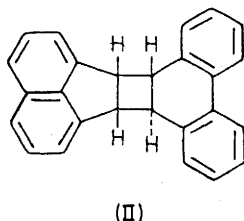
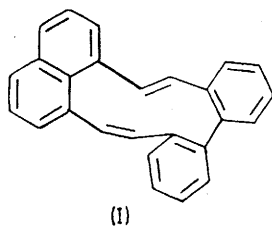


Synthesis and Photochemistry of 2,2'-Distyrylbiphenyl and 2,2'-Bis-(4-phenylbuta-1,3-dienyl)biphenyl

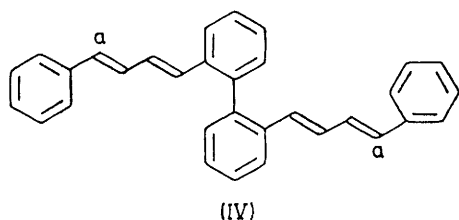
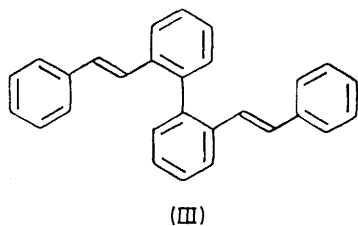
By C. D. Tulloch and W. Kemp,* Chemistry Department, Heriot-Watt University, Chambers St., Edinburgh EH1 1HX

2,2'-Distyrylbiphenyl and 2,2'-bis-(4-phenylbuta-1,3-dienyl)biphenyl have been prepared by Wittig reactions of 2,2'-bis(triphenylphosphoniomethyl)biphenyl dibromide with benzaldehyde and cinnamaldehyde, respectively, with sodium ethoxide as base. Their photolysis products have been shown by i.r., u.v., n.m.r., and mass spectra to be cyclobutane derivatives formed by intramolecular condensation.

MITCHELL and SONDHEIMER¹ have prepared, and studied the photolysis of, the eleven-membered ring compound (I); they showed that the photolysis gave a compound containing a cyclobutane ring *trans*-fused to a six-membered ring (II). Photolyses of two ana-

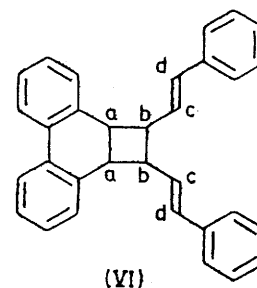
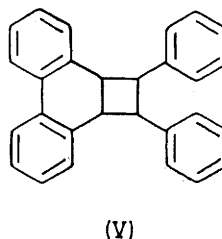


logous naphthalene derivatives [1,8-distyrylnaphthalene^{2,3} and 1,8-bis-(4-phenylbuta-1,3-dienyl)naphthalene⁴] have also been reported to give a cyclobutane ring. 2,2'-Distyrylbiphenyl (III) has previously been synthesised by Hall and Prakobsantisukh⁵ in 22% yield from the Wittig reaction between 2,2'-bis(triphenylphosphoniomethyl)biphenyl dibromide and benzaldehyde with butyl-lithium as base, but no information on its photolysis or that of the homologue (IV) has been available hitherto.



2,2'-Bis(triphenylphosphoniomethyl)biphenyl dibromide⁶ was treated with benzaldehyde or cinnam-

aldehyde in the presence of sodium ethoxide to give compounds (III) and (IV) (yields 30 and 50%, respectively). Photoirradiation of these products might have been expected to yield intermolecular condensation products, since the two distyryl or phenylbutadienyl residues will certainly be distant one from the other in the preferred conformation. However, the only products isolated after photoirradiation were compounds (V) and (VI), identified as follows.



The n.m.r. spectrum of compound (V) showed 18 aromatic protons and 2 pairs of cyclobutane protons (τ 6.15–6.4 and 6.7–7.0). Its mass spectrum showed several fragmentation series, each of which involved successive loss of CH. The two most intense peaks were due to the phenanthrene [m/e 178 (100.0%)] and stilbene ions [m/e 180 (77.8%)]. If no rearrangement occurs prior to fragmentation, these ions can only be formed if, in the photolysis product from (III), there is a linkage across the two $[\text{CH}]_n$ chains, *i.e.* a cyclobutane ring has been formed. The i.r. spectrum showed no evidence of a carbon-carbon double bond and the electronic absorption spectrum showed a loss of conjugation as compared with distyrylbiphenyl.

The n.m.r. spectrum of compound (VI) showed 18 aromatic protons, 4 alkene protons, and 4 groups of cyclobutane protons (each 1H; τ 5.95–6.3, 6.5–6.8, 6.95–7.5, and 7.6–8.2). The coupling constant for the two olefinic protons (16.5 Hz) is characteristic of a *trans*-double bond. The mass spectrum showed several fragmentation series, all involving successive loss of CH. The base peak (m/e 232) is due to the ion (IX). As the longest $[\text{CH}]_n$ chain in compound (IV) has $n = 4$,

¹ R. H. Mitchell and F. Sondheimer, *Tetrahedron Letters*, 1968, 2873.

² P. R. Houlton and W. Kemp, *Tetrahedron Letters*, 1968, 1045.

³ J. Meinwald and J. W. Young, *J. Amer. Chem. Soc.*, 1971, 93, 725.

⁴ P. R. Houlton and W. Kemp, *Tetrahedron Letters*, 1968, 4093.

⁵ D. M. Hall and B. Prakobsantisukh, *J. Chem. Soc.*, 1965, 6311.

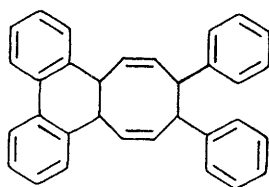
⁶ E. D. Bergmann, P. Bracha, I. Agrunat, and M. A. Kraus, *J. Chem. Soc. (C)*, 1967, 328.

Org.

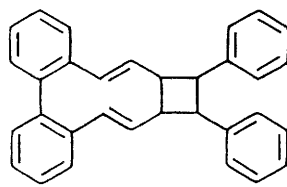
this ion can only be formed if, in the photolysis product from (IV), there is a linkage across the two $[\text{CH}]_n$ chains. Thus the photolysis product must have structure (VI), or one of the alternatives (VII) and (VIII). The presence of the phenanthrene ion [m/e 178 (19.2%)] and ion (IX) [m/e 232 (100%)] indicates (VI) as the likely structure. Structure (VII) can be discounted, as the two double bonds in this case are isolated from phenyl conjugation and a τ value of 4.7 would be expected; also the i.r. spectrum of the product shows a band at 905 cm^{-1} , characteristic of C-H on a cyclobutane ring.

The τ values for the cyclobutane protons in the photolysis product correspond to values for compounds similar to (V)¹ but not (VII),³ e.g. compound (II) shows τ 5.3–5.7 (2H), 6.2–6.6 (1H), and 6.9–7.3 (1H). Compound (X) shows τ 3.55 (2H) and 5.06 (2H).

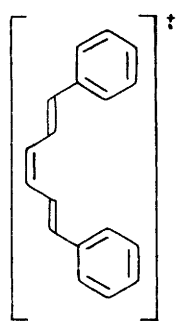
If the structure is (VI) one would expect an electronic absorption spectrum similar to that of styrene: product λ_{max} (cyclohexane) 221 nm ($\log \epsilon$ 4.42), 259 (4.39), and 293 nm (3.78); styrene λ_{max} 248 ($\log \epsilon$ 4.64) and 291 (4.54) nm, ν_{max} (C=C *trans*) 964 cm^{-1} .



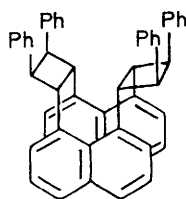
(VII)



(VIII)



(IX)



(X)

With regard to the stereochemistry of the photolysis products, models indicated that a cyclobutane ring *trans*-fused to the dihydrophenanthrene ring would be highly strained and difficult to form, whereas a *cis*-fused form showed much less strain and was more easily constructed. However, the complexity of the cyclobutane resonances appears to rule out the symmetrical forms unless the compounds are mixtures of the various stereoisomers. Spin decoupling experiments on the cyclobutane protons of compound (V) indicated that the two groups at τ 6.15–6.4 and 6.7–7.0 are coupling to each other, but no first-order splitting pattern was obtained through spin decoupling or by use of a 220 MHz instrument.

The complexity and width of the cyclobutane resonances for compound (VI) prevented any useful results being obtained from spin decoupling and variable temperature experiments or by use of the 220 MHz instrument.

It is noteworthy that whereas photocyclisation of 1,8-distyrylnaphthalene occurs intermolecularly to form a dimer³ (X), photocyclisation of the 2,2'-substituted biphenyls occurs intramolecularly, even though the stereochemistry of the starting materials would favour intramolecular photolysis to a greater extent in 1,8-distyrylnaphthalene than in the biphenyls.

EXPERIMENTAL

2,2'-Distyrylbiphenyl (III).—2,2'-Bis(triphenylphosphoniomethyl)biphenyl dibromide⁶ (6 g, 0.00695 mol) was dissolved in boiling absolute ethanol (50 cm³), and benzaldehyde (1.4 cm³, 0.014 mol) was added. The solution was added slowly with stirring under nitrogen to 0.4M-sodium ethoxide (50 cm³). The orange colour of the product was observed immediately. The mixture was stirred for 2 h, after which time the orange colour had completely disappeared from the solution, and the product (III) had precipitated out; m.p. 146–147° [from chloroform–light petroleum (b.p. 60–80°)] (lit.,⁵ 148–149°), yield 0.75 g (30%). I.r. and u.v. spectra agreed with those reported.⁵

Photolysis of 2,2'-Distyrylbiphenyl.—A 0.01M-solution of the biphenyl in cyclohexane was irradiated with a medium-pressure mercury vapour lamp while under reflux in a nitrogen atmosphere. The reaction was followed by recording the u.v. spectrum at intervals of 1 h. The peak at 295 nm decreased while a new peak at 273 nm appeared. The ratio $(A_{273} - A_{295})/A_{295}$ (A = optical density) reached a maximum value of 0.28 after 8 h. The cyclohexane was removed, and the product was dissolved in the minimum of chloroform and purified by preparative t.l.c. in 1:1 benzene–light petroleum (b.p. 60–80°) (R_F 0.90). 1,2,2a,10b-Tetrahydro-1,2-diphenylcyclobuta[1]phenanthrene (V) was obtained in 60% yield as an off-white solid, m.p. 202–203° (from chloroform–light petroleum) (Found: C, 93.1; H, 6.1. $\text{C}_{28}\text{H}_{22}$ requires C, 93.8; H, 6.2%), τ (CDCl_3) 2.1–3.1 (18H, aromatic), 6.15–6.4 (2H, cyclobutane), and 6.7–7.0 (2H, cyclobutane), λ_{max} (cyclohexane) 222 ($\log \epsilon$ 4.56), 228sh (4.51), 249 (4.06), 255 (4.09), 261 (4.14), 273 (4.18), 283 (4.20), and 294sh nm (4.05), m/e 358 (M^+ , 6.6%), 267 (10.4), 265 (16.7), 252 (13.0), 181 (13.3), 180 (77.8), 179 (32.6), 178 (100.0), and 165 (10.4).

2,2'-Bis-(4-phenylbuta-1,3-dienyl)biphenyl (IV).—2,2'-Bis(triphenylphosphoniomethyl)biphenyl dibromide⁶ (8.64 g, 0.01 mol) was dissolved in boiling absolute ethanol (125 cm³) and cinnamaldehyde (2.5 cm³, 0.02 mol) was added. This solution was added slowly with stirring under nitrogen to 0.2M-sodium ethoxide (125 cm³). The mixture was stirred for 1 h and filtered; the product (IV) (2.0 g, 50%) had m.p. 147–148° (from benzene–ethanol) (Found: C, 93.35; H, 6.6. $\text{C}_{32}\text{H}_{26}$ requires C, 93.6; H, 6.4%), λ_{max} (EtOH) 208 ($\log \epsilon$ 4.60), 229 (4.37), 323 (4.64), 336 (4.59), and 354 nm (4.40), τ 2.0–3.0 (aromatic + H_a) and 3.2–3.9, ν_{max} (C=C *trans*) 970–990 cm^{-1} (KBr).

Photolysis of 2,2'-Bis-(4-phenylbuta-1,3-dienyl)biphenyl.—

A 0.01M-solution of the biphenyl in cyclohexane was irradiated as for compound (III). The reaction was followed by u.v. spectroscopy (peaks at 320, 338, and 353 nm disappeared and peaks at 292 and 260 nm appeared). After 2 h the photolysis was complete. The cyclohexane was removed and the product was dissolved in the minimum of chloroform and purified by preparative t.l.c. in 1:1 benzene-light petroleum (R_F 0.90). 1,2,2a,10b-Tetrahydro-1,2-distyrylcyclobuta[1]phenanthrene (VI) was obtained in 50% yield as an off-white solid, m.p. (from benzene-ethanol) 99–100° (Found: C, 93.1; H, 6.6.

$C_{32}H_{26}$ requires C, 93.6; H, 6.4%), τ ($CDCl_3$) 2.0–3.0 (18H, aromatic), 3.0–4.4 (4H, alkene, conjugated to aromatic nucleus), 5.95–6.3 (1H, cyclobutane), 6.5–6.8 (1H, cyclobutane), 6.95–7.5 (1H, cyclobutane), and 7.6–8.2 (1H, cyclobutane), J_{ed} 16.5, J_{be} 9.5 Hz (from 220 MHz spectrum), m/e 410 (M^+ , 10.0%), 292 (13.2), 232 (100.0), 219 (10.6), 215 (26.6), 202 (10.1), 191 (11.4), 178 (19.2), 141 (15.4), 115 (13.3), and 91 (50.5).

We thank the S.R.C. for a grant (to C. D. T.).

[1/278 Received, March 15th, 1971]