Tetrahedron. Vol. 28, pp. 275 to 280. Pergamon Press 1972. Printed in Great Britain.

PHOTOCYCLIZATION OF SUBSTITUTED 1,4-DISTYRYLBENZENES TO DIBENZ [*a*,*h*] ANTHRACENES

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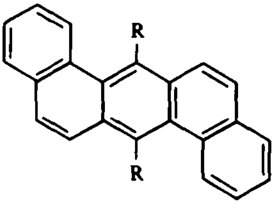
(*Received in the UK* 23 *June* 1971; *Accepted for publication* 25 *September* 1971)

Abstract—A photochemical route for the synthesis of 7,14-dimethyl-, 7,14-dichloro-, and 7,14-difluoro-dibenz[*a*,*h*]anthracene has been investigated. The 7,14-dimethyl derivative was obtained by photocyclization of either 2,5-distyryl- or 2,5-bis-(2-iodostyryl)-*p*-xylene, while the dichloro- and difluoro-dibenz[*a*,*h*]anthracene could be prepared only from the corresponding 2,5-bis-(2-iodostyryl)-1,4-dihalobenzenes. 2,5-Distyryl-1,4-dibromobenzene suffers debromination upon irradiation.

FOLLOWING OUR FINDINGS[1] that benz[*a*]anthracene derivatives, fluorinated in the so-called L region, can be prepared by photocyclization of appropriate 1,2-diarylethylenes, we extended our studies to include the synthesis of 7,14-difluorodibenz[*a*,*h*]-anthracene (**1**, R = F).

Dietz and Scholz[2] and Laarhoven *et al.*[3] have shown that irradiation of the unsubstituted 1,4-distyrylbenzene(**2**, R = H) does not lead to dibenz[*a*,*h*]anthracene (**1**, R = H) and have suggested that this is due to the low ΣF^*-values and localization energies of the atoms involved in the photocyclization of the intermediary monostyryl-compound (**3**, R = H) to **1**. It would be expected that if the 2- and 5-positions of the distyrylbenzene are blocked as in **2** (R ≠ H), the dibenz[*a*,*h*]anthracene skeleton would be formed.



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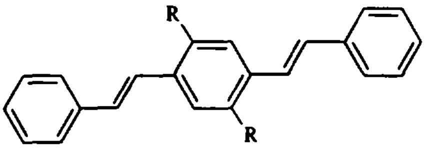

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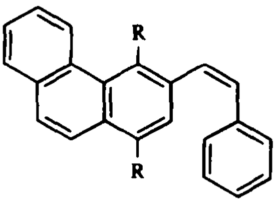

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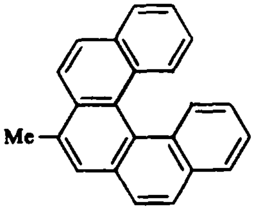

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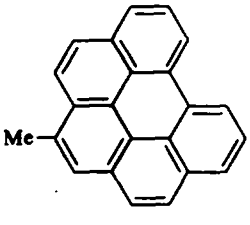

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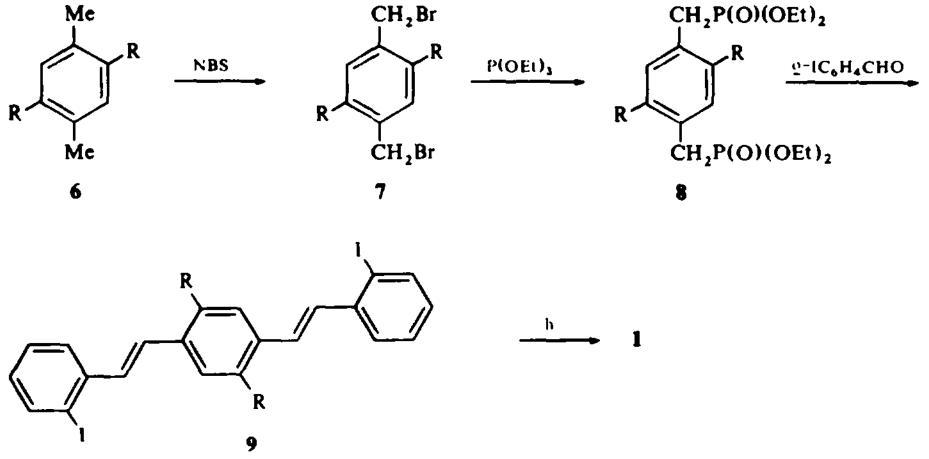
Indeed, *trans*, *trans*-2,5-distyryl-*p*-xylene (**2**, R = Me), which is prepared easily from 2,5-bis(bromomethyl)-*p*-xylene (**7**, R = Me)[4] and benzaldehyde by the Wittig–Arbuzov reaction, gave upon irradiation with a 450 Watt Hanovia high pressure mercury lamp 23% of 7,14-dimethyldibenz[*a*,*h*]anthracene (**1**, R = Me) after 1 hr. It is noteworthy that although demethylation has been reported to occur during the photolysis of *o*-methylstilbenes,[5] and 1,4-distyrylbenzene is cyclized mainly to dibenzo[*c*,*g*]phenanthrene and benzo[*g*,*h*,*i*]perylene,[2,3] we did not isolate **4** or **5**.

Unfortunately the conditions of photolysis useful in the case of the dimethyl compound, proved inapplicable to the halogenated distyrylbenzenes (**2**, R = Hal, including F), as the halogen atoms were eliminated during and after the photocyclization. Irradiation from a UV source of low intensity (75 W), did not cause significant dehalogenation of the chloro- and fluoro-distyrylbenzenes, but the cyclization to **1** proceeded extremely slowly.

We succeeded in preparing the halo-substituted dibenz[*a*,*h*]anthracenes, when Kupchan's modification[6] of the photocyclization of stylbenes was applied: 2,5-difluoro-*p*-xylene (**6**, R = F)[7] was converted in two steps to tetraethyl 2,5-bis(diethylphosphonomethyl)-1,4-difluorobenzene (**8**, R = F), which condensed with *o*-iodobenzaldehyde to give *trans*, *trans*-2,5-bis-(2-iodostyryl)-1,4-difluorobenzene (**9**, R = F). Irradiation for 5 hr caused cyclodehydroiodination to 7,14-difluorodibenz[*a*,*h*]anthracene (**1**, R = F) in 31% yield. Prolonged photolysis gave increasing quantities of monofluoro- and fluorine-free hydrocarbons.



6 **7** **8**

9

7,14-Dimethyl and 7,14-dichloro-dibenz[*a*,*h*]anthracene could be prepared in the same manner from *trans*, *trans*-2,5-bis-(2-iodostyryl)-*p*-xylene (**9**, R = Me) and *trans*, *trans*-2,5-bis-(2-iodostyryl)-1,4-dichlorobenzene (**9**, R = Cl), respectively, while the photocyclization of *trans*, *trans*-2.5-bis-(2-iodostyryl)-1,4-dibromobenzene (**9**, R = Br) (as well as that of **2**, R = Br) was accompanied by extensive debromination. The dibromo-compound (**1**, R = Br) could not be obtained analytically pure.

The structure of the 7,14-dihalodibenz[*a*,*h*]anthracenes was proved by the close resemblance of their electronic spectra to those of the halogen-free parent compound and of 7,14-dimethylbenz[*a*,*h*]anthracene (Table 1). The latter compound (obtained

TABLE 1

Compound	Electronic Spectra, λ_{max} nm (log ϵ)										
Dibenz[*a*,*h*]anthracene (**1**, R = H)[a,b]	273 (4·70)	285 (4·90)	295 (5·20)	306 (4·40)	320 (4·30)	332 (4·25)	349 (4·20)	364 (2·70)	373 (3·00)	384 (2·60)	394 (3·10)
7,14-Difluorodibenz[*a*,*h*]anthracene (**1**, R = F)[c]	273 (4·62)	278 (4·77)	290 (4·99)	299 (5·04)	313 (4·11)	329 (4·15)	349 (4·28)	362 (4·26)	378 (3·78)		399 (3·73)
7,14-Dichlorodibenz[*a*,*h*]anthracene (**1**, R = Cl)[e]		278 (4·30)	294 (4·45)	306 (4·53)		332 (4·06)	348 (4·09)	366 (4·10)		386 (3·98)	412 (3·45)
7,14-Dibromodibenz[*a*,*h*]anthracene (**1**, R = Br)[d,e]		287	296	306		330	348	365		385	411
7,14-Dimethyldibenz[*a*,*h*]anthracene (**1**, R = CH_3)[e,f]	273 (4·08)	282 (4·12)	293 (4·28)	305 (4·42)	315 (3·62)	332 (3·46)	351 (3·61)	369 (3·91)		390 (3·97)	410 (2·85)
7,14-Dimethyldibenz[*a*,*h*]anthracene (**1**, R = CH_3)[a,b]		283 (4·16)	293 (4·90)	306 (4·95)	322 (4·08)	335 (4·08)	352 (4·15)	370 (4·15)		291 (2·90)	408 (2·70)

[a] EtOH as solvent.

[b] After Mayneord and Roe.[9]

[c] $CHCl_3$ as solvent.

[d] Not analytical pure.

[e] Cyclohexane as solvent.

[f] Obtained from **2**, (R = Me) and from **9** (R = Me).

by both the methods described above) was identical with an authentic sample prepared by the "classical" route from 7,14-dibenz[*a*,*h*]anthraquinone.[8]

EXPERIMENTAL

trans, trans-2,5-*Distyryl*-p-*xylene* (**2**, R = Me). To a stirred soln of 4·06 g of phosphate **8** (R = Me)[4] in 70 ml dry DMF, was added dropwise 0·6 g NaOMe in 30 ml of the same solvent. After 5 min 2·12 g freshly distilled benzaldehyde was added at 25–30°. After 30 min at the same temperature, the mixture was poured on crushed ice to yield 36% of **2**, (R = Me) as yellow crystals; m.p. 200° (from C_6H_6 and EtOH); λ_{max} ($CHCl_3$) nm (log ϵ) 343 (4·30); ν^{KBr}_{max} 965 cm^{-1}. (Found: C, 92·7; H, 7·0. Calc. for $C_{24}H_{22}$: C, 92·9; H, 7·1%).

trans, trans-2,5-*Bis*-(2-*iodostyryl*-)-p-*xylene* (**9**, R = Me). A soln of 2·3 g **8** (R = Me) and 0·3 g NaOMe in 70 ml DMF was treated as above with 2·32 g *o*-iodobenzaldehyde[10] in 40 ml of the same solvent at 25° to yield 1·52 g (54%) of bright yellow crystals; m.p. 221–22° (from C_6H_6 and EtOH). λ_{max} ($CHCl_3$) nm (log ϵ) 340 (4·49); ν^{KBr}_{max} 960 cm^{-1}. (Found: C, 51·3; H, 3·7; I, 44·7. Calc. for $C_{24}H_{20}I_2$: C, 51·3; H, 3·6; I, 45·2%).

7,14-*Dimethyldibenz*[a,h]*anthracene* (**1**, R = Me). (a) A mixture of 155 mg **2** (R = Me), 64 mg I_2 and 150 ml purified cyclohexane was irradiated in a 3-necked photolysis tube of quartz, equipped with a gas inlet for N_2, a Teflon magnetic stirrer and a 450 Watt Hanovia high pressure mercury lamp. After 60 min, the UV spectrum of the soln ceased to change and the illumination was discontinued. The mixture was washed with $NaHSO_3$ aq, dried and concentrated. The residue was chromatographed on alumina under N_2 (mixtures of hexane-C_6H_6 serving as eluent). After recrystallization from C_6H_6 and EtOH 35 mg (23%) of **1** (R = Me) was obtained; m.p. and m.m.p. with an authentic sample[8] 204–205°.

(b) In the same apparatus as in (a), a soln of 200 mg **9**, (R = Me) in 150 ml purified cyclohexane was irradiated for 90 min. Column chromatography of the mixture gave 33 mg (23%) of **1** (R = Me) identical with the hydrocarbon from (a).

2,5-*Bis*(*bromomethyl*)1,4-*difluorobenzene* (**7**, R = F). A mixture of 27·4 g 2,5-difluoro-*p*-xylene (**6**, R = F) (prepared in four steps from 2,5-dimethylaniline[7]), 76·4 g NBS, 0·5 g benzoyl peroxide and 250 ml CCl_4 was refluxed until all the reagent had decomposed (2 hr) to yield 27·8 g (48%) of colorless crystals; m.p. 53–55° (from EtOH). ν^{KBr}_{max} 1210 cm^{-1} (C – F). (Found: C, 31·8; H, 2·3; Br, 52·9. Calc. for $C_8H_6Br_2F_2$: C, 32·0; H, 2·0; Br, 53·3%).

2,5-*Bis*(*diethylphosphonatomethyl*)1,4-*difluorobenzene* (**8**, R = F). A mixture of 8·7 g triethyl phosphite and 7·5 g **7** (R = F) was refluxed until evolution of EtBr ceased (20 min). The excess reagent was removed by distillation at 0·5 mm, and the residue triturated with hexane to give 9·3 g (90%) of yellow crystals of m.p. 74–75° (from hexane). $\nu^{CHCl_3}_{max}$ 1275 cm^{-1} (P – O); 1200 cm^{-1} (C – F). (Found: C, 46·2; H, 6·1. Calc. for $C_{16}H_{26}F_2O_6P_2$: C, 46·4; H, 6·3%).

trans, trans-2,5-*Bis*-(2-*iodostyryl*)-1,4-*difluorobenzene* (**9**, R = F) was prepared in 53% yield in the same way as **9** (R = Me) from 4·14 g **8** (R = F) and 4·64 g *o*-iodobenzaldehyde. Bright yellow crystals; m.p. 227–230° (from C_6H_6). λ_{max} (cyclohexane) nm (log ϵ) 350 (4.40); ν^{Nujol}_{max} 960 cm^{-1}; NMR ($CDCl_3$) τ ppm 2·85 (m, aromatic protons), 3·48 (m, *trans*-ethylenic protons). (Found: C, 46·6; H, 2·7; F, 7·1. Calc. for $C_{22}H_{14}F_2I_2$: C, 46·3; H, 2·5; F, 6·7%).

7,14-*Difluorodibenz*[a,h]*anthracene* (**1**, R = F). A soln of 560 mg of **9** (R = F) in 400 ml cyclohexane was placed in a 4·5 × 32 cm quartz tube of a Rayonet photochemical reactor fitted with 16 75 Watt UV lamps at a distance of 12 cm from the reaction vessel. N_2 was bubbled through the soln. After 5 hr the soln was washed with $NaHSO_3$ aq, dried and concentrated. The residue was chromatographed on alumina (hexane–C_6H_6 mixtures serving as eluent). The third fraction of the eluate afforded 96 mg (31%) of **1** (R = F) as pale yellow crystals; m.p. 213–215° (from C_6H_6). ν^{KBr}_{max} 1250 cm^{-1} (C – F). The NMR spectrum contained only a multiplet in the aromatic region (τ ppm 2·86). (Found, C, 84·4; H, 3·8; H, 11·7. Calc. for $C_{22}H_{12}F_2$: C, 84·1; H, 3·8; F, 12·1%).

The 2,4,7-*trinitrofluorenone complex* was prepared in, and recrystallized from, C_6H_6; red-brown needles, m.p. 210°. (Found: C, 66·9; H, 3·0; F, 5·8. Calc. for $C_{35}H_{17}F_2N_3O_7$: C, 66·9; 2·7; F, 6·0%).

2,5-*Bis*(*bromomethyl*)-1,4-*dichlorobenzene* (**7**, R = Cl) was prepared from 2,5-dichloro-*p*-xylene (**6**, R = Cl)[11] in the same way as the 2,5-difluoro-analog **7** (R = F). Colorless crystals, m.p. 112–114° (from EtOH). (Found: C, 29·0; H, 1·8. Calc. for $C_8H_6Bt_2Cl_2$: C, 28·8: H, 1·8%).

2,5-*Bis(diethylphosphonatomethyl)*-1,4-*dichlorobenzene* (**8**, R = Cl) was obtained in 96% yield from the foregoing dibromide (**7**, R = Cl) (10·5 g) and triphenyl phosphite (10·8 g) by the procedure described for the difluoro-compound **8** (R = F). Yellow crystals; m.p 87–89° (from petroleum ether). (Found: C, 42·5; H, 5·5; Cl, 15·8. Calc. for $C_{16}H_{26}Cl_2O_6P_2$: C, 42·9; H, 5·8; Cl, 15·9%).

trans, trans-2,5-*Bis*-(2-*iodostyryl*)-1,4-*dichlorobenzene* (**9**, R = Cl) was obtained in 83% yield from phosphonate **8** (R = Cl), (2·24 g) and *o*-iodobenzaldehyde (2·32 g). Bright yellow crystals; m.p. 250–252° (from xylene). λ_{max} (cyclohexane) nm (log ε) 340 (4·39); ν^{KBr}_{max} 958 cm^{-1}. (Found: C, 43·9; H, 2·5. Calc. for $C_{22}H_{14}Cl_2I_2$: C, 43·8; H, 2·3%).

7,14-*Dichlorodibenz*[a,h]*anthracene* (**1**, R = Cl). Irradiation of 318 mg of **9** (R = Cl) in 300 ml cyclohexane, under the conditions described for the difluoro-analog, afforded after 4 hr an orange semi-solid that was chromatographed on alumina (hexane-C_6H_6 mixtures serving as eluent). The eighth fraction of the eluate was recrystallized from C_6H_6 to yield 60·5 mg (33%) of **1** (R = Cl) as yellowish needles; m.p. 70–72°. (Found: C, 76·3; H, 3·5; Cl, 20·3. Calc. for $C_{22}H_{12}Cl_2$: C, 76·1; H, 3·5; Cl, 20·5%).

The first fraction of the eluate was a chlorine-free hydrocarbon that did not show the characteristic UV spectrum of dibenz[*a,h*]anthracene; fractions 5–7 showed absorptions similar to **1** (R = Cl) but did not contain the required amount of chlorine.

2,5-*Bis(bromomethyl)*-1,4-*dibromobenzene* (**7**, R = Br). Bromination of 26·4 g 2,5-dibromo-*p*-xylene (**6**, R = Br)[11] with 38·2 g NBS in 250 ml CCl_4, afforded 30·0 g (71%) of colorless crystals; m.p. 145–147° (from EtOH). (Found: C, 23·0; H, 1·4. Calc. for $C_8H_6Br_4$: C, 22·8; H, 1·4%).

2,5-*Bis(diethylphosphonatomethyl)*-1,4-*dibromobenzene* (**8**, R = Br) was formed in 65% yield from 21·1 g of **7** (R = Br) and 18·3 g triethyl phosphite by the procedure described above. Yellow crystals: m.p. 88–90° (from petroleum ether). (Found: C, 35·5; H, 4·5. Calc. for $C_{16}H_{26}Br_2O_6P_2$: C, 35·8; H, 4·8%).

trans, trans-2,5-*Distyryl*-1,4-*dibromobenzene* (**2**, R = Br). The foregoing phosphonate (5·36 g), 1·2 g NaOMe and 2·12 g benzaldehyde in 80 ml DMF gave 2·98 g (68%) of yellow crystals; m.p. 225–227° (from toluene). λ_{max} ($CHCl_3$) nm (log ε) 343 (4·37); ν^{KBr}_{max} 970 cm^{-1}. (Found: 59·7; H, 3·7; Br, 36·3. Calc. for $C_{22}H_{16}Br_2$: C, 60·0; H, 3·6; Br, 36·4%).

Attempts to convert **2**, (R = Br) into 2,5-*distyryl*-1,4-*dideuteriobenzene* (**2**, R = D) failed. Reaction of the dibromo-compound with either CaO_2, Zn powder and D_2O[12,13], or with excess BuLi, followed by hydrolysis with D_2O, did not lead to a bromine-free product. In both methods 10% of the mono-deuterated compound of m.p. 110–112° was obtained. (Found: C, 72·9; H, 4·8. Calc. for $C_{22}H_{16}BrD$: C, 72·9; H, 4·7%). (The total hydrogen content is calculated as ^1H in accordance with the analytical method)

trans, trans-2,5-*Bis*-(2-*iodostyryl*)-1,4-*dibromobenzene* (**9**, R = Br). As in the case of the dimethyl-compound **9** (R = Me), 2·68 g **8** (R = Br), 2·32 g *o*-iodobenzaldehyde and 0·60 g NaOME gave 1·75 g (51%) of yellow crystals; m.p. 300° λ_{max} ($CHCl_3$) nm (log ε) 335 (4·42); ν^{KBr}_{max} 960 cm^{-1}. (Found: C, 38·5; H, 1·9; Br, 23·2. Calc. for $C_{22}H_{14}Br_2I_2$: C, 38·2; H, 2·0; Br, 23·1%).

Irradiation of **2** *and* **9** (*R* = *Br*). When a soln of 880 mg **2** (R = Br) and 508 mg I_2 in 400 ml cyclohexane was irradiated for 60 hr under the conditions described for **9** (R = F) [or a soln of 346 mg **9** (R = Br) in 300 ml cyclohexane—for 4 hr] characteristic bands of the dibenz[*a,h*]anthracene system appeared in the UV spectra. In both cases, however, chromatography on alumina gave mainly bromine-free and monobromo-compounds. From **2** and **9** (R = Br) there were obtained 42 and 18 mg respectively, in the eighth fraction of the eluate that analysed approximately for $C_{22}H_{12}Br_2$, but could not be purified to a higher degree [mol. wt. (mass spectrograph) 436]. M.p. 200–204° (unsharp); λ_{max} (cyclohexane) nm (log ε) 287 (4·60), 296 (4·75), 306 (4·81), 330 (4·28), 348 (4·34), 365 (4·40), 385 (4·30), 411 (3·08).

Acknowledgement—The authors wish to thank Professor E. D. Bergmann for his advice.

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