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Photocyclisations of Unsaturated [2$_4$]Paracyclophanes

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The photocyclisation of [2$_4$]paracyclophanes with one or two unsaturated bridges, compounds *7* and *3*, gives [2$_3$](3,6)phenanthrenodiparacyclophane, *8*, and [2$_2$](2,13)pentahelicenoparacyclophane, *4*, respectively. In contrast, [2$_4$]paracyclophanetriene, *1*, does not give the heptahelicene derivative *2* on irradiation. The introduction of iodosubstituents in [2$_4$]paracyclophanetetraene allows for successful photocyclisations under nitrogen.

The photocyclisation of stilbenes under oxidative conditions to give phenanthrenes is one of the most studied and widely used organic photoreactions.[1–3] It has been applied to the synthesis of condensed aromatic systems and has proved especially useful for the synthesis of helicenes [4] and bridged annulenes.[5] In this paper we report an investigation of the photocyclisation of [2$_4$]paracyclophanes with one, two or three bridging double bonds as well as that of some iodosubstituted [2$_4$]paracyclophanetetraenes.

As previsouly reported, [2$_4$]paracyclophanetetraene, *13*, slowly decomposes on irradiation in the presence of air and iodine.[6] Mass spectra of the product mixture showed the presence of aromatic aldehydes, probably formed by photooxidation of the double bonds. Other cyclophanes, closely related to *13*, also decomposed on irradiation [7] and an attempt to use tetracyanoethylene as a hydrogen acceptor, as has been proposed,[8] was also unsuccessful. There might be several reasons for the failure of these photocyclisation. One is that the products might be photolabile and decompose as soon as they are formed, and this is clearly a risk for the more strained products when the irradiation is performed in the presence of air. However, all unsuccessful photocyclisations showed a slow disappearance of the starting materials rather than fast formation of decomposition products and, in at least one case, we were indeed able to prepare the desired product, bi-2,13-pentahelicenylene, by a similar photocyclisation.[9]

Unfavourable electronic effects could be another reason for the unsuccessful photocyclisation. [2$_4$]Paracyclophanetetraene, *13*, as well as (2,5)-furan, (2,5)-thiophene or (4,4′)-biphenyl analogues all contain a perimeter of conjugated π-electrons. The delocalisation of the π-electrons around the ring, which affects the UV and NMR spectra of these compounds and also their electrochemical behaviour on reduction to the anion radicals [10] and dianions,[11] could also effect the photocyclisation. Interruption of the conjugated π-electron system around the perimeter by hydrogenation of some of the double bonds in [2$_4$]paracyclophanetetraene, *13*, would make it possible to test this hypothesis.

During this work it also became clear that steric requirements for the photocyclisations must be considered. It is generally accepted that the photochemical formation of a dihydrophenanthrene from a *cis*-stilbene is a conrotatory process which leads to *trans* orientation of the two inner hydrogens in the product.[12] The proper conformation of the reactant is that of *cis*-stilbene with a twofold axis of symmetry perpendicular to the double bond (Scheme 1). The reaction is reversible and considered to occur in the singlet state.[1,12] The barrier of activation for the cyclisation of excited *cis*-stilbene [1] and *cis*-1,2-(2-naphtyl)ethylene [13] has been determined. In the latter case, the barriers are different for the three

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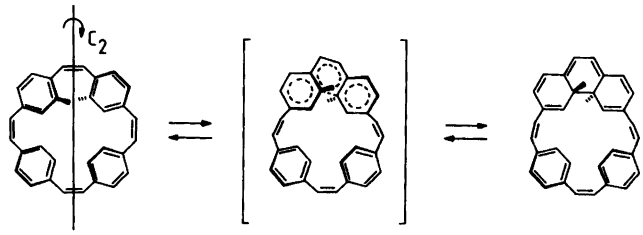
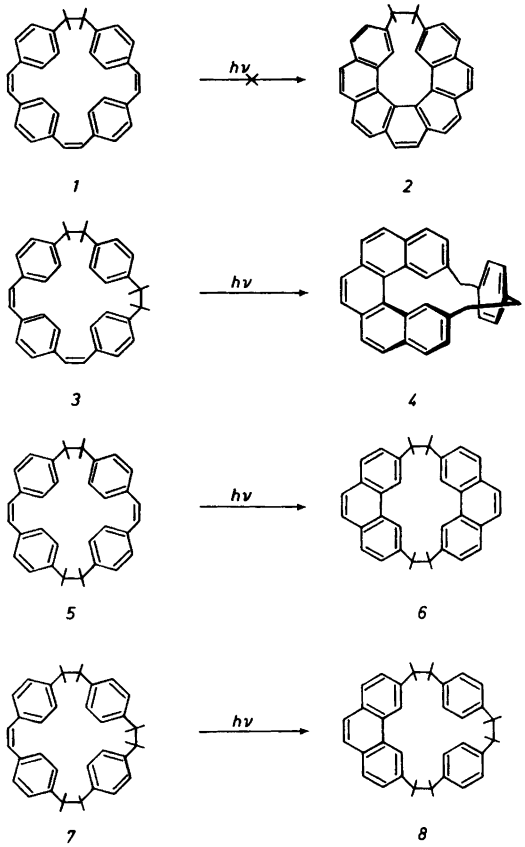
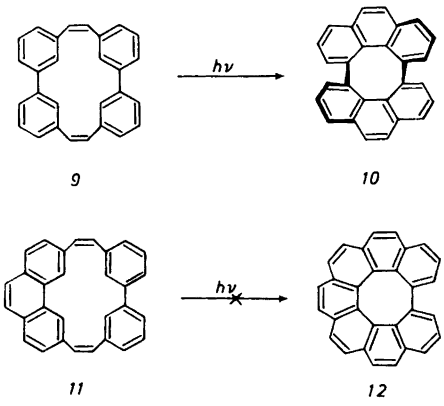


Scheme 1.

possible photocyclisations, and this can be rationalized as being due to steric effects.[14] Similarly, steric effects could be responsible for the failure of the photocyclisation of *13*. Successive saturation of the double bonds in *13* should result in more flexible cyclophanes and possibly decrease the contribution of steric effects to the barriers to cyclisation. Recently, we have been able to selectively reduce the double bonds in *13* by electrochemical reduction at constant



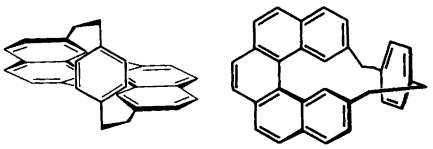


potential.[15] Thus, we have prepared [2$_4$]paracyclophanes with three double bonds, *1*, two double bonds, isomers *3* and *5*, and one double bond, *7*. The cyclophane *5* has also been prepared by a twofold Witting reaction from 4,4′-bibenzyldicarbaldehyde and the bistriphenylphosphonium salt from 4,4′-bis(bromomethyl)bibenzyl.[19]

RESULTS AND DISCUSSION

Photocyclisation of [2$_4$]*parabyclophanes.* Irradiation of [2$_4$]paracyclophanetriene, *1*, led to slow decomposition of the starting material. Apparently, cleavage of the cyclic π-electron system at only one site is not a sufficient condition for a successful photocyclisation in this series of cyclophanes.

[2$_4$]Paracyclophanediene, isomer *3* with the longer conjugated π-system, was converted nicely to a pentahelicene derivative, *4*, upon irradiation in cyclohexane at 254 nm. The structure of the product, [2$_2$](2,13)pentahelicenoparacyclophane, was determined from its UV, ^{1}H NMR and mass spectra. The UV spectrum is almost identical



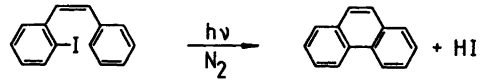
[2.2](2,13)Pentahelicenoparacyclophane *4*

with that of [5]helicene.[16] The chemical shifts for the protons in the pentahelicene part of the molecule are similar to those of the protons in [5]helicene, except for the inner protons which show an upfield shift of the signal by 1.2 ppm.[17] The shielding effect of the benzene ring (which must be essentially perpendicular to the pentahelicene part of *4*) is estimated to 0.5 ppm from the Bovey-Johnson equations.[18] Inspection of molecular models (CPK) of *4* reveals that the benzene ring must force the outer end of the pentahelicene apart, thereby increasing the angle and the distance between the inner hydrogens which results in decreased mutual deshielding. The protons in the bridges give rise to an ABCD spin system, and the shifts and coupling constants are consistent with a rather rigid structure.

The photocyclisation of the other isomer of [2_4]paracyclophanediene, *5*, gave [2_2](3,6)-phenanthrenophane, *6*, under the same conditions as above,the product being identical with that from hydrogenation of the corresponding diene *15*.[19]

Similarly, [2_4]paracyclophanemonoene, *7*, gives [2_3](3,6)phenanthrenodiparacyclophane, *8*, on irradiation. The ^{1}H NMR spectrum of the product shows a singlet and an AMX pattern for the phenanthrene protons, an AA'BB' pattern for the benzene protons and an AA'BB' pattern and a singlet for the protons on the bridges.

It has been suggested that the unsuccessful photocyclisation of *15* to *16* [20] and *11* to *12* [21] are due to the unfavourable *syn* conformations of the dienes. However, the closely related photocyclisation of *9* to *10* occurs readily.[19,22,23] The cyclophane *9* probably has a ground state conformation of D_2-symmetry,[19] and further approach of the benzene rings towards each other in the two *cis*-stilbene units to form the new carbon–carbon bonds should be facile.

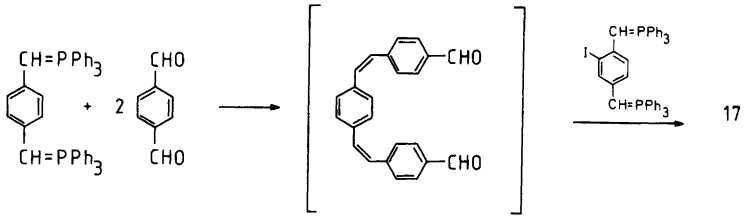


Scheme 2.

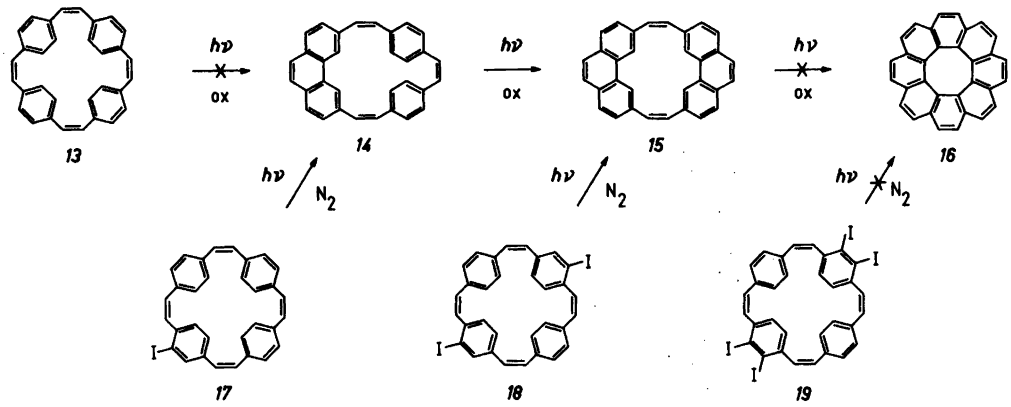
Photocyclisation of iodo-[2_4]*paracyclophanetetraenes.* As exemplified above, the photocyclisation of cyclophanes with *cis*-stilbene units is governed by rather subtle steric factors. Often, prolonged reaction times are needed which, due to the presence of air, can lead to photooxidation of the reactants and products. It may thus be advantageous to run the photocyclisation under an inert atmosphere, and this can be achieved if the cyclophane contains an iodine substituent adjacent to the double bond (see also Scheme 2).[24]

Multiple Wittig reactions can be used for the convenient synthesis of iodo-[2_4]paracyclophanetetraenes. Previously, we have reported the synthesis and photocyclisation of a di-iodo[2_4]-paracyclophanetetraene, *18*, to give *15*, [2_2]-(3,6)phenanthrenophanediene.[20] Similarly, photocyclisation of di-iodo[2_4](4,4')biphenyl-paracyclophanetetraene gave bi-2,13-pentahelicenyylene.[9] We have found that it is possible to prepare iodo[2_4]paracyclophanetetraene, *17*, by a fourfold Wittig reaction in a one pot reaction sequence from two mol of benzene-1,4-dicarbaldehyde and one mol each of the bistriphenylphosphonium salts from 1,4-bis(bromomethyl)benzene and 1,4-bis(bromomethyl)-2-iodobenzene (Scheme 3).

On irradiation, the monoiodocyclophane *17* gives *15* in the presence of air. If nitrogen is



Scheme 3.

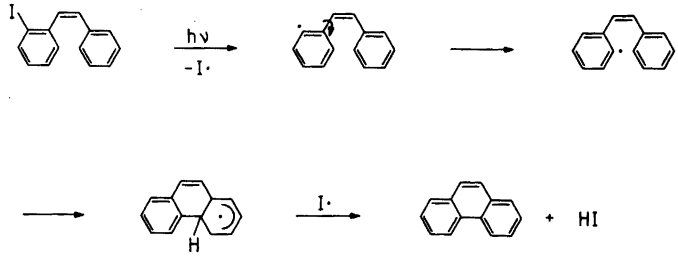


Scheme 4.

bubbled through the solution during the irradiation, the main product is [2_3](3,6)phenanthrenodiparacyclophanetriene, *14*. Hydrogenation of the product gives the saturated cyclophane *8*, described above.

We have also made an attempt to prepare [8]circulene, *16*, from a tetraiodo[2_4]paracyclophanetetraene, *19* (Scheme 4). The substitution pattern is set to ensure the proper location of the two iodines in the hypothetical intermediate (a di-iodo[2_2](3,6)phenanthrenophanediene) which might close to give [8]circulene. Unfortunately, this substitution pattern also favours the formation of benzyne derivatives.[24] The tetraiodo[2_4]-paracyclophanetetraene *19* was prepared from benzene-1,4-dicarbaldehyde and the bistriphenylphosphonium salt from 1,4-bis(bromomethyl)-2,3-di-iodobenzene by the usual Wittig reaction procedure. The bisphosphonium salt was prepared from 1,4-dimethylbenzene by a rather lengthy sequence of standard reactions. Irradiation of the cyclophane *19* under various conditions did not result in any detectable amount of [8]circulene, no product with the mass of 400 being observed by mass spectrometry.

Conclusion. Steric effects are of lesser importance in the photocyclisations of iodo[2_4]paracyclophanes than in photocyclisations of unsubstituted [2]paracyclophanes, which points to different mechanisms for the reactions. It is well-known that aryl iodides readily lose an iodine atom on irradiation,[24] and this is probably the first step in the photocyclisation of the iodocyclophanes discussed here. The hypothetical reaction sequence is shown in Scheme 5. For the photocyclisation of unsubstituted [2_4]paracyclophanes with bridging double bonds it is necessary to consider steric effects in the first excited singlet state and not only the ground state conformations. If the photocyclisation is too slow, or if the products are photo-oxidised, it should be advantageous to use a properly substituted iodo-stilbene-derivative.



Scheme 5.

EXPERIMENTAL

Melting points are uncorrected. UV spectra were recorded on a Beckman DK 2A, IR spectra on a Beckman IR 9, MS on an AEI MS 902 and NMR on a Bruker WH 270 instrument.

The [2$_4$]paracyclophanes *1*, *3*, *5* and *7* were prepared by selective electrochemical reduction of [2$_4$]paracyclophanetetraene, *13*, as previously described.[15]

Photocyclisations were performed using a Rayonet reactor (RPR-100) with low-pressure mercury lamps at 254 nm. Air was not excluded and catalytic amounts of iodine added in most reactions. The photoreactions were carried out in the standard water-coated quartz vessel in cyclohexane (spectroscopic grade) or benzene (A.R.) solution. The reactions were monitored by TLC and stopped when no starting material could be detected, usually after a few hours. The products were recrystallised from dichloromethane–methanol or sometimes purified by chromatography on silica gel.

[2$_4$]Paracyclophanediene, isomer *3*, (50 mg in 75 ml cyclohexane) gave after irradiation for 3.5 h at 254 nm *[2$_2$](2,13)pentahelicenoparacyclophane, 4* (29 mg, 60 %, m.p. 285 °C). UV [ethanol] (ε): 235 (81 500), 263 (sh), 271 (31 400), 293 (sh), 295 (31 600) nm. MS [IP 45 eV; *m/e* (% rel. int.)]: 408 (100, M^+), 303 (11), 302 (14), 301 (21), 276 (18). Abs. mass, obs. 408.187, calc. for $C_{32}H_{24}$ 408.188. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.86 (2 H, d, H_4), 7.81 and 7.65 (4 H, dd, $H_{5,6}$, J 8.5 Hz), 7.60 (2 H, s, H_7), 7.38 (2 H, dd, H_3, J 8.5 and 1.8 Hz), 7.26 (2 H, d, H_1), helicene protons, 6.91 and 6.77 (4 H, AA'BB'-pattern, J 8.5 Hz) parasubstituted ring protons, 3.12 (2 H, dt), 2.93 (4 H, m), and 2.18 (2 H, dt), J:s 13.5, 13.5, 13.5, 4.5, 4.5, and 4.5 Hz, methylene protons.

[2$_4$]Paracyclophanediene, isomer *5* (50 mg in 75 ml cyclohexane) gave after irradiation for 5 h at 254 nm *[2.2](3,6)phenanthrenophanne, 6* (30 mg, 58 %, m.p. 335–340 °C). UV [cyclohexane (ε)]: 247 nm (105 000). MS [IP 68 eV; *m/e* (% rel. int.)]: 408 (100, m^+), 217 (41), 204.5 (5), 204 (63), 203 (13), 202 (25), 191 (32). Abs. mass, obs. 408.18±0.01, calc. for $C_{32}H_{24}$ 408.19. ^{1}H NMR (270 MHz, $CDCl_2$): δ 9.17 (4 H, broad s, H_4), 7.64 (4 H, d, H_1), 7.48 (4 H, s, H_9), 7.37 (4 H, dd, H_2, J 1.7 and 8.3 Hz) phenanthrene protons, 3.62 (8 H, s) methylene protons.

[2$_4$]Paracyclophanemonoene, *7* (50 mg in 75 ml cyclohexane) gave after irradiation for 3.5 h at 254 nm *[2.2.2](3,6)phenanthrenodiparracyclophane, 8*, MS [IP 60 eV; *m/e* (% rel. int.)]: 412 (100, M^+), 307 (11), 217 (13), 207 (20), 206 (16), 205 (28), 204 (23), 203 (12), 202 (13), 191 (25). Abs. mass, obs. 412.203, calc. for $C_{32}H_{28}$ 412.219. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.80 (2 H, d, H_1) 7.63 (2 H, s, H_9), 7.53 (2 H, broad s, H_4), 7.48 (2 H, dd, H_2, J 1.5 and 8 Hz), phenanthrene protons, 6.82 and 6.60 (8 H, AA'BB'-pattern, J 8 Hz) parasubstituted ring protons, 3.04 and 2.95 (8 H, m), 2.94 (4 H, s) methylene protons.

[Iodo]2$_4$Paracyclophanetetraene, *17* (40 mg in 75 ml benzene) gave after irradiation, under nitrogen without addition of iodine, for 2 h at 254 nm *[2.2.2](3,6)phenanthrenodiparacyclophanediene, 14*,, after separation by preparative TLC in CCl_4 (13 mg, 41 %, m.p. 209–213 °C). MS [IP 60 eV; *m/e* (% rel. int.)]: 406 (100, M^+), 405 (10), 203 (12), and 202 (11). Abs. mass, obs. 406.171, calc. for $C_{32}H_{22}$ 406.172.

^{1}H NMR (270 MHz, $CDCl_3$: δ 8.16 (2 H, broad s, H_A), 7.87 (2 H, d, H_C), 7.69 (2 H, s, H_D), 7.47 (2 H, dd, H_B, J_{AB} 1 Hz, J_{BC} 8 Hz), 7.01 (4 H, d, H_E or $H_{E'}$), 6.86 (2 H, s, H_F), 6.75 (2 H, d, H_G or $H_{G'}$), 6.71 (4 H, d, H_E or $H_{E'}$l, $J_{EE'}$ 8 Hz) and 6.56 (2 H, d, H_G or $H_{G'}$, $J_{GG'}$ 12 Hz).

Some [2.2](3,6)phenanthrenophanediene, *15* (5 mg, 16 %, identified by comparison with authentic sample [20]) was also isolated.

The *Wittig reaction* was carried out as previously described.

Iodo[2$_4$]Paracyclophanetetraene, *17*, was prepared from 1,4-benzene dicarbaldehyde (10 mmol), the bisphosphonium salt from 1,4-bis-(bromomethyl)benzene (5 mmol), and the bisphosphonium salt from 2-iodo-1,4-bis(bromomethyl)benzene (5 mmol) in DMF at −40 °C. The dialdehyde and the unsubstituted bisphosphonium salt were mixed in DMF and lithium ethoxide in ethanol added slowly. When no further colour developed on addition of base, the iodo-substituted bisphosphonium salt was added, followed by more base. Work-up and chromatographic separation gave cyclophane *17* (180 mg, 7 %) together with small amounts of the unsubstituted and di-iodo [2$_4$]paracyclophanetetraenes. MS [IP 70 eV; *m/e* (rel. int.)]: 534 (100 %, M^+), 407 (12), 406 (16), 203 (12), 201 (15), 200 (16). Mol. wt., obs. 534.075±0.015, calc. for $C_{32}H_{23}I$ 534.086. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.75 (1 H, s, *ortho* to iodine), 7.34–7.13 (14 H, m, aromatic protons), 6.51–6.38 (8 H, m, olefinic protons).

Tetraiodo[2$_4$]paracyclophanetetraene, *19*. Benzene 1,4-dicarbaldehyde (3 mmol) and the bisphosphonium salt from 2,3-diiodo-1,4-bis-(bromomethyl)benzene (3 mmol) were reacted under the standard conditions to give the cyclophane *19* (90 mg, 6 %). ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.25 (4 H, s), 7.12 (8 H, s) aromatic protons, 6.48 (4 H, d) and 6.38 (4 H, d, J 12 Hz)

olefinic protons. MS [IP 70 eV; *m/e* (rel. int.)]: 912 (M^+, 3 %), 785 (25), 658 (18), 531 (10), 406 (39), 405 (47), 404 (100), 403 (25), 402 (28), 401 (22), 400 (28), 399 (17), 398 (31), 387 (31), 374 (31), 203 (33), 202 (50), 201 (33), 200 (39), and 199 (33). Abs. mass, obs. 911.776; calc. for $C_{32}H_{20}I_4$ 911.775.

The bistriphenylphosphonium salt from 2,3-diiodo-1,4-bis(bromomethyl)benzene was prepared from *p*-xylene as follows. A mixture of isomers (216 g) of dinitro-*p*-xylenes, obtained by nitration of *p*-xylene, was partially hydrogenated in toluene–ethanol 1:1 with palladium on charcoal as catalyst. The formation of a yellow compound, 2-amino-3-nitro-*p*-xylene, was followed by TLC. The product was purified by column chromatography with chloroform as eluent. The first yellow fractions gave *2-amino-3-nitro*-p-*xylene* (36 g, 20 %, m.p. 69–71 °C). ^{1}H NMR (270 MHz, $CDCl_3$): δ 6.85 and 6.32 (2 H, dd, J 7.3 Hz), 5.14 (2 H, s), 2.36 (3 H, s) and 2.11 (3 H, s). 2-Amino-3-nitro-*p*-xylene (36 g) was further hydrogenated under the same conditions as above to give *2,3-diamino*-p-xylene, which was recrystallised from iso-butanol (15 g, 51 %). IR (KBr): 3370 (s), 3260 (s), 3100–2600 (s, broad band), 2570 (s), 1670 (s), 1625(s), 1475 (s), 1310 (s), 1100 (s), 1025 (s), 792 (s) cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_2$): δ 6.78 (2 H, s), 3.34 (4 H, s), and 2.25 (6 H, s). MS [IP 70 eV; *m/e* (rel. int.)]: 136 (M^+, 100 %), 135 (30), 121 (9), 119 (12), 118 (17), 108 (11) and 104 (11).

2,3-Diamino-*p*-xylene (1.36 g) and sodium nitrite (2 g) were mixed with sulfuric acid (conc., 25 and 20 ml, respectively) in two separate flasks. The former solution was slowly added to the latter while the temperature was kept below 0 °C. Phosphoric acid (25 ml) was then added to the mixture and the temperature kept below 10 °C. The reaction mixture was poured onto crushed ice (300 ml) and potassium iodide (8 g). The mixture was stirred overnight, extracted with chloroform (3×150 ml) and treated with sodiumbisulphite. The solvent was distilled off and the residue, a light yellow oil, was chromatographed with tetrachloromethane as eluant. The first fractions gave *2,3-diiodo*-p-*xylene* (1.4 g, 40 %, m.p. 20 °C). ^{1}H NMR ($CDCl_3$): δ 7.1 (2 H, s) and 2.5 (6 H, s). MS [IP 70 eV; *m/e* (rel. int.)]: 358 (M^+, 100 %), 231 (33), 127 (14), 104 (67), 103 (33). 2,3-Diiodo-*p*-xylene (3.58 g) was refluxed in tetrachloromethane with NBS (3.9 g) and dibenzoyl peroxide as initiator for 24 h. The hot solution was filtered. From the cooled filtrate, a white crystalline precipitate was collected and purified by column chromatography with tetrachloromethane as eluent. The major fractions yielded *2,3-diiodo-1,4-bis(bromomethyl)benzene* (1.3 g, 225 %, m.p. 135–137 °C). IR: 2925 (m), 1460 (s), 1210 (s), 860 (s), and 650 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.46 (2 H, s), and 4.75 (4 H, s). MS [IP 70 eV; *m/e* (rel. int.)]: 516 (M^+, 22 %), 515 (17), 437 (80), 435 (80), 356 (57), 310 (14), 308 (14), 254 (12), 229 (14), 127 (30), 102 (100). 2,3-Diiodo-1,4-bis(bromomethyl)benzene (10 mmol) and triphenylphosphine (20 mmol) were heated in dry DMF overnight. After cooling, the solution was added to dry diethyl ether (500 ml). The precipitated phosphonium salt was collected, washed with dry ether and dried in vacuum at 110 °C before use.

Hydrogenations were carried out at room temperature and atmospheric pressure. The cyclophanes *15* and *14*, respectively, were dissolved in benzene (P.A.) and palladium on charcoal added and the mixtures were stirred under hydrogen. After 24 h the catalyst was filtered off, the solvent evaporated, and cyclophanes *6* and *8*, respectively, were collected and found to be identical with the products from the photocyclisations of cyclophanes *5* and *7*, respectively.

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REFERENCES

1. a. Muszkat, K. A. and Fischer, E. *J. Chem. Soc. B.* (1967) 662; b. Muszkat, K. A. *Top. Curr. Chem. 88* (1980) 89.
2. Blackburn, E. V. and Timmons, C. J. *Quart. Rev. 23* (1969) 482.
3. Houben-Weyl, *Methoden der Organischen Chemie,* Thieme, Stuttgart 1975, Band IV/5a, p. 511.
4. Wynberg, H. *Acc. Chem. Res. 4* (1971) 65; Martin, R. H. *Angew. Chem. 86* (1974) 727.
5. DuVernet, R. B., Wennerström, O., Lawson, J., Otsubo, T. and Boekelheide, V. *J. Am. Chem. Soc. 100* (1978) 2457 and references therein.
6. Thulin, B., Wennerström, O. and Högberg, H.-E. *Acta Chem. Scand. B 29* (1975) 138.
7. Strand, A., Thulin, B. and Wennerström, O. *Acta Chem. Scand. B 31* (1977) 521.
8. Bendig, J., Beyermann, M. and Kreysig, D. *Tetrahedron Lett.* (1977) 3659.
9. Thulin, B. and Wennerström, O. *Acta Chem. Scand. B 30* (1976) 688.
10. Gerson, F., Huber, W. and Wennerström, O. *Helv. Chim. Acta 61* (1978) 2763.

11. Ankner, K., Lamm, B., Thulin, B. and Wennerström, O. *Acta Chem. Scand. B 32* (1978) 155; *J. Chem. Soc. Perkin Trans. 2* (1980) 1301.
12. Cuppen, T. J. H. M. and Laarhoven, W. H. *J. Am. Chem. Soc. 94* (1972) 5914.
13. Wismonski-Knittel, T., Fischer, G. and Fischer, E. *J. Chem. Soc. Perkin Trans. 2* (1974) 1930.
14. Muszkat, K. A., Sharafi-Ozeri, S., Seger, G. and Pakkanen, T. A. *J. Chem. Soc. Perkin Trans. 2* (1975) 1517.
15. Ankner, K., Lamm, B., Thulin, B. and Wennerström, O. *Acta Chem. Scand. B 33* (1979) 391.
16. Bergmann, E. D. and Szmuskoviez, J. S. *J. Am. Chem. Soc. 73* (1951) 5153.
17. Martin, R. H., Defay, N., Figeys, H. P., Flammang-Barbieux, M., Cosyn, J. P., Gelbcke, M. and Schurter, J. J. *Tetrahedron 25* (1969) 4985.
18. Johnson, C. E. and Bovey, F. A. *J. Chem. Phys. 29* (1958) 1012.
19. Thulin, B. and Wennerström, O. *Acta Chem. Scand. B 37* (1983) 297.
20. Thulin, B. and Wennerström, O. *Acta Chem. Scand. B 30* (1976) 369.
21. Leach, D. N. and Reiss, J. A. *Aust. J. Chem. 32* (1979) 361.
22. Thulin, B. and Wennerström, O. *Tetrahedron Lett.* (1977) 929.
23. Leach, D. N. and Reiss, J. A. *J. Org. Chem. 43* (1978) 2484.
24. Sharma, R. K. and Kharasch, N. *Angew. Chem. 80* (1968) 69.
25. Thulin, B., Wennerström, O., Somfai, I. and Chmielarz, B. *Acta Chem. Scand. B 31* (1977) 135; Thulin, B., Wennerström, O. and Somfai, I. *Acta Chem. Scand. B 32* (1978) 109.

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