

## Overcrowded Molecules. Part X.<sup>1</sup> Photoreactions of Photochromic ( $\alpha$ -Phenylethylidene)(substituted methylene)succinic Anhydrides

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The photochemical, electrocyclic reactions and *E-Z* isomerisation of benzylidene-, diphenylmethylene-, and isopropylidene-( $\alpha$ -phenylethylidene)succinic anhydrides and of bis-( $\alpha$ -phenylethylidene)succinic anhydrides are reported. Cyclisation reactions are believed to occur by  $n \rightarrow \pi^*$  excitation of one of the two largely independent chromophores in the molecule, and the dependence of product composition on temperature is attributed to competing thermal processes (disrotatory ring opening and 1,5-hydrogen shifts) from the 1,8a-dihydronaphthalene intermediates. Structural assignments of the products, 1,2-dihydronaphthalene-2,3-dicarboxylic anhydrides, are based on n.m.r. studies.

In Part VII,<sup>2</sup> we reported that (*E*)- and (*Z*)-benzylidene-(diphenylmethylene)succinic anhydrides (1a) and (2a) underwent photochemical conrotatory ring closure exclusively onto one of the phenyls of the diphenylmethylene group to give the red *r*-1,*c*-8a- and *r*-1,*t*-8a-dihydronaphthalene intermediates (5a) and (6a) respectively, which underwent two competing thermal processes, *viz.* disrotatory ring opening to the isomeric succinic anhydrides (2a) and (1a), or a 1,5-hydrogen shift to give the *r*-1,*c*-2- and *r*-1,*t*-2-dihydronaphthalene-2,3-dicarboxylic anhydrides (8a) and (9a), respectively.

When (*E*)-benzylidene-(*E*)-( $\alpha$ -phenylethylidene)succinic anhydride (1b) in benzene, hexane, or chloroform, in the absence of oxygen, was exposed to radiation of

wavelength 366 nm, the solution changed rapidly from yellow to red. The colour change could be reversed thermally or by exposure to a tungsten-halogen lamp. On prolonged irradiation at 366 nm, the solution became colourless and a quantitative yield of the anhydrides (8b) and (9b) was obtained. Photochemical conrotatory ring closure, in accord with the Woodward-Hoffmann selection rules<sup>3</sup> occurs exclusively onto the phenyl of the  $\alpha$ -phenylethylidene group to give the red 1,8a-dihydronaphthalene intermediate (5b), which undergoes a thermal 1,5-hydrogen shift to the anhydride (8b) or thermal disrotatory ring opening to the succinic anhydride (2b). The latter, in turn, cyclises to the isomeric 1,8a-dihydronaphthalene intermediate (6b), which

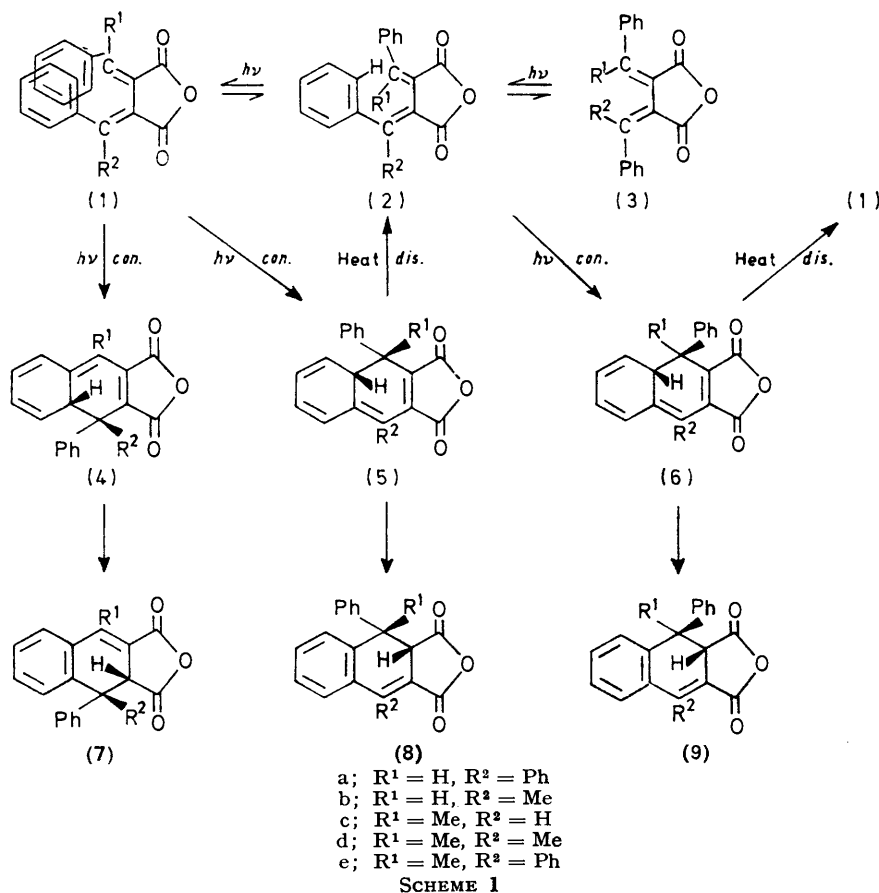
<sup>1</sup> Part IX, H. G. Heller and R. M. Megitt, *J.C.S. Perkin I*, 1974, 923.

<sup>2</sup> R. J. Hart and H. G. Heller, *J.C.S. Perkin I*, 1972, 1321.

<sup>3</sup> R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1968, **1**, 17; 'The Conservation of Orbital Symmetry,' Academic Press, New York, 1970.

undergoes a thermal 1,5-hydrogen shift to the anhydride (9b) or disrotatory ring opening back to the succinic anhydride (1b). The variation of product composition with temperature (see Table 1) indicates that the activation energy for the 1,5-hydrogen shift is lower than for the disrotatory ring opening process.

disrotatory ring opening of the 1,8a-dihydronaphthalene intermediate (6c) as a possible route for the observed *Z-E* isomerisation [(2c) → (1b)]. That ring closure of the anhydride (2c) did not occur was established as follows: on irradiation at 366 nm of an aliquot sample of the (*E,Z*)-anhydride (2c) in benzene for 30 h, the



As in the previous examples, (*E*)-benzylidene-(*Z*)-(α-phenylethylidene)succinic anhydride (2c) did not undergo photochemical ring closure onto the phenyl of the benzylidene group, accounting for the absence of the anhydride (9c) in the product and excluding thermal

solution changed from yellow to red, and 37% isomerisation of the anhydride (2c) took place [based on the amount of remaining anhydride (2c) and the yield of the anhydrides (8b) and (9b)]. A second aliquot sample was irradiated as before for the same period but with simultaneous exposure to white light from a tungsten-halogen lamp. No red colour was produced, as the white light caused rapid reversal of the 1,8a-dihydronaphthalene intermediates to the succinic anhydrides from which they were formed, and thus isomerisation and 1,5-hydrogen shifts through these intermediates were prevented; 67% of the (*E,Z*)-succinic anhydride (2c) isomerised under these conditions to give a mixture containing the (*E,E*)-, (*Z,E*)-, and (*Z,Z*)-succinic anhydrides (1b), (2b), and (3b). Exposure of a third aliquot sample to the tungsten-halogen lamp alone, for the same period, caused 33% isomerisation of the (*E,Z*)-anhydride (2c) to give a mixture containing the (*E,E*)-, (*Z,E*)-, and (*Z,Z*)-anhydrides (1b), (2b), and (3b). Thus the *Z-E* isomerisation which could have taken place through the 1,8a-dihydronaphthalene intermediate (6c) is no more than 3%. As product composition was determined by

TABLE 1

Product composition from photochemical reactions (at 366 nm) of arylmethylene-(α-phenylethylidene)succinic anhydrides

Reaction conditions			Product composition (%)					
Reactant	Solvent *	Temp. (°C)						
(1b) or (2c)	C	-8	(8b)	{	(9b)	{		
	C	19					100	0
	B	54					75	25
	B	80					65	35
	T	110					35	65
(1d)	B	9	(8d)	{	(9d)	{		
	C	54					100	0
	B	80					80	20
(2d)	B	9	(8d)	90	(9d)	10		
(2d) or (3d)	B	54	(8d)	55	(9d)	45		
	B	80	(8d)	55	(9d)	45		

No thermal isomerisation occurred at these temperatures.

\* C = chloroform, B = benzene, T = toluene.

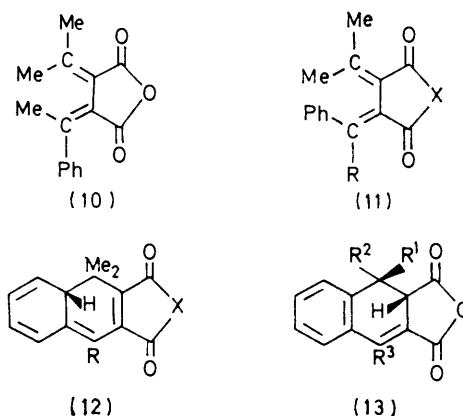
n.m.r. studies with an inherent experimental error estimated at  $\pm 2\%$ , this figure is not significant. On prolonged irradiation at 366 nm, the (*E,Z*)-succinic anhydride (2c) in benzene or chloroform, at various temperatures, gave the same product composition of the anhydrides (8b) and (9b) as was obtained on irradiation of the (*E,E*)-isomer (1b) under similar conditions (see Table 1). Direct photochemical isomerisation of the succinic anhydride (2c) to its isomer (1b) occurred prior to other rearrangement reactions.

On exposure of the (*E,E*)-succinic anhydride (1b) in benzene to u.v. and white light, a 60 : 40 photostationary state mixture of the (*E,E*)- and (*Z,E*)-succinic anhydrides (1b) and (2b) was obtained. The experiments involving simultaneous irradiation with u.v. and white light show that *Z-E* isomerisation of the benzylidene and  $\alpha$ -phenylethylidene groups and *E-Z* isomerisation of the benzylidene group take place but not *E-Z* isomerisation of the  $\alpha$ -phenylethylidene group; *cf.* the (*E*)-succinic anhydride (1e).

On irradiation at 366 nm without exclusion of oxygen, the succinic anhydride (1b) gave 1-methyl-4-phenyl-naphthalene-2,3-dicarboxylic anhydride.<sup>4</sup> As the 1,2-dihydronaphthalenes do not aromatise on prolonged irradiation under similar conditions, oxidation of the 1,8a-dihydronaphthalene intermediates (5b) and (6b) is believed to take place.

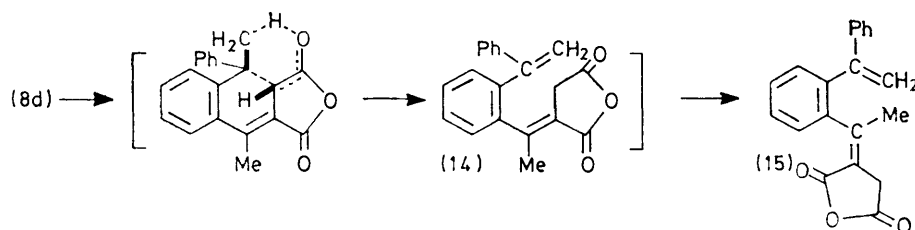
On irradiation at 366 nm, (*Z,Z*)-bis-( $\alpha$ -phenylethylidene)succinic anhydride (3d) in benzene underwent *Z-E* isomerisation to the corresponding (*E,Z*)-succinic anhydride (2d), since the same mixture of anhydrides (8d) and (9d) was obtained on irradiation of the (*E,Z*)-anhydride (2d) as initial reactant under similar conditions (see Table 1). Irradiation of (*E,E*)- and (*E,Z*)-bis-( $\alpha$ -phenylethylidene)succinic anhydrides (1d) and (2d) in

compound, m.p. 162–164° on prolonged irradiation, was reported by Stobbe<sup>5</sup> in 1911. This work was re-investigated and n.m.r. studies confirm the *Z-E* isomerisation of the (*Z*)-isomer (10) in benzene on irradiation at 366 nm, and establish the structure of the



colourless compound to be the anhydride (13;  $R^1 = R^2 = R^3 = \text{Me}$ ) formed by photochemical ring closure of the (*E*)-anhydride (11;  $R = \text{Me}$ ,  $X = \text{O}$ ), followed by a thermal 1,5-hydrogen shift.

On irradiation at 366 nm, a solution of (*E,E*)-bis-( $\alpha$ -phenylethylidene)succinic anhydride (1d) in benzene gave a quantitative yield of the anhydride (8d). On prolonged irradiation at 366 nm of this anhydride (8d) in benzene at 54°, the (*Z*)-succinic anhydride (15) was formed in near quantitative yield, presumably through a photochemical Norrish Type II reaction<sup>6</sup> of reactant (8d), followed by photochemical *E-Z* isomerisation of the resulting (*E*)-anhydride (14) (Scheme 2). Its structure was assigned from its n.m.r. spectrum which showed two doublets ( $J_{gem} 1 \text{ Hz}$ ) at  $\tau 4.45$  and 4.70, a broad



SCHEME 2

chloroform or benzene gave mixtures of 1,*r*-2-dihydro-*c*-1,4- and 1,*r*-2-dihydro-*t*-1,4-dimethyl-1-phenyl-naphthalene-2,3-dicarboxylic anhydrides (8d) and (9d) by the same sequence of reactions as described for the rearrangements of the (*E*)- and (*Z*)-succinic anhydrides (1a) and (2a), and (*E,E*)- and (*E,Z*)-succinic anhydrides (1b) and (2b). The product composition of anhydrides (8d) and (9d) is temperature dependent (see Table 1).

*Z-E* Isomerisation of (*Z*)-isopropylidene-( $\alpha$ -phenylethylidene)succinic anhydride (10) in chloroform to the yellow photochromic (*E*)-isomer (11;  $R = \text{Me}$ ,  $X = \text{O}$ ) on exposure to sunlight, and formation of a colourless

absorption at 6.92 due to the methylene hydrogens, and a triplet ( $J 2 \text{ Hz}$ ) at 7.82 due to the allylic coupled methyl group which is not deshielded by the carbonyl group of the anhydride [*cf.* (*E*)- and (*Z*)-( $\alpha$ -phenylethylidene)succinic esters<sup>7</sup>]. Double resonance irradiation at  $\tau 6.92$  caused the methyl triplet at  $\tau 7.82$  to collapse to a singlet.

(*E*)-Diphenylmethylene-( $\alpha$ -phenylethylidene)succinic anhydride (1e) in benzene underwent preferential but not exclusive photochemical ring closure onto one of the phenyls of the diphenylmethylene group to give a

<sup>5</sup> H. Stobbe, *Ber.*, 1905, **38**, 3893.

<sup>6</sup> G. R. McMillan, J. G. Calvert, and J. N. Pitts, jun., *J. Amer. Chem. Soc.*, 1964, **86**, 3602.

<sup>7</sup> H. G. Heller and M. Szewczyk, preceding paper.

<sup>4</sup> R. J. Hart, Ph.D. Thesis, University College of Wales, Aberystwyth, 1970.

25:75 mixture of 1,2-dihydro-4-methyl-1,1-diphenyl-naphthalene-2,3-dicarboxylic anhydride (7e) and 1,7-2-dihydro-*c*-1-methyl-1,4-diphenyl-naphthalene-2,3-dicarboxylic anhydride (8e) through their corresponding 1,8a-dihydronaphthalene intermediates (4e) and (5e). Neither photochemical *E-Z* isomerisation of the (*E*)-succinic

follow from the n.m.r. data recorded in Table 2. The composition of mixtures was determined by measuring the relative intensity by integration of characteristic absorptions of each component.

The cyclisation reactions of bis(arylmethylene)succinic anhydrides (1) onto one of two possible phenyl

TABLE 2

N.m.r. ( $\tau$ values, $J$ in Hz) and m.p. data for 1,2-dihydronaphthalene-2,3-dicarboxylic anhydrides [general formula (13)]											
Compound	M.p. (°C)	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	2-H	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	$J_{H,R^1}$	$J_{H,R^2}$	$J_{H,R^3}$
(8b)	148—150	H	Ph	Me	5.74oct	5.30d		7.25d	7.5		2.5
(9b)	188—189	Ph	H	Me	6.02oct		5.75d	7.37d		15.5	2.5
(8d)	185—186	Me	Ph	Me	6.15q	7.73s		7.35d			2.4
(9d)	157—158	Ph	Me	Me	5.69q		8.45s	7.27d			2.4
(7e)	229—230	Ph	Ph	Me	5.11q			7.42d			2.4
(8e)	177—179	Me	Ph	Ph	5.92s	7.66s					
(13; R <sup>1</sup> = R <sup>2</sup> = R <sup>3</sup> = Me)	163—164	Me	Me	Me	6.36l	8.15s	8.89s	7.29d			2.5

anhydride (1e) [*cf.* (*E,E*)-succinic anhydride (1b)] nor thermal disrotatory ring opening of the 1,8a-dihydronaphthalene intermediate (5e) occurred to any appreciable extent because the resulting (*Z*)-succinic anhydride

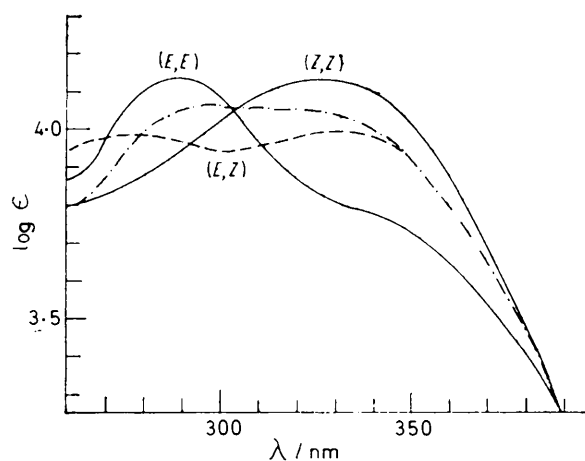


FIGURE 1 U.v. spectra of (*E,E*)-, (*E,Z*)-, and (*Z,Z*)-bis-( $\alpha$ -phenylethylidene)succinic anhydrides (1d), (2d), and (3d), and of a molar solution of a 1:1 mixture of (*E,E*) and (*Z,Z*)-anhydrides (--- · ---), in chloroform

(2e) would be expected to undergo photochemical ring closure followed by a thermal 1,5-hydrogen shift to yield the anhydride (9e) [*cf.* (2a)  $\rightarrow$  (9a)]. Anhydride (9e) could not be detected in the product.

N.m.r. studies show that in 1,2-dihydronaphthalene-2,3-dicarboxylic anhydrides (13) an equatorial hydrogen atom or methyl group at C-1 (R<sup>1</sup>) *cis* to the axial methine hydrogen at C-2 is deshielded by a carbonyl group and gives a signal at lower field than the corresponding axial hydrogen atom or methyl group (R<sup>2</sup>) *trans* to the methine hydrogen at C-2, and that a methyl group (R<sup>3</sup>) at C-4 is deshielded by a carbonyl group and gives a doublet signal owing to allylic coupling with the hydrogen atom at C-2. Derivatives (8b) and (9b), having an *ax-eq* and an *ax-ax* arrangement of methine hydrogen atoms at C-1 and C-2, give  $J_{1,2}$  values of 7.5 and 15.5 Hz respectively.<sup>2</sup> Assignment of structure and stereochemistry

<sup>2</sup> M. D. Cohen, H. W. Kaufman, D. Sinnreich, and G. M. J. Schmidt, *J. Chem. Soc. (B)*, 1970, 1035.

groups can be explained by  $n \rightarrow \pi^*$  excitation of one of two largely independent chromophores.

Evidence for independent chromophores is provided by the X-ray crystallographic analysis of (*E,E*)-dianisylidenesuccinic anhydride, which shows that the molecule is non-planar with a 30° angle between the planes of the anisylidene groups.<sup>8</sup> Non-planarity, due to steric interactions of the MeOC<sub>6</sub>H<sub>4</sub> groups in the fixed (*E,E*)-configuration, prevents effective delocalisation of the  $\pi$ -electrons over the butadiene system. The close similarity of the u.v. spectrum of (*E,Z*)-bis-( $\alpha$ -phenylethylidene)succinic anhydride (2d) with the combined spectra of the corresponding (*E,E*)- and (*Z,Z*)-succinic anhydrides (1d) and (3d) (Figure 1), supports this view as does the observation by Freudenberg and Kempermann<sup>9</sup> that

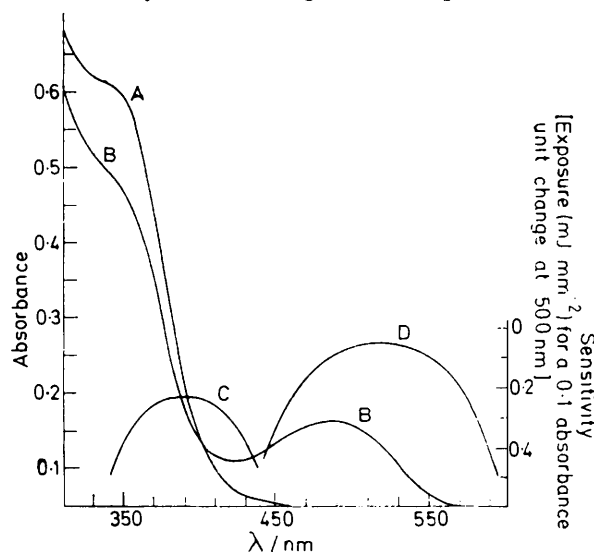
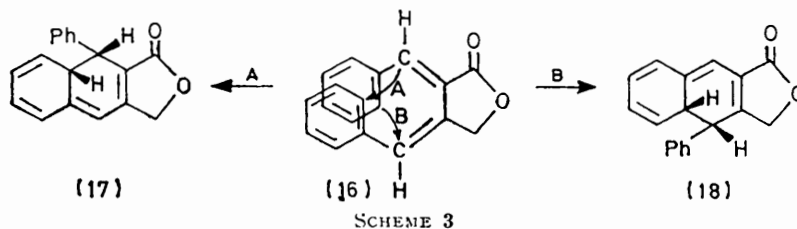


FIGURE 2 U.v. spectrum of a 10<sup>-4</sup>M solution of diphenylmethylene(isopropylidene)-*N*-phenylsuccinimide (11; R = Ph, X = NPh) in hexane, before (A) and after irradiation (B) at 366 nm, and the sensitivity to colouration (C) and to bleaching (D) of the imide in polymethyl methacrylate matrix (Tensol 6 cement, I.C.I. Ltd.)

the u.v. spectrum of dimethyl (*E,E*)-dibenzylidenesuccinate closely resembled that of methyl cinnamate and differed markedly from that of 1,4-diphenylbutadiene.

<sup>9</sup> K. Freudenberg and T. Kempermann, *Annalen*, 1957, **602**, 184.

Evidence for  $n \rightarrow \pi^*$  excitation initiating the cyclisation of bis(arylmethylene)succinic anhydrides (1) and (2) to 1,8a-dihydronaphthalene intermediates (4) and (5), is provided by studies † on the effect of wavelength of irradiation on the rate of electrocyclic ring closure of diphenylmethylene(isopropylidene)-*N*-phenylsuccinimide (11; R = Ph, X = NPh), by measuring the energy of radiation required to produce an absorbance change of 0.1 at the maximum of the long wavelength absorption band (500 nm) of the red 1,8a-dihydronaphthalene intermediate (12; R = Ph, X = NPh). The plot of sensitivity (rate of cyclisation) against wavelength of irradiating light shows that the change in sensitivity does not relate to the main absorption of the imide and that the wavelength at which sensitivity is greatest lies partly outside its main absorption band (Figure 2). It is believed that the change in sensitivity relates to the weak  $n \rightarrow \pi^*$  absorption band of the imide. Irradiation of the (*E*)-succinic anhydride (1a) below 330 nm causes *E*-*Z* isomerisation<sup>2</sup> and is presumed to involve  $\pi \rightarrow \pi^*$  excitation of the anhydride (1a).



Two paths A and B for photochemical cyclisation involving  $n \rightarrow \pi^*$  excitation of succinic anhydrides (1) and (2) to 1,8a-dihydronaphthalene intermediates (4), (5), and (6) are possible. Path A involves attack from the doubly bonded carbon of the excited state chromophore onto the *ortho*-position of the phenyl group; whereas path B involves attack from the *ortho*-position of the phenyl group of the excited state chromophore onto the double bond. As (*E,E*)-2,3-dibenzylidene- $\gamma$ -butyrolactone (16) cyclises by path A to give products from the intermediate (17) and none from intermediate (18) through path B,<sup>11</sup> it is tentatively suggested that, in an analogous manner, anhydrides (1) and (2) cyclise by path A only.

#### EXPERIMENTAL

U.v. spectra were measured for solutions in chloroform unless stated otherwise with a Unicam SP 1800 or a Hilger-Gilford reaction kinetics spectrometer; n.m.r. spectra were obtained for solutions in deuteriochloroform with a Perkin-Elmer R12 (60 MHz) or a Varian HA100 (100 MHz) spectrometer (tetramethylsilane as internal standard except when monitoring photochemical reactions when an external standard was used). Solvents were dried and fractionally distilled before use. Petroleum refers to the fraction b.p. 60–80°. Reactions were carried out under oxygen-free nitrogen, prepared by passing 'white-spot' nitrogen through

† These studies were carried out by Dr. R. M. Megit<sup>10</sup> in collaboration with Dr. R. Hurditch, Allen Clark Research Centre, The Plessey Co. Ltd., Caswell as part of a wider programme on the applications of organic photochromic compounds to optical storage and display systems, and will be reported in detail later.

Fieser's solution,<sup>12</sup> then through concentrated sulphuric acid, and then passing through a column (3 ft) of copper wool in a copper tube heated at 300°, followed by a glass spiral. The preparation of succinic anhydrides has been described previously.<sup>7</sup> Photochemical reactions were carried out for 0.1–0.5% w/v solutions of the anhydrides in benzene, or chloroform. For irradiation at 366 nm, an assembly of four 125 W mercury vapour discharge lamps with Wood's glass filters (type MBW, Thorn Lighting) in a reflecting aluminium housing were used. Normal running temperature of the photoreactor was 54°. Photoreactions at higher temperatures were carried out in boiling solvent, and at lower temperatures, in a flask with an outer glass jacket through which a cooled solution of water and ethylene glycol circulated. Photoreactions were complete when the solutions, which initially changed from yellow to red, became colourless. Solvent was removed and product composition determined by n.m.r. spectroscopy. For simultaneous irradiation at 366 nm and with white light, a 10 mm cuvette containing a solution of the succinic anhydride in deuteriochloroform was exposed to radiation on one side only, from a 250 W mercury discharge lamp (type ME/D, Thorn Lighting) with a filter (type OX1, Chance-Pilkington)

and a 150 W tungsten-halogen lamp (type A1/216, Phillips), by using a 10% transmission mirror. The progress of the reaction was monitored by measuring the n.m.r. spectrum of the solution periodically.

(*E,E*)-Benzylidene-( $\alpha$ -phenylethylidene)succinic anhydride (1b) (250 mg) in deuteriochloroform (4 ml) was irradiated (50 h) with u.v. and white light simultaneously to give a photostationary state consisting of a 60:40 mixture of (*E,E*)- and (*Z,E*)-succinic anhydrides (1b) and (2b) respectively. Separation could not be achieved by fractional crystallisation or column chromatography on silica gel with petroleum as eluant. The (*Z,E*)-isomer showed n.m.r. signals at  $\tau$  3.48br (1H, s, olefinic hydrogen shielded by the phenyl group) and 7.16 (3H, d, *J* 1 Hz, long range coupling with the olefinic hydrogen, CH<sub>3</sub>).

(*E,Z*)-Benzylidene-( $\alpha$ -phenylethylidene)succinic anhydride (2c) under similar conditions gives a 45:18:12:25 mixture of (*E,Z*)-, (*E,E*)-, (*Z,E*)-, and (*Z,Z*)-succinic anhydrides (2c), (1b), (2b), and (3b). Removal of solvent followed by trituration with ether gave the sparingly soluble (*Z,Z*)-benzylidene-( $\alpha$ -phenylethylidene)succinic anhydride (3b), pale yellow plates (from benzene-petroleum), m.p. 195–196° (Found: C, 78.2; H, 4.8. C<sub>18</sub>H<sub>14</sub>O<sub>3</sub> requires C, 78.65; H, 4.9%),  $\lambda_{\text{max}}$  352 nm (log  $\epsilon$  4.30),  $\tau$  1.95–2.80 (11H, complex m, olefinic hydrogen and aromatics), 7.38 (3H, d, *J* 1 Hz, long range coupling with olefinic hydrogen, CH<sub>3</sub>). The anhydrides (8b) and (9b), obtained on irradiation of the (*E,E*)- or (*E,Z*)-succinic anhydrides (1b) and

<sup>10</sup> R. M. Megit, Ph.D. Thesis, University College of Wales, Aberystwyth, 1972.

<sup>11</sup> R. J. Hart, H. G. Heller, and P. J. Strydom, Paper 28, IVth I.U.P.A.C. Symposium on Photochemistry, Baden-Baden, 1972

<sup>12</sup> L. F. Fieser, *J. Amer. Chem. Soc.*, 1924, **24**, 2639.

(2c) in benzene (see Table 1) were separated by fraction-crystallisation from carbon tetrachloride. *r*-1,*c*-2-*Dihydro-4-methyl-1-phenylnaphthalene-2,3-dicarboxylic anhydride* (8b) formed needles, m.p. 148—150° (Found: C, 79.2; H, 4.9.  $C_{19}H_{14}O_3$  requires C, 78.6; H, 4.9%),  $\lambda_{max}$  (hexane) 226, 233, and 296 nm (log  $\epsilon$  4.18, 4.15, and 4.11). *r*-1,*t*-2-*Dihydro-4-methyl-1-phenylnaphthalene-2,3-dicarboxylic anhydride* (9b) formed needles, m.p. 188—189° (Found: C, 78.4; H, 4.9%),  $\lambda_{max}$  302 (log  $\epsilon$  3.97).

1,2-Dihydro-1,1,4-trimethylnaphthalene-2,3-dicarboxylic anhydride (13;  $R^1 = R^2 = R^3 = Me$ ) was obtained in quantitative yield from the photorearrangement of (*Z*)- or (*E*)-isopropylidene-( $\alpha$ -phenylethylidene)succinic anhydride (10) or (11;  $R = Me$ ,  $X = O$ ) in benzene, and formed needles (from chloroform-petroleum), m.p. 163—164° (lit.,<sup>5</sup> 162—164°) (Found: C, 74.35; H, 5.75. Calc. for  $C_{15}H_{14}O_3$ : C, 74.35; H, 5.8%),  $\lambda_{max}$  (hexane) 228, 235, and 299 nm (log  $\epsilon$  4.13, 4.14, and 4.17).

On boiling (100 h) in xylene at 140°, the (*Z*)-succinic anhydride (10) isomerised to the (*E*)-isomer (11;  $R = Me$ ,  $X = O$ ), yellow needles from petroleum, m.p. 132—133°. The mixed m.p. with an authentic sample<sup>7</sup> was undepressed.

The anhydrides (8d) and (9d), obtained on irradiation at 366 nm of the (*E,E*)-, (*E,Z*)-, and (*Z,Z*)-succinic anhydrides (1d), (2d), and (3d) in benzene (see Table 1) were separated by dissolving them in ether, adding petroleum, and allowing the ether to evaporate off slowly at room temperature.

1,*r*-2-*Dihydro-t*-1,4-dimethyl-1-phenylnaphthalene-2,3-dicarboxylic anhydride (9d) separated in needles, m.p. 157—158° (Found: C, 79.0; H, 5.4.  $C_{20}H_{16}O_3$  requires C, 78.9; H, 5.3%),  $\lambda_{max}$  304 (log  $\epsilon$  4.13). 1,*r*-2-*Dihydro-c*-1,4-dimethyl-1-phenylnaphthalene-2,3-dicarboxylic anhydride (8d) was obtained from a second crop of crystals, needles, m.p. 185—186° (Found: C, 78.8; H, 5.4%),  $\lambda_{max}$  304 nm (log  $\epsilon$  4.11).

On prolonged irradiation at 366 nm of the (*E,E*)-succinic anhydride (1d) or its photoproduct, the anhydride (8d), in benzene at 54°, (*Z*)-{ $\alpha$ -[*o*-(1-phenylvinyl)phenyl]ethylidene}-succinic anhydride (15) was formed in near quantitative yield.

(*E*)-Diphenylmethylene-( $\alpha$ -phenylethylidene)succinic anhydride (1e) (100 mg) in toluene (20 ml) was irradiated (24 h) at 54°. Solvent was removed and the residue crystallised from ether-petrol as previously described. 1,2-*Dihydro-4-methyl-1,1-diphenylnaphthalene-2,3-dicarboxylic anhydride* (7e) separated in needles, m.p. 229—230° (Found: C, 82.0; H, 5.1.  $C_{25}H_{18}O_3$  requires C, 81.9; H, 4.95%),  $\lambda_{max}$  305 nm (log  $\epsilon$  4.01). A later crop of crystals gave 1,*r*-2-*dihydro-c*-1-*methyl-1,4-diphenylnaphthalene-2,3-dicarboxylic anhydride* (8e), plates, m.p. 177—179° (Found: C, 81.7; H, 5.1%),  $\lambda_{max}$  312 nm (log  $\epsilon$  4.04).

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