# Photocyclisations of 1,4-Diarylbut-1-en-3-ynes. Part III.[1] Scope and Limitations of the Reaction

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The photoreactivity of a large series of diarylbutenynes has been studied in order to establish the scope of this photocyclisation reaction. The conditions for an optimal yield of photocyclisation products are discussed. On addition of iodine to the butenyne solution, irradiation gives rise to iodo-derivatives of the normal cyclisation products, whereas in the presence of iodine and with benzene as the solvent the corresponding phenyl substitution products are found. The cyclisations are regiospecific and ring closure always takes place between C-4 and an *ortho*-position of the aryl group at C-1. Only low yields are obtained when the aryl residue at C-1 is a phenyl group because of its low reactivity in radical additions. Overcrowding of aromatic groups in the product formed in this type of photocyclisation has no great effect on its yield. Factors that sometimes interfere with the cyclisation are easy intersystem crossing due to substituents with heteroatoms and the occurrence of side reactions such as dimerisation. In other cases the yields are mostly better than 50%.

In Part II [1] the results of a mechanistic study of photocyclisation of diarylbutenynes were presented. It appeared that the formation of 1-phenylphenanthrene (4) by irradiation of 1-($\alpha$-naphthyl)-4-phenylbut-1-en-3-yne (1) in an aprotic solvent (hexane or benzene) occurred *via* radical intermediates. The singlet-excited parent compound, in which the acetylene bond has a non-linear *trans*-configuration (1)*, picks up a hydrogen atom at C-3, and the resulting radical (2) undergoes ring-closure by intramolecular homolytic addition to the naphthyl residue. Hydrogen abstraction from (3) then leads to the stable, aromatic end-product (Scheme 1).

For optimal results in synthetic application of this type of photocyclisation, several experimental conditions can be varied in order to increase the reaction rate, to improve the yield, or to minimize the formation of side-products. Consequently, in this report on the scope and limitations of the reaction, the formation or otherwise of cyclisation products from a large variety of diarylbutenynes has not always been studied under completely equivalent conditions. The rationale for the choice of the conditions for individual compounds originates from the following considerations.

In general the use of fluorescent tube lamps (300 or 360 nm, depending on the wavelengths of absorption) suffices to obtain good results. A high pressure light source (HPK 125) may be used to accelerate slow conversions.

To restrict photodimerisation [2,3] of the butenynes the irradiations are performed at rather low concentrations. In most experiments $5 \times 10^{-4}$—$5 \times 10^{-3}$M solutions were used.

In the presence of oxygen, product formation is always slightly faster than under nitrogen but at the same time the amount of oxygen-containing side-products increases. Therefore, irradiation under nitrogen is generally preferable.

Photocyclisations in hexane are about twice as fast as those in benzene because the former solvent is a better hydrogen donor. Still higher rates are observed in methanol but in this protic solvent the cyclisation product arises *via* ionic intermediates as a consequence of photoprotonation of the starting compound at C-3.[1]

Increased reaction rates are also observed on addition of iodine to the irradiation mixture. The effect is twofold; iodine functions as an oxidant, thus promoting hydrogen abstraction from the intermediate (3), and it provides an alternative source for the formation of radicals from (1)*. These will then have an iodine atom at C-3 as in (5) and (6) (Scheme 1). As a consequence of the latter effect, irradiation in the presence of iodine will always lead to a mixture of cyclisation products among which at least the normal and a corresponding, iodinated product [(4) and (4a), respectively], are present; (4a) can be the main product when large amounts of iodine (100 mol %) are used. The formation of an iodinated end-product can largely be suppressed by irradiation at short wavelengths (high pressure lamp). As a consequence of the photolability of iodoaromatic compounds, reductive deiodination [4] *via* radical (7) occurs when (4a) is irradiated at short wavelengths in

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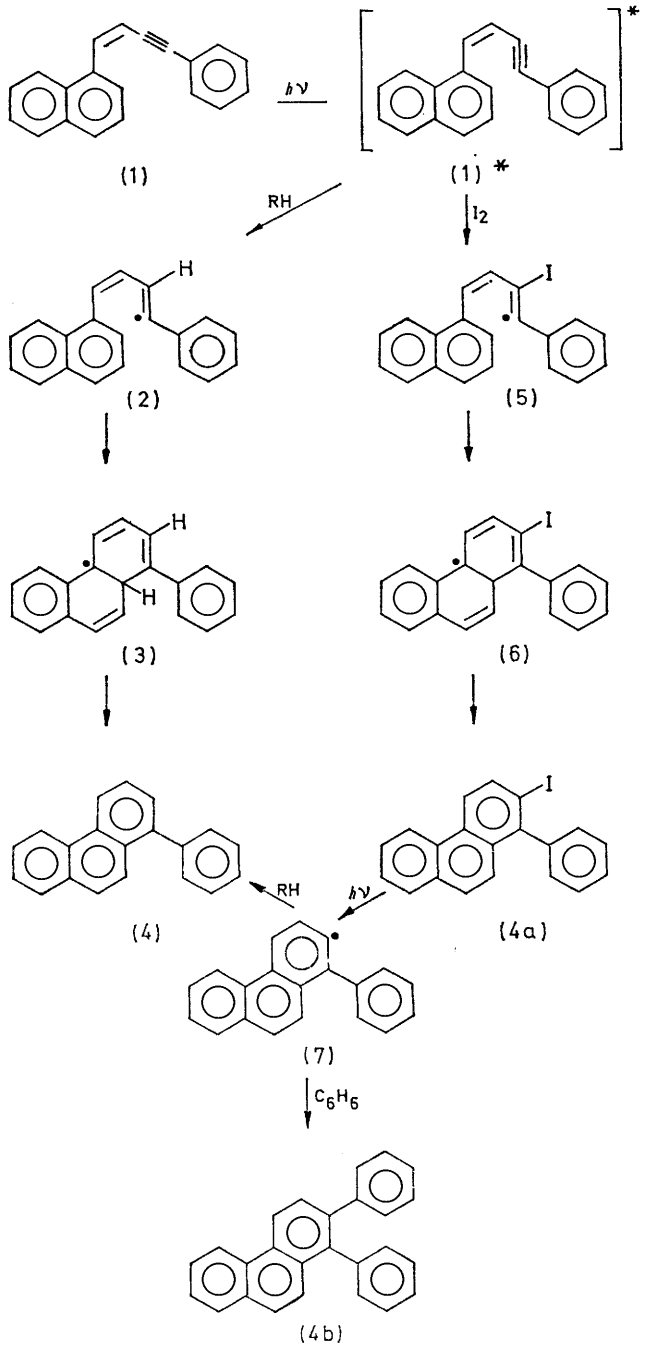
[1] Part II, A. H. A. Tinnemans and W. H. Laarhoven, preceding paper.

[2] M. Herberhod and G. S. Hammond, *Ber. Bunsengesellschaft, Phys. Chem.*, 1968, **72**, 309.

[3] G. T. Kwiatkowski and D. B. Selley, *Tetrahedron Letters*, 1968, 3471.

[4] R. K. Sharma and N. Kharasch, *Angew. Chem.*, 1968, **80**, 69.

hexane or in methanol; in benzene as solvent (7) is almost completely converted [5,6] into the phenyl-substituted end-product (4b). Care has to be taken in using iodine when products are formed which are themselves able to undergo photodehydrocyclisation, because this photoreaction is always strongly catalysed by an oxidant like iodine (see *e.g.* photocyclisation of 4,5-diphenyltriphenylene [7]).

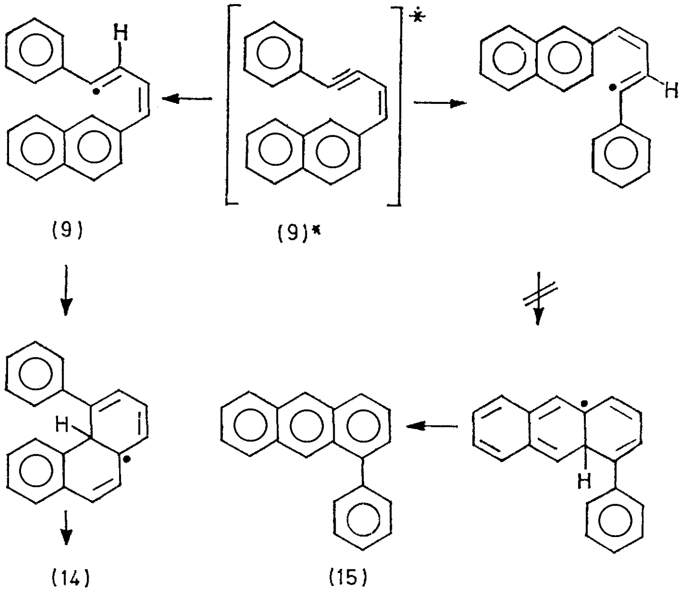


Scheme 1

Taking into account the influence of experimental conditions on the occurrence of photocyclisation of butenynes, their behaviour on irradiation has been investigated in relation to the structure of the starting compound.

As most of the products have not been described before their structures had to be elucidated. This was done by u.v., n.m.r., and mass spectroscopy. In particular the sterically hindered molecules show interesting spectroscopic properties. They are given in Table 4—8. The similarities between the spectral data within each series (phenanthrenes, benzo[*c*]phenanthrenes, and triphenylenes) furnish convincing proof of the proposed structures. Differences in the n.m.r. spectra between sterically hindered and related planar molecules were always consistent with the expected ring current effects in the overcrowded compounds.

*Influence of the* 1-*Aryl Group*.—Results with several 4-phenylbutenynes containing various 1-aryl residues are given in Table 1. It is apparent that the compounds (1), (9), and (10) give very similar results. On irradiation of these compounds at 360 nm for 4—6 h in the presence of an equimolar amount of iodine the iodinated derivatives could be obtained as the main products in 50, 44, and 32% yield, respectively. The butenyne containing the large 2-benzo[*c*]phenanthryl residue (11) gave a mixture of cyclic dimers under all circumstances, even at very low concentrations, as indicated by n.m.r. and mass spectroscopic data. This may be due to excimer formation.



Scheme 2

The fact that the cyclisation of the β-naphthyl derivative (9) is completely regiospecific deserves attention. Of two possible products, (14) and (15), only the former was found (Scheme 2). This may be ascribed to the

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[5] W. Wolf and N. Kharasch, *J. Org. Chem.*, 1965, **30**, 2493.

[6] S. M. Kupchan and H. C. Wormser, *J. Org. Chem.*, 1965, **30**, 3792; *Tetrahedron Letters*, 1965, 359.

[7] A. H. A. Tinnemans and W. H. Laarhoven, *J. Amer. Chem. Soc.*, 1974, **96**, 4617.

higher reactivity of the α- than the β-position of naphthalene in homolytic addition.

A similar argument can be used to explain the very low susceptibility to cyclisation of 1,4-diphenylbutenyne (8) which yields only a mixture of *cis–trans* isomers on irradiation; even under the most forcing conditions, less than 2% of a cyclisation product was obtained. In homolytic arylation of aromatic compounds the reaction rates of toluene and naphthalene relative to benzene are 1.7 and 24, respectively.[8] In agreement with this explanation the photoreactivity of 1,4-diphenylbutenyne was appreciably increased by the introduction of methyl substituents at the *meta*-positions of the 1-phenyl residue [see (12)] whereas a *para*-methoxy-substituent as in (13) had no noticeable influence. In homolytic arylation the reactivity of mesitylene[8] relative to benzene is 11.6.

TABLE 1

Photoreactivity of diarylbutenynes ArCH=CH–C≡CPh

| Compound | Ar | Cyclisation product | Yield (%) | Method [a] |
|---|---|---|---|---|
| (8) | Phenyl | 1-Phenylnaphthalene (35) | 2 | III |
| (1) | α-Naphthyl | 1-Phenylphenanthrene (4) | 55 | I |
| (9) | β-Naphthyl | 4-Phenylphenanthrene (14) | 55 | I |
| (10) | 3-Phenanthryl | 1-Phenylbenzo[*c*]phenanthrene (36) | 60 | II |
| (11) | 2-Benzo[*c*]phenanthryl | *b* | | |
| (12) | 3,5-Dimethylphenyl | 1,3-Dimethyl-8-phenylnaphthalene (37) | 44 | III |
| (13) | 4-Methoxyphenyl | *c* | | III |

[a] I, Fluorescence lamp; λ 300 or 360 nm, depending on the absorption of the compound under study. II, Same lamp and 5 mol % iodine added to the solution. III, High pressure Hg lamp, 100 mol % iodine added, quartz vessel. [b] Only dimers formed. [c] Only *cis-trans* isomerisation occurred.

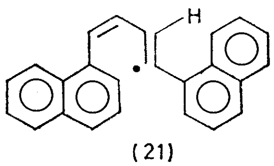
TABLE 2

Photoreactivity of diarylbutenynes ArCH=CH–C≡CR

| Compound | Ar | R | Cyclization product | Yield (%) | Method [a] |
|---|---|---|---|---|---|
| (16) | Phenyl | α-Naphthyl | *b* | | III |
| (17) | α-Naphthyl | α-Naphthyl | 1-(α-Naphthyl)phenanthrene (38) | 22 | III |
| (18) | β-Naphthyl | α-Naphthyl | 4-(α-Naphthyl)phenanthrene (39) | 58 | I |
| (19) | β-Naphthyl | H | Phenanthrene [c] | Trace | III |
| (20) | β-Naphthyl | $CH_3$ | 4-Methylphenanthrene [c] | Trace | III |

[a] See Table 1. [b] Only *cis–trans* isomerisation occurred. [c] Mainly cyclic dimers formed.

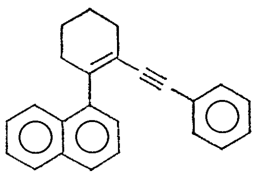
*Influence of the Group at* C-4.—Replacement of the 4-phenyl group in compounds (8), (1), and (9) (Table 1) by an α-naphthyl residue gave qualitatively similar results. 4-(α-Naphthyl)-1-phenylbutenyne (16) did not cyclize on irradiation; the α- and β-naphthyl derivatives (17) and (18) gave the expected cyclisation products (Table 2). Even under forcing conditions the yield of the photocyclisation product from (17) was much lower than that from (1). A large amount of the starting compound was restored on irradiation. One explanation might be that in the intermediate radical (21), the planarity of the α-naphthylvinyl system containing the unpaired electron is highly distorted by steric interaction between the hydrogen atoms at C-3 and the *peri*-position. This may lead to increased delocalisation of the unpaired electron over the naphthyl residue and reduced reactivity of the radical in the subsequent addition step. With (18) such an effect was not observed, which might be due to the higher sensitivity of the β-naphthyl residue for radical additions in comparison with the α-naphthyl system. In the presence of iodine, (18) gave 38% 3-iodo-4-(α-naphthyl)phenanthrene.



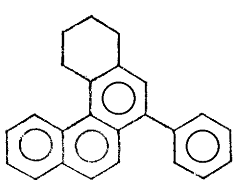
(21)

Replacement of the 4-aryl system in diarylbutenynes by hydrogen or a methyl group as in (19) and (20), results in the formation of cyclodimers as the main products on irradiation. Even at low concentrations ($10^{-5}$M) only traces of monomeric photocyclisation products were found.

*Influence of Substituents and Steric Factors.*—As explained above, the introduction of methyl substituents in the 1-aryl system, at an *ortho-* or *para*-position relative to the ring atom concerned in the cyclisation step can considerably accelerate the formation of a photocyclisation product. Introduction of methyl substituents in the 4-aryl group as in (22) and (23), and of various substituents ($CH_3$, $CH_2OH$, $OCH_3$) at *meta*-positions of the 1-aryl system as in (24), (25), and (13) had, however, no influence. The same is true when a tetramethylene bridge is erected over the olefinic bond of (1) as in (33), which gives the expected cyclisation product 1,2,3,4-tetrahydro-6-phenylbenzo[*c*]phenanthrene (34) in 45% yield on irradiation in hexane at 300 nm. From (22)—



(33)



(34)

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[8] G. H. Williams, 'Homolytic Aromatic Substitution,' Pergamon, Oxford, 1960, ch. 4.

TABLE 3

Photoreactivity of substituted diarylbutenynes ArCH=CH−C≡CR

| Compd. | Ar | R | Cyclization product | Yield (%) | Method [a] |
|---|---|---|---|---|---|
| (22) | β-Naphthyl | 3,5-Dimethylphenyl | 4-(3,5-Dimethylphenyl)phenanthrene (40) | 65 | I |
| (23) | 3-Phenanthryl | 3,5-Dimethylphenyl | 1-(3,5-Dimethylphenyl)benzo[*c*]phenanthrene (41) | 45 | II |
| (24) | 4-Methyl-α-naphthyl | Phenyl | 1-Phenyl-9-methylphenanthrene (42) | 54 | I |
| (25) | 4-Hydroxymethyl-α-naphthyl | 3,5-Dimethylphenyl | 1-(3,5-Dimethylphenyl)-9-hydroxymethylphenanthrene (43) | 62 | I |
| (26) | 4-Methoxycarbonyl-α-naphthyl | 3,5-Dimethylphenyl | *b* | | I |
| (27) | 2-Methyl-α-naphthyl | Phenyl | 1-Phenylphenanthrene [c] (4) | 50 | I |
| (28) | 1-Bromo-β-naphthyl | Phenyl | 4-Phenylphenanthrene [d] (14) | 10 | III |
| (29) | 8-Phenyl-β-naphthyl | Phenyl | 4,5-Diphenylphenanthrene (44) | 65 | I |
| (30) | 1-Phenyl-9-phenanthryl | Phenyl | 4,5-Diphenyltriphenylene (45) | 60 | I |
| (31) | 1-(3,5-Dimethylphenyl)-9-phenanthryl | 3,5-Dimethylphenyl | 4,5-Bis-(3,5-dimethylphenyl)triphenylene (46) | 65 | I |
| (32) | 5,7-Dimethyl-3-phenanthryl | 3,5-Dimethylphenyl | | <1 | II |

[a] See Table 1. [b] *cis–trans* Isomerisation occurred. [c] A trace of 2-benzylphenanthrene was formed. [d] Together with benzo[*e*]pyrene.

TABLE 4

M.p.s and u.v. spectra in methanol (α and *p* bands) of substituted phenanthrenes

| | | $\lambda_{max.}$/nm (log ε) | |
|---|---|---|---|
| Compound | M.p. (°C) | *p* Bands | α Bands |
| Phenanthrene [a] | | 273 (4.18), 281 (4.14), 292.5 (4.30) | 329 (2.52), 337 (2.40), 345 (2.46) |
| (4) | 74—76 [b] | [275 (4.27)], [284 (4.14)], 298 (4.16) | 333 (2.56), 341 (2.35), 350 (2.43) |
| (4a) * | 166—168 | [280 (4.52)], [289 (4.40)], [297.5 (4.16)] | 329 (2.47), 337 (2.54), 345 (2.50) |
| (4b) * | 150—151 | [298 (4.24)] | 330 (2.72), 343 (2.68), 350 (2.65) |
| (42) | 96—98 | [277 (4.32)], [290 (4.16)], 301.5 (4.16) | 336 (2.71), 341 (2.52), 352 (2.66) |
| (42a) * | 93—95 | [281.5 (4.53)], [290 (4.41)], 301.5 (4.15) | 323 (2.54), 339 (2.67), 348 (2.47), 356 (2.62) |
| (42b) * | 171—173 | [301 (4.20)] | 336 (2.74), 348 (2.67), 356 (2.66) |
| (43) | 158—160 | [280 (4.21)], 290 (4.10)], 300.5 (4.17) | 335 (2.74), 351 (2.70) |
| (38) | 116—118 [c] | 277 (4.48), 297.5 (4.37) | 333 (2.69), 350 (2.43) |
| (14) | 82—84 [d] | [275 (4.36)], [282 (4.27)], 296 (4.13) | 334 (2.62), 349 (2.58) |
| (14a) † | 160—162 | [280 (4.24)], 292.5 (4.20), 305 (4.26) | 337 (2.76, 345 (2.53), 354 (2.73) |
| (14b) † | 185—187 | 299 (4.17) | 336 (2.83), 352 (2.79) |
| (40) | 91—93 | [276 (4.28)], [282 (4.20)], 296 (4.12) | 333 (2.72), 349 (2.71) |
| (40a) † | 164—167 | [280 (4.23)], 292 (4.18), 305.5 (4.22) | 338 (2.78), 353.5 (2.82) |
| (40b) † | 240—241 | [290 (4.26)], 298 (4.21) | 336 (2.44), 352 (2.55) |
| (39) | 150—152 [e] | 276 (4.29), 285 (4.30), 297 (4.28) | 333 (2.84), 349 (2.76) |
| (39a) † | 137—140 | 280 (4.44), 292 (4.40), 304.5 (4.31) | 337 (2.87), 345 (2.56), 354 (2.80) |
| (39b) † | 146—149 | 288—294 (4.29), 299 (4.32) | 334 (2.99), 353 (2.85) |
| (44) | 169—171 | [310 (4.21)] | 355 (2.82), 372 (2.72) |
| (44a) † | 135—140 | [319 (4.19)] | 361 (2.88), 379 (2.81) |

* Extra 2-substituent. † Extra 3-substituent.

[a] Data from ref. 9. [b] 79—79.5 °C (A. L. J. Beckwith and M. J. Thompson, *J. Chem. Soc.*, 1961, 73). [c] 117.5—118 °C (W. E. Bachmann and N. C. Deno, *J. Amer. Chem. Soc.*, 1949, **71**, 3062). [d] 80.5—81.5 °C (A. D. Campbell, *J. Chem. Soc.*, 1954, 3659). [e] 108—110 °C (R. J. Hayward, A. C. Hopkinson, and C. C. Leznoff, *Tetrahedron*, 1972, **28**, 439).

TABLE 5

M.p.s and u.v. spectra in methanol (α and *p* bands) of some benzo[*c*]phenanthrenes and triphenylenes

| | | $\lambda_{max.}$/nm (log ε) | |
|---|---|---|---|
| Benzo[*c*]phenanthrene [a] | M.p. (°C) | *p* Bands | α Bands |
| Compound | | 296 (4.13), 303 (4.07), 315 (4.06) | 325 (3.67), 353 (2.63), 372 (2.38) |
| (36) | 109—113 | [307 (4.05)], [318 (3.93)] | [340 (3.68)] |
| (36a) * | 131—133 | [314 (4.19)], [326 (4.02)] | [337 (3.83)], 368 (2.66), 385 (2.39) |
| (36b) * | 232—234 | [325 (4.06)] | [340 (3.80)], 365 (2.80), 383 (2.41) |
| (41) | 143—145 | [307 (4.07)], 321 (3.94) | [333 (3.81)] |
| (41a) * | 200—203 | [314 (4.17)], [327 (3.99)] | [339 (3.75)], 369 (2.57) |
| (41b) * | 182—184 | [323 (4.06)] | [339 (3.98)] |
| (34) | 119—121 | [300 (4.12)], 307 (4.17) | 341 (2.94), 358 (2.79) |
| Triphenylene [a] | | 273 (4.40), 284 (4.26) | 321 (2.90), 327 (2.88), 333 (2.88) |
| (45) | 150—152 | 267 (4.76), 287 (4.60) | |
| (45a) † | 254—260 | [290 (4.60)], [310 (4.32)] 272 (4.74) | |
| (46) | 189—191 | 269 (4.74), 291.5 (4.54) | |

* Extra 2-substituent. † Extra 3-substituent.

[a] Data from ref. 9.

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[9] E. Clar, ' Polycyclic Hydrocarbons,' Academic Press, London, vol. 1, 1964.

(24) iodinated cyclisation products were also obtained by irradiation with an equivalent amount of iodine in 45, 36, and 48% yield, respectively.

It is remarkable that the presence of the methoxycarbonyl substituent in (26) apparently prohibits photocyclisation. In all experiments with this compound only *cis–trans* isomerisation and decomposition were observed leaving substantial amounts (20%) of unchanged starting compound. The resistance to photocyclisation of this compound might be due to very fast intersystem crossing, resulting in a preference for isomerisation *via* the triplet excited state.

TABLE 6

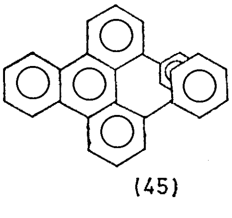
δ Values (p.p.m.) in $CS_2$ extrapolated to zero concentration for substituted phenanthrenes

| Compound | H-1 | H-2 | H-3 | H-4 | H-5 | H-6 | H-7 | H-8 | H-9 | H-10 | Others |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Phenanthrene [a] | 7.76 | 7.48 | 7.54 | 8.55 | 8.55 | 7.54 | 7.48 | 7.76 | 7.61 | 7.61 | |
| (4) | | | | 8.59 | 8.59 | | | | 7.57 | 7.75 | 7.40 (5 H, phenyl), 7.42—7.84 (5 H, m) |
| (4a) | | | 8.06 | 8.32 | 8.57 | 7.46 [b] | 7.64 [b] | 7.73 | 7.57 | 7.27 | 7.09—7.23 (2 H, m, phenyl), 7.34—7.64 (3 H, phenyl) |
| (4b) | | | 7.59 | 8.62 | 8.64 | 7.45 [b] | 7.60 [b] | 7.74 | 7.51 | 7.51 | 7.05 (5 H, s, phenyl), 7.07—7.28 (5 H, phenyl) |
| (42) | | | | 8.56 | 8.62 | 7.48 [b] | 7.62 [b] | 7.92 | | 7.58 | 2.59 (3 H, s, $CH_3$), 7.38 (5 H, m, phenyl), 7.26—7.62 (2 H, m) |
| (42a) | | | 7.98 | 8.25 | 8.56 | 7.57 | 7.54 | 7.88 | | 7.11 | 2.57 (3 H, s, $CH_3$), 7.05—7.23 (2 H, m, phenyl), 7.33—7.48 (3 H, m, phenyl) |
| (42b) | | | 7.55 | 8.60 | 8.65 | 7.48 [b] | 7.62 [b] | 7.92 | | 7.32 | 2.58 (3 H, s, $CH_3$), 7.04 (5 H, s, phenyl), 7.08—7.26 (5 H, m, phenyl) |
| (43) [c] | | | | 8.61 | 8.70 | | | 8.10 | | 7.83 | 1.76 (s, OH), 2.36 (6 H, s, $2CH_3$), 4.97 (2 H, s, $CH_2$), 7.07 (3 H, s, phenyl), 7.41—7.71 (4 H, m) |
| (14) | 7.73 | 7.48 | 7.32 | | 7.60 | 6.95 | 7.29 | 7.66 | 7.63 | 7.63 | 7.36 (5 H, s, phenyl) |
| (14a) | 7.48 | 8.07 | | | 7.34 | 6.92 | 7.26 | 7.66 | 7.62 | 7.62 | 7.10—7.27 (2 H, m, phenyl), 7.43—7.55 (3 H, m, phenyl) |
| (14b) | 7.79 | 7.45 | | | 7.28 | 6.85 | 7.24 | 7.65 | 7.62 | 7.62 | 6.88—7.21 (10 H, m, phenyl) |
| (40) | 7.71 | 7.46 | 7.30 | | 7.66 | 6.97 | 7.30 | 7.64 | 7.60 | 7.60 | 2.32 (6 H, s, $2CH_3$), 6.92 (3 H, s, phenyl |
| (40a) | 7.44 | 8.07 | | | 7.36 | 6.94 | 7.29 | 7.65 | 7.60 | 7.60 | 2.36 (6 H, s, $2CH_3$), 6.77 (2 H, s, *o*-phenyl), 7.05 (1 H, s, *p*-phenyl) |
| (40b) | 7.90 | 7.58 | | | 7.61 | | 7.39 | 7.80 | 7.74 | 7.74 | 2.23 (6 H, s, $2CH_3$), 6.73 (2 H, s, *o*-phenyl), 6.85 (1 H, s, *p*-phenyl), 6.92—7.18 (6 H, m) |
| (39) | | | | | | 6.71 | 7.09 | | | | 6.97—7.92 (15 H, m) |
| (39a) | 7.56 | 8.14 | | | | 6.69 | | | 7.65 | 7.65 | 6.99—7.67 (8 H, m), 7.77—8.00 (2 H, m) |
| (39b) | 7.93 | 7.46 | | | | 6.63 | 7.04 | | | | 6.83 (5 H, m, phenyl), 7.05—7.39 (6 H, m), 7.58—7.81 (5 H, m) |
| (44) | 7.64 | 7.40 | 6.98 | | | 6.98 | 7.40 | 7.64 | 7.56 | 7.56 | 6.43 (4 H, d, *o*-phenyl), 6.91 (4 H, t, *m*-phenyl), 6.94 (2 H, m, *p*-phenyl) |
| (44a) | 7.35 | 8.05 | | | | 6.98 | 7.36 | 7.58 | 7.54 | 7.52 | 5.96—7.16 (10 H, m) |

[a] Data from K. D. Bartle and J. A. S. Smith, *Spectrochim. Acta*, 1967, **23A**, 1689. [b] These δ values represent the extreme values of a complex multiplet for H-6 and -7. [c] Spectrum measured in $CDCl_3$.

As is apparent from the results with (27) and (28) a methyl or halogeno-substituent at the ring position involved in the photocyclisation is completely lost during irradiation. Compound (27) gave unsubstituted 1-phenylphenanthrene in the same yield as (1), and only a trace of a rearranged product, 2-benzylphenanthrene, could be detected in the reaction mixture. Compound (28) gave unsubstituted 4-phenylphenanthrene in the presence of iodine, accompanied by the secondarily formed photodehydrocyclisation product, benzo[*e*]pyrene, but no trace of bromo-substituted products.

An attractive aspect of the photocyclisation reaction is that large substituents (phenyl, 3,5-dimethylphenyl) in the 1-aryl group which cause strong steric interactions with the 4-aryl system in the starting compound, do not inhibit photocyclisation. Compounds (29)—(31) give highly overcrowded cyclisation products in good yield [*e.g.* (45) from (30)]. In view of these results it is remarkable that the presence of a methyl substituent at C-5 (and C-7) in (32) is apparently prohibitive for photocyclisation. From (29) and (30), irradiated in the presence of iodine, the corresponding iodinated cyclisation products were also obtained in 26 and 44% yield.



(45)

## EXPERIMENTAL

General experimental details are given in the preceding paper.[1] U.v. data in brackets refer to inflections. N.m.r. interpretations were done by decoupling or tickling, and by comparison with spectra of known compounds. The symbols d, t, *etc.* refer both to first and higher order signals.

All irradiations of 1,4-diarylbutenynes and the isolation of the products were carried out in the same way. The procedures used for the preparations of 1-phenylphenanthrene are given as examples. Physical data for the products obtained are given in Tables 4—8.*

1-*Phenylphenanthrene* (4).—A solution of 1-(α-naphthyl)-4-phenylbut-1-en-3-yne (1) (175 mg, 0.7 mmol) in methanol (1 l) was irradiated in a quartz vessel in the Rayonet reactor at 300 nm. The reaction was followed by t.l.c. and u.v. spectroscopy. At the end of the reaction, when starting material could no longer be detected (8—10 h), the solution was light yellow. The solvent was distilled off, and the residue was chromatographed over silica gel with hexane–benzene (4 : 1) as eluant to remove polymers and oxidation products. The eluate was purified by chromatography on $Al_2O_3$. Elution with benzene–hexane (1 : 9) gave 1-phenylphenanthrene (4) in 55% yield, m.p. (from methanol) 74—76°. The same result was obtained by irradiation in hexane or benzene. The reaction time was then 12—20 h.

TABLE 7

δ Values (p.p.m.) in $CS_2$ extrapolated to zero concentrations for substituted benzo[*c*]phenanthrenes [a]

| Compound | H-3 | H-4 | H-9 | H-10 | H-11 | H-12 | Others |
|---|---|---|---|---|---|---|---|
| Benzo[*c*]phenanthrene [b] | 7.48 | 7.86 | 7.86 | 7.48 | 7.54 | 8.97 | |
| (36) | | | 7.55 | 7.08 | 6.79 | 7.72 | 7.54—7.99 (8 H, m), 6.73—6.99 (5 H, m) |
| (36a) | 8.15 | 7.53 | 7.48 | 7.08 | 6.93 | 7.83 | 8.12 (1 H, d, *o*-phenyl), 7.68 (2 H, s), 7.62 (2 H, s), 7.20 (1 H, t, *m*-phenyl), 6.76 (1 H, t, *p*-phenyl), 6.38 (1 H, t, *m*-phenyl), 5.75 (1 H, d, *o*-phenyl) |
| (36b) | 7.55 | 7.90 | 7.48 | 7.02 | 6.77 | 7.84 | 7.65 (2 H, s), 7.68 and 7.76 (2 H, AB), 6.57 (5 H), 6.86—7.15 (5 H, m, phenyl) |
| (41) | | | 7.56 | 7.07 | 6.78 | 7.77 | 1.93 (6 H, s, $2CH_3$), 7.53—7.86 (7 H, m), 6.43 (1 H, s, *p*-phenyl), 6.52 (2 H, m, *o*-phenyl) |
| (41a) | 8.14 | 7.48 | 7.48 | 7.09 | 6.93 | 7.84 | 1.56 (3 H, s, $CH_3$), 2.34 (3 H, s, $CH_3$), 5.30 (1 H, s, *o*-phenyl), 6.37 (1 H, s, *p*-phenyl), 7.59 (2 H, s), 7.66 (2 H, s), 7.69 (1 H, s, *o*-phenyl) |
| (41b) | 7.54 | 7.86 | 7.48 | | 6.75 | 7.75 | 1.71 (6 H, s, $2CH_3$), 6.21 (s, *p*-phenyl), 6.87—7.18 (6 H, m), 7.64 (2 H, s), 7.66 and 7.74 (2 H, AB) |
| (34) | | | | 7.72 | | 8.61 | 1.65—2.15 (4 H, m), 3.09 (2 H, t), 3.52 (2 H, t), 7.16 (s, H-5), 7.34br (5 H, s, phenyl), 7.37—7.53 (3 H, m), 7.65 and 7.55 (1 H, part AB) |

[a] δ Values for the phenyl groups are temperature dependent; the values given are at room temperature. [b] Data from K. D. Bartle and D. W. Jones, *J. Chem. Soc.* (*A*), 1969, 437.

TABLE 8

δ Values (p.p.m.) in $CS_2$ extrapolated to zero concentration for substituted triphenylenes [a]

| Compound | H-1 | H-2 | H-3 | H-6 | H-7 | H-8 | H-9 | H-12 | Others |
|---|---|---|---|---|---|---|---|---|---|
| Triphenylene [a] | 8.51 | 7.55 | 7.55 | 7.55 | 7.55 | 8.51 | 8.51 | 8.51 | |
| (45) | 8.33 | 7.46 | 6.95 | 6.95 | 7.46 | 8.33 | 8.44 | 8.44 | 6.40 (4 H, d, *o*-phenyl), 6.85 (4 H, t, *m*-phenyl), 6.91 (2 H, m, *p*-phenyl), 7.51 (q, H-10, -11) |
| (45a) | 8.03 | 8.09 | | 6.97 | 7.39 | 8.26 | | | 7.44—7.65 (m, H-10, -11), 6.0—7.2 (10 H, phenyl), 8.27—8.50 (m, H-9, -12) |
| (46) | 8.32 | 7.41 | 6.97 | 6.97 | 7.41 | 8.32 | 8.41 | 8.41 | 2.04 (12 H, s, $4CH_3$), 6.07 (4 H, s, *o*-phenyl), 7.50 (q, H-10, -11), 6.61 (2 H, s, *p*-phenyl) |

[a] δ Values for the phenyl groups are temperature dependent; the values given are at room temperature. [b] Data from N. Jonathan, S. Gordon, and B. P. Dailey, *J. Chem. Phys.*, 1962, **36**, 2443.

2-*Iodo*-1-*phenylphenanthrene* (4a) *and* 1,2-*Diphenylphenthrene* (4b).—The solvent was evaporated from the mixture obtained on irradiation of a solution of (1) (0.7 mmol, 175 mg) and iodine (0.7 mmol, 175 mg) in benzene (1 l) for *ca.* 6 h at 360 nm. The residue was chromatographed on silica and eluted with benzene–hexane (1 : 3) to remove polar side-products. The remaining mixture was separated by column chromatography on $Al_2O_3$. Elution with benzene–hexane (1 : 9) gave (4) as a first fraction in *ca.* 10% yield. Elution with benzene–hexane (1 : 6) gave 2-iodo-1-phenylphenanthrene (4a) as a second fraction in 50% yield. This was sublimed at 150° and 1 mmHg and crystallized from methanol to obtain an analytically pure sample. The third product, 1,2-diphenylphenanthrene (4b) was eluted from the column with benzene–hexane (1 : 4) in 5% yield.

Compound (4b) can be obtained in much better yield by irradiation of the pure iodinated compound (4a) in benzene with a high pressure lamp. To this end a solution of (4a) (1 mmol, 380 mg) in benzene (350 ml) was irradiated for 20 h. After washing the solution with a $NaHSO_3$ solution and water the benzene layer was dried ($MgSO_4$) and the solvent evaporated. The light green residue was chromatographed on $Al_2O_3$. Elution with benzene–hexane (1 : 9) gave 10% (4). Elution with benzene–hexane (1 : 4) gave the photosubstitution product (4b) in 88% yield.

1-Phenylnaphthalene (35) was obtained in only 2% yield after 30 h irradiation of (8). The product was identical with that obtained by irradiation of 1,4-diphenylbutadiene in benzene.[10,11]

1,3-Dimethyl-8-phenylnathphalene (37) was an oil, *m*/*e* 232 ($M^+$), $\lambda_{max.}$ ($CH_3OH$) 232 (log ε 4.61) and 288 nm (3.86), δ($CS_2$) 1.89 (3 H, s, $CH_3$), 2.40 (3 H, s, $CH_3$), 6.92 (s, H-2), 7.06 (dd, H-7), 7.13—7.33 (6 H, m), 7.37 (s, H-4), and 7.59 (dd, H-5).

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* The indices a and b are used to indicate end-products containing an additional iodo or phenyl substituent, as in Scheme 1.

[10] G J. Fonken, *Chem. and Ind.*, 1962, 1327.

[11] C. C. Leznoff and R. J. Hayward, *Canad. J. Chem.*, 1970, **48**, 1842.