# Fulvenes and Thermochromic Ethylenes. Part LXXXIII.[1] 'Double Dibenzotropones' within $C_6$-$C_7$-$C_6$-$C_7$-$C_6$ Ring Systems. Synthesis of Bisbenzo[4,5]cyclohepta[1,2-a:2',1'-d]benzene-5,7-dione and Bisbenzo-[4,5]cyclohepta[1,2-a:1',2'-d]benzene-5,13-dione

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Condensation of pyromellitic anhydride with phenylacetic acid (2 mol. equiv.) gave the two isomeric di-γ-lactones of 4,6-bis-(α-hydroxystyryl)isophthalic acid (IX) and 2,5-bis-(α-hydroxystyryl)terephthalic acid (X) in the ratio of 5:3. 4,6-Bis-(2-phenylethyl)isophthalic acid (XI) and 2,5-bis-(2-phenylethyl)terephthalic acid (XIII), formed by reduction of (IX) and (X), respectively, have been cyclized and dehydrogenated to bisbenzo[4,5]-cyclohepta[1,2-a:2',1'-d]benzene-5,7-dione (III) and bisbenzo[4,5]cyclohepta[1,2-a:1',2'-d]benzene-5,13-dione (IV).

SINCE the first syntheses of dibenzo[a,d]cyclohepten-5-one (I) and its 10,11-dihydro-derivative (II),[2] exploration of these systems has been conducted in two directions: (a) the study of the 'aromaticity' and the spatial structure of 5H-dibenzo[a,d]cycloheptene derivatives,



(I)    (II)

(III)    (IV)

(V)    (VI)
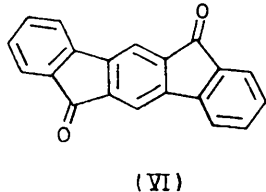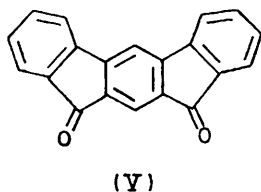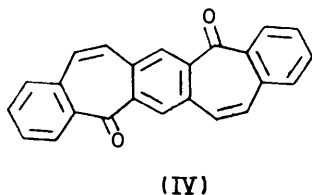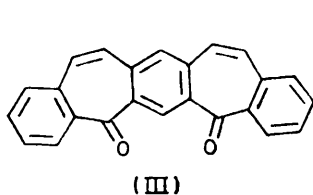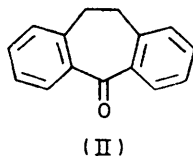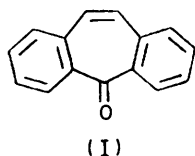
with special reference to dibenzotropones and dibenzo-heptafulvenes[3] and (b) the preparation of psycho-pharmacological agents of the amitriptyline type.[4] Several benzo- and dibenzo-derivatives of (I) and (II) have been studied,[5-7] and the present paper describes

the syntheses of two new linearly annulated $C_6$-$C_7$-$C_6$-$C_7$-$C_6$ polycyclic systems (III) and (IV) closely related to (I). These systems may be considered as 'double dibenzotropones': the preparation of the analogous 'double fluorenones,' (V) and (VI), has been reported.[8]

The method of approach was the general synthesis of dibenzo[a,d]cyclohepten-5-one derivatives, in which the seven-membered ring is constructed by an intramolecular Friedel–Crafts acylation.[2,9] A double Perkin condensation (under the Gabriel–Weiss modification [10,11]) of phenylacetic acid (VII) and pyromellitic anhydride (VIII) gave a mixture of the two isomeric di-γ-lactones (IX) and (X), in the ratio of 5:3. The two isomers were separated by repeated fractional recrystallization. The structural assignments of (IX) and (X) were based on unambiguous chemical degradations (see below). The preparation of (IX) and (X) by condensation of (VIII) and (VII) had been reported, but their structures had not been previously established.[12] The n.m.r. spectra of (IX) and (X) were consistent with their structures. The symmetry of (X) was reflected in the downfield aromatic singlet at δ 8·49 (in $FSO_3H$) representing two magnetically equivalent protons ortho to the carbonyl groups. In the case of (IX), the two non-equivalent protons of the central benzene ring gave two singlets at δ 8·38 and 8·63 (in $FSO_3H$); the latter is probably due to the proton ortho to the two carbonyl groups. A priori, either of the two dilactones (IX) and (X) could exhibit geometrical isomerism around each of its olefinic bonds. In each case, three geometrical configurations should be considered: $(Z,Z)$, $(Z,E)$, and $(E,E)$. It has previously been noted that this type of condensation gives almost

[1] Part LXXXII, I. Agranat and S. Dinur, *Chemica Scripta* (Sweden), in the press.

[2] (a) W. Treibs and H.-J. Klinkhammer, *Chem. Ber.*, 1950, 83, 367; (b) E. D. Bergmann, E. Fischer, D. Ginsburg, Y. Hirshberg, D. Lavie, H. Mayot, A. Pullman, and B. Pullman, *Bull. Soc. chim. France*, 1951, 18, 684; (c) A. C. Cope and S. W. Fenton, *J. Amer. Chem. Soc.*, 1951, 73, 1668.

[3] (a) E. D. Bergmann, *Progr. Org. Chem.*, 1955, 3, 81; (b) E. D. Bergmann, *Chem. Rev.*, 1968, 68, 41.

[4] (a) C. Kaiser and C. L. Zirkle in 'Medicinal Chemistry,' part II, 3rd edn., ed. A. Burger, Wiley-Interscience, New York, 1970, p. 1470; (b) G. N. Walker, D. Alkalay, A. R. Engle, and R. J. Kempton, *J. Org. Chem.*, 1971, 36, 466.

[5] E. D. Bergmann and R. Ikan, *J. Org. Chem.*, 1963, 28, 3341.

[6] E. D. Bergmann and I. Agranat, *J. Chem. Soc. (C)*, 1971, 3532.

[7] I. Agranat and D. Avnir, *J.C.S. Chem. Comm.*, 1973, 362.

[8] (a) W. Deuschel, *Helv. Chim. Acta*, 1951, 34, 168; (b) W. Deuschel, *ibid.*, 1951, 34, 2403; (c) L. Chardonnens and R. Ritter, *ibid.*, 1955, 38, 393; (d) L. Chardonnens and H. Chardonnens, *ibid.*, 1958, 41, 2109; (e) L. Chardonnens and J. Rody, *ibid.*, 1959, 42, 1328.

[9] S. O. Winthrop, M. A. Davis, G. S. Myers, J. G. Gavin, R. Thomas, and R. Barber, *J. Org. Chem.*, 1962, 27, 230.

[10] S. Gabriel, *Ber.*, 1885, 18, 3470.

[11] R. Weiss, *Org. Synth.*, Coll. Vol. II, 1943, p. 61.

[12] A. Schönberg and G. Schütz, *Chem. Ber.*, 1961, 94, 667.

exclusively the (Z)-isomer of the condensation product.[13] The n.m.r. absorption of the vinyl protons of (IX) appears at δ 6·45 [CDBr₃; (Me₃Si)₂; 140°] and is consistent with the (Z,Z)-configuration.[14] [The n.m.r. spectrum of (X) could not be taken in CDBr₃ for solubility reasons.] The same conclusion may be drawn from the n.m.r. spectra of (IX) and (X) in FSO₃H, in which the vinyl protons gave singlets at δ 7·26 and 7·12 respectively. For comparison, the vinyl protons of

phthalic acid (XIII) in 95% yield and traces of the di-γ-lactone (XIV). The structures of the saturated di-γ-lactones (XII) and (XIV) and the acids (XI) and (XIII) were supported by the spectroscopic evidence. The pattern of the aliphatic absorptions in the n.m.r. spectra of the ' saturated ' di-γ-lactones was approximately A₂X: δ (XII) 2·95—3·35 (4H, m) and 5·60—5·72 (2H, t); δ (XIV) 3·20—3·26 (4H, d) and 5·60—5·82 (2H, m). In the aromatic region, the absorptions due
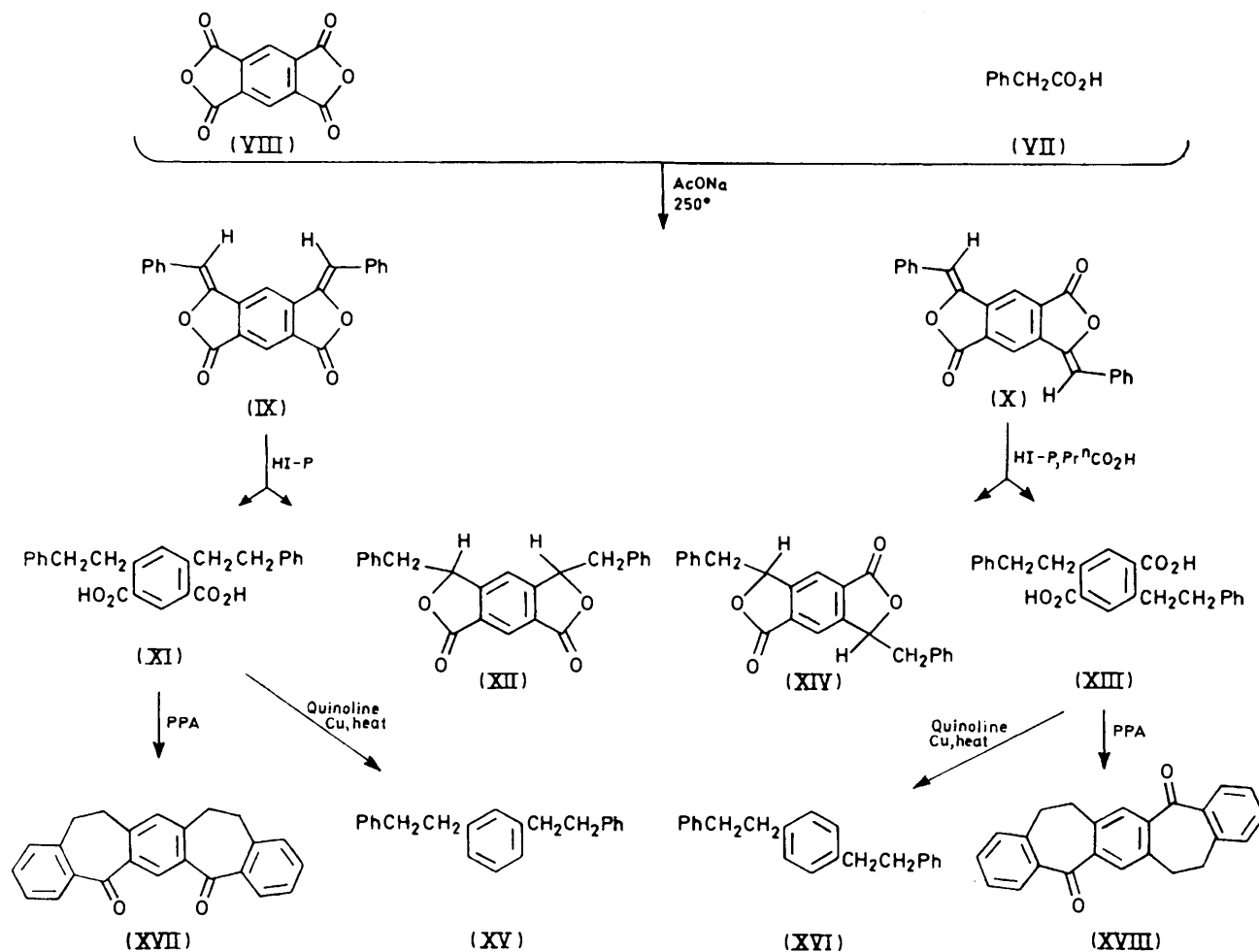


(Z)-3-benzylidenephthalide appear in FSO₃H at δ 7·16. This aspect of the problem was not clarified unequivocally since the relevant olefinic bonds were to be removed in later steps of the syntheses of (III) and (IV). The extensive conjugation in the two unsaturated di-γ-lactones was indicated by the long wavelength u.v. absorption maxima.

Reduction and hydrogenolysis of (IX) with red phosphorus and boiling aqueous hydriodic acid (68%) proceeded in the usual manner, yielding the isophthalic acid (XI) as the major product and traces of the di-γ-lactone (XII). Under identical conditions, (X) failed to react. The reduction and hydrogenolysis of (X) were effected only with red phosphorus and aqueous hydriodic acid (68%) in boiling butyric acid, affording the tere-

to the protons of the central benzene rings of (XII) and (XIV) reflected the different symmetries of the two structures [δ (XII) 8·08—8·12 (1H, d) and 6·80—6·84 (1H, d) while δ (XIV) 7·60 (2H, d)]. The signal of the proton ortho to the two carbonyl groups in (XII) was significantly shifted upfield (0·37 p.p.m.) relative to the corresponding absorption of (IX). Apparently, the reduction of the olefinic double bonds of (IX) causes the neighbouring carbonyl groups in (XII) to be tilted out of the plane of the central benzene ring [relative to their orientation in (IX)].

The preparation of the di-acids (XI) and (XIII) per-

[13] G. Berti, Gazzetta, 1956, 86, 655.
[14] J. Rigaudi and P. Derible, Bull. Soc. chim. France, 1965, 3047, 3055, 3061.

mitted a straightforward chemical proof of their structures, and of the structures of (IX) and (X). Decarboxylation of (XI) in boiling quinoline in the presence of copper powder gave 1,3-bis-(2-phenylethyl)-benzene (XV), which was identical with an authentic sample of (XV) prepared by a catalytic hydrogenation of (E,E)-1,3-distyrylbenzene. An analogous decarboxylation of (XIII) gave 1,4-bis-(2-phenylethyl)-benzene (XVI), identical with an authentic sample of (XVI) prepared according to the literature.[15]

Double cyclizations of the diacids (XI) and (XIII) with polyphosphoric acid (PPA) at elevated temperatures afforded the diones (XVII) and (XVIII). In order to affect the ' double cyclizations,' considerably higher temperatures, compared with the ordinary temperatures (100°) employed in the 'mono cyclization,'[2] were required [140° for (XVII) and 155° for (XVIII)]. This difference of behaviour may be due to the insolubility of the diacids (XI) and (XIII) in PPA at the lower temperatures, and the second cyclization

tropones ' [(III) and (IV)] is [as in the case of (I)] negligible.

The spatial structure of (I) has been determined by X-ray crystallography,[17] and it has been established that the molecule of (I) (in the solid state) is not planar: the seven-membered ring is in the boat conformation, and the two benzene nuclei planes are inclined to each other at the angle of 39°. Furthermore, the bond lengths and angles indicate that there is no contribution from the dipolar (' aromatic ') structure. The dipole moments of (I) and its 3-chloro- and 3,7-dichloro-derivatives (in solution) are also in accord with the non-planar conformation.[18] A few conclusions pertaining to the spatial structures of the pentacyclic diketones (III), (IV), (XVII), and (XVIII) may be drawn from their n.m.r. spectra (Table 1). The absorptions of the aromatic protons *ortho* to the carbonyl groups give some indication of the spatial orientation of the carbonyl groups relative to their neighbouring benzene nuclei. These protons may be divided into two types; type (a)

TABLE 1

N.m.r. spectra and i.r. carbonyl bands of compounds (I)—(IV), (XVII), and (XVIII)

δ

| Compound | H-6 | H-4 | Other aromatic | CH=CH bridge | $CH_2CH_2$ bridge | $\nu_{C=O}/cm^{-1}$ [d] |
|---|---|---|---|---|---|---|
| (I) [a] | | 8·13—8·23 (m) | 7·30—7·59 (m) | 6·88 (s) | | 1645 |
| (II) [a] | | 7·97—8·06 (m) | 7·18—7·52 (m) | | 3·18 (s) | 1650 |
| (III) [b] | 8·90 (s) | 8·12—8·21 (m) | 7·34—7·60 (m) | 6·96 (s) | | 1647 |
| (IV) [c] | 8·31 (s) | 8·13—8·24 (m) | 7·36—7·54 (m) | 7·06 (AB) | | 1642 |
| (XVII) [a] | 8·71 (s) | 7·90—8·00 (m) | 7·04—7·45 (m) | | 3·13 (s) | 1641 |
| (XVIII) [a] | 7·87 (s) | 7·90—8·00 (m) | 7·16—7·47 (m) | | 3·22 (s) | 1650 |

[a] N.m.r. spectra in $CDCl_3$ ($Me_4Si$). [b] N.m.r. spectra in $CDBr_3$ [$(Me_3Si)_2$; 100°]. [c] N.m.r. spectra in $CDBr_3$ [$(Me_3Si)_2$; 130°]. [d] I.r. spectra in Nujol.

might possibly be retarded after the first cyclization has occurred. In spite of the extreme conditions the ' double cyclizations ' followed the normal course: rearrangements of the conjugate acids of the diketones did not occur[7,16] and the products had the expected linearly annulated structures. The i.r. carbonyl absorption of the two diketones appeared at 1641 (XVII) and 1650 cm⁻¹ (XVIII), in accord with the 1650 cm⁻¹ band of (II) The aliphatic protons of the seven-membered rings gave a singlet at δ 3·13 (XVII) and 3·22 (XVIII): the corresponding singlet of (II) appeared at δ 3·18. The absorptions in the aromatic region of the n.m.r. spectra were also in accord with the structures of the diketones (see below).

Dehydrogenation of (XVII) and (XVIII) with N-bromosuccinimide in the presence of benzoyl peroxide followed by triethylamine gave the desired diketones (III) and (IV) respectively. The i.r. carbonyl absorptions appeared at 1647 (III) and 1642 cm⁻¹ (IV), indicating hardly any shift from the respective frequencies of (I) (1645 cm⁻¹), (II), (XVII), and (XVIII). From this point of view, the dipolar character in each of the seven-membered rings of the ' double dibenzo-

consists of the protons of the central benzene nuclei [H-6 in (III) and (XVII); H-6 and H-14 in (IV) and (XVIII)]; type (b) consists of the protons of the end-benzene nuclei [H-4 and H-8 in (III) and (XVII); H-4 and H-12 in (IV) and (XVIII)]. The absorptions of the protons of type (b) are very similar to the corresponding absorptions of (I) and (II) which appear as multiplets at δ 8·13—8·23 (I) and 7·90—8·00 (II). The downfield shifts of the former absorptions relative to the latter ones indicates that the tilting of the carbonyl group out of the planes of the benzene nuclei is smaller in the unsaturated ketone (I) than in its 10,11-dihydro-derivative (II). In considering the protons of type (a), a distinction should be made between the diketones with a σ-symmetry [(III) and (XVII)] and the diketones with an *i*-symmetry [(IV) and (XVIII)]. The remarkable downfield shifts of H-6 in the cases of (III) and (XVII) [δ 8·90 (III) and 8·71 (XVII)] should be attributed to the diamagnetic anisotropy of two *ortho*-carbonyl groups. In spite of the overcrowding in these systems, the degree of tilting of the two carbonyl groups out of the planes of the benzene nuclei is relatively small. The difference in these shifts between (III) and (XVII) is

[15] T. Kauffmann, C. Kosel, and W. Schoeneck, *Chem. Ber.*, 1963, **96**, 999.

[16] D. E. Pearson and C. A. Buehler, *Synthesis*, 1971, 455.

[17] H. Shimanouchi, T. Hata, and Y. Sasada, *Tetrahedron Letters*, 1968, 3573.

[18] H. Weiler-Feilchenfeld and A. Solomonovici, *J. Chem. Soc. (B)*, 1971, 869.

approximately the same as the respective difference between (I) and (II) (0·2 p.p.m.). In the $i$-isomers, the difference in the chemical shifts of the protons of type (a) between the unsaturated diketone (IV) and its 7,8,15,16-tetrahydro-derivative (XVIII) is much more pronounced, 0·44 p.p.m. [δ (H-6) (IV) 8·31 while δ (H-6) (XVIII) 7·87]. In the case of (IV), the introduction of two olefinic bridges forces the molecule into a steric configuration in which a smaller deviation from planarity relative to that in (XVIII), is attained. The n.m.r. absorptions due to the protons of the olefinic bridges appeared in the case of (III) as a singlet (δ 6·96) while in the spectra of (IV), an AB quartet at δ 6·93 and 7·18 ($J$ 13 Hz) was observed. This magnetic non-equivalence may be due to the effect of each carbonyl group of one cycloheptene ring on the neighbouring olefinic proton of the other cycloheptene ring. Such an effect may operate in the case of (IV) [(C(5)=O on H-7 and C(13)=O on H-15] but not in the case of (III). For comparison, the protons of the CH=CH bridge in (I) give a singlet at δ 6·88. It is doubtful whether this probe may serve as a criterion for evaluating the dipolar (' aromatic ') character in the seven-membered ring of (I).[19,20] However, even if it may, the contribution (if any) of the dipolar (' aromatic ') character in the ' double dibenzotropones ' (III) and (IV) remains practically unaltered compared with that of (I).

Finally, we discuss the mass spectra of the diketones (III), (IV), (XVII), and (XVIII). Under electron

TABLE 2

Relative intensities of some prominent signals in the mass spectra of compounds (I)—(IV), (XVII), and (XVIII)

| | Signal intensity(%) | | |
|---|---|---|---|
| Compound | $M^{+\cdot}$ | $[M - CO]^{+\cdot}$ | $[M - 2CO]^{+\cdot}$ |
| (I) | 88 | 100 | |
| (II) | 96 | 100 | |
| (III) | 29 | 20 | 100 |
| (IV) | 100 | 5·6 | 44 |
| (XVII) | 100 | 47 | 11 |
| (XVIII) | 100 | 46 | 13 |

impact, the primary fragmentation path involves a step-wise loss of two CO molecules as well as a loss of one CO molecule from the molecular ions ($M^{+\cdot}$) of the diketones.[21] This process is reminiscent of the behaviour of aromatic quinones.[22] Table 2 summarizes the relative intensities of the signals representing $M^{+\cdot}$, $[M - CO]^{+\cdot}$, and $[M - 2CO]^{+\cdot}$. In the ' unsaturated ' diketones [(III) and (IV)], $[M - 2CO]^{+\cdot}/[M - CO]^{+\cdot} \gg 1$ while in the ' saturated ' diketones [(XVII) and (XVIII)], $[M - 2CO]^{+\cdot}/[M - CO]^{+\cdot} < 1$. In all the four diketones, $M^{+\cdot}/[M - CO]^{+\cdot} > 1$. Thus, the elimination of two carbonyl groups from the molecular ions of (III) and (IV) proved to be the favoured process of the fragmentation path, while the loss of one carbonyl group was sig-

[19] I. Agranat, Ph.D. Thesis, The Hebrew University of Jerusalem, Jerusalem, 1966, p. 122.
[20] Cf. M. Rabinovitz, I. Agranat, and E. D. Bergmann, Tetrahedron, 1966, 22, 225.
[21] M. Rabinovitz, I. Agranat, D. Shapiro, E. D. Bergmann, and C. Lifshitz, Israel J. Chem., 1969, 7, 769.

nificantly inferior. The driving force for the preferred electron impact elimination of two carbonyl groups from the ' double dibenzotropones ' may be the stabilization gained by the formation of the aromatic radical cations of dibenzo[a,j]anthracene [from $M(III)^{+\cdot}$] and dibenzo-[a,h]anthracene [from $M(IV)^{+\cdot}$] (or their rearrangement products). In the ' saturated ' diketones, such a driving force does not exist; the preferred process is the elimination of one rather than two carbonyl groups. The most striking feature in the mass spectra of the diketones is the high intensity of the signal representing $[M - 2CO]^{+\cdot}$ in (III): it is the only case in which $[M - 2CO]^{+\cdot}/M^{+\cdot} > 1$. This interesting behaviour, which is even more pronounced than the fragmentation of 9,10-anthraquinone,[22,23] should not be attributed solely to stability of the aromatic $[M - 2CO]^{+\cdot}$ species. It is likely that a further important driving force for the $M^{+\cdot} \longrightarrow [M - CO]^{+\cdot} \longrightarrow [M - 2CO]^{+\cdot}$ fragmentation is the relief of the overcrowding around the carbonyl groups of $M^{+\cdot}$. This picture is consistent with the kinetic energy evidence. In (IV), (XVII), and (XVIII), the transformations $[M - CO]^{+\cdot} \longrightarrow [M - 2CO]^{+\cdot}$ as well as $M^{+\cdot} \longrightarrow [M - 2CO]^{+\cdot}$ were substantiated by the appropriate metastable transitions. Only in the case of (III), however, the metastable transition due to $M^{+\cdot} \longrightarrow [M - 2CO]^{+\cdot}$, was absent. In the overcrowded radical ion of (III), the transformation $M^{+\cdot} \longrightarrow [M - CO]^{+\cdot}$ is apparently completed in the source before acceleration.

EXPERIMENTAL

M.p.s were taken on a Unimelt Thomas–Hoover capillary melting point apparatus. Above 300°, m.p.s were taken in capillaries in a salt ($KNO_3$–$NaNO_2$) bath.[11] I.r. spectra were recorded on a Perkin-Elmer 457 spectrophotometer in Nujol and in KBr discs. U.v. spectra were recorded on a Unicam SP 800 and a Varian Techtron 635 spectrophotometers. N.m.r. spectra were taken on a Varian HA-100 spectrometer at 30° and are reported in p.p.m. relative to $Me_4Si$ (internal standard) unless otherwise stated. In some cases $(Me_3Si)_2$ served as an internal standard. Mass spectra were measured in a Varian MAT-311 instrument operating at 70 eV, employing the direct insertion technique. Metastable transitions were detected by the defocusing method (alteration of accelerating voltage mode). The mass spectra of all the new compounds reported below contained the appropriate molecular ion peaks.

4,6-Bis-(α-hydroxystyryl)isophthalic Acid Di-γ-lactone (IX) and 2,5-Bis-(α-hydroxystyryl)terephthalic Acid Di-γ-lactone (X).—As described for the preparation of 3-benzylidenephthalide,[11] a mixture of pyromellitic anhydride (VIII) (82·7 g, 0·379 mol), phenylacetic acid (VII) (120·0 g, 0·882 mol), and freshly fused sodium acetate (5·0 g) was immersed in a salt-bath heated at 250° (flask temperature, 235—240°). After a few min, carbon dioxide and water began to be evolved, and within 30 min, most of the theoretical quantity of water had distilled over. After

[22] J. H. Beynon, R. A. Saunders, and A. E. Williams, ' The Mass Spectra of Organic Molecules,' Elsevier, Amsterdam, 1969, pp. 204—209.
[23] L. W. Hall and R. W. A. Oliver, Org. Mass Spectrometry, 1969, 2, 801.

3·5 h at 265° (flask temperature, 250°), the resulting orange-red solid was cooled to 200° and triturated with acetic acid (700 ml). Filtration, washing with methanol, and drying afforded 98 g (77% yield) of a crude mixture of (IX) and (X). The two isomers (IX) and (X) were separated by a fractional recrystallization from dimethylformamide (DMF) or from nitrobenzene as follows. DMF method: a sample (10 g) of the crude mixture of lactones was dissolved in boiling DMF (850 ml), and the mixture filtered. A mixture (1·2 g) of (IX) and (X) was collected on the filter paper. A second filtration at 40—50° gave 1·5 g of pure (X), and a third filtration at room temperature gave 2·6 g of (IX). After each filtration, the product was washed with methanol. The first crop (mixture) was combined with the residue obtained after evaporating the filtrate to dryness, and recrystallized in the same manner, to give additional crops of pure (IX) and (X). Nitrobenzene method: the crude mixture of lactones (9 g) was dissolved in boiling nitrobenzene (180 ml) and the mixture filtered. A mixture (1·8 g) of (IX) and (X) was collected on the filter paper. A second filtration at 80° gave 1·5 g of pure (X), and a third filtration at room temperature gave 3·0 g of (IX). After each filtration, the product was washed with benzene and hexane. The first crop (mixture) was combined with the residue obtained after evaporating the filtrate to dryness, and recrystallized in the same manner to give additional crops of pure (X) and (IX). The yields of the practically pure isomers, after the recrystallization and the separation steps, were 28% (IX) and 18% (X). The two lactones can easily be separated by t.l.c. on neutral silica [benzene–ethyl acetate (100 : 1); $R_F$ values (24°) (IX) 0·67 (blue-yellow fluorescence), (X) 0·82 (orange fluorescence)]. The lactone (X) obtained by the foregoing fractional recrystallizations was pure, while (IX) contained traces of (X) which could not be removed even after repeated fractional recrystallizations. A pure sample of (IX), free of (X), was finally obtained by p.l.c. (silica): (IX), yellow *needles*, m.p. 322° (from DMF) (lit.,[12] 330°); $v_{max.}$ (Nujol) 1815sh, 1782 (C=O), 1660, 1630, 1100, 990, and 980 cm⁻¹, $\lambda_{max.}$ (CH₂Cl₂) 250 (log ε 3·53), 275 (3·59), 343 (4·51), 356sh (3·95), 394 (3·77), 416sh nm (3·67), δ [CDBr₃; (Me₃Si)₂; 140°] 6·45 (2H, s), 7·22—7·48 (6H, m), 7·72—7·82 (4H, m), 7·97 (1H, s), and 8·38 (1H, s), δ (FSO₃H) 7·26 (2H, s), 8·11 (10H, s), 8·38 (1H, s), and 8·63 (1H, s) (Found: C, 78·5; H, 3·85. C₂₄H₁₄O₄ requires C, 78·7; H, 3·85%); (X), yellow-orange *needles*, m.p. 412° (from DMF) (lit.,[12] 375°), $v_{max.}$ (Nujol) 1760 (C=O), 1665, 1070, 990, and 780 cm⁻¹, $\lambda_{max.}$ (CH₂Cl₂) 250 (log ε 4·00), 355 (4·50), and 410 nm (3·97), δ (FSO₃H) 7·19 (2H, s), 7·84 (10H, s), and 8·49 (2H, s) (Found: C, 78·7; H, 3·65%).

4,6-*Bis*-(2-*phenylethyl*)*isophthalic Acid* (XI) *and* 4,6-*Bis*-(1-*hydroxy*-2-*phenylethyl*)*isophthalic Acid Di-γ-lactone* (XII).
— CAUTION. During the reaction described below, a white solid, presumably PH₄I,[24] accumulated in the reflux condenser. Its reaction with water is extremely exothermic, giving the toxic flammable phosphine; in some instances it may lead to explosions.[25] As a precaution, the reaction should be stopped from time to time, and the reflux condenser should carefully be washed.

A mixture of compound (IX) (28 g, 76 mmol), red phosphorus (45 g), and hydriodic acid (d 1·94; 68%; 250 ml) was refluxed with vigorous mechanical stirring for 36 h; during the first 30 h, more phosphorus (20 g) and

hydriodic acid (150 ml) were added. The yellow colour of the starting lactone (IX) disappeared after 8 h. The hot mixture was poured on ice and the solid was filtered off and washed with ammonia solution (25%) until the extract no longer gave a precipitate on acidification. The *acid* (XI) (23·5 g, 82%) had m.p. 209—210° (from toluene), $v_{max.}$ (Nujol) 1680 (C=O), 1600, 1300, 1253, and 692 cm⁻¹, $\lambda_{max.}$ (EtOH) 220 (log ε 4·60), 250sh (4·05), 288 (3·24), 296sh (3·21), and 325sh nm (1·78), δ [CDBr₃; (Me₃Si)₂; 140°] 2·84—3·50 (8H, m), 6·90 (1H, s), 6·85—7·35 (10H, m), 8·56 (1H, s), and 8·95 (2H, s) (Found: C, 77·1; H, 6·0. C₂₄H₂₂O₄ requires C, 7·0; H, 5·9%).

The product (XII) insoluble in ammonia was extracted with boiling methylene chloride (500 ml). The extract was filtered, washed with dilute sodium hydroxide and water, dried (MgSO₄), and evaporated to dryness. The residue yielded almost colourless crystals of (XII), m.p. 180—183° (from butan-1-ol); a pure *sample* was obtained by p.l.c., $v_{max.}$ (Nujol) 1777 (C=O), 1631, 1170, 1068, 985, and 699 cm⁻¹, $\lambda_{max.}$ (CH₃CN) 230 (log ε 4·21), 266 (3·01), 270 (2·98), 279 (2·98), and 289 nm (2·91), δ [CDBr₃; (Me₃Si)₂] 2·95—3·35 (4H, m), 5·70 (1H, t, J 6 Hz), 6·82 (1H, d, J 3·5 Hz), 6·93—7·35 (10H, m), and 8·10 (1H, d, J 3·5 Hz) (Found: C, 78·05; H, 5·1. C₂₄H₁₈O₄ requires C, 77·8; H, 4·9%).

2,5-*Bis*-(2-*phenylethyl*)*terephthalic Acid* (XIII) *and* 2,5-*Bis*-(1-*hydroxy*-2-*phenylethyl*)*terephthalic Acid Di-γ-lactone* (XIV).—A mixture of compound (X) (22·5 g, 61 mmol), red phosphorus (40 g), hydriodic acid (d 1·94; 68%; 200 ml), and butyric acid (400 ml) was refluxed with vigorous mechanical stirring for 49 h. During the first 40 h, more phosphorus (10 g) and hydriodic acid (90 ml) were added. The yellow colour of the starting lactone (X) disappeared after ca. 12 h. The mixture was cooled and the solids were filtered off and washed with acetic acid and water. The solids were repeatedly extracted with boiling ammonia solution (25%) until the extracts no longer gave a precipitate on acidification. Recrystallization from ethanol afforded the *acid* (XIII) (17 g, 75%), m.p. 266°, $v_{max.}$ (Nujol) 1696 (C=O), 1651, 1605, 1287, 1254, 756, and 700 cm⁻¹, $\lambda_{max.}$ (EtOH) 245sh (log ε 3·99) and 298 nm (3·36), δ [(CD₃)₂SO] 3·00 (8H, m), 7·25 (10H, s), and 7·74 (1H, s) (Found: C, 77·3; H, 6·05. C₂₄H₂₂O₄ requires C, 7·0; H, 5·9%).

The filtrate (butyric acid–acetic acid–water solution) was evaporated to dryness and the residue (traces) was recrystallized from propan-1-ol, affording crystals of the *dilactone* (XIV), m.p. 209—210°, $v_{max.}$ (KBr) 3040, 2920, 2855, 1750 (C=O), 1605, 1360, 1175, 991, 695, and 587 cm⁻¹, $\lambda_{max.}$ (CH₂Cl₂) 242 (log ε 4·07), 288 (3·52), and 300 nm (3·55), δ [CDBr₃; (Me₃Si)₂] 3·23 (4H, d, J 6 Hz), 5·75 (2H, t, J 6 Hz), 6·98—7·23 (10H, m), and 7·60 (2H, s) (Found: C, 77·75; H, 5·1. C₂₄H₁₈O₄ requires C, 77·8; H, 5·1%).

(E,E)-1,4-*Distyrylbenzene*.[26]—A magnetically stirred suspension of benzyltriphenylphosphonium bromide (22 g, 50·1 mmol) and benzene-p-dicarbaldehyde (3·0 g, 22·5 mmol) in methanol (100 ml) was treated dropwise, in an inert atmosphere under anhydrous conditions at room temperature, with a solution of sodium methoxide in methanol (1·1 g sodium in 15 ml methanol). Following the addition of the base, a clear solution was formed, and after 2 min, a solid precipitated. The mixture was stirred for an additional 1 h and the solid filtered off (4·7 g) and washed

²⁴ B. V. Gregorovich, K. S. Y. Liang, D. M. Clugston, and S. F. MacDonald, *Canad. J. Chem.*, 1968, **46**, 3291.

²⁵ *Cf.* F. J. Villani, C. A. Ellis, R. F. Travers, and C. Bigos, *J. Med. Chem.*, 1964, **7**, 457 (note 9).
²⁶ *Cf.* H. Oediger and K. Eiter, *Annalen*, 1965, **682**, 58.

with methanol. Recrystallization from toluene afforded 1,4-distyrylbenzene (1·7 g, 27%) as pale yellowish leaflets, m.p. 261—262° (lit.,[27] 266—267), $v_{max.}$ (KBr) 3080, 3060, 3030, 1600, 1515, 1490, 1450, 1075, 985, 970, 960, 870, 815, 745, 690, and 550 cm⁻¹, $\lambda_{max.}$ (dioxan) 246 (log ε 4·16), 250sh (4·07), 345s (4·70), and 355 nm (4·74) (Found: C, 93·95; H, 6·2. Calc. for $C_{22}H_{18}$: C, 93·6; H, 6·4%).

(E,E)-1,3-*Distyrylbenzene*.[28]—A double Wittig reaction of benzene-m-dicarbaldehyde and benzyltriphenylphosphonium bromide (sodium methoxide in methanol) was carried out in an analogous manner to the foregoing preparation. (E,E)-1,3-Distyrylbenzene was obtained as needles, m.p. 170° (lit.,[27b,28] 170—172°), $v_{max.}$ (KBr) 3020, 1600, 1485, 1445, 960, 785, 740, and 685 cm⁻¹, $\lambda_{max.}$ (EtOH) 231 (log ε 4·27), 301 (4·77), 311 (4·76), and 325sh nm (4·58) (Found: C, 93·15; H, 6·75. Calc. for $C_{22}H_{18}$: C, 93·6; H, 6·4%).

1,3-*Bis-(2-phenylethyl)benzene* (XV).—(a) A mixture of the diacid (XI) (0·8 g, 2 mmol), freshly distilled quinoline (10 ml), and copper–bronze powder (0·2 g) was refluxed for 1 h and poured into cold dilute hydrochloric acid. The resulting oil was extracted with ether, and the organic solution was washed successively with sodium hydrogen carbonate solution and water, dried (MgSO₄), and evaporated to dryness. Recrystallization of the residue from a little ethanol afforded (XV) as needles, m.p. 56° (lit.,[29] 56—57°), $v_{max.}$ (KBr) 3060, 3020, 2920, 2860, 1603, 1490, 1453, 785, 758, 742, 695, and 505 cm⁻¹, $\lambda_{max.}$ (EtOH) 251sh (log ε 1·58), 257sh (1·74), 262 (1·83), 265 (1·84), 268 (1·81), 271 (1·74), and 275sh nm (1·49), δ (CDCl₃) 2·86 (8H, s), 6·88—7·08 (4H, m), and 7·18 (10H, s) (Found: C, 92·05; H, 7·5. $C_{22}H_{22}$ requires C, 92·25; H, 7·75%).

(b) A solution of (E,E)-1,3-distyrylbenzene (0·365 g, 1·3 mmol) in benzene–acetic acid (1 : 1) (100 ml) containing a little platinum oxide was hydrogenated at 3 atm (Parr instrument) for 3 h. After removal of the catalyst, the solvents were evaporated off in vacuo. The residual brown oil was dissolved in methylene chloride and the solution was washed successively with water, sodium hydrogen carbonate, and water, dried (MgSO₄), and evaporated to dryness. Column chromatography of the residual oil on neutral alumina and elution with benzene afforded (XV) as needles, m.p. 56° (from ethanol) identical (mixed m.p., i.r. spectra) with a sample of (XV) prepared via method (a) (Found: C, 92·45; H, 7·8%).

1,4-*Bis-(2-phenylethyl)benzene* (XVI).—(a) A mixture of the diacid (XIII) (1·5 g, 4 mmol), freshly distilled quinoline (70 ml), and copper–bronze powder (0·5 g), was refluxed for 2·5 h and poured into cold dilute hydrochloric acid. The resulting oil was extracted with ether and the organic solution was washed successively with sodium hydrogen carbonate solution and water, dried (MgSO₄), and evaporated to dryness. Recrystallization from ethanol–ethyl acetate (5 : 1; 7 ml) gave (XVI) (0·4 g). A second recrystallization from ethanol (10 ml) afforded (XVI) as leaflets, m.p. 89—90° (lit.,[15] 90—91°), $v_{max.}$ (Nujol) 1596, 808, 742, 697, and 540 cm⁻¹, $\lambda_{max.}$ (EtOH) 224 (log ε 4·24), 251sh (266), 256sh (2·81), 262 (2·92), 264 (2·90), 267 (2·92), 271 (2·88), and 276 nm (2·70), δ (CDCl₃) 2·88 (8H, s) and 7·06—7·26 (14H, m).

(b) A suspension of (E,E)-1,4-distyrylbenzene in benzene–acetic acid (1 : 1) containing a little platinum oxide was

hydrogenated at 3 atm (Parr instrument) according to the literature.[15] The completion of the reaction was indicated by the disappearance of the intense blue fluorescence of the starting material. The product (XVI) after two recrystallizations from ethanol melted at 89—90°; mixed m.p. with a sample of (XVI) prepared via method (a), 89—90°.

12,13,15,16-*Tetrahydrobisbenzo[4,5]cyclohepta[1,2-a:2′,1′-d]benzene-5,7-dione* (XVII).—At 140° and under anhydrous conditions, the diacid (XI) (5·0 g, 13 mmol) was added to polyphosphoric acid (Fluka; 100 ml). The red mass was kept at 140° with vigorous mechanical stirring for 8·5 h and then poured into ice–water (1·5 kg). After the complex had completely disintegrated, the mixture was extracted with methylene chloride and the organic fractions were washed successively with water, aqueous sodium hydrogen carbonate solution and water, dried (MgSO₄), and evaporated to dryness under vacuum. Recrystallization of the residue from benzene (15 ml) afforded 1·7 g (38%) of (XVII), m.p. 158—160°. An analytical sample, m.p. 161°, was obtained by a second recrystallization and treatment with active charcoal, $v_{max.}$ (Nujol) 1641 (C=O), 1597, 1297, 1219, 1028, 977, 937, 756, 719, and 600 cm⁻¹, $\lambda_{max.}$ ($CH_2Cl_2$) 275 (log ε 4·56) and 346 nm (4·15), δ (CDCl₃) 3·13 (8H, s), 7·02 (1H, s), 7·04—7·45 (6H, m), 7·90—8·00 (2H, m), and 8·71 (1H, s) (Found: C, 84·95; H, 5·2. $C_{24}H_{18}O_2$ requires C, 85·2; H, 5·35%).

7,8,15,16-*Tetrahydrobisbenzo[4,5]cyclohepta[1,2-a:1′,2′-d]-benzene-5,13-dione* (XVIII).—At 155° and under anhydrous conditions, the diacid (XIII) (10·0 g, 26 mmol) was added to polyphosphoric acid (Fluka; 200 ml). The resulting yellow complex was kept at 155° for 3 h with vigorous mechanical stirring. During the reaction, the complex turned from yellow to brown. Subsequently, it was poured into ice–water (1·5 kg). After it had completely disintegrated, the mixture was extracted with methylene chloride. The organic fraction was washed successively with water, sodium hydrogen carbonate solution and water, dried (MgSO₄), and evaporated to dryness under vacuum. Recrystallization of the residue from butan-1-ol (140 ml) afforded 6·0 g (66%) of (XVIII) as brownish crystals. An analytical sample was obtained by treating a boiling chloroform solution of (XVIII) with active charcoal. The diketone (XVIII) was obtained as yellow crystals, m.p. 212—214°, $v_{max.}$ (Nujol) 1650 (C=O), 1600, 1288, 1238, 982, 940, 899, and 751 cm⁻¹, $\lambda_{max.}$ ($CH_3CN$) 286 (log ε 4·41) and 354 nm (3·31), δ (CDCl₃) 3·22 (8H, s), 7·16—7·47 (6H, m), 7·87 (2H, s), and 7·90—8·00 (2H, m) (Found: C, 85·1; H, 5·4. $C_{24}H_{18}O_2$ requires C, 85·2; H, 5·35%).

*Bisbenzo[4,5]cyclohepta[1,2-a:2′,1′-d]benzene-5,7-dione* (III).—To a boiling solution of compound (XVII) (0·54 g, 1·6 mmol) in carbon tetrachloride (500 ml), N-bromosuccinimide (0·656 g, 3·6 mmol) was added and the mixture was stirred and refluxed for 2 h, then cooled and filtered, and the solid succinimide was washed with carbon tetrachloride. Freshly distilled (over KOH) triethylamine (8 ml) was added to the filtrate and refluxing was continued for 4 h. After cooling, the product was filtered off (more could be obtained by washing the filtrate with dilute hydrochloric acid and water, drying, and concentrating it),

[27] (a) T. W. Campbell and R. N. McDonald, *J. Org. Chem.*, 1959, **24**, 1246; (b) W. H. Laarhoven, Th. J. H. M. Cuppen, and R. J. F. Nivard, *Tetrahedron*, 1970, **26**, 1069; (c) S. Misumi and M. Kuwana, *Bull. Chem. Soc. Japan*, 1960, **33**, 711.

[28] *Cf.* K. Friedrich and H. G. Henning, *Chem. Ber.*, 1959, **92**, 2944.

[29] (a) K. Sisido and S. Kato, *J. Soc. Chem. Ind. Japan*, 1941, **44**, 25B (*Chem. Abs.*, 1941, **35**, 4369); (b) K. Sisido, *ibid.*, 1941, **44**, 55B (*Chem. Abs.*, 1941, **35**, 4370); (c) K. Sisido and Y. Yusikawa, *J. Amer. Chem. Soc.*, 1948, **70**, 1608.

triturated with dilute hydrochloric acid, filtered off again, washed with water, dried, and recrystallized from n-butyl acetate (20 ml). The diketone (III) was obtained (20% yield) as yellow *needles*, m.p. 216—217°, $\nu_{max}$ 1647 (C=O), 1632, 1601, 1590, 1031, 909, 807, and 730 cm$^{-1}$, $\lambda_{max}$ (CH$_2$Cl$_2$) 254 (log $\epsilon$ 4·56) and 330 nm (4·63), $\delta$ [CDBr$_3$; (Me$_3$Si)$_2$; 100°] 6·96 (4H, s), 7·34—7·60 (7H, m), 8·12—8·21 (2H, m), and 8·90 (1H, s) (Found: C, 86·1; H, 4·4. C$_{24}$H$_{14}$O$_2$ requires C, 86·2; H, 4·2%).

*Bisbenzo*[4,5]*cyclohepta*[1,2-a:1′,2′-d]*benzene*-5,13-*dione* (IV).—To a boiling solution of compound (XVIII) (1·0 g, 2·9 mmol) in carbon tetrachloride (300 ml), *N*-bromo-succinimide (1·15 g, 6·4 mmol) and dibenzoyl peroxide (0·08 g) were added. The mixture was stirred and refluxed for 2 h, cooled, filtered, and the solid succinimide was washed with carbon tetrachloride. Freshly distilled tri-ethylamine (15 ml) was added to the filtrate and refluxing was continued for 4 h. After cooling, the product (0·330 g)

was filtered off [more (0·200 g) could be obtained by washing the filtrate with dilute hydrochloric acid and water, drying, and then concentrating it], triturated with dilute hydro-chloric acid, filtered off again, washed with water, dried, and recrystallized from n-butyl acetate–benzene. The diketone (IV) was obtained (50% yield) as golden glittering *needles*, m.p. 314—315°, $\nu_{max}$ (Nujol) 1642 (C=O), 1592, 1320, 1151, 951, 910, 810, and 492 cm$^{-1}$, $\lambda_{max}$ (C$_6$H$_6$) 361 (log $\epsilon$ 4·49), 425sh nm (3·54), $\delta$ [CDBr$_3$; (Me$_3$Si)$_2$; 130°] 6·93 and 7·18 (4H, AB, $J$ 13 Hz), 7·36—7·54 (2H, m), 8·13— 8·24 (2H, m), and 8·31 (2H, s) (Found: C, 85·35; H, 4·3. C$_{24}$H$_{14}$O$_2$ requires C, 86·2; H, 4·2%).