The Photochemistry of 2-Vinyldiphenylacetylene and Related Compounds

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Irradiation of solutions of 2-vinyldiphenylacetylene (5) under anaerobic conditions gives 2-phenylnaphthalene (9) in 90% yield. Several derivatives of (5) behave similarly. The reaction is ascribed to the primary formation of a cyclic allene (29), as has been proposed previously for the analogous photocyclization of 1,4-diarylbutenynes into phenylaromatic compounds. The end-product arises from (29) either *via* a 1,5-hydrogen shift or by addition and elimination of a proton. Irradiation of 2-ethynylstilbene (21) also yields (9), but 1-ethynylphenanthrene (22) is formed as a side-product.

IN a previous communication [1] we reported the formation of 2-vinyldiphenylacetylene (5) and 2-ethynylstilbene (21) as a result of the photoelimination of hydrogen chloride from the chloro-2-vinylstilbenes (1) and (3), and (20), respectively. It was noticed that the photoelimination products underwent photocyclization on prolonged irradiation, yielding 2-phenylnaphthalene. In this paper the photocyclization of (5) and (21) is studied under various conditions and with a number of substitution products of (5), and a mechanism is proposed for the reaction.

Though 2-vinyldiphenylacetylenes can be obtained by short irradiation of α- or β-chloro-2-vinylstilbene, better yields are achieved on treatment of these stilbenes with potassium t-butoxide in refluxing toluene. In this way 2-vinyldiphenylacetylene (5), several substitution products ([6)—(8), (14), (17)] and 2-ethynylstilbene (21) were prepared in 90—100% yield (Scheme 1). The compounds were purified by column chromatography on silica, using hexane as the eluent.

All these products, dissolved in hexane (c 10^{-3} mol l^{-1}) which was previously degassed with a stream of oxygen-free argon, gave the corresponding 2-phenylnaphthalenes in fair to good yields (50—90%) on irradiation in a Rayonet photoreactor at 300 nm. Compounds (17) and (21), which contain a stilbene moiety, gave rise also to the formation of a 4a,4b-dihydrophenanthrene derivative, which was converted into the corresponding phenanthrene derivative, possibly by residual oxygen.*

Irradiation of the compounds (5), (17), and (21) in methan[^{2}H]ol gave 2-phenylnaphthalene derivatives containing the label at that α-carbon atom of the naphthalene group which corresponds with an α-acetylene carbon atom in the parent compound (Scheme 2). According to n.m.r. the deuterium incorporation in the products (23)—(25) varied from 50 to 70%. This partial incorporation of the label points to the occurrence of two parallel processes in this solvent, one involving the addition of a proton (H^+ or D^+) at some stage of the reaction and another involving an intramolecular hydrogen shift or the abstraction of a hydrogen atom from the solvent by some intermediate. In methanolic solution the latter possibility could largely be excluded because irradiation of (5) in perdeuteriomethanol gave the same amount of deuterium incorporation as found in CH_3OD.

It is very improbable that the pathway *via* a cationic intermediate is effected by the addition of a proton to the parent compound after excitation as pictured in Scheme 3. In that case a cation (26) should arise, which is very similar to the cation (27) occurring in the photoelimination of α-chloro-2-vinylstilbene (1). This reaction carried out in methanol leads to the substitution product (28) as a side-product,[1] but in the photocyclization of (5) no trace of methoxylated products is found.

A mechanism which is in accord with the experimental data and the considerations given above is proposed in Scheme 4. In this mechanism the photocyclization of 2-vinyldiphenylacetylenes and 2-ethynylstilbene proceeds *via* a primary photoreaction leading to a cyclic allene (29) or (30), from which the end-product (9) arises *via* an intramolecular 1,5-hydrogen shift, *via* addition and elimination of a proton (in protic solvents) and possibly *via* addition and elimination of a hydrogen atom (in aprotic solvents). A similar cyclic allene (32) was previously proposed [3] as an intermediate in the photocyclization of the 1,4-diarylbutenyne (31) and its occurrence in that type of reaction has been supported by flash photolysis experiments.[4]

It is noteworthy that the photocyclizations of vinyldiphenylacetylenes and diarylbutenynes show several differences, which are not fully explained by the supposition of the occurrence of corresponding intermediates. The photocyclization of (31) in CH_3OD leads to 100% deuterium incorporation at the relevant position of the product (33), the reaction is catalysed by amines,[3] and the addition of iodine to the solvent causes incorporation of iodine in the product [5] (see Scheme 4). The photocyclization of vinyldiphenylacetylenes in CH_3OD is only accompanied by *partial* incorporation of the label, catalysis by amines could not be established unequivocally, and the formation of iodinated products in the presence of iodine was not observed. The differences may point to a more polar intermediate in the latter reaction [more like (34)]. In such an intermediate the

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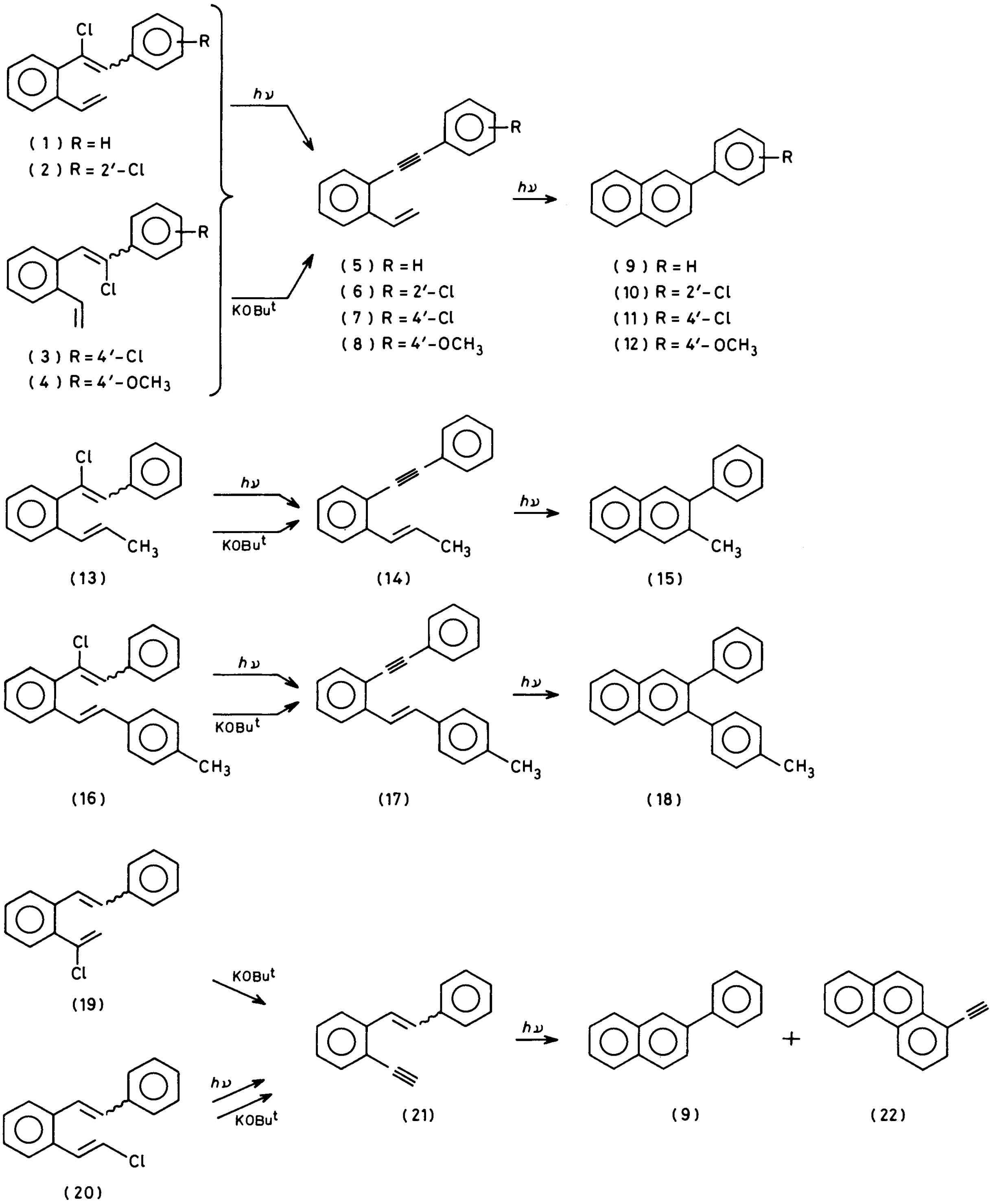
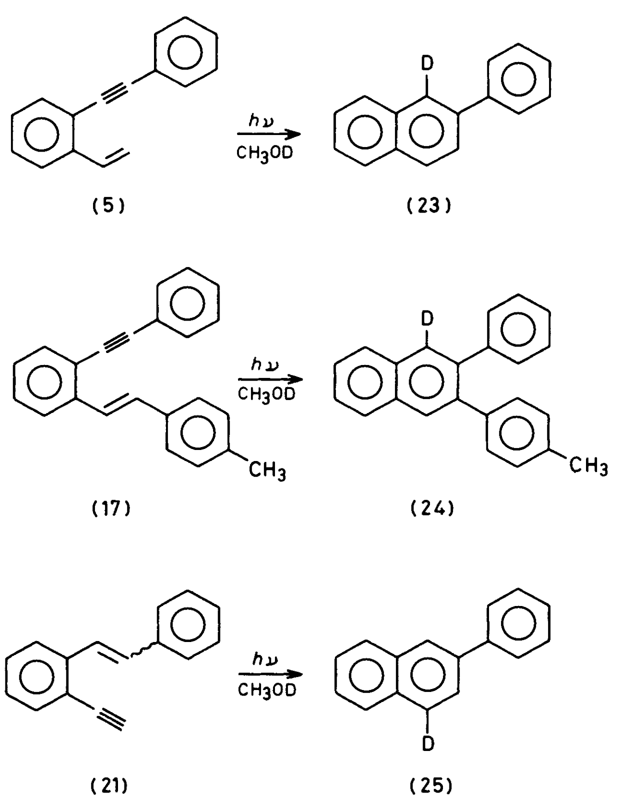
* Compound (17), irradiated in 'oxygen-free' hexane, gave only a very small amount of the phenanthrene derivative, but (21) under quite similar conditions (not in methanol!) gave 1-ethynylphenanthrene as the main product. Similar dehydrogenations under strictly anaerobic conditions have been observed previously in the photodehydrocyclization of 4,5-diphenylimidazole [2a] and of α-phenyl-2-vinylstilbene.[2b]


Cl
R
(1) R = H
(2) R = 2′-Cl
R
Cl
(3) R = 4′-Cl
(4) R = 4′-OCH$_3$
hν
KOBu^t
R
(5) R = H
(6) R = 2′-Cl
(7) R = 4′-Cl
(8) R = 4′-OCH$_3$
hν
R
(9) R = H
(10) R = 2′-Cl
(11) R = 4′-Cl
(12) R = 4′-OCH$_3$
Cl
CH$_3$
(13)
hν
KOBu^t
CH$_3$
(14)
hν
CH$_3$
(15)
Cl
CH$_3$
(16)
hν
KOBu^t
CH$_3$
(17)
hν
CH$_3$
(18)
Cl
(19)
KOBu^t
hν
KOBu^t
Cl
(20)
(21)
hν
(9)
+
(22)

Scheme 1



SCHEME 2

aromatic stabilization of the parent compound should be largely retained, which is not the case in the corresponding intermediate (35) formed from (31).

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded on a Varian T60 or a Bruker WH90 spectrometer in $CDCl_3$ solution and with tetramethylsilane (δ 0) as an internal standard. U.v. spectra were measured with a Cary 15 or a Perkin 555 spectrometer in methanol solution. Mass spectra were obtained using a Varian SM2B or a Finnigan 2000 spectrometer. Elemental analyses of the compounds synthesized were in agreement with theoretical values. Irradiations were performed in a Rayonet RPR 100 or 200 photoreactor under anaerobic conditions. To that aim a stream of argon, previously purified and dried through a BTS catalyst, phosphorus pentaoxide, silica, and potassium hydroxide, was led through the solutions. Reaction mixtures were separated by column chromatography over alumina (Baker) or silica (Merck 0.063—0.200). In general hexane was used as the eluent, but sometimes the polarity of the eluent was increased by the addition of increasing amounts of chloroform.

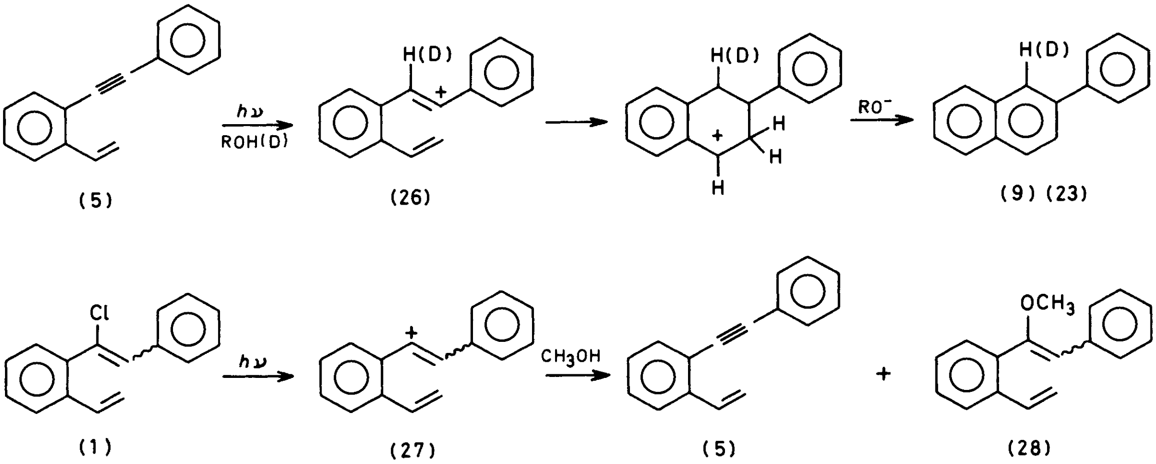
The syntheses of α-chloro-2-vinylstilbene (1) and 2-(α-chlorovinyl)- and 2-(β-chlorovinyl)-stilbenes (19) and (20) have been described previously.[1] The other α-chloro-2-vinylstilbenes were prepared in a similar way.

α,2′-Dichloro-2-vinylstilbene (2).—*cis* (oil); δ 5.23 (1 H, dd) and 5.61 (1 H, dd, methylene protons), 6.92 (1 H, dd, –CH=), and 6.58—7.58 (9 H, m, H_β and aromatic protons); $\lambda_{max.}$ (log ε) 247 nm (4.14); $\lambda_{min.}$ (log ε) 230 nm (4.06); *m/e* (%) 276(28), 274(32), 241(46), 239(100), and 204(62); *trans* (oil); δ 5.34 (1 H, dd) and 5.76 (1 H, dd, methylene protons), 7.12; (1 H, dd, –CH=), 6.84 (1 H, s, H_β), and 7.22—8.0 (8 H, m, aromatic protons); $\lambda_{max.}$ (log ε) 269(4.09, sh), 265(4.13, sh), 261(4.16, sh), and 247(4.28); $\lambda_{min.}$ (log ε) 230 nm (4.17); *m/e* (%) 276(33), 274(58), 241(33), 239(100), and 204(75).

β,4′-Dichloro-2-vinylstilbene (3).—*cis* (oil); δ 5.28 (1 H, dd) and 5.64 (1 H, dd, methylene protons), 6.86 (1 H, dd, –CH=), 7.13 (1 H, s, Hα), and 7.00—7.66 (8 H, m, aromatic protons); $\lambda_{max.}$ (log ε) 250 nm (4.12); *trans* (oil); δ 5.28 (1 H, dd) and 5.65 (1 H, dd, methylene protons), 6.90 (1 H, dd, –CH=), 7.06 (s, 1 H, H_α), and 6.78—7.55 (8 H, m, aromatic protons); $\lambda_{max.}$ (log ε) 278(4.10) and 251 nm (4.24).

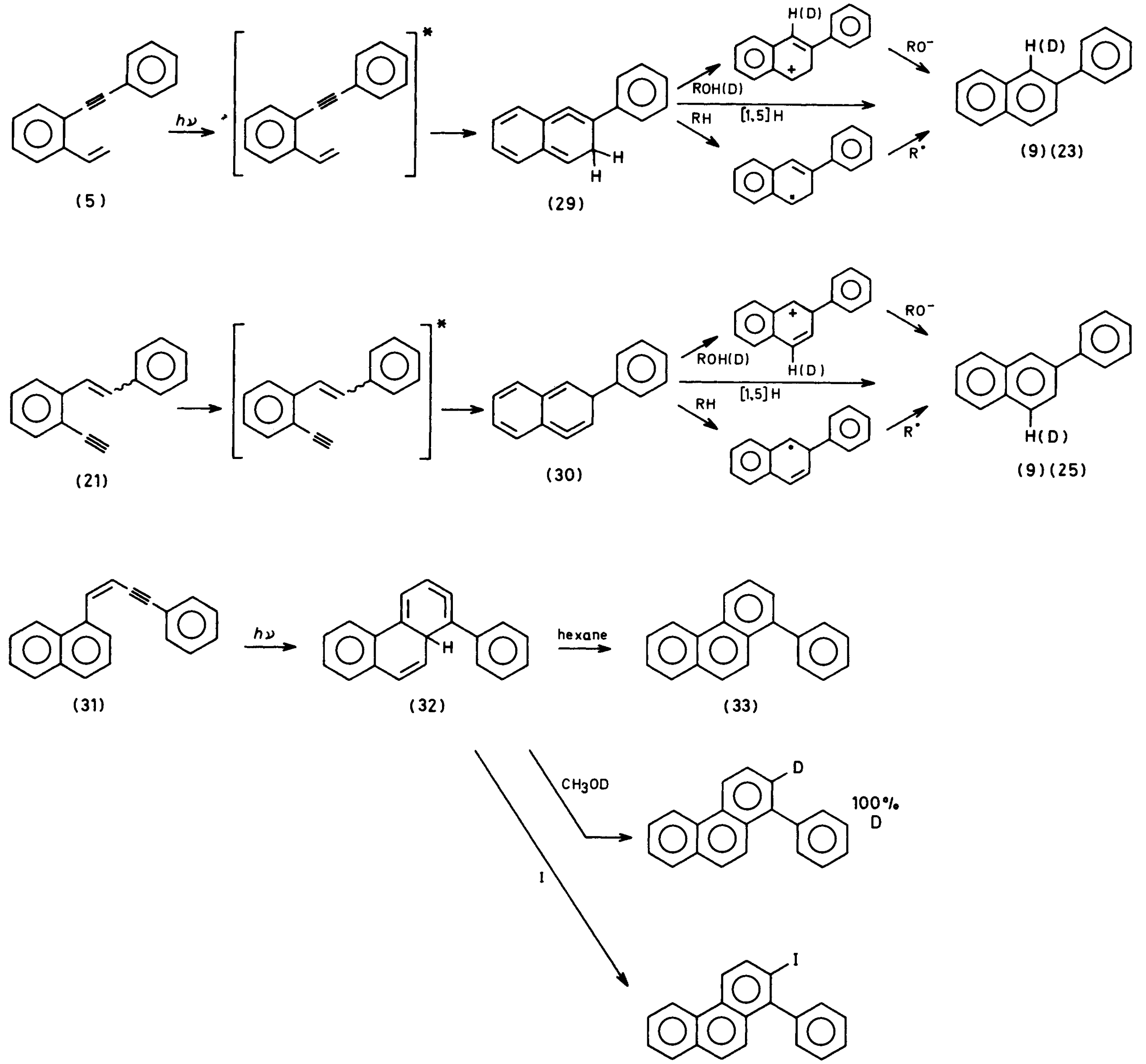
β-Chloro-4′-methoxy-2-vinylstilbene (4).—*trans* (oil); δ 3.77 (3 H, s, OCH_3), 5.26 (1 H, dd) and 5.62 (1 H, dd, methylene protons), and 6.51—7.66 (10 H, m, all other protons). The *cis*-isomer was not obtained in pure form.

α-Chloro-2-propenylstilbene (13).—Oil, mixture of isomers; δ 1.55—1.84 (3 H, 4 s, CH_3) and 5.57—7.80 (12 H, m, all other protons); *m/e* (%) 256(9), 254(17), 239(15), 219(64), 204(100), 203(69), and 202(62).



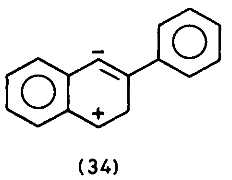
SCHEME 3

α-Chloro-2-(4-methylstyryl)stilbene (16).—Oil, mixture of isomers; δ 2.24—2.32 (3 H, 4 s, CH_3) and 6.5—7.8 (16 H, m); $\lambda_{max.}$ 300 and 255 nm; *m/e* (%) 332(3), 330(9), 295(50), 206(36), 205(37), 204(61), 203(41), 193(37), 192(94), 191(100), and 189(57).

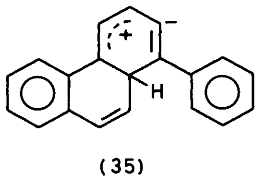


Scheme 4

Preparation of Vinyldiphenylacetylenes (5)—(8), (14), *and* (17), *and of 2-Ethynylstilbene* (21).—An appropriate chloro-2-vinylstilbene (1—1.5 g, see Scheme 1) was dissolved in toluene (50 ml) and potassium t-butoxide (1—1.5 equivalents) was added. The mixture was refluxed for 16 h, then cooled and carefully neutralized with 1N-HCl solution. The water layer was extracted several times with toluene and the collected toluene layers were dried over $MgSO_4$. After evaporation of the solvent the residue was separated by column chromatography over silica. Yields were 90—100%.



(34)



(35)

2-Vinyldiphenylacetylene (5). Oil; δ 5.37 (1 H, dd, *J* 1.2 and 10.5 Hz) and 5.84 (1 H, dd, *J* 1.2 and 17 Hz, methylene protons), and 7.14—7.67 (10 H, m, all other protons); $\lambda_{max.}$ (log ε) 308(4.11), 296(4.16, sh), 290(4.24), 282(4.17, sh), 275(4.13, sh), 244(4.28, sh), and 239 nm (4.29); *m/e* (%) 204(100), 203(82), and 202(65).

2'-Chloro-2-vinyldiphenylacetylene (6). Oil; δ 5.28 (1 H, dd, *J* 1.2 and 11 Hz) and 5.27 (1 H, dd, *J* 1.2 and 17.5 Hz, methylene protons), and 6.97—7.52 (9 H, m, all other protons); $\lambda_{max.}$ (log ε) 307(4.36), 295(4.36), 287(4.46), 279(4.39, sh), 272(4.34), 249(4.51), and 232 nm (4.49); *m/e* (%) 240(40), 238(88), 203(75), and 202(100) (Found: M^+, 238.170. Calc. for $C_{16}H_{11}Cl$: *m/e*, 238.172).

4′-Chloro-2-vinyldiphenylacetylene (7). Oil; δ 5.36 (1 H, dd, *J* 1.2 and 11 Hz) and 5.74 (1 H, dd, *J* 1.2 and 17.5 Hz, methylene protons), 6.98 (1 H, dd, *J* 11 and 17.5 Hz, –CH=), and 7.00—7.68 (8 H, m, aromatic protons); $\lambda_{max.}$ (log ε) 310(4.22), 300(4.26, sh), 292.5(4.28), 277(4.24), 257(4.39), 248(4.37, sh), and 246 nm (7.36); *m/e* (%) 240(36), 238(86), 203(71), and 202(100) (Found: M^+, 238.170. Calc. for $C_{16}H_{11}Cl$: *m/e* 238.172).

4′-Methoxy-2-vinyldiphenylacetylene (8). Oil; δ3. 93 (3 H, s, OCH_3), 5.35 (1 H, dd, *J* 1.2 and 10.5 Hz) and 5.76 (1 H, dd, *J* 1.2 and 17 Hz, methylene protons), and 6.60—7.56 (9 H, m, all other protons); $\lambda_{max.}$ (log ε) 299(4.47), 293(4.45, sh), 255(4.53), and 246 nm (4.48, sh).

trans-*2-Propenyldiphenylacetylene* (14). Oil; δ 1.92 (3 H, dd, *J* 1.2 and 7.0 Hz, CH_3), 6.31 (1 H, qd, *J* 7.0 and 15.6 Hz, =C*H*–CH_3), 6.97 (1 H, qd, *J* 1.5 and 15.6 Hz, C*H*=CH), and 7.11—7.62 (9 H, m, aromatic protons); $\lambda_{max.}$ (log ε) 309(3.94, sh), 299(4.23, sh), 292(4.32), 284(4.30), 277(4.25, sh), 258(4.40, sh), 254(4.42), and 246 nm (4.38); *m/e* (%) 218(71), 217(53), 203(38), 204(47), and 192(100) (Found: M^+, 218.111. Calc. for $C_{17}H_{14}$: *m/e*, 218.110. The *cis*-isomer was not isolated in pure form.

2-(4-Methylstyryl)diphenylacetylene (17). *cis*, oil; δ 2.29 (s, 3 H, CH_3), 6.65 (1 H, d, *J* 12.3 Hz, $=CH_\beta$), 6.86 (1 H, d, $=CH_\alpha$), and 7.02—7.67 (13 H, m, aromatic protons); $\lambda_{max.}$ (log ε) 298(4.25, sh), 279(4.35), and 274 nm (4.35); *trans*, m.p. 96—97 °C; δ 2.35 (3 H, s, CH_3), and 7.06—7.76 (15 H, m, all other protons); $\lambda_{max.}$ (log ε) 317(4.35), 280(4.57), and 276(4.56, sh); $\lambda_{min.}$ (log ε) 296(4.26) and 244 nm (4.10); *m/e* (%) 295(23), 294(100), 293(27), 279(59), and 278 (23) (Found: M^+, 294.141. Calc. for $C_{23}H_{18}$: *m/e*, 294.141).

2-Ethynylstilbene (21). *cis*, oil; δ 3.30 (1 H, s, ≡CH), 6.69 and 6.83 (2 H, AB, *J* 12 Hz, CH=CH), and 7.00—7.99 (9 H, m, aromatic protons); $\lambda_{max.}$ (log ε) 286(3.64), 253(4.09 sh), and 242 nm (4.18); *trans*, oil; δ 3.39 (1 H, s, ≡CH) and 7.08—8.00 (11 H, m, all other protons); $\lambda_{max.}$ (log ε) 289(4.26), 255(4.12), and 244 nm (4.15).

Irradiation Products.—2-Phenylnaphthalene (9) was formed from (5) by irradiation in hexane or methanol for 1 h in 80% yield (20% polymeric products) after separation by column chromatography, m.p. 102—103 °C (lit.,[6,7] 101—102, 104 °C).

2-(2-Chlorophenyl)naphthalene (10) was formed from (6) by irradiation in methanol (yield 100%) or in hexane for 40 min (yield 91%), m.p. 63—64 °C; δ 7.17—7.62 (8 H, m) and 7.77—7.93 (3 H, m) (aromatic protons); $\lambda_{max.}$ (log ε) 304(3.29, sh), 274(3.81, sh), 266(3.83, sh), and 240 nm (4.37).

2-(4-Chlorophenyl)naphthalene (11) was formed from (7) by irradiation in hexane (yield 80%), m.p. 137—139 °C (lit.,[8] 136.5—138 °C); δ 7.06—8.02 (m, aromatic protons); $\lambda_{max.}$ (log ε) 296(4.05), 286(4.12), and 252 nm (4.64).

2-(4-Methoxyphenyl)naphthalene (12) was formed from (8) by irradiation in hexane (yield 70%), m.p. 136—137 °C (lit.,[6,7] 136—137, 132 °C); δ 3.87 (3 H, s, OCH_3) and 6.77—8.01 (11 H, m, aromatic protons).

2-Methyl-3-phenylnaphthalene (15) was formed from (14) by irradiation in hexane (yield 60%), m.p. 60—63 °C; δ 2.40 (3 H, s, CH_3) and 7.00—7.91 (11 H, m, aromatic protons); $\lambda_{max.}$ (log ε) 299(3.42, sh), 289(3.57, sh), 281(3.74), 272(3.73 sh), 266(3.72, sh), 238(4.32), and 228 nm (4.39).

2-Phenyl-3-(*p*-tolyl)naphthalene (18) was formed from (17) by irradiation in hexane for 16 h or in methanol (yield 75%), m.p. 70.5—71 °C; δ 2.33 (3 H, s, CH_3), 7.07 (4 H, s, aromatic *p*-tolyl protons), 7.24 (5 H, s, phenyl), 7.48 [2 H, m, H(6) and H(7)], 7.87 [2 H, s, H(1) and H(4)], and 7.87 [2 H, m, H(5) and H(8)]; $\lambda_{max.}$ (log ε) 290(4.14, sh), 278(4.34, sh), 254(4.83), and 243 nm (4.75); *m/e* (%) 295(43), 294(100), 293(20), 279(33), 278(33), 212(36), 192(46), and 191(35) (Found: M^+, 294.143. Calc. for $C_{23}H_{18}$: *m/e* 294.141).

1-Ethynylphenanthrene (22) was formed from (21) by irradiation in hexane in the presence of iodine. The yield was 50% after separation from (9) (20%) and polymeric products (30%); δ 3.49 (1 H, s, ≡CH), 7.06—7.93 (6 H, m, aromatic protons), 8.33 [1 H, d, *J* 9.0 Hz, H(10)], and 8.62 [2 H, m, H(4) and H(5)]; $\lambda_{max.}$ (log ε) 302(4.20), 2.58(4.57), and 242 nm (4.37).

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