim 1000$) * and 265 mμ ($\varepsilon = 55$), and a trough at 248 mμ ($\varepsilon = 47$).

The tetramethyl ester, m. p. 134°, was prepared by heating the acid (0·2 g.) under reflux for 7 hr. with methyl alcohol (5 ml.) and concentrated sulphuric acid (0·1 g.). The *ester* formed crystals from methyl alcohol (Found: C, 58·6; H, 5·9%; *M*, 356. $C_{18}H_{22}O_8$ requires C, 59·0; H, 6·0%; *M*, 366). The ester was titrated with perbenzoic acid, by the normal procedure, and shown to possess 1·1 ethylenic bonds (αβ-double bonds are generally relatively inert to perbenzoic acid [19,20]). The *tetraethyl ester*, m. p. 81°, was prepared similarly (Found: C, 62·8; H, 7·1. $C_{22}H_{30}O_8$ requires C, 62·5; H, 7·15%).

In further experiments no marked change in the yield of adduct was produced by wide variations in the proportion of maleic anhydride. Thus, 0·50 g. of maleic anhydride gave an 88% yield after 24 hr. The yield was found to be approximately proportional to the time of irradiation. An increase in the reaction temperature to 80° markedly decreased the yield.[21] The addition of acetone (10 ml.) before irradiation led to no significant decrease in yield. In the absence of maleic anhydride, this proportion of acetone in benzene was found to reduce the yield of fulvene to *ca.* 25% of that obtained when pure benzene was used.[11]

Thermal Decomposition of the Benzene–Maleic Anhydride Adduct.—The adduct (0·05 g.) was heated *in vacuo*, at 360° for 30 min. in a system having traps at 25° and −70°. Maleic acid (m. p. 135—136°, mixed m. p. 135—137°; infrared spectrum identical with that of the authentic material) collected in the first trap, and only water (m. p. 0°) and benzene (m. p. 3·5°; ultraviolet spectrum identical with that of the authentic material) appeared in the second. A little involatile tar was also formed. Maleic acid must have been present as the anhydride under the conditions of pyrolysis. The absence of fulvene from the benzene was recognised both visually and by the lack of absorption at 360 mμ.[11,22]

Infrared Data.—Peaks are listed as strong (s), medium (m), or weak (w). Wavelengths are in μ.

Benzene–maleic anhydride adduct: 3·4 (s), 5·45 (m), 5·7 (s), 7·7 (w), 8·0 (m), 8·2 (m), 8·4 (m), 8·7 (w), 9·25 (s), 9·5 (m), 10·0 (w), 10·4 (m), 10·9 (s), 11·2 (w), 12·2 (m), 12·6 (m), 13·1 (m), 14·0 (m), 14·4 (m), 14·6 (m).

Adduct acid: 3·2 (s), 3·4 (s), 5·8 (s), 7·1 (s), 7·5 (m), 7·8 (m), 7·9 (m), 8·2 (s), 8·5 (m), 8·6 (m), 8·95 (w), 9·3 (w), 9·4 (w), 9·85 (w), 10·0 (w), 10·2 (w), 10·4 (w), 11·35 (s), 12·0 (m), 12·4 (w), 13·0 (m), 13·75 (m), 14·6 (w).

Tetramethyl ester: 3·0 (w), 3·4 (s), 3·7 (w), 5·75 (s), 7·6 (m), 7·7 (w), 8·0 (m), 8·4 (s), 8·7 (s), 9·0 (w), 9·3 (m), 9·6 (w), 9·8 (m), 10·0 (w), 10·6 (m), 11·1 (m), 11·8 (w), 12·1 (m), 13·0 (w), 13·3 (m).

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* These values are rather uncertain owing to limitations of the spectrometer in this region.

[19] Wild, " Estimation of Organic Compounds," Cambridge University Press, 1953, p. 34.
[20] Bodendorf, *Arch. Pharm.*, 1930, **268**, 491.
[21] Bryce-Smith and Lodge, unpublished observations.
[22] Angus and Bryce-Smith, *J.*, 1960, 1409.