Photoreactivity of Quinoline Derivatives. Part 2.[1] Photodimers of trans-4-Styrylbenzo[h]quinoline

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The solution-phase photochemistry of trans-4-styrylbenzo[h]quinoline (1) was reinvestigated with the aim of obtaining more detailed information about the photodimerization reaction. Four new isomeric (benzoquinolyl)-diphenylcyclobutanes (5)—(8) were isolated in addition to the previously described cyclobutane derivative (4). Mass and ^{1}H n.m.r. spectra provided valuable information about the structures, configurations, and conformations of these compounds. The effects of monomer concentration, irradiation time, and the presence of oxygen are briefly discussed with a view to preparative applications of the photodimerization.

A PRELIMINARY study[1] of the solution-phase photochemistry of trans-4-styrylbenzo[h]quinoline (1) revealed that, after a rapid trans–cis isomerization [(1) ⇌ (2)], dibenzo[c,i]phenanthridine (3) and di(benzoquinolyl)-diphenylcyclobutane (4) are formed as a result of dehydrocyclization and dimerization, respectively. Although the formation of other products of isomerization or dehydrocyclization is not likely, only one of the eleven possible cyclobutane isomers has been isolated hitherto. Since the photoreaction mixtures proved to be particularly complex, and since the ^{1}H n.m.r. spectra of fractions obtained during isolation and purification of the above mentioned compounds suggested the presence of dimers with configurations different from that of (4), we re-examined the photoreaction of (1) with the aim of obtaining more detailed information about the photo-dimerization. Careful experimental work, involving thin-layer and column chromatography, resulted in the isolation of four more dimers, (5)—(8).

*Structures, Configurations, and Conformations.*—The mass spectra of the five photodimers showed molecular

ions at m/e 563, in agreement with their dimeric structure. The n.m.r. signals obtained for the four ring protons of the five photodimers were in each case symmetrical, corresponding to an AA'BB'-type spectrum. Of the eleven possible configurations, only seven contain an element of symmetry, but two of these which have all substituents on the same side of the cyclobutane ring are unlikely for steric reasons. The remaining configurations are depicted [(4)—(8)].

The fragmentation patterns in the mass spectra permitted a clear differentiation between head-to-tail (ht) and head-to-head (hh) stereoisomers. The two pathways of ring fragmentation for ht configurations (4) and (5) are equivalent, and only one monomer ion fragment, [PhCH=CHBq]$^{+·}$ (m/e 281), could be produced (symmetric splitting). On the other hand, three stilbene ion fragments, [PhCH=CHBq]$^{+·}$ (m/e 281), [PhCH=CHPh]$^{+·}$ (m/e 180), and [BqCH=CHBq]$^{+·}$ (m/e 382), are expected for hh isomers (6)—(8) (symmetric and asymmetric splitting). Since the two ring-splitting processes might not occur with comparable ease, the intensity of the fragment ions cannot be readily predicted.

Ionization voltages of 75 eV produced very similar

[1] Part 1, F. Andreani, R. Andrisano, G. Salvadori, and M. Tramontini, *J. Chem. Soc. (C)*, 1971, 1007.

mass spectra for the five stereoisomers. The most prominent peak was at m/e 281, suggesting that the


(1)

(2)

(3)

(4)
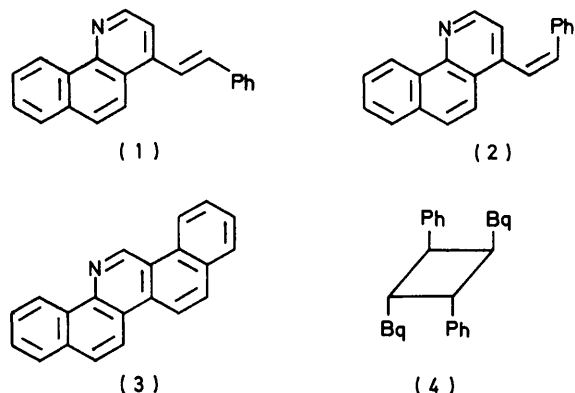
Bq = 4-benzoquinolyl

cyclobutane ring structure readily undergoes symmetric racture to give a fragment with a mass one half that of the parent ion. However, fragment ions at m/e 180 and 382 were determined to be completely absent with absolute certainty only in the mass spectra of two dimers, (4) and (5). Because quantitative thermal dimer ⟶ dimer isomerizations were not observed when these two compounds were heated at the minimum temperature necessary to record their mass spectra, we concluded

temperatures. On the basis of these results, we concluded that the dimers (6)—(8) must belong to the hh-configuration class.

The ^{1}H n.m.r. spectra of the five compounds (4)—(8) were in agreement with the proposed stereoisomeric structures. In addition to the aliphatic hydrogen multiplet mentioned above, all the spectra showed an aro-

(4)   (5)

head — to — tail

(6)   (7)   (8)

head — to — head
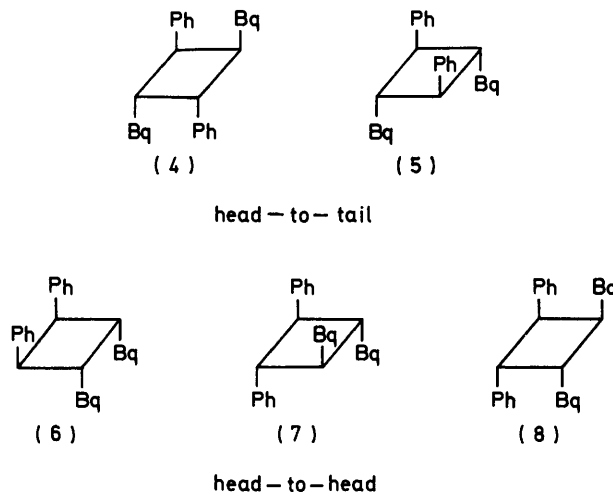
matic multiplet corresponding to 26 protons (see Table). Only the absorption pattern of the cyclobutyl protons,

^{1}H N.m.r. spectra of di(benzoquinolyl)diphenylcyclobutanes (4)—(8) (δ values)

	Structure	ArH	Cyclobutane protons				
			Low-field half-spectrum AA′	High-field half-spectrum BB′	Centre of spectrum	$\Delta\delta_{obs.}$	$\Delta\delta_{calc.}$
ht	(4)	9.35 (2 H, m), 8.95 (2 H, d), 8.15—6.95 (22 H, m)	5.60—5.20 [a]	5.20 [a]—4.80	5.20	0.40	0.40
	(5)	9.35 (2 H, m), 9.05 (2 H, d), 8.00—7.00 (22 H, m)	5.00—4.55	4.35—3.90	4.45	0.65	0.60
hh	(6)	9.20 (2 H, m), 8.75 (2 H, d), 8.05—7.20 (22 H, m)	5.67—5.45	4.80—4.58	5.125	0.87	0.80
	(7)	9.30 (2 H, m), 9.05 (2 H, d), 8.05—7.00 (22 H, m)	4.80—4.55	4.35—4.10	4.45	0.45	0.60
	(8)	9.20 (2 H, m), 8.95 (2 H, d), 8.10—7.20 (18 H, m), 6.95—6.35 (4 H, m)	5.35—5.125 [a]	5.125 [a]—4.90	5.125	0.225	0.40

[a] Superimposition of lines was insignificant.

that they have the ht-type configuration. However, peaks at m/e 180 and 382 were observed in the spectra of the remaining three dimers, although in differing abundances. The intensities of the two diagnostic peaks of the dimer (7) differed slightly, the lesser representing 25% of the base peak. The spectrum of the dimer (6) showed the two peaks of equal intensity, each representing ca. 3% of the base peak. The mass spectrum of the dimer (8) was almost identical with that of the dimer (5), and the intensities of the two peaks were so low that their value for diagnostic purposes appeared dubious. Pyrolysis experiments at the minimum temperature required to record mass spectra demonstrated, however, that the dimer (6) isomerized considerably, but not quantitatively, to the dimer (4), and the dimer (8) isomerized in a nearly quantitative manner to yield the dimer (5) and was completely stable at lower

however, permitted both the confirmation of the distinction made on the basis of the mass spectra between ht and hh isomers and the assignment of configuration to the ht dimers (4) and (5) and to the hh dimer (7). It is known that one half of the AA′BB′ spectrum of the ht isomers always covers, independently of chemical shift, a frequency interval approximately double that for the hh isomers.[2,3] Further differentiation within the two classes of stereoisomers can be obtained from more specific spectral features.[3] For example, the two types of ht isomers could be immediately differentiated since a theoretical A_2B_2 system with a half-spectrum of seven lines would be expected on the basis of molecular symmetry (C_{2v}) for cyclobutanes with configuration (5).[4]

On the basis of the above observations, the configurations of the ht dimers (4) and (5) were easily assigned. Their half-spectra did in fact exhibit a frequency interval (ca. 24—27 Hz) approximately double that for the hh isomers (6)—(8) (ca. 13—15 Hz). In addition only isomer (5) of the two ht isomers showed a half-spectrum which,

[2] H. Ulrich, D. V. Rao, F. A. Stuber, and A. A. R. Sayigh, *J. Org. Chem.*, 1970, **35**, 1121.
[3] G. Montaudo, S. Caccamese, and V. Librando, *Org. Magnetic Resonance*, 1974, **6**, 534.
[4] H. Günther, *Angew. Chem. Internat. Edn.*, 1972, **11**, 861.

in its number of peaks (seven) and their relative intensities, was in agreement with the expected A_2B_2 spin system. Although a lack of fine structure in the spectra of hh dimers (6)—(8) prevented any differentiation within this class of compounds, we were able to assign the configuration to dimer (7), since it is known that in 1,2,3,4-tetrasubstituted cyclobutane derivatives such as dimers (4)—(8), in which the spatial arrangement of the four cyclobutyl protons is *trans,trans,trans*, the centre of the AA'BB' multiplet always falls at higher field than for isomeric configurations having two pairs of *cis* protons.[3,5,6] The cyclobutyl proton multiplet was, in fact, centred at δ *ca.* 4.45 in the spectra of isomers (5) and (7), and at δ *ca.* 5.15 in the spectra of (4), (6), and (8) (see Table). These results were in agreement with the configurations previously assigned to ht dimers (4) and (5) and, in addition, permitted the unequivocal determination of the configuration of dimer (7), since it is the only hh dimer with a *trans,trans,trans* cyclobutyl proton configuration. However, the signals at δ 4.45 and 5.15 although being well enough separated to permit the distinction of configurations (5) and (7) from (4), (6), and (8), are both shifted to lower field with respect to analogous examples in the literature.[3,5,6] This may be attributed to the fact that compounds (4)—(8) contain four aryl groups (two of which have considerable steric bulk), which would favour a limited number of inflexible conformations in which the aromatic rings would deshield the cyclobutyl protons. For the dimers (6) and (8), which could not be differentiated since both showed the spectroscopic characteristics of hh dimers having two pairs of *cis*-protons, the configurations were assigned by evaluating the shift in the n.m.r. shielding value which would be experienced by the cyclobutyl protons as a result of the magnetic field of the aromatic rings.

Conformational analysis of the five stereoisomers (4)—(8) led to the conclusion that the most stable conformation of an aryl group bound to a carbon atom of a cyclobutane ring (*e.g.* C-1, see Figure 1) always corresponds to that in which the plane of the aryl ring forms an angle θ of *ca.* 30° with the plane containing the C(1)–H and C(1)–Ar bonds. All other possible angles between these two planes would give less favourable conformations. On the basis of these considerations, made more evident by inspection of molecular models, the most stable conformations were assigned to each dimer (4)—(8). Figure 2 shows that whereas each of the stereoisomers (4), (6), and (8) has only one possible conformation, compounds (5) and (7) both have four energetically equivalent conformations. Dimers (6) and (8) are characterized, as are the other three isomers, by two pairs of configurationally equivalent cyclobutyl protons and the lack of equal response of each pair to the aromatic shielding effect is responsible for the differences in chemical shifts of the two half-spectra, AA' and BB'.

[5] W. H. Laarhoven, Th. J. H. M. Cuppen, and R. J. F. Nivard, *Tetrahedron*, 1970, **26**, 1069.

[6] H. Shechter, W. J. Link, and G. V. D. Tiers, *J. Amer. Chem. Soc.*, 1963, **85**, 1601.

The shielding shift values of each pair of configurationally equivalent protons were calculated by summing the shielding shift value of each of the two constituent protons (evaluated by means of the Johnson and Bovey diagram [7] and reported in p.p.m. in Figure 1). Thus two values of shielding were obtained for each configuration and their absolute difference (calc. $\Delta\delta$) was then compared with the experimental value derived from the ^{1}H n.m.r.
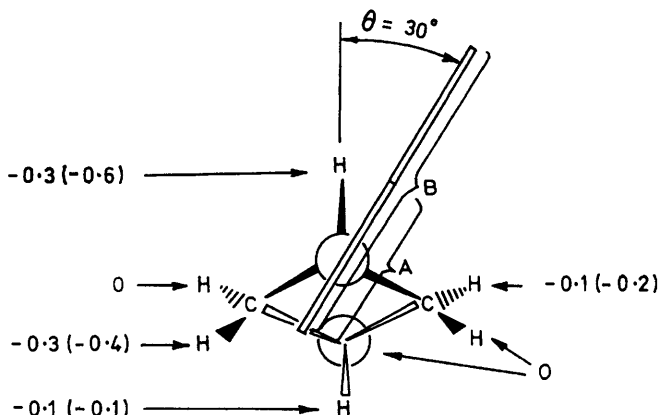

FIGURE 1 Most probable conformation ($\theta = 30°$) of the phenyl (A) or 4-benzoquinolyl (B) group bound to a cyclobutane ring and the shift in the ^{1}H n.m.r. shielding values (p.p.m.) experienced by each of the remaining seven protons as a result of the magnetic field of the two aromatic rings. The shielding values are always zero or negative (paramagnetic shift). The first shielding value is due to the phenyl and the value in parentheses to the benzoquinolyl group

spectrum (see Table). This procedure was applied to all five isomers (4)—(8) and proved particularly successful in differentiating the dimer (8) from the dimer (6) whose calculated and experimental $\Delta\delta$ values were considerably larger than those for compound (8).

Photochemical Reactions.—Even with low monomer concentrations, the photoreaction was accompanied by precipitation, varying in degree with the solvent, both in the irradiated solutions and on the walls of the quartz immersion well. The intensity of light reaching the solution was thus considerably reduced. We were therefore able to study the effects neither of solvents with different polarities nor of a large range of monomer concentrations. Benzene proved to be the solvent with which the irradiations could be effected with the highest concentrations of monomer without dimer precipitation, even after long time intervals. Nitrogen was bubbled through the irradiated solutions to exclude air except in the case where we desired to study the effect of oxygen.

Reaction mixtures were analysed quantitatively by g.l.c. under conditions for which it had been determined by use of authentic samples that there was a good separation of compounds (1)—(3), yet with no dimer interference, since none was revealed at the detector. With all column types employed, all attempts to obtain characteristic dimer peaks failed because of the dimers' thermal decomposition in the injection port. The

[7] C. E. Johnson, jun., and F. A. Bovey, *J. Chem. Phys.*, 1958, **29**, 1012.

quantitative g.l.c. determination of the monomers (1)—(3) in reaction mixtures was therefore achieved by the internal standard method, and the extent of dimerization was evaluated by difference and verified by

contrast, in the presence of oxygen, the photodehydro-cyclization reaction competed with isomerization and dimerization. A typical composition of the reaction mixture obtained after irradiating a 0.25% (w/v) solution
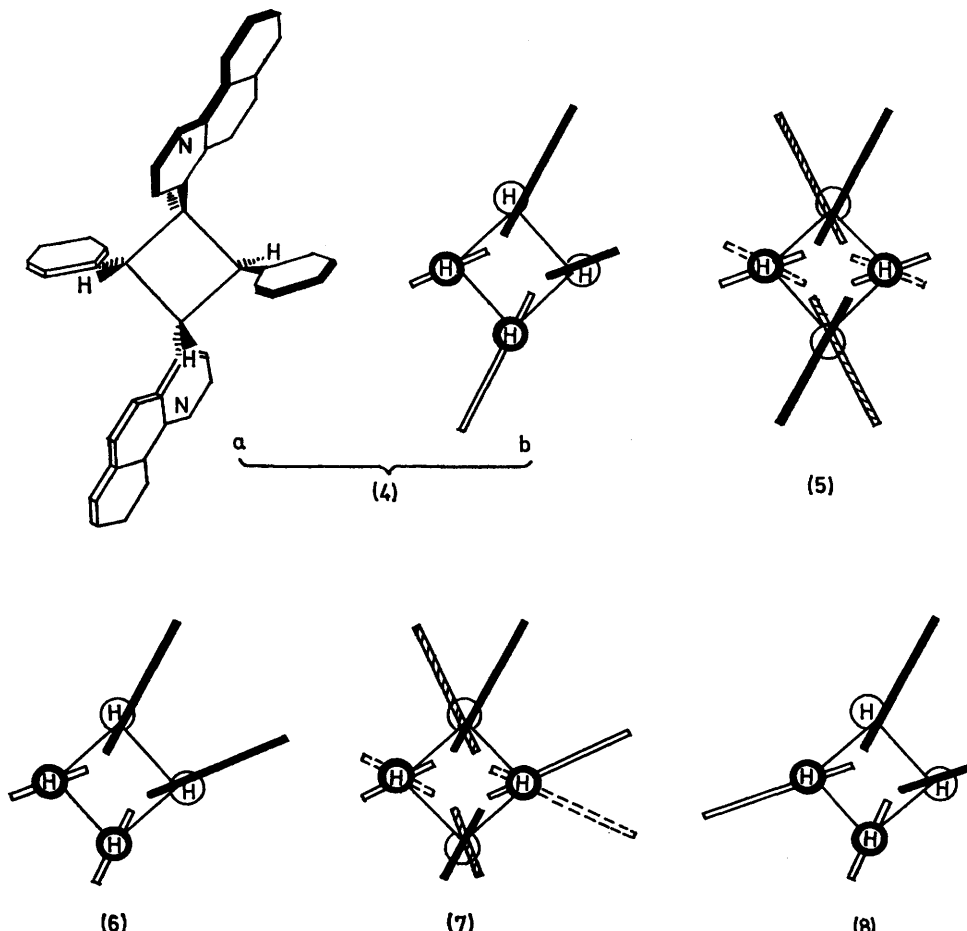

FIGURE 2 Configurations and most stable conformations of the five cyclobutane stereoisomers (4)—(8). Arrangement (4a) is a real projection; while (4b) and (5)—(8) are schematic in that the angle between the cyclobutane ring plane and the C—Ar bond has been distorted to ca. 90°

column chromatography. For irradiation times up to 4 h, this method proved valid, since the quantity of by-products was negligible. For longer irradiation times, however, the extent of dimerisation had to be determined by u.v. spectroscopy after t.l.c. separation. The same procedure was adopted to obtain the proportion of each dimer.

Effect of Oxygen.—The extents of dimerization obtained after irradiating (1) for 4 h in nitrogen and in oxygen were similar. In the inert atmosphere, however, dibenzo[c,i]phenanthridine (3) was formed in very small quantities, even after long irradiation times, probably because it was not possible to obtain total deaeration of the irradiated solutions with the nitrogen flow. In

of monomer (1) for 15 h was: (1), 4.0%; (2), 8.0%; (3), 18%; extent of dimerization 50%; by-products, 20%.

The initial rate of dibenzo[c,i]phenanthridine (3) production was zero for the irradiation of pure *trans*-4-styrylbenzo[h]quinoline (1) and finite for the irradiation of the *cis*-isomer (2). A pure sample of (3), irradiated under the same conditions in which it was formed, proved stable; its formation, therefore, occurred irreversibly only in the presence of oxidants and *via* the *cis*-isomer (2). These results are in general agreement with those reported for the photocyclization of stilbene analogues.[5,8-14]

[8] E. V. Blackburn and C. J. Timmons, *Quart. Rev.*, 1969, **23**, 482.

[9] P. Bortolus, G. Cauzzo, and U. Mazzucato, *Z. phys. Chem.*, 1969, **63**, 29.

[10] D. D. Morgan, S. W. Horgan, and M. Orchin, *Tetrahedron Letters*, 1970, 4347.

[11] W. H. Laarhoven, Th. J. H. M. Cuppen, and R. J. F. Nivard, *Tetrahedron*, 1970, **26**, 4865.

[12] E. V. Blackburn and C. J. Timmons, *J. Chem. Soc. (C)*, 1970, 172.

[13] E. V. Blackburn, C. E. Loader, and C. J. Timmons, *J. Chem. Soc. (C)*, 1970, 163.

[14] T. Sato and T. Morita, *Bull. Chem. Soc. Japan*, 1972, **45**, 1548.

Effects of Time and Concentration.—Since both by-product formation and photodehydrocyclization are favoured by the presence of oxygen, the effects of monomer concentration and irradiation time on the dimerization were studied under a nitrogen flow. For the above-mentioned reasons, *trans*-4-styrylbenzo[*h*]quinoline (1) was irradiated at concentrations of 0.25, 1.0, and 1.5% (w/v). Isomerization consistently competed with dimerization, which nevertheless occurred at these three concentrations with respective yields of *ca.* 30, 50, and 60% after 4 h irradiation. The high dimerization extent even at low monomer concentrations shown by the present styrylbenzo[*h*]quinoline system is a characteristic which distinguishes it from other mono-olefinic systems.[2,6,15] After 4 h irradiation all reaction mixtures contained all dimers except (8). However, only the dimers (4) and (6) showed good yields. For example, at a 1.0% w/v concentration of (1), the dimers (4) and (6) each represented *ca.* 25% of the reaction mixture, whereas the dimers (5) and (7) constituted only 1.5 and 0.5%, respectively. The remaining portions of the reaction mixture consisted of monomers (1) and (2). There was no substantial difference in composition for the analogous irradiation of the *cis*-monomer (2). In agreement with the assigned configurations, the initial rate of formation of dimers (4)—(7) was zero for irradiation of pure *cis*-4-styrylbenzo[*h*]quinoline (2) and finite for the irradiation of the *trans*-isomer (1). The dimer (8) should have shown a finite initial rate of formation for the irradiation of pure *cis*-4-styrylbenzo[*h*]quinoline (2) and zero for the irradiation of the *trans*-isomer (1). Unfortunately, the rate of formation of (8) at the concentrations studied was so low that it could only be revealed after long (>4 h) irradiation times, when both monomers (1) and (2) were almost at equilibrium, as demonstrated by the fact that, as the reaction proceeded, their ratio approached a constant value. The rates of formation for each dimer followed the order: (6) > (4) ≫ (7) ≃ (5) ≫ (8). The extent of dimerization after 4 h was always over 50% of the quantity obtained after 15 h, even when the monomer (1) was irradiated at a concentration of 0.25% w/v. Irradiation after this period did not lead to notable increases in dimerization extent, which, if anything, tended to diminish, as demonstrated by a 48 h irradiation. The distribution of the individual isomeric dimers does, however, differ after long irradiation times from that observed after 4 h. A typical product distribution after 15 h irradiation of monomer (1) at a concentration of 1.0% (w/v) was: (1), 4.5%; (2), 11%; (4), 50%; (6), 7.0%; (5), 6.5%; (8), 6.0%; (7), trace; (3), trace; by-products, 14%.

The irradiation of solutions in benzene of each dimer at concentrations which, because of their limited solubility, did not exceed 0.3% w/v, yielded after a short time all the compounds obtained by irradiating (1).

Even apparent dimer ⟶ dimer isomerizations occurring faster than monomer formation were observed. For example, dimers (5) and (8) were formed much more rapidly from (8) and (5), respectively, than from the monomers. To elucidate this surprising finding, we irradiated very dilute solutions (0.01—0.05% w/v) of each monomer (concentrations close to that which would be expected from photolysis of the very dilute starting dimer solutions). We were thus able to verify that the formation rates of the dimers differed from those observed at higher monomer concentrations. In particular, formation of dimers (5) and (8), as would be expected, was favoured by very low monomer concentrations.

The quantitative determination of initial dimer remaining after 5 and 30 min of irradiation permitted us to determine that the photochemical stabilities of each dimer followed the order: (5) > (8) ≃ (4) ≫ (6) ≫ (7), which, in view of the formation rates, is not in contrast with the compositions of the reaction mixtures after 4 and 15 h.

Conclusions.—Although the dimers (4)—(7) are definitely derived from the monomer (1), the dimer (8) is most likely derived from the *cis*-monomer (2). Unfortunately, we were not able to demonstrate this directly, because of the high rate of *cis* ⇌ *trans* isomerization relative to the formation of (8). All dimers are in equilibrium with the original monomers and a direct dimer ⟶ dimer photoisomerization may be reasonably excluded. Therefore, the composition of the reaction mixture is always the result of a complex interaction between the formation and photolysis rates of each dimer. Since it was demonstrated that the rate of individual dimer formation and (presumably) the rate of photolysis vary with concentration, we conclude that although the composition of the reaction mixture after a given irradiation time may not be predictable it is possible, within certain limits, to increase the formation of some dimer configurations over others by manipulating such factors as monomer concentration and irradiation time. However, high monomer dilutions or long irradiation times favour the irreversible formation of by-products.

EXPERIMENTAL

Microanalyses were performed for all the compounds with a Hewlett–Packard 185 CHN analyser and results were within ±0.4% of the theoretical values. [1]H N.m.r. spectra were obtained from samples in deuteriochloroform solution with a JEOL C-60 HL instrument (tetramethylsilane as internal standard). Mass spectra were determined with a JEOL D-100 spectrometer. U.v. spectra were recorded with a Unicam SP 700 spectrophotometer. G.l.c. was conducted by using a dual column Carlo Erba Fractovap GV instrument equipped with flame ionization detectors and 2.5 m × 4 mm i.d. stainless steel columns packed with 5% methyl phenyl silicone (SE-52) on Chromosorb W(60—80 mesh). Authentic samples and 4-phenylbenzo[*h*]quinoline [1] as the internal standard were used for calibration. The operational parameters were: column temperature 275 °C (isothermal); injection port temperature 210 °C; detector

[15] G. Mark, H. Mattaus, F. Mark, J. Leitich, D. Henneberg, G. Schomburg, I. V. Wilucki, and O. E. Polansky, *Monatsh.*, 1971, **102**, 37.

temperature 300 °C; carrier gas nitrogen at 75 ml min⁻¹, hydrogen at 60 ml min⁻¹ and air at 250 ml min⁻¹; attenuation, $10^2 \times 16$. Unless otherwise specified, column chromatographic separations were carried out with Merck Kieselgel 60 (70—230 mesh ASTM). T.l.c. was performed on Merck precoated plates (silica gel 60 without fluorescent indicator, thickness 0.25 mm). The chromatograms were developed by the stepwise elution technique [16] for qualitative analyses; carbon tetrachloride–ethyl acetate (9 : 1) and trichloroethylene–ethyl acetate (9 : 1) were the solvent systems, and spots were located by inspection under u.v. light. Multiple-elution t.l.c.[16] was used for quantitative dimer estimations. The solvent system was trichloroethylene–ethyl acetate (9 : 1), and the dimers were located with u.v. light, eluted with pyridine, and spectrophotometrically estimated by the usual procedures (measurement wavelength 350 nm).

trans-4-Styrylbenzo[h]quinoline (1), described in a previous paper, was obtained by means of a method improved according to Tilak's suggestion.[17] 3-(1-Naphthylamino)-1-styrylpropan-1-one [1] (15 g) and triphenylmethyl chloride (14 g) were dissolved in methylene chloride (250 ml). Formic acid (60 ml) in methylene chloride (300 ml) was added dropwise at room temperature and with stirring during 2 h. The mixture was then refluxed for 15 min, cooled in an ice-bath, and carefully made alkaline with 20% w/v sodium hydroxide solution (375 ml), added dropwise with stirring. The organic layer was recovered, washed with water, dried (Na₂SO₄), and evaporated. The residue, dissolved in a minimal amount of benzene, was chromatographed on a column with benzene as eluant. Crude *trans*-4-styrylbenzo[h]quinoline (1) (7 g) was recrystallized from ethanol (yield 5 g, 33%); this product was homogeneous on t.l.c. and g.l.c. and could be used without further purification for the irradiation experiments. Among the by-products, α-naphthylamine, 1,2,3,4-tetrahydro-4-styrylbenzo[h]quinoline,[1] and 1-phenyl-2-(4-benzoquinolyl)ethane [1] were identified.

Photoreactions.—Irradiations of both small and large solution volumes were carried out in reaction vessels with identical characteristics except for available capacity: a flat bottom permitted the use of a stirring bar and angled joints allowed bubbling and gas escape (oxygen or nitrogen).

The vessels were designed to accommodate double-walled quartz immersion wells which permitted water cooling of lamps and solutions whose temperature during irradiation was never higher than 25 °C. Small volumes (*ca.* 100 ml) of solution were irradiated by means of a Hanau TQ-81 u.v. lamp and large volumes (*ca.* 1 000 ml) by means of a 400 W 400 LQ medium-pressure mercury lamp (Applied Photophysics Ltd.). Solutions were deaerated in the dark for 0.5 h by bubbling through nitrogen, which was then continued until the end of the irradiation.

Isolation of the Dimers (4)—(8).—A procedure is given below for the isolation of dimers from a solution of *trans*-4-styrylbenzo[h]quinoline (1) (1 000 ml; 1% w/v) irradiated for 15 h under nitrogen. The procedure proved to be generally valid, and was used for all the irradiations described in this paper. After the irradiation was complete, the solution was concentrated by rotary evaporation. Work-up of the oily residue, involving addition of trichloroethylene (100 ml) and trituration, yielded a white crystalline precipitate which was filtered off and washed with more trichloroethylene (50 ml). It was identified as pure (4) [about 70% of the amount of (4) formed upon irradiation]. The combined filtrate and washings were concentrated by rotary evaporation and the residual oil was applied to a silica gel column which was eluted with trichloroethylene. The fractions obtained were not homogeneous on t.l.c., always containing mixtures of monomers (1)—(3).* After the eluate was free of the highest R_F materials (t.l.c.), elution with trichloroethylene–ethyl acetate (9 : 1) afforded a satisfactory separation of each dimer. Fractions containing the same dimer were combined and evaporated to dryness *in vacuo*, to give a residue which was then recrystallized. For each dimer (in order from the fastest to the slowest moving), the crystallization solvents and m.p.s (°C) were: (7), ethanol, 211—213; (4), chloroform, 294—296; (8), toluene, 285—287; (6), ethanol–chloroform, 253—255; (5), ethanol–benzene, 245—247.

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* Satisfactory separation of the three monomers could be achieved by using a column of Merck aluminium oxide 90 standardized according to Brockmann and eluting with trichloroethylene.

[16] K. Randerath, ' Thin-layer Chromatography,' Academic Press, New York and London, 1964, p. 45.
[17] B. D. Tilak, T. Ravindranathan, and K. N. Subbaswami, *Tetrahedron Letters*, 1966, 1959.