Overcrowded Molecules. Part IX.[1] Fatigue-free Photochromic Systems involving (E)-2-Isopropylidene-3-(mesitylmethylene)succinic Anhydride and N-Phenylimide

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(E)-2-Isopropylidene-3-(mesitylmethylene)succinic anhydride and N-phenylimide undergo reversible photochemical conrotatory ring closure reactions to form 1,8a-dihydronaphthalene intermediates, which do not experience ring opening up to 160°. This is presumably because of steric interactions between the 1- and 8a-methyl substituents which must occur in the allowed disrotatory mode. Neither a methyl shift nor elimination of ethane occurs at this temperature: these thermally stable photochromic systems thus do not exhibit irreversible side reactions.

PHOTOCHROMIC properties in organic molecules arise usually from heterolytic or homolytic cleavage of sigma bonds to give ionic, dipolar, or radical coloured species, which recombine or undergo irreversible side reactions often involving oxygen or solvent. In the case of spiropyrans and related systems, small amounts of degradation products markedly affect the photochromic properties of the system.[2] Salicylaldehyde anils are claimed to be free from fatigue but they are photochromic only in the crystal modification or in rigid glassy solutions at low temperatures.[3-5]

Fulgides and fulgimides generally show a yellow-to-red colour change on irradiation at 366 nm, which is reversed by white light. The red 1,8a-dihydronaphthalene intermediates which are formed undergo side reactions including thermal disrotatory ring opening, a thermal 1,5-hydrogen shift to yield 1,2-dihydronaphthalene derivatives, and, in some cases, oxidation to fully aromatic compounds.[6,7] On irradiation, the colour of a

[1] Part VIII, J. S. Hastings and H. G. Heller, *J.C.S. Perkin I*, 1972, 1839.

[2] 'Photochromism,' ed. G. H. Brown, Wiley-Interscience, New York, 1971.

[3] M. D. Cohen. G. M. J. Schmidt, and S. Flavian, *J. Chem. Soc.*, 1964. 2041.

[4] M. D. Cohen, Y. Hirshberg, and G. M. J. Schmidt, *J. Chem. Soc.*, 1964, 2051.

[5] R. Potashnik and M. Ottolenghi, *J. Chem. Phys.*, 1969, 51, 3671.

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

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

solution of (E)-2-benzylidene-3-isopropylidene-N-phenylsuccinimide (2; Ar = Ph) in benzene changed rapidly from pale yellow to orange-red; then on prolonged irradiation the solution became colourless and a quantitative yield of 1,2-dihydro-1,1-dimethyl-N-phenylnaphthalene-2,3-dicarboximide (4) was obtained, formed through a thermal 1,5-hydrogen shift in the 1,8a-dihydronaphthalene intermediate (3; R = H).
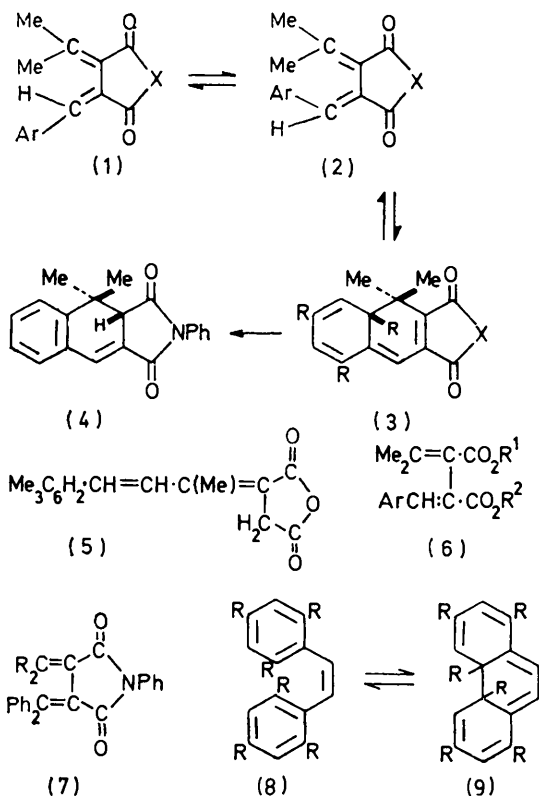
Irradiation of the pale yellow (E)-2-isopropylidene-3-(mesitylmethylene)succinic anhydride and N-phenylimide (2; Ar = mesityl) at 366 nm in the crystal state, in a rigid plastic matrix, and in benzene produced a red colouration attributed to the 1,8a-dihydronaphthalene intermediates (3; R = Me). The colour change was reversed on exposure to white light but not by heating to 160°. On prolonged irradiation, EZ-isomerisation occurred, giving, in deuteriochloroform solutions, photostationary systems consisting of 70% (E)- and 30% (Z)-anhydride, and of 74% (E)- and 26% (Z)-N-phenylimide, respectively. Further irradiation of the solutions in sealed tubes for 400 h at 54° and then for 200 h at 160° caused no change, and no other products were detected.

Whereas thermal 1,5-hydrogen shifts are well-documented,[8] thermal and photochemical 1,3- and 1,5-methyl shifts are rare.[9] The *ortho*-methyl substituents in the (E)-anhydride and the (E)-N-phenylimide (2; Ar = mesityl) prevent a 1,5-shift in the 1,8a-dihydronaphthalene intermediates (3; R = Me). Further, the allowed

[8] R. B. Woodward and R. Hoffman, ' The Conservation of Orbital Symmetry,' Academic Press, New York, 1970.

thermal disrotatory ring opening reaction did not occur at 160°, presumably because of steric interaction between the 1- and 8a-methyl groups. Ring opening of the red hexamethyldihydrophenanthrene (9; R = Me) is twenty times slower at 25° than of the unsubstituted hydrocarbon (9; R = H).[10]

Although the anhydride and the N-phenylimide (2; Ar = mesityl) gave thermally stable fatigue-free red 1,8a-dihydronaphthalene intermediates, their rate of photocolouration was low compared with those of other fulgimides, *e.g.* (7; R = Ph or Me) (see Table 1). In

TABLE 1

Photocolouration reactions

Imide	Thermal half-life ($t_{\frac{1}{2}}$/min) at 21 °C	Colouring at 390—405 nm; O.D. change of 0·1 at 490 nm. Exposure in mJ mm⁻²
(2; Ar = mesityl, X = NPh)	∞	10
(7; R = Ph)	180	0·13
(7; R = Me)	20	0·55

Samples in rigid plastic matrix.

These studies were carried out in collaboration with Dr. R. Hurditch, Allen Clark Research Centre, Plessey Co. Ltd., Caswell, as part of a wider programme on applications of organic photochromic compounds to optical storage and display. and will be reported in detail later.

this respect, the anhydride and imide (2; Ar = mesityl) resemble *cis*-hexamethylstilbene (8; R = Me), which undergoes photocolouration with a much lower quantum
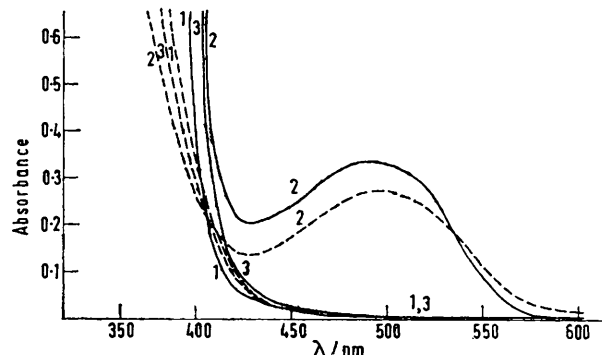
Spectral changes in irradiation of 2-diphenylmethylene-3-isopropylidene-N-phenylsuccinimide (7; R = Me) (initial solution 1·63 × 10⁻⁴M in toluene) (– – – –) and (E)-2-isopropylidene-3-(mesitylmethylene)succinic anhydride (2; Ar = mesityl, X = O) (initial solution 1·28 × 10⁻²M in benzene) (———), at 21° in a 10 mm cell; curve 1, spectrum prior to irradiation; curve 2, spectrum showing maximum colouration after irradiation at 366 mm; curve 3, spectrum after exposure of coloured solution to white light.

yield than does *cis*-stilbene (8; R = H).[10] The Figure shows parts of the spectra of the anhydride (2; Ar = mesityl, X = O) and the imide (7; R = Me) before and after u.v. irradiation, and after decolouration with white light.

Condensation of benzaldehyde with diethyl isopropylidenesuccinate gave the (E)-2-benzylidene-3-isopropylidenesuccinic half ester (6; Ar = Ph, R^1 = H, R^2 = Et),

[9] V. Boekelheide and E. Sturm, *J. Amer. Chem. Soc.*, 1969, **91**, 902.

[10] K. A. Muszkat and E. Fischer, *J. Chem. Soc. (B)*, 1967, 662.

which was hydrolysed to the diacid (6; Ar = Ph, $R^1 = R^2 = H$) and thence converted into the (E)-anhydride (2; Ar = Ph, X = O). Treatment of the anhydride with aniline in benzene gave a mixture of succinamic acids which reacted with acetyl chloride to yield the N-phenylimide (2; Ar = Ph, X = NPh). No Z-isomers were detected in these reactions.

Our investigations and a literature survey have shown that aromatic aldehydes condense with succinic esters to give exclusively (E)-arylmethylenesuccinic acid derivatives.[6] The present studies demonstrate that aromatic aldehydes with ortho-substituents are an exception to this rule. ortho-Substituents appear to disturb the fine balance between the steric and electronic effects controlling the stereoselectivity of the reaction.

The (Z)-2-isopropylidene-3-(mesitylmethylene)succinic half ester (6; Ar = mesityl, $R^1 = H$, $R^2 = Et$) was obtained in 76% yield, as the sole product from the condensation of mesitaldehyde with diethyl isopropyl-idenesuccinate in the presence of an equimolar amount of potassium t-butoxide in t-butyl alcohol. Base-catalysed hydrolysis to the diacid, followed by ring closure to the anhydride (1; Ar = mesityl, X = O) with acetyl chloride was not accompanied by ZE-isomerisation.

The (E)-2-isopropylidene-3-(mesitylmethylene)succinic half ester (6; Ar = mesityl, $R^1 = H$, $R^2 = Et$) was obtained as the sole product in 86% yield by using the same reactants but in the presence of a three molar excess of potassium t-butoxide in t-butyl alcohol. Hydrolysis of the half ester to the diacid, reaction of the half ester with anilinomagnesium bromide to give the succinamic acids, and ring closure of the succinamic acids and the diacids with acetyl chloride to give the imide and the anhydride (2; Ar = mesityl) were not accompanied by any detectable EZ-isomerisation. The only other product isolated along with the anhydride (2; Ar = mesityl, X = O) was a small amount of (E,E)-(3-mesityl-1-methylprop-2-enylidene)succinic an-hydride (5), which is believed to be formed via the condensation of diethyl isopropenylsuccinate (a by-product from the Stobbe condensation of acetone with diethyl succinate to yield diethyl isopropylidene-succinate [11]) with mesitaldehyde. Condensation of mesi-tylvinyl methyl ketone with diethyl succinate in the presence of potassium t-butoxide in t-butyl alcohol gave only (Z)-[(2E)-3-mesityl-1-methylprop-2-enylidene]-succinic anhydride (5). Assignment of stereochemistry to the isomers (5) was based on n.m.r. spectra. The (E,E)-anhydride showed an allylically coupled methyl group deshielded by the carbonyl, giving a triplet centred at τ 7·40. The (E,Z)-anhydride, in the absence of this deshielding influence, showed the corresponding triplet centred at τ 7·81.

From the condensation of 2,6-dichlorobenzaldehyde with diethyl isopropylidenesuccinate in the presence of potassium t-butoxide in t-butyl alcohol under a variety of conditions, only the (Z)-2,6-dichlorobenzylidene-(isopropylidene)succinic half ester (6; Ar = $2,6\text{-}Cl_2C_6H_3$,

$R^1 = Et$, $R^2 = H$) was obtained, and this was converted into the (Z)-diacid and hence into the (Z)-anhydride (1; Ar = $2,6\text{-}Cl_2C_6H_3$, X = O). No ZE-isomerisation was detected. On irradiation at 366 nm in benzene, a photostationary system containing 80% (E)- and 10% (Z)-anhydride was obtained, but no photochromism was observed. No degradation or rearrangement products were detected after further irradiation of the equilibrium mixture for 400 h at 40°.

The stereochemistry of the (E)- and (Z)-half esters, the dimethyl esters, the anhydrides, and the imides and

TABLE 2

N.m.r. data (τ values) for arylmethylene(isopropylidene)-succinic acid derivatives

	=CH	CH₃	CH₃
Ar = mesityl			
(Z)-Anhydride (1; X = O)	2·50	7·38	7·59
(E)-Anhydride (2; X = O)	2·20	7·55	8·72
(Z)-Imide (1; X = NPh)	2·61	7·36	7·63
(E)-Imide (2; X = NPh)	2·17	7·57	8·75
(Z)-Half ester (5; $R^1 = H$, $R^2 = Et$)	3·16	7·70	7·94
(E) Half ester (5; $R^1 = H$, $R^2 = Et$)	2·10	7·68	8·46
(Z)-Diester (5; $R^1 = R^2 = Me$)	3·12	7·70	7·95
(E)-Diester (5; $R^1 = R^2 = Me$)	2·17	7·72	8·45
Ar = 2,6-dichlorophenyl			
(Z)-Half ester (5; $R^1 = H$, $R^2 = Et$)	3·30	7·66	7·86
(Z)-Anhydride (1; X = O)	2·62	7·36	7·55
(E)-Anhydride (2; X = O)	2·42	7·55	8·62
Ar = phenyl			
(Z)-Anhydride (1; X = O)	2·4	7·42	7·60
(E)-Anhydride (2; X = O)	2·28	7·52	8·38
(E)-Imide (2; X = NPh)	2·34	7·60	8·45
Imide (7; R = Me)		7·66	8·70

the compositions of mixtures of isomers were determined by n.m.r. spectroscopy. In (E)-arylmethylene(iso-propylidene)succinic acid derivatives the olefinic hydro-gen atom and one of the methyl groups are deshielded by the carbonyl groups, and the other methyl group is shielded by the aryl group. The (Z)-isomers show the olefinic proton signal at higher field and that of the methyl group trans to the carbonyl at lower field (by ca. 1 p.p.m.) [6] (see Table 2).

EXPERIMENTAL

U.v. spectra were measured with a Unicam SP 1800A spectrometer; n.m.r. spectra were obtained for solutions in deuteriochloroform with a Perkin-Elmer R12 (60 MHz) spectrometer (tetramethylsilane as internal standard except in photochemical reactions when an external standard was used). Solvents and reactants were carefully purified before use. Reaction mixtures were acidified to pH 2 with 5M-hydrochloric acid. Petrol refers to light petroleum, b.p. 60—80°. For photoreactions, an assembly of four 125 W mercury discharge lamps (type MBW/U, A.E.I. Lamp and Lighting Co., Leicester) with Wood's glass filters was used. Samples in rigid plastic matrix were prepared by dissolving the imides in a polyester monomer (Plasticraft, supplied by Turner Research Laboratories, Leeds) which was then polymerised at 60°. Films were lapped with emery paper to a thickness of ca. 1 mm and polished.

(E)-2-Benzylidene-3-isopropylidene-N-phenylsuccinimide

[11] C. G. Overberger and C. W. Roberts, J. Amer. Chem. Soc., 1949, 71, 3618.

(2; Ar = Ph, X = NPh).—The crude succinamic acids obtained from (E)-2-benzylidene-3-isopropylidenesuccinic anhydride [12] (3·6 g) and aniline (1·75 g) in benzene (100 ml) after boiling for 3 h were dissolved in acetyl chloride (100 ml) and the solution was boiled for 2 h. Acetyl chloride was removed and the residue was crystallised from petrol giving the N-phenylimide (2·3 g), pale yellow needles, m.p. 123° (Found: C, 79·2; H, 5·7; N, 4·6. $C_{20}H_{17}NO_2$ requires C, 79·2; H, 5·7; N, 4·6%), $\lambda_{max.}$ (CHCl$_3$) 257 and 315 nm (log ε 4·30 and 4·20), τ 2·34 (1H, s, olefinic), 2·50—2·70 (10H, complex m, ArH), 7·60 (3H, s, Me cis to CO), and 8·45 (3H, s, Me trans to CO).

2-Diphenylmethylene-3-isopropylidene-N-phenylsuccinimide (7; R = Me).—The crude succinamic acids obtained from diphenylmethylene(isopropylidene)succinic anhydride [13] (15·2 g) and aniline (4·7 g) in benzene (75 ml) after boiling for 1 h were dissolved in acetyl chloride (50 ml) and the solution was boiled for 1 h. Acetyl chloride was removed and the residue crystallised from benzene–petrol giving the N-phenylimide (17 g), pale yellow needles, m.p. 210—211° (Found: C, 82·4; H, 5·6; N, 3·7. $C_{26}H_{21}NO_2$ requires C, 82·3; H, 5·6; N, 3·7%), $\lambda_{max.}$ (benzene) 280 and 341 nm (log ε 3·78 and 3·59), τ 2·45—2·75 (15H, complex m, ArH), 7·66 (3H, s, Me cis to CO), and 8·70 (3H, s, Me trans to CO).

(Z)-2-Isopropylidene-3-(mesitylmethylene)succinic Anhydride (1; Ar = mesityl, X = O).—Equimolar amounts of mesitaldehyde and diethyl isopropylidenesuccinate were added to a 10% excess of potassium t-butoxide in t-butyl alcohol and the mixture was boiled for 2 h. Solvent was removed and the residue acidified. Work-up gave the (Z)-half ester (76% yield), which was hydrolysed with aqueous ethanolic 10% potassium hydroxide; the (Z)-diacid was precipitated by addition of hydrochloric acid. A solution of the dry diacid in acetyl chloride was boiled for 1 h. Acetyl chloride was removed and the residue crystallised from benzene–petrol giving the anhydride (72% yield), pale yellow plates, m.p. 140—141° (Found: C, 76·2; H, 6·7. $C_{17}H_{18}O_3$ requires C, 75·5; H, 6·7%), $\lambda_{max.}$ (EtOH) 271 and 336 nm (log ε 4·04 and 3·79), τ 2·50 (1H, s, olefinic), 3·05 (2H, s, ArH), 7·38 (3H, s, Me cis to CO), 7·59 (3H, s, Me trans to CO), 7·67 (3H, s, p-Me), and 7·77 (6H, s, o-Me).

(E)-2-Isopropylidene-3-(mesitylmethylene)succinic Anhydride (2; Ar = mesityl, X = O).—Condensation was carried out as in the previous experiment in the presence of a 300% excess of potassium t-butoxide in t-butyl alcohol, giving the (E)-half ester in 86% yield. A sequence of reactions similar to that used for the (Z)-isomer gave the (E)-anhydride (48%), pale yellow needles, m.p. 191—192° (from petrol) (Found: C, 75·5; H, 6·9%), $\lambda_{max.}$ (EtOH) 232 and 293 nm (log ε 3·91 and 4·25), τ 2·20 (1H, s, olefinic), 3·12 (2H, s, ArH), 7·55 (3H, s, Me cis to CO), 7·69 (3H, s, p-Me), 7·84 (6H, s, o-Me), and 8·72 (3H, s, Me trans to CO). A second small crop of crystals from the petrol mother liquors gave (E,E)-(3-mesityl-1-methylprop-2-enylidene)-succinic anhydride (5), pale yellow needles, m.p. 130—131° (from petrol) (Found: C, 76·0; H, 6·7. $C_{17}H_{18}O_3$ requires C, 75·5; H, 6·7%), $\lambda_{max.}$ (EtOH) 310 nm (log ε 4·24), τ 2·65 (1H, d, $J_{3,4}$ 16 Hz, olefinic), 3·04 (2H, s, ArH), 3·60 (1H, d, $J_{3,4}$ 16 Hz, olefinic), 6·40 (2H, ill-defined q, CH$_2$), 7·40 (3H, t, J 2 Hz, Me cis to CO), and 7·65 (9H, s, o- and p-Me).

The n.m.r. spectra of the (E)- and (Z)-mesitylmethylene-

[12] H. Stobbe, Ber., 1905, **38**, 3893.
[13] H. Stobbe, Ber., 1905, **38**, 3673.
[14] D. V. N. Hardy, J. Chem. Soc., 1936, 398.

succinic half esters, dimethyl esters (prepared from the diacids with ethereal diazomethane) and anhydrides showed that no isomerisation occurred on hydrolysis or treatment with acetyl chloride.

(Z)-[(2E)-3-Mesitylprop-2-enylidene]succinic Anhydride (5).—Mesitylvinyl methyl ketone (9·4 g) and diethyl succinate (8·7 g) were added to potassium t-butoxide [from potassium (2 g)] in t-butyl alcohol (100 ml) and the mixture was boiled for 2 h. The half ester was hydrolysed and the diacid treated with acetyl chloride to give the (Z,E)-anhydride, obtained as pale yellow prisms, m.p. 160—161° (from benzene–petrol), $\lambda_{max.}$ (EtOH) 235 and 289 nm (log ε 4·18 and 4·29), τ 1·90 (1H, d, $J_{3,4}$ 16 Hz, olefinic), 2·75 (1H, d, $J_{3,4}$ 16 Hz, olefinic), 3·04 (2H, s, ArH), 6·38 (2H, ill-defined q, CH$_2$), 7·62 (6H, s, o-Me), 7·69 (3H, s, p-Me), and 7·81 (3H, t, J 2 Hz, Me trans to CO).

(E)-2-Isopropylidene-3-(mesitylmethylene)-N-phenylsuccinimide (2; Ar = mesityl, X = NPh).—The (E)-2-isopropylidene-3-(mesitylmethylene)succinic half ester (6; Ar = mesityl, R^1 = H, R^2 = Et) (1·5 g) in ether (100 ml) was added to a solution of anilinomagnesium bromide [14] [prepared by addition of aniline (0·93 g) to ethylmagnesium bromide, obtained from the reaction of ethyl bromide (1·09 g) with magnesium (0·24 g) in ether]. The mixture was acidified and the liberated succinamic acids were extracted with ether. The solution was dried (MgSO$_4$), filtered, and evaporated. The crude succinamic acids were dissolved in acetyl chloride (30 ml) and the solution was boiled for 1 h. Acetyl chloride was removed and the residue crystallised from petrol giving the N-phenylimide, pale yellow needles, m.p. 180—181° (Found: C, 80·6; H, 6·6; N, 4·1. $C_{23}H_{23}NO_2$ requires C, 80·0; H, 6·7; N, 4·1%), $\lambda_{max.}$ (hexane) 256 and 310 nm (log ε 4·32 and 4·02), τ 2·17 (1H, s, olefinic), 2·61 (5H, s, Ph), 3·16 (2H, s, ArH), 7·57 (3H, s, Me cis to CO), 7·70 (3H, s, p-Me), 7·82 (6H, s, o-Me), and 8·75 (3H, s, Me trans to CO).

(Z)-2-[2,6-Dichlorobenzylidene]-3-isopropylidenesuccinic Anhydride (1; Ar = 2,6-Cl$_2$C$_6$H$_3$, X = O).—Equimolar amounts of 2,6-dichlorobenzaldehyde and diethyl isopropylidenesuccinate were added to a 100% excess of potassium t-butoxide in t-butyl alcohol and the mixture was boiled for 1 h. The crude (Z)-half ester was converted into the (Z)-anhydride by the method already described, giving needles (from acetic acid), m.p. 205—206° (Found: C, 53·8; H, 3·9. $C_{14}H_{10}Cl_2O_3$,AcOH requires C, 53·8; H, 3·95%), $\lambda_{max.}$ (EtOH) 216, 251, and 269 nm (log ε 4·34, 3·02, and 3·44), τ 2·54—2·78 (2H, m, ArH), 2·62 (2H, s, ArH and olefinic), 7·36 (3H, s, Me trans to CO), and 7·55 (3H, s, Me cis to CO).

Photoreactions.— 1,2-Dihydro-1,1-dimethyl-N-phenylnaphthalene-2,3-dicarboximide (4) was obtained in quantitative yield from photorearrangement of (E)-2-benzylidene-3-isopropylidene-N-phenylsuccinimide (2; Ar = Ph, X = NPh) (0·5 g) in benzene (40 ml) and petrol (360 ml) at 366 nm. The imide (4) formed needles (from petrol), m.p. 157—158° (Found: C, 79·2; H, 5·6; N, 4·5. $C_{20}H_{17}NO_2$ requires C, 79·2; H, 5·7; N, 4·6%), τ 2·30—2·80 (9H, m, ArH), 2·41 (1H, d, $J_{2,4}$ 2·75 Hz, 4-H), 6·43 (1H, d, $J_{2,4}$ 2·75 Hz, 2-H), 8·07 (3H, s, equatorial Me deshielded by CO), and 8·83 (3H, s, axial Me).

A solution of (E)-2-isopropylidene-3-(mesitylmethylene)-N-phenylsuccinimide (2; Ar = mesityl, X = NPh) (100 mg) in deuteriochloroform (0·6 ml) in a sealed n.m.r. tube was irradiated (366 nm) at 54° for 400 h. The colour changed from pale yellow to deep red and a photostationary

system containing 74% (E)- and 26% (Z)-anhydride was reached within 24 h. (On heating at 160° in the vapour of boiling cyclohexanol, the red colour did not fade.) No further change occurred on irradiation at 160° for a subsequent 200 h. The ratio of imides was monitored by measuring the relative intensities of the methyl n.m.r. absorptions at τ 8·75 [(E)-imide] and 7·36 [(Z)-imide] and the relative intensities of the olefinic absorptions at τ 2·17 and 2·62, respectively. No other products were detected by n.m.r. spectroscopy or by t.l.c. The concentration of the red 1,8a-dihydronaphthalene intermediate (3; R = Me, X = PhN) was too low to be detected by n.m.r. spectroscopy. On exposure to white light, the intermediate underwent photoreversal to the (E)-imide with regeneration of the pale yellow colour. No decrease was detected in absorbance at the maximum of the long-wavelength band at 490 nm for the 1,8a-dihydronaphthalene intermediate (3; R = Me) (Hilger–Gilford reaction kinetics spectrometer) over a period of 80 h at room temperature. (Z)-2-Isopropylidene-3-(mesitylmethylene)-N-phenylsuccinimide (1; Ar = mesityl, X = NPh) could not be separated from its (E)-isomer (2) by column chromatography or fractional crystallisation. Its n.m.r. spectrum [superimposed on that of the (E)-imide] showed τ 2·62 (1H, s, olefinic), 2·61 (5H, s, Ph), 3·16 (2H, s, ArH), 7·36 (3H, s, Me *cis* to CO), 7·63 (3H, s, Me *trans* to CO), and 7·78 (9H, s, *o*- and *p*-Me).

Solutions of (E)- and (Z)-isopropylidene(mesitylmethylene)succinic anhydrides (2) and (1) (Ar = mesityl, X = O) in deuteriochloroform in sealed n.m.r. tubes were irradiated under the same conditions as described for the imide (2; Ar = mesityl, X = NPh). Colours of solutions changed from pale yellow to deep red, and the same photostationary system was obtained for each solution, consisting of 70% (E)- and 30% (Z)-anhydride. The ratio of anhydrides was monitored by measuring the relative intensities of the methyl n.m.r. absorptions at τ 8·72 and 7·38 for (E)- and (Z)-anhydride, respectively. The red 1,8a-dihydronaphthalene intermediate was stable at 160° but underwent photoreversal with regeneration of the pale yellow colour when exposed to white light.

A solution of (Z)-2-[2,6-dichlorobenzylidene]-3-isopropyl-idenesuccinic anhydride (1; Ar = 2,6-$Cl_2C_6H_3$, X = O) (50 mg) in deuteriochloroform (0·5 ml) in an n.m.r. tube was irradiated as before for 500 h. The colour changed from pale to deep yellow but no colour reversal occurred on exposure to white light. The photostationary state showed 90% (E)- and 10% (Z)-anhydride. No n.m.r. absorptions due to degradation, elimination, or rearrangement products were detected. (E)-2-[2,6-Dichlorobenzylidene]-3-isopropylidenesuccinic anhydride (2; Ar = 2,6-$Cl_2C_6H_3$, X = O) was not isolated. Its n.m.r. spectrum [superimposed on that of the (Z)-isomer] showed τ 2·42 (1H, s, olefinic), 2·50—2·85 (3H, m, ArH), 7·53 (3H, s, Me *cis* to CO), and 8·63 (3H, s, Me *trans* to CO). The ratio of anhydrides was determined from the relative intensities of the methyl absorptions at τ 8·64 and 7·36 for the (E)- and (Z)-anhydrides, respectively.