Photochemical Behaviour of Bridged Compounds. Part II.[1] Photolytic and some Ground State Reactions of Carbonyl-bridged Anhydrides and their Decarbonylation Products

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7-Oxonorborn-2-ene-5,6-dicarboxylic anhydrides (I) and cyclohexa-1,3-diene-5,6-dicarboxylic anhydrides (II), with various substituting or fused groups, give substituted benzenes (III) in substitution-dependent yields when irradiated at 2537 Å. A possible rationale for the photolytic decarbonylation is discussed. Some synthetic and ground state reactions of the systems studied are also described.

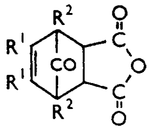
In Part I,[1] the novel photochemical removal of the anhydride group in conjunction with decarbonylation of substituted norbornen-7-ones (I) was described. Further

$$\text{(I)} \xrightarrow[-\text{CO}]{h\nu} \text{(II)} \xrightarrow[-(\text{CO}+\text{CO}_2)]{h\nu} \text{(III)} \qquad (1)$$

study revealed that the dienes (II) formed both in the thermal[2] and the photochemical decarbonylation processes underwent on photolysis the same CO + CO_2 elimination. In both cases the aromatic hydrocarbons (III) were formed in substitution-dependent yields. Meanwhile some of these results have been duplicated and described along with other observations;[3,4] this stimulated the publication of the present Report.

Photochemical decarbonylation of ketones was considered until recently[5] a less probable reaction in solution than in the gas phase. However numerous examples have now been recorded (see later). Almost invariably a particular driving force is identifiable in these processes, *e.g.*, strain relief, formation of thermodynamically stable molecules, and/or mesomeric stabilisation of the intermediate radicals.

The decarbonylation of substituted norbornen-7-ones was therefore examined in the hope that substituted bicyclohexenes and other interesting products would be formed. In the compounds (I) the anhydride group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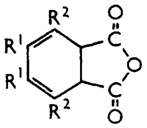
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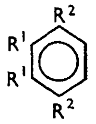
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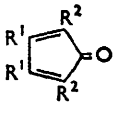
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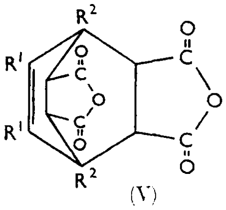
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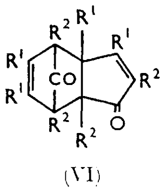
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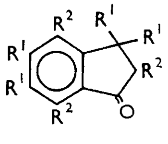
(VII)

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[1] B. Fuchs, *Israel J. Chem.*, 1965, **3**, 44p.

[2] (*a*) M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, 1965, **65**, 261; (*b*) C. F. H. Allen, *Chem. Rev.*, 1962, **62**, 653; 1945, **37**, 209.

[3] R. N. Warrener and J. B. Bremner, (*a*) *Angew. Chem.*, 1966, **78**, 305; (*b*) *Tetrahedron Letters*, 1966, 5691.

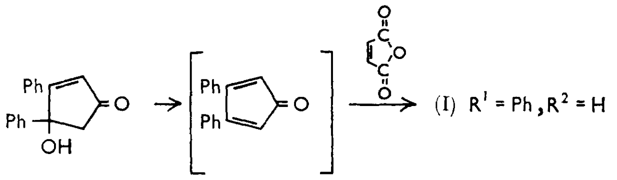
[4] H. Prinzbach, R. Kitzing, E. Druckrey, and H. Achenbach, *Tetrahedron Letters*, 1966, 4265.

[5] R. Srinivasan in 'Advances in Photochemistry,' Interscience, New York, 1963, vol. I, p. 83.

was intended to fulfil two functions: (*a*) to prevent open-chain triene formation (as obtained in non-fused systems [6–8]) by prohibiting the conrotatory opening of the six-membered ring, and (*b*) to make possible oxidative removal of the dicarboxylic function to give products of potential interest.

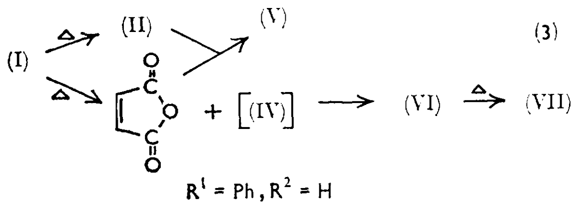
As outlined already,[1] the reaction takes an unusual course. The results shown [Table 1 and equation (1)] only include the aromatic hydrocarbons isolated. In all cases additional products still bearing the anhydride group have been observed in small yields. These are still under scrutiny and will be described in due course. It is, however, noteworthy that in numerous cases the dienes (II) could be isolated after incomplete irradiation.

Although the carbonyl-bridged anhydride (I; $R^1 = Ph$, $R^2 = H$) is mentioned in review articles [2] together with other analogues, it has apparently not been isolated, since no properties are recorded.[9a] It was therefore synthesised, from 5-hydroxy-1,5-diphenylcyclopenten-3-one (anhydracetonebenzil [10]) and maleic anhydride [equation (2)], and characterised, as was its thermal decarbonylation product, the diene (II; $R^1 = Ph$, $R^2 = H$). The thermal decarbonylation was accomplished by refluxing a bromobenzene solution of the ketone (I; $R^1 = Ph$, $R^2 = H$) in an inert atmosphere [the dienes are generally oxygen-sensitive at high temperatures as well as when irradiated (see later)]. The first insoluble product was the bis-anhydride (V; $R^1 = Ph$, $R^2 = H$,[9b] followed, on concentration of the solution, by the diene (II; $R^1 = Ph$, $R^2 = H$). Chromatography of the mother-liquor gave 3,3,5,6-tetraphenylindanone (VII); the latter is known [9c] to be formed from the dimer (VI; $R^1 = Ph$, $R^2 = H$) by decarbonylation and subsequent thermal rearrangement [equation (3)].



(2)

The bridged ketone (I; $R^1 = Ph$, $R^2 = Me$) decomposes in the same way to give the known [2,9d] bis-anhydride (V) and the diene (II; $R^1 = Ph$, $R^2 = Me$) followed by the dimer (VI; $R^1 = Ph$, $R^2 = Me$).[11] This is obviously a transformation involving a retro Diels–Alder process competing with the decarbonylation to (II) and followed by different cyclo-additions, *viz.*, formation of the bis-adduct (V) and dimerisation of (IV). This is apparently characteristic of the adducts (I) of maleic anhydride with dimerising cyclopentadienones (IV; $R^2 = H$ or Me),[2] whereas in the case of those adducts derived from stable monomers (IV; *e.g.*, $R^2 = Ph$), only a slight colouring of the solution is observed along with decarbonylation to the diene (II).



(3)

The photo-decarbonylation of (I) apparently provides the diene (II), the subsequent excitation of which causes its fragmentation to (II), CO, and CO_2. This sequence is suggested by certain observations in this work. Thus Table 1 shows slightly but consistently higher yields from the dienes (II) and the latter are occasionally isolated after incomplete irradiation of (I).

The photo-decarbonylation of ketones is amply documented; [5,8,12,13] saturated ketones seem to photolyse according to well established alternative patterns, one of which is the decarbonylation process. On the other hand,[13,14] a feature which greatly facilitates decarbonylation is the presence of $\beta\gamma$-unsaturation in the molecule. Typical examples are cyclopenten-4-one [8] and derivatives,[13] indan-2-one derivatives,[12,13] cyclohepta-1,3-dien-6-one,[19b] norbornen-7-one,[6a] and $\beta\gamma$-unsaturated 19-oxosteroids; [14] furthermore, a $\beta\gamma$-cyclopropane ring exerts the same effect, as exemplified by thujone,[13] bicyclo[3,1,0]hexan-3-one,[8] cyclopropylpropan-2-one,[8] etc.

In $\beta\gamma$-unsaturated ketones, it is the geometry of the molecules which determines their electronic spectral properties.[15–19] Compounds featuring a non-coplanar arrangement of the $\beta\gamma$-unsaturated ketone exhibit unusual strong $n \longrightarrow \pi^*$ transitions.[15,16] This has been attributed to the overlap of the non-bonding

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[6] (*a*) D. I. Schuster, H. F. T. Lee, A. Padwa, and P. G. Gassman, *J. Org. Chem.*, 1965, **30**, 2262; (*b*) see, however, P. G. Gassman and P. G. Pape, *J. Org. Chem.*, 1964, **29**, 160; (*c*) C. J. Norton, Ph.D. Dissertation, Harvard University, 1955.

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[8] J. G. Calvert and J. N. Pitts, jun., 'Photochemistry,' Wiley, New York, 1966, ch. 5.

[9] (*a*) C. F. H. Allen and L. J. Sheps, *Canad. J. Res.*, 1934, **11**, 171; (*b*) C. F. H. Allen and E. W. Spanagel, *J. Amer. Chem. Soc.*, 1933, **55**, 3773; (*c*) C. F. H. Allen and J. A. VanAllan, *J. Org. Chem.*, 1955, **20**, 315; (*d*) C. F. H. Allen and J. A. VanAllan, *J. Amer. Chem. Soc.*, 1942, **64**, 1261.

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[12] G. Quinkert, *Pure Appl. Chem.*, 1964, **9**, 607.

[13] J. E. Starr and R. H. Eastman, *J. Org. Chem.*, 1966, **31**, 1393.

[14] (*a*) J. Hill, J. Iriarte, K. Schaffner, and O. Jeger, *Helv. Chim. Acta.*, 1966, **49**, 292; (*b*) D. E. Poel, H. Wehrli, K. Schaffner, and O. Jeger, *Chimia* (*Switz.*), 1966, **20**, 110.

[15] H. Labhart and G. Wagnière, *Helv. Chim. Acta.*, 1959, **42**, 2219.

[16] R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 1956, 2302.

[17] S. Winstein, L. deVries, and R. Orloski, *J. Amer. Chem. Soc.*, 1961, **83**, 2020.

[18] E. M. Kosower, W. D. Closson, H. L. Goering, and J. C. Gross, *J. Amer. Chem. Soc.*, 1961, **83**, 2013.

[19] (*a*) J. Meinwald, S. L. Emerman, N. C. Yang, and G. Büchi, *J. Amer. Chem. Soc.*, 1955, **77**, 4401; (*b*) O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *J. Amer. Chem. Soc.*, 1962, **84**, 1220.

p-orbital of the oxygen atom with the π-orbital of the double bond in its ground state; the orbitals are energetically similar. On the other hand, when the two chromophores are coplanar, the system has a ' normal ' low extinction $n \longrightarrow \pi^*$ band[6,16-18] but may exhibit an additional $\pi \longrightarrow \pi^*$ transition at relatively high wavelength (200—250 mμ), where a charge transfer is involved.[15] The geometrical array of the bridged ketones (I) apparently meets the requirements for the latter behaviour,[6,17] this is also reflected in their electronic absorption spectra (Table 2). This feature is probably responsible for the first step in our photolytic process, namely the decarbonylation to the diene (II);† the excitation initiating it is apparently the $\pi \longrightarrow \pi^*$ transition. This assertion is supported by the finding (also mentioned by Schuster *et al.*[6a]) that long-wavelength irradiation with ' Pyrex ' filters suppresses the rate as well as the yield of decarbonylation; also no photosensitisation was observed in such experiments. Decarbonylation of saturated ketones is generally initiated by $n \longrightarrow \pi^*$ excitation (*e.g.*, at 313 mμ).[8] This is still considered as an alternative, though less efficient, way of photolysing the systems we deal with and may lead to different excited intermediates and products.[3b]

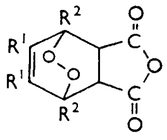
The formation of stable species in the various stages of the described processes constitutes undoubtedly an important driving force, *viz.*, the evolution of CO and CO_2, the formation of conjugated dienes and aromatic compounds, and the allylic stabilisation of the (diradical) intermediate. This could also provide a reason for observations such as the low yield of aromatic product (III) in the photolysis of the cyclopentaphenanthrenone–maleic anhydride adduct (IX) (Table 1, entry 5), which may reflect the reluctance of (IX) to undergo a first-step transformation from a phenanthrene into a 9,10-phenanthraquinonoid structure. This is supported by the fact that thermal decomposition of (IX) requires very high temperatures and does not yield the corresponding diene of type (II) but what we believe to be a product with the double bonds rearranged.[20] In the case of the cyclopentacenaphthylenone derivative (X), the strain relief[21] in changing from an acenaphthylene to an acenaphthene quinonoid structure might facilitate the process (I) $\longrightarrow$ (II). Finally, there is the similarity in ready occurrence of the thermal and the photolytic decarbonylation, both of which give the same primary products (II). This could be understood from symmetry considerations: both processes must be and are able to occur in the favourable sigmasymmetric fashion.[22]

TABLE 1

Yields (%) of aromatic product (III)

	R^1	R^2	Irradiation of ketone (I)	 diene (II)
1	Ph	Me	86	98
2	Ph	Ph	64	65
3	Ph	H	42	51
4	1,8-Naphthylene	Et	32	49
5	*oo'*-Biphenylene	Ph	22	*a*

[a] Unavailable (see text)



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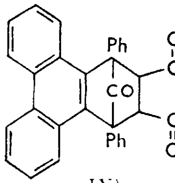

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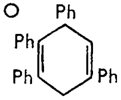
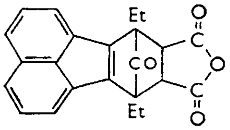


(XII)



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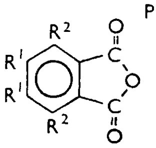

(XI)

For the second photolytic step, the elimination of the anhydride function (CO + CO_2) from (II), it is difficult at this stage to make a definite assignment and further investigation is necessary. However, in a chemical attempt to achieve it, by treatment of (II) with lead tetra-acetate in pyridine,[23] no aromatic hydrocarbon could be isolated and the correspondingly substituted phthalic anhydrides (XI) were obtained instead.

We believe that the variation in yields of aromatic hydrocarbon (Table 1) stems, at least in part, from the difference between the absorption spectra of the products and those of the starting materials and intermediate dienes (Table 2). Specifically, the aromatic products which absorb strongly at the irradiated wavelength could effectively suppress the first photochemical process and thus cause a smaller yield. Another factor which most likely affects the yields is the nature of the bridgehead substituents [(R^2) in (I) and (II)]. Alkyl[13] or phenyl[12] substituents must stabilise the diradicals formed in the excited state. Support for the assumption of diradical formation[12] is to be found in the high sensitivity to molecular oxygen during photolysis (as well as in the ground state—see previously). As expected, this sensitivity is lower for the phenyl substituted compounds (R^2 = Ph) and very high in the others (R^2 = H or alkyl), from which peroxides (VIII) have actually been isolated and characterised.[20]

In a recent communication by Warrener and Bremner[3b] it is stated that photolysis of (I) and (II) ($R^1 = R^2$ = Ph) gives mainly 1,2,3,5-tetraphenylbenzene. We could not detect any isomers in our products; melting points and g.l.c. showed absolute homogeneity. We suggest that

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† Other examples of systems featuring the discussed $\pi \longrightarrow \pi^*$ (charge transfer) transition, are to be found in the literature; some of them have also been successfully decarbonylated.[6a,8,12-14,16-19]

[20] B. Fuchs, unpublished results.

[21] V. Balasubramaniyan, *Chem. Rev.*, 1966, **66**, 567.

[22] D. S. Lemal and S. D. McGregor, *J. Amer. Chem. Soc.*, 1966, **88**, 1335.

[23] E. E. van Tamelen and S. P. Pappas, *J. Amer. Chem. Soc.*, 1963, **85**, 3297.

in their case a different excited species is involved, caused by the entirely different range of irradiation[3b] (high pressure Hg lamp, 'Pyrex' filter, and benzene solution). The strained non-planar intermediate may take advantage of the excitation in this range to rearrange. A similar process has been described recently by Theis and Dessy;[24] albeit this yields the rearranged diene (XIII) by photo-induced electrocyclic closure of 1,3,4,6-tetraphenylhexatriene.

TABLE 2

Electronic absorption spectra of (I), (II), and (III): $\lambda_{max.}$ in mμ (log ε)

	R^1	R^2	(I)	(II)	(III)
1	Ph	Me	227(4·16) 256(3·96)	225(4·01) 235sh(3·9) 271(3·63)	235(4·01) 276sh(3·0) 300sh(2·4)
2	Ph	Ph	226(4·33) 265sh(4·02)	216(4·19) 235(4·24) 317(4·05)	247(4·44) 274sh(4·18)
3	Ph	H	232(4·28) 288(3·97)	231(4·20) 266(3·71)	232(4·36) 248sh(4·06)
4 [b]	1,8-Naphthylene	Et	213(4·11) 232(4·65) 260(3·75) 271(3·73) 320(4·03) 327(4·13) 334(4·00) 345(3·70) 351(3·78)	243(4·47) 260sh(4·25) 339(3·96) 356(4·06) 372(3·96)	242(4·72) 264(4·44) 269(4·44) 281(4·31) 292(4·20) 310(3·70) 324(3·97) 358(4·15) 375(4·11)
5 [c]	*oo*′-Biphenylene	Ph	214(3·92) 222(3·92) 254(4·04) 262(4·13) 271(3·82) 286(3·79) 298(3·47) 310(3·78)	*a*	236(4·55) 260, 270sh 282(4·66)

[a] Unavailable (see text). [b] Formula (X) for (I). [c] Formula (IX) for (I).

EXPERIMENTAL

The u.v. spectra were recorded with a Perkin-Elmer 137 spectrophotometer with tetrahydrofuran as solvent. No attempts to obtain more accurate spectra were made, since, for most of the anhydrides, absolute elimination of impurities is exceedingly difficult. The i.r. spectra were measured with a Perkin-Elmer 237 spectrophotometer (chloroform solutions or potassium bromide discs), and n.m.r. spectra were recorded with a Varian A-60 spectrometer (deuteriochloroform solutions with tetramethylsilane as internal standard). Mass spectra were obtained with an Atlas CH4 instrument. The g.l.c. analyses were performed with a Beckmann GC-2 instrument equipped with a SE-30 column, at 220°.

Irradiations were carried out with a low-pressure Hg lamp (Hanau NK 6/20) in a quartz well at *ca.* 25°. Absolute ether solutions * (*ca.* 10^{-4}M) were swept with inert gas prior to and during photolysis. Yields are reported (Table 1) from those experiments in which no further change occurred on continued irradiation.† They were determined by filtering the products through basic alumina; only the aromatic hydrocarbons were eluted. Identity and homogenity were established by m. p., g.l.c. analysis, and i.r., u.v., n.m.r., and mass spectra.

The only new aromatic hydrocarbon is 7,10-*diethylfluoranthene* (Table 1, entry 4), m. p. 144°, M^+ 258, τ 8·51 (3H, triplet), 6·75 (2H, quadruplet), and 1·5—2·6 (8H, multiplet) (Found: C, 92·8; H, 7·1. $C_{20}H_{18}$ requires C, 93·0; H, 7·0%). All other products have been described as have the starting materials[2] except for (I and II; R^1 = Ph, R^2 = H).

7-*Oxo*-2,3-*diphenylnorborn*-2-*ene*-5,6-*dicarboxylic Anhydride* (I; R^1 = Ph, R^2 = H).—5-Hydroxy-1,5-diphenylcyclopenten-3-one[9,10] (10 g.) and maleic anhydride (10 g.) were heated in a pressure bottle at 135° for 6 hr. The mixture was cooled and triturated with dichloromethane. An insoluble high-melting solid was collected (5·5 g.). The filtrate was concentrated and poured on to a column of silica gel (Matheson; 300 g.). Elution with chloroform gave a little ketonic material; acetone–chloroform (1 : 9) eluted the main fraction. Crystallisation from dichloromethane–carbon tetrachloride gave the *anhydride* (I; R^1 = Ph, R^2 = H) (5 g., 34%), m. p. 165° (decomp.) $\nu_{max.}$ (CO) 1785, 1798, 1835, and 1870 cm.$^{-1}$, τ 6·1 (4H, octuplet), 2·7 (10H singlet), M^+ 330 (Found: C, 75·8; H, 4·5; O, 19·6. $C_{21}H_{14}O_4$ requires C, 76·3; H, 4·3; O, 19·4%).

Thermal Decarbonylation of (I; R^1 = Ph, R^2 = H).—A solution of (I; R^1 = Ph, R^2 = H) (1 g.) in bromobenzene (30 ml.) was swept with nitrogen, refluxed for 4 hr. in an atmosphere of nitrogen, and cooled. The solid anhydride (V; R^1 = Ph, R^2 = H)[9b] (105 mg.) was collected, m. p. 350°.

The filtrate was concentrated *in vacuo* and hexane was added to yield the *diene* (II; R^1 = Ph, R^2 = H) (380 mg., 42%), m. p. 128—129° (from ether–pentane under nitrogen because of the sensitivity of the product when heated to oxygen as well as to chlorinated solvents such as carbon tetrachloride), $\nu_{max.}$ (CO) 1790 and 1872 cm.$^{-1}$, τ 5·85 (2H, quadruplet) and 2·9 (10H, multiplet), M^+ 302 (Found: C, 79·5; H, 4·6. $C_{20}H_{14}O_3$ requires C, 79·4; H, 4·7%).

The mother-liquor was filtered through a column of basic alumina to yield 3,3,5,6-tetraphenylindanone (XII), i.r. spectrum identical with that of an authentic sample prepared from 5-hydroxy-1,5-diphenylcyclopenten-3-one.[9c]

Thermal Decarbonylation of (I; R^1 = Ph, R^2 = Me).—This was performed under the same conditions as described for (I; R^1 = Ph, R^2 = H). The keto-anhydride (1 g.) yielded the dianhydride (V; R^1 = Ph, R^2 = Me)[9b] (60 mg.), m. p. 320—321° and the diene (II; R^1 = Ph, R^2 = Me)[10d] (300 mg., 33%), m. p. 157—158°. The mother-liquor provided dimer (VI; R^1 = Ph, R^2 = Me)[11] (22 mg.).

Lead Tetra-acetate Oxidation of (II; R^1 = Ph, R^2 = Ph, Me, or H).—The diene-anhydride (II) (100 mg.), in pyridine (2 ml.) or benzene (5 ml.), was treated with an excess of lead tetra-acetate. The reaction mixture was heated for 5 min. on a steam-bath, cooled, and poured into an excess of 3N-hydrochloric acid. Extraction with ether provided the known phthalic anhydrides (XI; R^1 = Ph, R^2 = Ph, Me or H)[2a] as the only isolable products.

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* Use of pure acetone as solvent did not alter the results appreciably.

† In experiments where irradiation was incomplete, concentration of the solution provided, in varying yields, (I) and/or (II). The mother-liquor contained the aromatic hydrocarbon (III) with minor by-products.

[24] R. J. Theis and R. E. Jessy, *J. Org. Chem.*, 1966, **31**, 4248.