JOURNAL
OF
THE CHEMICAL SOCIETY

PERKIN TRANSACTIONS II
Physical Organic Chemistry

The Photochemistry of Di-*p*-cumenylfulgide (Bis-*p*-cumenylmethylenesuccinic Anhydride)

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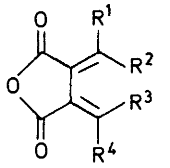
The photochemistry of the title compound in the solid and in solution at low temperatures has been investigated. The solid *E,E*-isomer gives the *E,Z*-isomer plus a dimer F; one crystal form of the *E,E*-isomer is reversed photochromic. The solid *Z,Z*-isomer also gives the dimer F, whereas the *E Z*-isomer appears to give the *E,E*-isomer as the primary photoproduct. In methylcyclohexane–isohexane at −185° the *E,E*-isomer is isomerised to *E,Z*; the latter is reversibly isomerised into *Z,Z* but also gives two dimers, one of them F. At −100° the same isomerisation processes occur, with in addition reversible conversion of the *E,Z*-isomer into the 1,8a-dihydrophenylnaphthalene. At these low temperatures the isomerisation of the *E,E*- to the *Z,Z*-isomer proceeds *via* the *E,Z*-form. The isomerisation processes do not proceed through the dihydrophenylnaphthalenes or cyclobutenes.

In a previous paper[1] we treated qualitatively the photochemistry of bis-*p*-methoxybenzylidenesuccinic anhydride: we described its three geometrical isomers and the conditions for their interconversion. Heller and his co-workers have since reported[2-4] on the thermal and photochemical reactions of a variety of other fulgides and fulgimides. They give structural assignments to the geometric isomers of these materials and of the corresponding fulgenic acids; Elbe and Köbrich[5] also discuss the assignments for the latter. The structure assignments are based mainly on n.m.r. spectroscopy, although evidence based on the chemical shift of the vinyl proton signal is sometimes ambiguous.[1] However, combination of the n.m.r. results with a crystal structure analysis[1] gives confidence in the general correctness of the picture. In keeping with the other authors[2-5] we adopt the *E,Z* nomenclature for isomers A—C: *E* and *Z* are respectively equivalent to *trans* and *cis* as used previously.[1]

The mechanisms of interconversion of these isomers are potentially complex. Thus the photoconversion of A into B and C could be either simultaneous (C ⟵ A ⟶ B) or consecutive (A ⟶ C ⟶ B) processes. Further, the isomerisations could proceed by electrocyclic 4π or 6π rearrangements. Symmetry-allowed reactions are shown in Scheme 1.



Isomer	R^1	R^2	R^3	R^4
A (≡ *E*, *E*)	H	Ar	Ar	H
B (≡ *Z*, *Z*)	Ar	H	H	Ar
C (≡ *E*, *Z*)	Ar	H	Ar	H

Santiago and Becker[6] have shown that irradiation of dibenzylidenesuccinic anhydride in a low-temperature glass gives rise to a 1,8a-DHPN. Heller and his co-workers found[2-4] that a number of fulgides and fulgimides give 1,8a-DHPNs photochemically; these undergo two competitive thermal reactions, one ring opening to the isomeric fulgides, and the second a 1,5-hydrogen shift yielding 1,2-dihydrophenylnaphthalenes. The latter process occurs even on prolonged irradiation at room temperature. Both groups of workers assumed

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[1] M. D. Cohen, H. W. Kaufman, D. Sinnreich, and G. M. J. Schmidt, *J. Chem. Soc.* (*B*), 1970, 1035. There are a number of errors in this paper. For the B isomer, for the crystal form $P2_1/c$, a should have been 15.47 Å, and the two structures are in fact identical; for this structure $U = 1\,604$ Å^3, $D_c = 1.391$ g cm^{-3}. For the A isomer, the cell dimensions of the form described on p. 1036 lead to an unreasonable density. We have not been able to produce this form again and assume that data were obtained for a crystal of some foreign substance. Thus for A, there is only the form for which the structure was solved. Crystals of C have $U = 3346$ Å^3, $D_c = 1.333$ g cm^{-3}. In Table 1 the vinyl proton frequency for the acid Aa should be 454.0 Hz.

[2] R. J. Hart and H. G. Heller, *J.C.S. Perkin I*, 1972, 1321.

[3] H. G. Heller and R. M. Megit, *J.C.S. Perkin I*, 1974, 923.

[4] H. G. Heller and M. Szewczky, *J.C.S. Perkin I*, 1974, 1487.

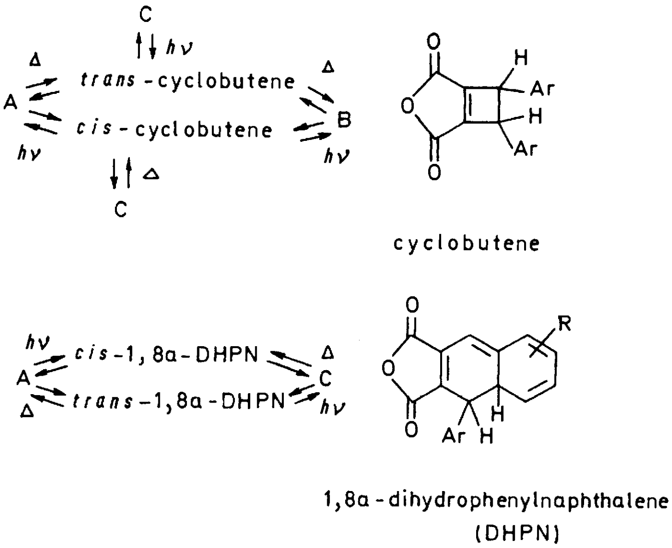
[5] H.-L. Elbe and G. Köbrich, *Chem. Ber.*, 1974, **107**, 1654.

[6] A. Santiago and R. S. Becker, *J. Amer. Chem. Soc.*, 1968, **90**, 3654.

that the red colour produced on irradiating some crystalline fulgides is due to 1,8a-DHPN formation.

To determine the degree of participation of these electrocyclic processes in the isomerisation it is desirable to compare the reaction at low and high temperatures, and to use various excitation wavelengths so that the results of exciting the fulgides and the intermediates, if any, can be distinguished. With the hope that it would be sufficiently soluble to allow low temperature work we prepared bis-*p*-cumenylmethylenesuccinic anhydride (A—C; Ar = p-Pr^{i}C$_6$H$_4$), and this indeed proved to be amenable to study. We here report on the photochemistry of this compound both in solution and in the solid.

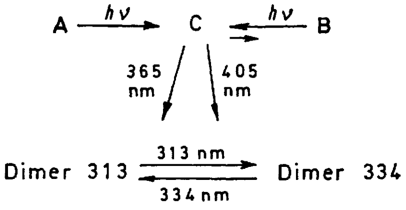
The A isomer of this compound was prepared *via* the Stobbe condensation and gave on irradiation in solution isomers B and C. Structure assignments are based on n.m.r. spectroscopy. Irradiation of solid A gave two major products, C and a new material (F). The latter proved to be a dimer containing a cyclobutane ring. In addition, one of the two crystal forms of A shows the interesting phenomenon of reversed photochromism (see Experimental section). Solid B gives F only on photolysis. Solid C gives A together with other products which are apparently derived from A.



SCHEME 1

The problem of the factors determining isomerisation or dimerisation in solid-state reactions is an interesting one; in some cases the relative yields of the two products have been shown to be a function of the history of the crystal.[7] Our information from the present study is unfortunately too limited to contribute; thus we know neither the crystal structures of the reactants which give F, nor has the stereochemistry of this dimer been fully elucidated. Nor can we say much of reversed photochromy except that the photocolour does not appear to be due to 1,8a-DHPN, that it is not formed *via* a free radical intermediate, and that it involves a thermally activated step.

Most of the low-temperature studies were of solutions in methylhexane–isohexane. In this solvent B, and to a lesser extent C, show spontaneous spectral changes below −105° indicative of aggregation. At −185° irradiation of A gives initially only C, with a quantum yield $\phi(\mathrm{A} \longrightarrow \mathrm{C})$ of 0.45; subsequently there is gradual formation of B. At this temperature C gives rise to B in a photoreversible process with $\phi(\mathrm{B} \longrightarrow \mathrm{C}) \gg \phi(\mathrm{C} \longrightarrow \mathrm{B})$. In addition, prolonged irradiation yields two other products, one absorbing at 334 nm and proving to be identical with F, and the second absorbing at 313 nm and probably also being dimeric. We interpret our experiments at this low temperature as shown in Scheme 2. The dimerisations presumably occur in monomer aggregates present in the glasses. When methyltetrahydrofuran, a good 'solvator', is used as solvent no dimer formation was found.



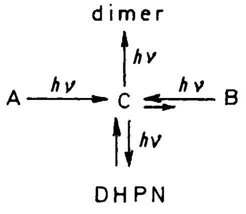
SCHEME 2

At −100° and higher temperatures we observed formation of 1,8a-DHPN, in addition to isomerisation. The results are interpreted as shown in Scheme 3.

The quantum yield for conversion of A into C at −100° is practically identical (0.48) to that for the lower temperature. Thus there is no indication of the DHPN providing an additional pathway for this isomerisation. Heller and Szewczyk [4] found that in related compounds at room temperature <3% of the isomerisation occurs *via* DHPNs.

At neither of the temperatures was there found any evidence for accumulation of cyclobutenes, nor for their participation as intermediates in the isomerisations.

It is of interest that prolonged irradiation in our system leads to a dimer, whereas in Heller's systems [2-4] at room temperature such irradiation leads to 1,2-DHPNs, and that these two products have similar u.v. absorption properties. The evidence for the structures of these products appears to be unequivocal, but we are nevertheless presently undertaking an *X*-ray analysis of our dimeric product.



SCHEME 3

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[7] I. Ron, Ph.D. Thesis, Weizmann Institute of Science, 1971; G. M. J. Schmidt, *Pure Appl. Chem.*, 1971, **27**, 647.

EXPERIMENTAL AND RESULTS

*Synthesis and Qualitative Photochemistry of Di-*p*-cumenylfulgide.*—The compound was prepared as by Stobbe and Härtel[8] *via* dicumenylfulgenic acid which was treated by acetyl chloride. We refer to the product as isomer A.

A 1% solution of A in methylcyclohexane was irradiated under nitrogen at 10—15° by an external 500 W high pressure mercury lamp through Pyrex–Corning glass filters 5 860 + 7 380 (transmission peak *ca.* 366 nm) until the ratio of optical densities at 290 and 390 nm dropped to 1.8. The solvent was then removed under high vacuum in the cold. Two products, B and C, were formed; n.m.r. analysis showed [A] : [B] : [C] = (30—35) : (5—10) : (55—60). The three compounds were separated, with substantial losses, by column chromatography (silica gel H, ratio 1 : 40, under pressure of nitrogen). There were obtained also traces of other, unidentified, products.

N.m.r. spectra of bis-*p*-cumenylmethylenesuccinic anhydrides and related compounds*

Compound	CHMe_2 ^{a}	ArH	=CH	Solvent
(*E*)-Cumenylmethylene(methylene)succinic anhydride	8.76 (6 H)	2.53 ^{b} (4 H)	2.32 ^{c} (1 H)	$CDCl_3$
(*E*)-Cumenylmethylene(methylene)succinic acid	8.85 (6 H)	2.53 ^{b} (4 H)	2.7 ^{b} (1 H)	NaOD–D_2O
(*E*,*E*)-Biscumenylmethylenesuccinic acid	9.11 (12 H)	2.77,^{d} 3.17 ^{e} (8 H)	2.53 ^{b} (2 H)	NaOD–D_2O
(*E*,*E*)-Biscumenylmethylenesuccinic anhydride (A)	8.88 (12 H)	3.15 ^{b} (8 H)	2.10 ^{b} (2 H)	$CDCl_3$
(*E*,*Z*)-Biscumenylmethylenesuccinic anhydride (C)	8.76 (6 H),	2.25,^{d} 2.77 ^{e} (4 H),	2.22 ^{b} (1 H)	CCl_4
	8.71 (6 H)	2.48,^{d} 2.82 ^{e} (4 H)	2.43 ^{b} (1 H)	
(*Z*,*Z*)-Biscumenylmethylenesuccinic anhydride (B)	8.74 (12 H)	2.05,^{d} 2.75 ^{e} (8 H)	2.73 ^{b} (2 H)	$CDCl_3$

^{a} Doublet. ^{b} Singlet. ^{c} Triplet (J 2 Hz). ^{d} AA′ doublet (J 9 Hz). ^{e} BB′ doublet (J 9 Hz).

* Tetramethylsilene as internal reference.

On longer irradiation, to an optical density ratio of 1.65, two further products were obtained, one of which proved to be a dimer F. Less satisfactory conversions resulted from use of other filters or of benzene or ethanol as solvents.

A solution of A in methylcyclohexane was divided in two, and iodine was added to one of these samples. The two solutions were then irradiated in parallel at room temperature for two days under air. The iodine-containing solution gave the phenylnaphthalene (16%), whereas the other solution gave the DHPN (absorption spectrum) but no phenylnaphthalene. Thus the DHPN is not oxidised under these conditions in the absence of iodine.

Properties of and Assignment of Structures to A—C and F.—The di-*p*-cumenylfulgenic acid, apparently identical with the yellow compound prepared by Stobbe and Härtel,[8] is of *E,E*-configuration, by comparison of its n.m.r. spectrum with that of the corresponding *p*-methoxy-acid. This is as expected from studies of the Stobbe condensation.[2,5] The acid was cyclised to A which is therefore also *E,E*. This assignment also derives from the n.m.r. spectrum, τ ($CDCl_3$) 3.15 (A_4, ArH); in acetone, on the other hand, these protons give rise to an A_2B_2 system, while the vinyl protons give a signal at τ 2.10 (*cf.* ref. 1). Compound B is assigned the *Z,Z*-configuration, the aromatic protons constituting an AA′BB′ system giving a double doublet (τ 2.05 and 2.75), while the vinyl proton signals appear at higher field, as in other systems.[1,2,4] Compound C is the *E,Z*-isomer, with a spectrum very similar to that of the *p*-methoxy-derivative.[1]

(E,E)-*Bis-*p*-cumenylmethylenesuccinic Anhydride A.*—This forms two orange-red crystal forms,[8] (i) rods from hexane or acetyl chloride, space group $P1$ or $P\bar{1}$, a = 15.77, b = 16.41, c = 8.36 Å, α = 95° 25′, β = 97° 3′, γ = 99° 56′, Z = 4, U = 2 105 Å^3, D_c = 1.135 g cm^{-3}; (ii) thin transparent plates from light petroleum, $P2_1/c$, a = 15.91, b = 10.35, c = 13.20 Å, β = 92° 30′, Z = 4, U = 2 121 Å^3, D_c = 1.127 g cm^{-3}. Both forms have m.p. 110—111° (lit.,[8] 112—113°) (Found: C, 80.0; H, 6.7. Calc. for $C_{24}H_{24}O_3$: C, 80.0; H, 6.7%). The mass spectrum taken at 128° was satisfactory, m/e 360 (M^+), and scanning to m/e 720 showed no sign of dimer. The n.m.r. spectra of the isomers are given in the Table, and the u.v. absorption spectra in Figure 1.

(Z,Z)-*Bis-*p*-cumenylmethylenesuccinic Anhydride B.*—This was obtained as needles from hexane and rhombs from benzene–light petroleum; the two forms proved structurally identical, with space group $P2_1/c$, a = 16.52, b = 10.74, c = 23.19 Å, β = 92° 30′, Z = 8, U = 4 110 Å^3, D_c = 1.163 g cm^{-3}; m.p. 145—146°.

This is the only isomer which gives measureable emission. Excitation at −185° of a solution in methylcyclohexane–isohexane (2 : 1) with light of wavelength 370—405 nm produces emission with $\lambda_{max.}$ 510 nm.

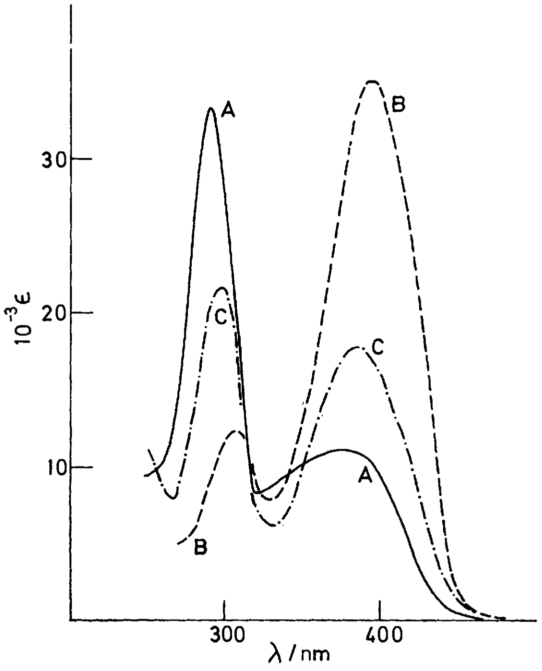

FIGURE 1 Absorption spectra of the biscumenylmethylenesuccinic anhydrides in methyl cyclohexane–isohexane (2 : 1) at room temperature: A, *E,E*; B, *Z,Z*; C, *E,Z*

(E,Z)-*Bis-*p*-cumenylmethylenesuccinic Anhydride C.*—This forms orange prisms on slow concentration of a solution in light petroleum; space group $P2_1/c$, a = 13.48, b = 12.58, c = 12.41 Å, β = 105°, Z = 4, U = 2 033 Å^3, D_c = 1.176

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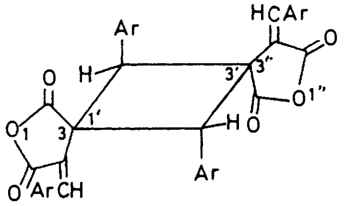
[8] H. Stobbe and R. Härtel, *Annalen*, 1911, **380**, 1, 59, 72.

g cm^{-3}; m.p. 73—75°. The mass spectrum taken at 142° and 4mA was satisfactory.

All the experimental data are compatible with the above assignment: Thus the u.v. spectra (Figure 1) are almost superposable on those of the corresponding *p*-methoxy-isomers.[1] The R_F values lie in the order B > C > A, as expected, and in keeping with the generalisation B > A given by Paetzold and Ilge.[9] The packing efficiency would be expected to be higher for the *Z,Z*- than for the *E,E*-isomer, and we calculate higher density for A than for B. Further, in most of the cases studied only the *Z,Z*-isomer is fluorescent,[9] as for compound B. Finally, the cell dimensions suggest the same assignment, but this argument is not conclusive. None of our isomers is the same as the ' dicumylideneisofulgide ' of Stobbe and Härtel,[8] which they describe as citron yellow with m.p. 112°. The structure of this material remains an open question.

*2′,4′-Di-*p*-cumenyl-4,4″-bis-*p*-cumenylmethylene-2,2″,5,5″-tetraoxotetrahydrofuran-3-spiro-1′-cyclobutane-3′-spiro-3″-tetrahydrofuran F.*—This exists in two crystal forms, (i) prisms from ethyl acetate, m.p. 231—233°, space group $P1$ or $P\bar{1}$, $a = 11.43$, $b = 10.47$, $c = 9.48$ Å, $\alpha = 81° 47'$, $\beta = 109° 18'$, $\gamma = 102° 53'$, $Z = 1$; (ii) colourless prisms by slow concentration of a light petroleum solution, m.p. 228—230°, space group $P1$ or $P\bar{1}$, $a = 13.31$, $b = 15.05$, $c = 12.89$ Å, α 112° 33′, $\beta = 89° 4'$, $\gamma = 104° 6'$, $Z = 2$ (Found: C, 79.9; H, 6.7. Calc. for $C_{48}H_{48}O_6$: C, 80.0; H, 6.7%); ($CDCl_3$) 8.84 (12 H, d, CH_3, J 7 Hz), 8.76 (12 H, d, CH_3, J 7 Hz), 7.07 (2 H, m, CH–CH_3, J 7 Hz), 4.85 (2 H, s, cyclobutane), 3.17, 2.83, 2.75, and 2.28 (16 H, aromatic), and 2.27 (2 H, m, vinyl); $\lambda_{max.}$ (methylcyclohexane) 334 nm (ε 43 500); ν (KBr) 2 950, 2 910, (CH,CH_3), 1 820, 1 760 (cyclic anhydride), 1 625 (phenyl and/or C=C), 1 594, 1 225, 1 075, 1 050, 1 000, 945, 933, and 775 cm^{-1}; molecular weight (Hitachi–Perkin-Elmer 115, ethyl acetate) 673, 669 [dimer requires 720 (monomer gives 363)]; *m/e* 720 (22%, M^+) and 360 (100); when *m/e* 720 is taken as 100 then 721 ($M^+ + 1$, 65), 702 (23), 676 ($M^+ - CO_2$, 10), 677, 603 (55), 264 (<5, stilbene derivative), and 358 (25), indicating a cyclobutane dimer. Peak heights vary between runs making structure assignment difficult. This dimer was hydrolysed by methanolic KOH followed by acidification, giving one major product (60—80%) which in turn gave a tetramethyl ester on treatment with diazomethane in ether. The suggested structure is F, with group positions and stereochemistry not established. From the photobehaviour of the solids and solutions it seems that F can be formed from B and C.



Ar = p-Pr^{i}C$_6$H$_4$

Photochemistry of the Fulgide in the Solid.—Isomer A in both crystal forms is photoactive, the rods being converted into products more rapidly than the plates. Both forms give the same products in vacuum, and these products with traces of others in air or oxygen. The main product is C; appreciable quantities of dimer F are formed after *ca.* 30% conversion, and traces of the B isomer were found.

Rods of A show reversed photochromism, a phenomenon described previously for some semicarbazones:[10] irradiation of whole or powdered rods in vacuum, air, or oxygen gives no visually observable change of colour, but on subsequent standing in the dark the samples develop a deep orange-to-red colour which in turn fades on long standing or on re-irradiation. The colour development is thermally activated: it is not observed when a sample which has been irradiated is held below 0°, but is if the sample is then warmed. The colour is associated with a broad absorption (470—>600 nm). Its intensity is marked for excitation with light of wavelength 313 or 450—560 nm, but is much weaker for exciting wavelength 340—380, 405, or 436 nm. On repeated cycling the intensity of the colour developed decreases. Partial solution in methylcyclohexane, in the absence of air, of rods which were strongly coloured in the above way gave solutions with no absorption at 460—500 nm; separate experiments showed that solutions of the corresponding 1,8a-DHPN absorb in this range and are stable under these conditions. Thus the red species is not the DHPN. The rods give no e.s.r. signals immediately after irradiation or on subsequent standing in the dark. However, both rods and plates gave very long lived signals on irradiation of freshly powdered material, but we have found no evidence that these signals are related to the photochromic phenomenon.

Solid B irradiated by sunlight in vacuum at 0—5° was converted into one main product, identical to the dimer F formed from solid A (m.p., n.m.r., u.v., mass spectrum).

Solid C irradiated by sunlight in vacuum for ten days was completely converted into a mixture giving an n.m.r. spectrum similar to that of the mixture obtained from solid A. Only A was found in high yield and it is probably the primary photoproduct. These results are in marked contrast with those obtained for solutions (see below).

Kinetic Measurements in Solution at Low Temperatures.—As solvent for these studies we used methylcyclohexane–isohexane (2 : 1). Analysis of composition was from the absorption spectra: a computer program was written which fitted the sum of the weighted known spectra of the isomers to the measured spectrum by a least-squares procedure. The input data consisted of the extinction coefficients of the isomers, the initial concentration of the solution, and the spectrum after irradiation measured at 10 nm intervals throughout the range 270—440 nm. The procedure was tested by analysing an unknown mixture of the isomers, preparing a mixture of the isomers of the calculated concentrations, and showing the identity of the spectra in the two cases.

To use this method there are required the absorption spectra of the isomers at the particular temperature used. We found that on cooling a solution of B there is a marked change in spectrum (decrease in the 400 nm band and appearance of a new band at 360 nm) on cooling below −100°. This apparently results from aggregation of the solute.[11,12] A similar but less drastic effect occurs with

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[9] R. Paetzold and H.-D. Ilge, *Journal für Signalaufzeichnungs Materialien*, 1975, **2**, 93.

[10] F. J. Wilson, I. M. Heilbron, and M. M. T. Sutherland, *J. Chem. Soc.*, 1914, **105**, 2812; I. M. Heilbron, H. E. Hudson, and D. Huish, *ibid.*, 1923, **123**, 2273.

[11] E. Fischer, *J. Phys. Chem.*, 1973, **77**, 859.

[12] M. D. Cohen, Y. Hirshberg, and G. M. J. Schmidt, *J. Chem. Soc.*, 1964, 2060.

isomer C, but no such change was found with compound A. Solutions of all the isomers were found to obey Beer's law at room temperature. Because of these spectral changes we were unable to obtain extinction coefficients for B for temperatures below −100°. Those of C at −185° could be estimated by way of completely converting A into C by irradiation at −185°, where no aggregation takes place, and very little B is formed.

(a) *Irradiation at* −185°. Irradiation of a solution of isomer A at −185° gives initially C only; beyond 50% conversion small concentrations of B are observable. From the initial portions of the curves of concentration *versus* time we calculated the quantum yield of the isomerisation: $\phi(\mathrm{A} \longrightarrow \mathrm{C}) = 0.45$. Under the same conditions isomer C undergoes a much slower reversible conversion into isomer B. In these irradiations no products other than the three isomers were obtained.

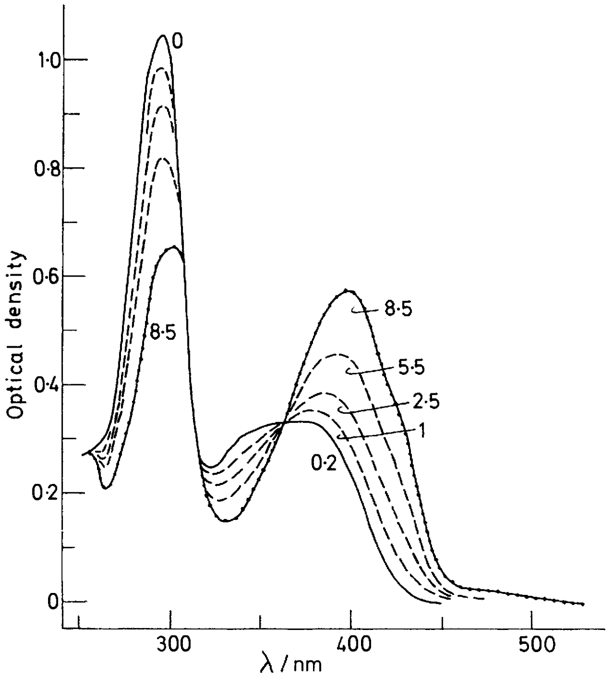

FIGURE 2 Spectra of a solution initially of isomer A (2.56 × 10^{-5}M in methyl cyclohexane–isohexane) after various times of irradiation with 334 nm light at −100° (irradiation times in min as indicated)

(b) *Irradiation at* −100°. At this temperature there occurs, in addition to the isomerisations, ring closure to the 1,8a-DHPNs (characterized by absorption at long wavelengths; $\lambda_{\text{max.}}$ *ca.* 480 nm). The DHPN concentration in the photostationary state proved to be strongly wavelength-dependent.

Irradiation of A with 334 nm light (Figure 2) gives initially results very similar to those for −185°: $\phi(\mathrm{A} \longrightarrow \mathrm{C}) = 0.48$. On further irradiation absorption due to DHPN appears; the delay on irradiation with 365 or 405 nm light is less obvious. Irradiation of B with light of wavelength 334 nm gives initially C only, without signs of DHPN (Figure 3) [$\phi(\mathrm{B} \longrightarrow \mathrm{C}) = 0.14$]; with 365 or 405 nm, DHPN formation is found, but seemingly not from the start. Irradiation of C at any of the three wavelengths gives rise to DHPN absorption immediately (*e.g.* Figure 4). The variation of the photostationary concentration of DHPN with wavelength suggests that the formation of this product is photoreversible; this was confirmed by converting it back into the butadiene(s) by light of λ > 450 nm. Figure 4 shows also the spectrum of ' pure ' DHPN obtained by assuming that curve 3 corresponds to 20% conversion.

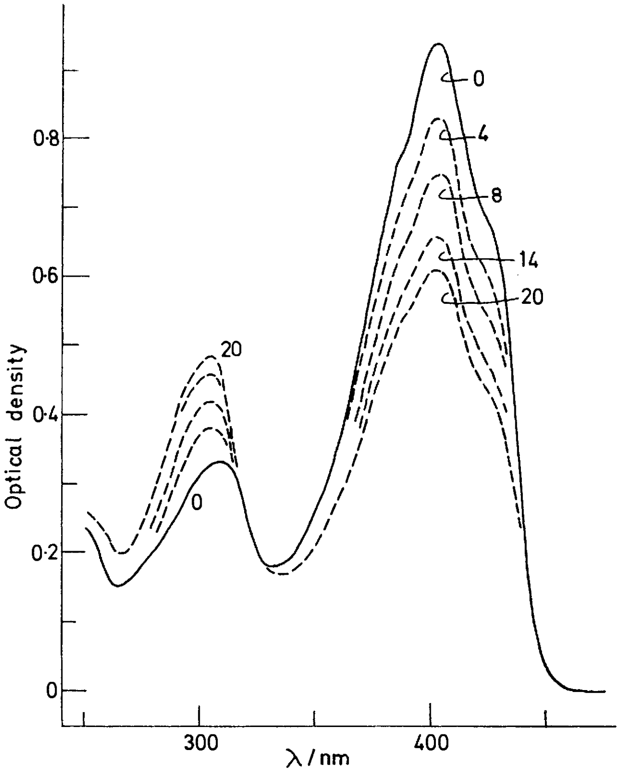

FIGURE 3 Spectra of a solution initially of isomer B (2.25 × 10^{-5}M in methyl cyclohexane–isohexane) after various times of irradiation with 334 nm light at −100° (irradiation times in min as indicated)

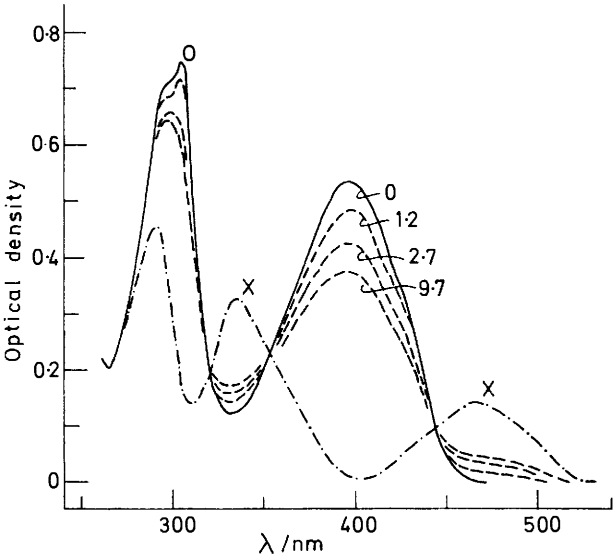

FIGURE 4 Spectra of a solution initially of isomer C (3.78 × 10^{-5}M in methyl cyclohexane–isohexane) after various times (in min as indicated) of irradiation with 405 nm light at −100°. Curve X is the spectrum of the DHPN, assuming 20% conversion in curve 2.7

This spectrum is reminiscent of that of the dihydrophenanthrenes.[13] The absorption due to the DHPN disappears on heating above room temperature.

In those cases where the absorption by DHPN was appreciable it was not possible to determine the concentrations of the various products by our method.

(c) *Prolonged irradiations.* On irradiation of A at −185° there is first established the photoequilibrium between the isomers, and then gradually a new absorption band ($\lambda_{max.}$ 334 nm) appears, while the bands near 300 and 400 nm decrease in intensity. In the case of B, present in aggregated form at this temperature, there is an initial drop only in the long-wavelength band, and subsequently the 334 nm band appears. Only in the case of C is there no change in shape or position of the initial bands during their decrease in intensity which accompanies the increase in absorption at 334 nm (Figure 5). We conclude that C is the direct precursor of the product which gives rise to this new absorption; as expected isosbestic points are found only when the isomer irradiated is C. Figure 5 also shows the 'calculated' spectrum of the dimer. The 334 nm absorption remains unchanged on warming to room temperature, so that it was possible to isolate the product. It proved to be identical to the dimer F, obtained previously from A and B in the solid state.

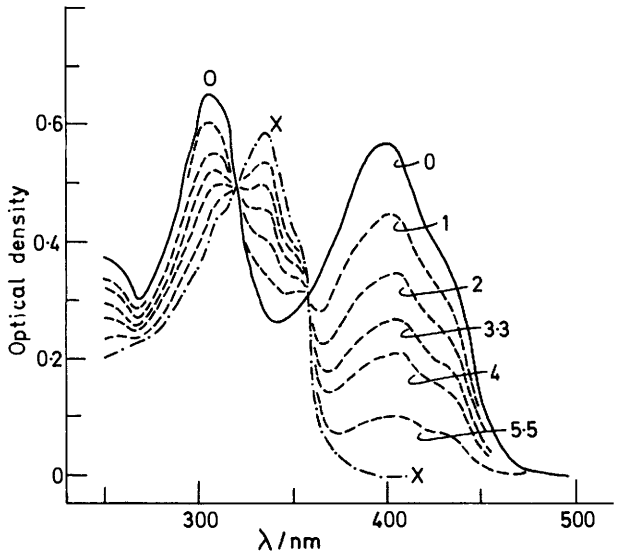

Figure 5 Spectra changes in a 'photostationary' mixture of isomers A—C (initially 2.87×10^{-5}M, A in methylcyclohexane–isohexane) on irradiation (*t*/min as indicated) with 405 nm light at −185°. Curve X is the spectrum of the dimer, extrapolated from the above, assuming no absorption of the dimer at 400 nm

One must assume that for a dimer to be formed in such a viscous medium the reactant molecules are present as aggregates. This was known to be true of B and to a lesser extent of C. The results suggest that also in the case of A cooling brings about aggregation, even though there is no corresponding marked change in absorption spectrum. In order to test this, solutions were prepared of the three isomers in methyltetrahydrofuran, a solvent which was expected to prevent aggregation as a result of its high solvation power. Indeed, cooling of these solutions to −185° gave no spectral changes suggestive of aggregation, and irradiation of the solutions at this temperature gave rise to isomerisation only, with no further changes being found on prolonged exposure to the light.

As mentioned previously, when C is irradiated with 405 nm light in methyl cyclohexane–isohexane at −100°, there occurs initially formation of DHPN. On prolonged irradiation dimer F is formed, and, because of the reversibility of the C–DHPN interconversion, there is a concomitant drop in the concentration of the DHPN.

We find that the dimer F is itself photolabile, and can be transformed reversibly at −185° to a material having $\lambda_{max.}$ 313 nm.

Because of this effect the product distribution after long-time irradiation of C is dependent on exciting wavelength. The 313 nm absorbing species was not isolated but presumably is also dimeric.

Additional data are given in Supplementary Publication No. SUP 21837 (11 p., 1 microfiche).*

We thank Dr. A. Mandelbaum for the mass spectral analyses, Mr. J. Halfon for the crystallographic constants, and Dr. J. Bernstein for writing the computer programme used in the analyses.

[5/405 *Received, 27th February,* 1975]

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II,* 1975, Index issue.

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