Overcrowded Molecules. Part XIII.[1] Thermally Stable Photochromic Systems involving (*E*)-2-Isopropylidene-3-(naphthylmethylene)succinic Anhydrides and *N*-Phenylimides

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(*E*)-2-Isopropylidene-3-(α- or β-naphthylmethylene)succinic anhydrides and *N*-phenylimides undergo reversible photochemical ring closure to form orange or red 4.4a-dihydrophenanthrenes (DHPs) which are thermally stable at ambient temperature presumably because of their fused benzene rings. The potentially multiphotochromic yellow (*E.E*)-3.3′-di-isopropylidene-2.2′-(naphthalene-2.6-diyldimethylidyne)disuccinic bis-*N*-imide gives. on irradiation at 366 nm. the thermally stable red DHP. Attempts to cyclise this DHP or to detect a double ring closure of the bis-imide proved unsuccessful.

PHOTOCHROMIC organic compounds have important applications in optical information storage and display systems provided that they allow image retention indefinitely in the dark and undergo many thousands of forward and reverse colour changes without photodegradation, in conjuction with other properties. Some studies on thermally stable photochromic compounds resistant to irreversible side reactions are reported.[2]

When (*E,E*)-dibenzylidene-*N*-phenylsuccinimide (1a) in benzene was irradiated at 366 nm, the colour of the solution changed from pale yellow to red. The change could be reversed thermally or by exposure to white light. As reported previously,[3] we believe that the red colour is due to the *cis*-1,8a-dihydronaphthalene intermediate (DHN) (2a), formed by photochemical conrotatory ring-closure of the imide (1a), and that the reverse process occurs in white light. In the absence of oxygen, the DHN (2a) undergoes two competing thermal reactions: a 1,5-H shift to yield *cis*-1,2-dihydro-1,*N*-diphenylnaphthalene-2,3-dicarboximide (3a) and disrotatory ring-opening to give the (*E,Z*)-dibenzylidene-*N*-phenylsuccinimide (4a) which, in turn, undergoes photochemical ring closure followed by a 1,5-H shift to yield the *trans*-1,2-dihydronaphthalene derivative (5a). As

the rates of these competing reactions vary with temperature, there is a dramatic change in the product depending on the temperature at which the photoreaction is carried out. At 18 °C the *cis*-dihydronaphthalene (3a) was obtained in over 70% yield, and at 80 °C the reaction gave the *trans*-isomer (5a) in over 80% yield, together with 1,*N*-diphenylnaphthalene-2,3-dicarboximide as the only other product in each case. The imide (1a) is thermally stable in boiling benzene. The structures and stereochemistry of the dihydronaphthalenes (3a) and (5a) follow from their n.m.r. spectra, which show $J_{1.2}$ 7.5 and 15.0 Hz, characteristic of *cis* (*eq–ax*)- and *trans* (*ax–ax*)-arrangements of hydrogen atoms at C-1 and C-2, respectively.

In contrast, naphthalene derivatives (3c) and (5c) could not be detected as photoproducts from the irradiation of (*E,E*)-benzylidene (mesitylmethylene)succinic anhydride (1c; X = O) or *N*-phenylsuccinimide (1c; X = NPh) in benzene for 4 weeks at 54 °C. The red DHNs (9; R¹ = Ph, R² = H) and (9; R¹ =ᵢH, R² = Ph) were formed, indicating exclusive ring closure on to the mesityl group, and photoequilibration of (1c) with its geometrical isomers occurred. The DHN (9; R¹ = Ph, R² = H) is thermally stable whereas the DHN (9; R¹ = H, R² = Ph) undergoes thermal side reactions much

[1] Part XII, J. S. Hastings, H. G. Heller, and K. Salisbury, *J.C.S. Perkin I*, 1975, 1995.
[2] R. C. Bertelson in ' Techniques of Chemistry,' ed. G. H. Brown, vol. 3, ch. 10.
[3] R. J. Hart and H. G. Heller, *J.C.S. Perkin I*, 1972, 1321; H. G. Heller and M. Szewczyk *ibid.*, 1974, 1487.

more slowly (K 6.25 × 10⁻⁶ s⁻¹ at 26 °C) than the DHN (2a) (K 1.0 × 10⁻⁴ s⁻¹ at 23 °C). In the DHN (9; R^1 = Ph, R^2 = H), disrotatory ring opening is presumably prevented by steric interactions between the 1-phenyl and 8a-methyl substituents (*cf.* ref. 4) whereas in the DHN (9; R^1 = H, R^2 = Ph) steric interaction between the 1-hydrogen atom and the 8a-methyl group is less severe but still greater than the interaction between the 1- and 8a-hydrogen atoms in the DHN (2a).

Reports [5,6] that a fused benzene ring can stabilise intermediates from photoreactions and reduce or eliminate thermal side reactions suggested that naphthyl-substituted dimethylenesuccinic anhydrides and imides should be stable photochromic compounds.

Condensation of α- or β-naphthaldehyde with diethyl isopropylidenesuccinate gave the (*E*)-isopropylidene-(naphthylmethylene)succinic half ester (6; Ar = naphthyl, R^1 = H, R^2 = Et) which was hydrolysed to the diacid (6; Ar = naphthyl, R^1 = R^2 = H) and treated with acetyl chloride. The resulting anhydride (7; Ar = naphthyl, X = O) with aniline gave a mixture of succinamic acids which, on treatment with acetyl chloride, gave the imide (7; Ar = naphthyl, X = NPh). (*E,E*)-2-Benzylidene-3-(β-naphthylmethylene)succinic anhydride (1b) was prepared by a similar procedure, from diethyl (*E*)-benzylidenesuccinate and β-naphthaldehyde.


(1)

(4)

hν con. | heat / dis. | *hν* con.

(2)

(3)

(5)
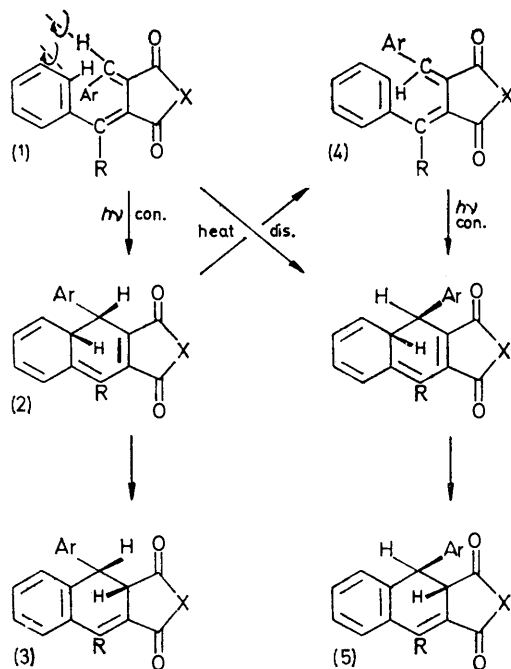
a; R = H, Ar = Ph, X = NPh
b; R = H, Ar = β-naphthyl, X = O
c; R = H, Ar = mesityl, X = O or NPh

No *Z*-isomers were detected in these reactions.[2,3,7] Irradiation of the yellow (*E*)-2-isopropylidene-3-(β-naphthylmethylene)succinic anhydride and *N*-phenyl-

⁴ H. G. Heller and R. M. Megit, *J.C.S. Perkin I*, 1974, 923.
⁵ C. J. Timmons, E. V. Blackburn, and C. E. Loader, *J. Chem. Soc. (C)*, 1970, 163.

imide (7b; X = O or NPh, respectively) at 366 nm in the crystal state, in a rigid plastic matrix, and in benzene or

(6)

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(7)

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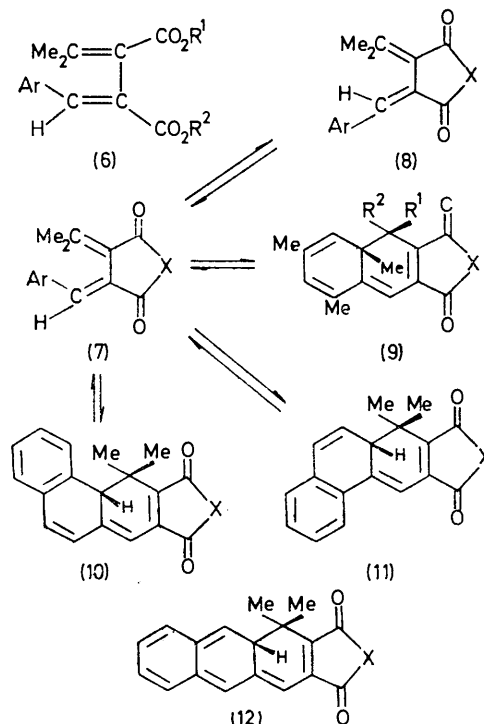
a; Ar = α-naphthyl
b; Ar = β-naphthyl
c; Ar = mesityl

deuteriochloroform, produced a red colouration (λ_{max} 485 nm) attributed to the 4,4a-dihydrophenanthrene intermediates (DHPs) (10; X = O or NPh). The colour change was reversed on exposure to white light but did not occur in the dark. It is believed that thermal disrotatory ring opening and the 1,5-hydrogen shift are prevented by the increase in activation energy arising from stabilisation of the DHPs by the fused benzene ring. On prolonged irradiation, *EZ*-isomerisation occurred giving, in benzene solutions, photostationary states consisting of 60% *E*- and 40% *Z*-anhydride or *N*-phenylimide, respectively. As no other products could be detected, ring closure on to the 3-position of the naphthyl group to give the less stable dihydroanthracene intermediate (12), expected to undergo a 1,5-hydrogen shift, was not a competing photoreaction.

(*E*)-2-Isopropylidene-3-(α-naphthylmethylene)succinic anhydride and imide (7a; X = O or NPh) showed similar photochromic properties with a hypsochromic shift of the long wavelength absorption band of the DHPs (11; X = O or NPh) (λ_{max} 465 nm) indicating that photocyclisation does occur on the α-position of the naphthyl group and that the fused benzene ring again stabilises the DHPs. On prolonged irradiation, *EZ*-isomerisation took place giving photostationary states

⁶ R. S. Becker and J. Michl, *J. Amer. Chem. Soc.*, 1966, **88**, 5931.
⁷ H. G. Heller and B. Swinney, *J. Chem. Soc. (C)*, 1967, 2452.

consisting of 20% E- and 80% Z-anhydride or 55% E- and 45% Z-imide, respectively.

In contrast, an analogous photoreaction of (E,E)-2-benzylidene-3-(β-naphthylmethylene)succinic anhydride (1b) in benzene at 20 °C resulted in a colour change from yellow to orange-red, but on prolonged irradiation the solution became colourless and a quantitative yield of cis-1,2-dihydro-1-(β-naphthyl)naphthalene-2,3-dicarboxylic anhydride (3b) was obtained, presumably by photochemical conrotatory ring closure of the anhydride (1b) to the DHN (2b), followed by a 1,5-hydrogen shift.

The structure and stereochemistry of (3b) follow from a comparison of its n.m.r. and u.v. spectra with those of

chemical ring closure (the latter either by consecutive or concomitant processes) would give rise to red and, presumably in view of the long-conjugated system involved, blue intermediates [(16) and (17)], respectively.

The bis-half-ester (13; R^1 = H, R^2 = Et) was obtained by condensation of naphthalene-2,6-dicarbaldehyde with a two molar excess of diethyl isopropylidene-succinate. Hydrolysis of the bis-half-ester gave the tetra-acid (13; R^1 = R^2 = H), treatment of the bis-half-ester with anilinomagnesium iodide gave the succinamic acids, and ring closure of the tetra-acid and succinamic acids gave the dianhydride and bis-imide (14), respectively. The red dianhydride was insoluble in most
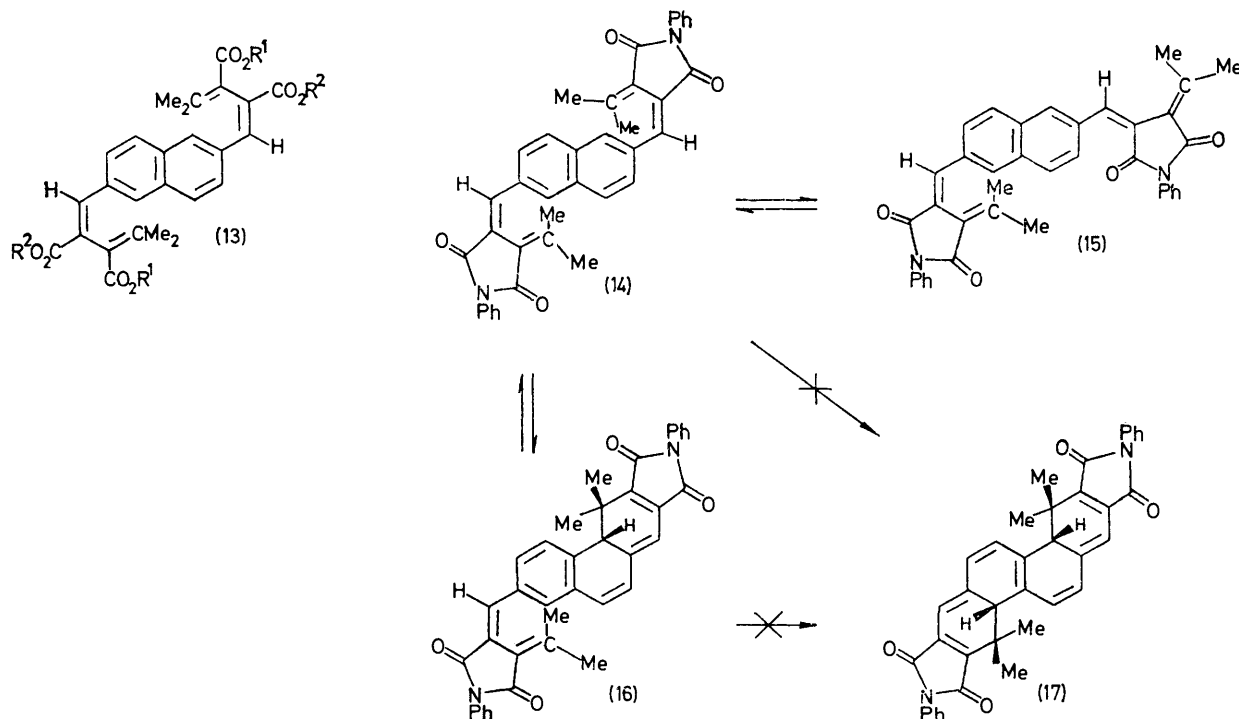
cis- and trans-1,2-dihydro-1,N-diphenylnaphthalene-2,3-dicarboximides [(3a) and (5a)]. In view of the exclusive photochemical cyclisation of the imide (1a) and the corresponding anhydride on to the mesityl group, the absence of phenanthrene derivatives from the photoreaction of the anhydride (1b) is attributed to exclusive ring closure on to the phenyl group rather than the alternative possibility that the DHP formed by ring closure on to the β-naphthyl group does not undergo a 1,5-H shift.

Organic compounds which undergo more than one light-induced reversible major colour change have not been reported before, to our knowledge. A single compound which could show the primary colour changes, depending on irradiation conditions, would provide the first example of multiphotochromism and the basis for a multicolour reversible image forming system. (E,E)-3,3'-Di-isopropylidene-NN'-diphenyl-2,2'-(naphthalene-2,6-diyldimethylidyne)disuccinimide (14) is potentially such a compound in which a single or a double photo-

organic solvents. The structure and stereochemistry of the yellow (E,E)-bis-imide (14), follows from the similarity of its n.m.r. spectrum to that of the E-imide (7b; X = NPh), its analysis, and its molecular weight (determined by mass spectrometry). The bis-half-ester (13; R^1 = H, R^2 = Et) and the tetra-acid (13; R^1 = R^2 = H) were shown to be E,E-isomers from the n.m.r. spectrum of the tetramethyl ester (13; R^1 = R^2 = Me), prepared by the action of diazomethane on the tetra-acid.

Like the E-imide (7b; X = NPh), the bis-imide (14) underwent a yellow to red colour change in the crystal state and in benzene or deuteriochloroform on irradiation at 351—356, 366, or 404 nm, attributed to the formation of the E-DHP (16) and its Z-isomer. The colour change was reversed by white light but did not occur in the dark. The bis-imide (14), as a film in rigid plastic matrix between two microscope slides, was irradiated at 366 nm while changes in absorbance were monitored at 514 and 633 nm with low-intensity radiation from argon ion and

helium neon lasers, respectively. In the case of the imide (7b; X = NPh) changes in absorbance of 0.02 at 514 nm could be detected readily. The bis-imide (14) was not photochromic at room temperature or at −196 °C. On prolonged irradiation, the yellow film was bleached. (These studies were carried out in collaboration with Dr. R. Hurditch at the 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.) Flash photolysis [8] of the bis-imide (14) in chloroform (ca. 10^{-3} M) showed the red photocoloured intermediate but no transient with an absorption in the region 550—650 nm, arising from the double ring closure.

A double ring closure would result in loss of stability due to benzene ring fusion in the intermediate (17), leading to a ready thermal 1,5-hydrogen shift (cf. photoreactions of aryl-substituted 1,2-dimethyleneindanes).[9] No phenanthrene derivatives were obtained on prolonged irradiation at 366 nm. As before, EZ-isomerisation occurred, giving in deuteriochloroform solutions a photostationary state consisting of 33% E,E- and 67% E,Z-bis-imide [(14) and (15), respectively].

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

	=CH	CH₃	CH₃
Ar = α-naphthyl			
(E)-Anhydride (7a; X = O)	1.71	7.60	8.73
(Z)-Anhydride (7a; X = O)		7.50	7.35
(E)-Imide (7a; X = NPh)	1.73	7.58	8.74
(Z)-Imide (7a; X = NPh)		7.52	7.30
Ar = β-naphthyl			
(E)-Half-ester (6b; R¹ = H, R² = Et)		7.74	8.39
(E)-Anhydride (7b; X = O)		7.51	8.38
(Z)-Anhydride (7b; X = O)		7.48	7.28
(E)-Imide (7b; X = NPh)		7.50	8.39
(Z)-Imide (7b; X = NPh)		7.60	7.36
Ar = 2,6-dinaphthyl			
(E,E)-Bis-half ester (13; R¹ = H, R² = Et)		7.72	8.31
(E,E)-Tetraester (13; R¹ = R² = Me)		7.83	8.39
(E,E)-Bis-imide (14)		7.48	8.34
(E,Z)Bis-imide (15)	{	7.52	8.43
	{	7.58	7.35

The stereochemistry of the half esters, esters, anhydrides, and imides and the compositions of mixtures of isomers were determined by n.m.r. spectroscopy. In (E)-isopropylidene(naphthylmethylene)succinic acid derivatives, the olefinic hydrogen atom and one of the methyl groups are deshielded by a carbonyl group and the other methyl group is shielded by the naphthyl group. Z-Isomers show the signal of the methyl group trans to the carbonyl group at lower field (by ca. 1 p.p.m.).[4,10] When not reported, the signal of the olefinic hydrogen atom is obscured by the absorptions of the naphthyl protons.

EXPERIMENTAL

U.v. spectra were measured for solutions in chloroform (unless stated otherwise) with a Unicam SP 1800A spectro-

meter, and n.m.r. spectra for solutions in deuteriochloroform with a Perkin-Elmer R12 (60 MHz) spectrometer (tetramethylsilane as internal standard except when monitoring photochemical reactions, for which an external standard was used). Molecular weight determinations were carried out with an A.E.I. MS9 spectrometer. Photochemical reactions were carried out for 0.1—0.5% w/v solutions of the anhydrides or imides in benzene at 54 °C and irradiated at 366 nm with an assembly of four 125 W mercury vapour discharge lamps with Woods glass filters (type MBW, Thorn lighting) in a reflecting aluminium housing. Studies of solutions in deuteriochloroform or spectroscopic studies for ca. 1.5 × 10^{-4} M-solutions of the anhydrides or imides in benzene at 20 °C were carried out in 2 mm and 10 mm cells, respectively, exposed to radiation from a 250 W mercury discharge lamp (type ME/D) with a filter (type OX1, Chance-Pilkington) focused on one side of the cell. Solvents were dried and fractionally distilled before use. Petroleum refers to the fraction b.p. 60—80°. The work-up of condensation reactions is described in detail in an earlier paper.[10] Rigid plastic matrix refers to polymethyl methacrylate (Tensol 6, I.C.I. Ltd.)

(E,E)-Dibenzylidene-N-phenylsuccinimide (1a).—A mixture of diethyl succinate (87 g, 0.5 mol) and benzaldehyde (106 g, 1 mol) was added dropwise to a stirred suspension of sodium hydride (60 g of 80% dispersion in oil; 2 mol) in toluene (500 ml) containing a few drops of ethanol to initiate the vigorous exothermic reaction. The mixture was then stirred (2 h) and acetic acid added to decompose any unchanged sodium hydride. The organic layer was washed with 5M-hydrochloric acid and water and extracted with 4M-sodium carbonate solution. The aqueous extracts were acidified and the liberated half ester was boiled with ethanolic 10% potassium hydroxide (500 ml). On cooling, dipotassium dibenzylidenesuccinate separated and was filtered off and acidified. The resulting diacid (76 g) was boiled (2 h) with acetyl chloride (300 ml). Acetyl chloride was removed and the residue was crystallised from ethanol, giving (E,E)-dibenzylidenesuccinic anhydride (45 g) as yellow plates (from ethanol), m.p. 202—203° (lit.,[11] 203—204°), τ 2.05 (2 H, s, =CH) and 2.6—3.2 (10 H, complex m, ArH).

2,3-Dibenzylidene-N-phenylsuccinamic acid (17 g) [obtained by boiling (4 h) a solution of dibenzylidenesuccinic anhydride (17.5 g) and aniline (6 g) in benzene (600 ml)] was dissolved in acetyl chloride (80 ml). Acetyl chloride was removed and the residue crystallised from acetic acid giving the (E,E)-imide (1a) (15 g), yellow needles, m.p. 200—201° (Found: C, 82.15; H, 4.95; N, 4.05. $C_{24}H_{17}NO_2$ requires C, 82.0; H, 4.9; N, 4.0%), λ_{max} 294 and 336 nm (log ε 4.61 and 4.12), τ 2.10 (2 H, s, =CH) and 2.4—3.3 (15 H, complex m ArH).

(E,E)-Benzylidene(mesitylmethylene)succinic Anhydride (1c; X = O) and N-Phenylimide (1c; X = NPh).—A mixture of dimethyl succinate (14.6 g, 0.1 mol) and mesitaldehyde (14.8 g, 0.1 mol) was added to a stirred suspension of sodium hydride (4.8 g of 60% dispersion in oil; 0.1 mol) in ether (400 ml). Work-up gave the half-ester (24 g), which yielded dimethyl mesitylmethylenesuccinate (b.p. 145—147° at 1.2 mmHg) on treatment with diazomethane in ether. A mixture of the dimethyl ester (5.5 g 0.02 mol) and benzaldehyde (2.1 g, 0.02 mol) was added to sodium hydride (1.0 g

[9] H. G. Heller and K. Salisbury, J. Chem. Soc. (C), 1970, 399, 873.
[10] H. G. Heller and M. Szewczyk, J.C.S. Perkin I, 1974, 1483.
[11] H. Stobbe and P. Naoúm, Ber., 1904, 37, 2240.

[8] G. Porter and M. A. West in ' Techniques of Chemistry,' eds. A. Weissberger and G. Hemmes, vol. 6, part 2.

of 60% dispersion in oil; *ca.* 0.02 mol) in ether (250 ml) containing methanol (0.5 ml) to initiate the reaction, and the mixture was boiled (1 h). Work-up gave the half-ester (7 g) which was hydrolysed with aqueous ethanolic 4% sodium hydroxide (100 ml). Removal of solvent followed by acidification gave the diacid, which was boiled (1 h) with acetyl chloride (150 ml). Acetyl chloride was removed and the residual gum was crystallised from petroleum giving the (E,E)-*anhydride* (1c; X = O), yellow needles, m.p. 136—137° (Found: C, 79.2; H, 5.5. $C_{21}H_{18}O_3$ requires C, 79.2; H, 5.7%). $\lambda_{max.}$ (EtOH) 251 and 291 nm (log ε 3.69 and 4.12), τ 2.09 (2 H, two s, =CH), 2.2—2.65 (5 H, complex m, Ph), 3.11 (2 H, s, ArH), 7.72 (3 H, s, *p*-Me), and 7.84 (6 H, s, *o*-Me).

The half-ester in ether was added to ethereal anilinomagnesium bromide; the mixture was acidified and the liberated succinamic acids were boiled with acetyl chloride (*cf.* ref. 4). Acetyl chloride was removed and the residue crystallised from benzene–petroleum, giving pale yellow needles of (E,E)-*benzylidene(mesitylmethylene)-N-phenylsuccimide* (1c; X = NPh), m.p. 191—192° (Found: C, 82.6; H, 5.9; N, 3.6. $C_{27}H_{23}NO_2$ requires C, 82.4; H, 5.9; N, 3.6%), $\lambda_{max.}$ (EtOH) 214, 251, and 290 nm (log ε 4.53, 3.75, and 4.15), τ 2.20 and 2.30 (2 H, s, =CH), 2.4—2.8 (10 H, complex m, Ph), 3.26 (2 H, s, ArH), 7.77 (3 H, s, *p*-Me), and 7.86 (6 H, s, *o*-Me).

(E)-2-*Isopropylidene-3-(β-naphthylmethylene)succinic Anhydride* (7b; X = O).—Diethyl isopropylidenesuccinate (11 g, 0.05 mol), β-naphthaldehyde (7.8 g, 0.05 mol), and potassium t-butoxide (6 g, 0.06 mol) in t-butyl alcohol (300 ml), heated for 40 min, gave the (E)-half-ester (6b; $R^1 = H$, $R^2 = Et$) (13 g), which was hydrolysed to the diacid (6b; $R^1 = R^2 = H$) (10.5 g). Treatment of the diacid with acetyl chloride gave the (E)-*anhydride* (7b; X = O) (7.8 g), yellow needles from benzene–petroleum, m.p. 149—150° (Found: C, 77.6; H, 5.1. $C_{18}H_{14}O_3$ requires C, 77.7; H, 5.1%), $\lambda_{max.}$ 274 and 345 nm (log ε 4.27 and 4.22).

(E)-2-*Isopropylidene-3-(β-naphthylmethylene)-N-phenylsuccinimide* (7b; X = NPh).—The crude succinamic acids obtained from the (E)-anhydride (7b; X = O) and aniline (0.4 g) in benzene (70 ml) after boiling for 4 h were dissolved in acetyl chloride (40 ml). The excess of acetyl chloride was removed and the residue crystallised from methanol giving the N-*phenylimide* (7b; X = NPh) (0.7 g), pale yellow needles, m.p. 151° (Found: C, 81.5; H, 5.55; N, 4.0. $C_{24}H_{19}NO_2$ requires C, 81.6; H, 5.4; N, 4.0%), $\lambda_{max.}$ 274 and 337 nm (log ε 4.41 and 4.29).

(E)-2-*Isopropylidene-3-(α-naphthylmethylene)succinic Anhydride* (7a; X = O).—Diethyl isopropylidenesuccinate (22 g), α-naphthaldehyde (16 g), and sodium (5 g) dissolved in ethanol (100 ml), heated for 4 h, gave, after work-up and hydrolysis of the half-ester, (E)-2-isopropylidene-3-(α-naphthylmethylene)succinic *acid* (6a; $R^1 = R^2 = H$), pale yellow rods, m.p. 205—206° (from 80% aqueous acetic acid) (Found: C, 73.0; H, 5.2. $C_{18}H_{16}O_4$ requires C, 73.0; H, 5.4%). Treatment of the diacid (6a; $R^1 = R_2 = H$) with acetyl chloride gave the yellow *anhydride* (7a; X = O), m.p. 139—140° [from petroleum (b.p. 100—120°)](Found: C, 77.9; H, 5.0. $C_{18}H_{14}O_3$ requires C, 77.7; H, 5.1%) $\lambda_{max.}$ 275 and 366 nm (log ε 3.97 and 3.95).

(E)-2-*Isopropylidene-3-(α-naphthylmethylene)-N-phenylsuccinimide* (7a; X = NPh).—The imide was prepared from the anhydride (7a; X = O) as described for the previous example and was obtained as yellow *cubes*, m.p. 147—149°

(from acetic acid) (Found: C, 81.7; H, 5.3; N, 3.7. $C_{24}H_{19}NO_2$ requires C, 81.6; H, 5.4; N, 4.0%), $\lambda_{max.}$ 350 (log ε 4.02).

(E,E)-2-*Benzylidene-3-(β-naphthylmethylene)succinic Anhydride* (1b).—Diethyl (E)-benzylidenesuccinate (13.1 g, 0.05 mol), β-naphthaldehyde (7.8 g, 0.05 mol), and potassium t-butoxide (6 g, 0.06 mol) in t-butyl alcohol (300 ml), heated for 15 min, gave ethyl (E,E)-benzylidene-(β-naphthylidene)succinate (8 g, 49%), cubes from ether–petroleum, m.p. 144—145°, τ 2.05 and 2.10 (2 H, two s, =CH), 2.12—2.96 (12 H, complex m, ArH), 5.83 (2 H, q, *J* 7.5 Hz, CH_2), and 8.88 (3 H, t, *J* 7.5 Hz, CH_3). Hydrolysis of the ester (4 g) gave the diacid which, on boiling with acetyl chloride (80 ml), gave the (E,E)-*anhydride* (1b) (3.4 g), yellow plates from chloroform–petroleum, m.p. 145—146° (Found: C, 80.9; H, 4.3. $C_{22}H_{14}O_3$ requires C, 81.0; H, 4.3%), $\lambda_{max.}$ 280, 312, and 396 nm (log ε 4.40, 4.36, and 4.03), τ 2.00 and 2.06 (2 H, two s, =CH), and 2.21—3.48 (12 H, complex m, ArH).

Photoreactions.—cis-1,2-*Dihydro-1,N-diphenylnaphthalene 2,3-dicarboximide* (3a) was obtained in 70% yield on irradiation (5 h) of the (E,E)-imide (1a) (100 mg) in benzene (300 ml) at 18 °C with rigorous exclusion of oxygen,[3] as plates (from acetic acid), m.p. 228—230° (Found: C, 81.8; H, 4.85. $C_{24}H_{17}NO_2$ requires C, 82.0; H, 4.9%), $\lambda_{max.}$ 312 (log ε 4.08), τ 2.3—3.2 (15 H, complex m, ArH and 4-H), 5.18 (1 H, d, $J_{1,2}$ 7.5 Hz, 1-H), and 5.83 (1 H, q, $J_{1,2}$ 7.5, $J_{2,4}$ 2.8 Hz, 2-H). 1,N-*Diphenylnaphthalene-2,3-dicarboximide* was obtained as needles (from acetic acid), m.p. 225—226° (Found: C, 82.35; H, 4.35; N, 3.8. $C_{24}H_{15}NO_2$ requires C, 82.5; H, 4.35; N, 4.0%), $\lambda_{max.}$ 351 and 364 nm (log ε 3.58 and 3.65), τ 1.60 (1 H, s, 4-H) and 1.8—2.80 (14 H, complex m, ArH).

When the imide (1a) was irradiated as above in benzene at 80 °C, trans-1,2-*dihydro-1,N-diphenylnaphthalene-2,3-dicarboximide* (5a) was obtained in 80% yield as needles (from acetic acid), m.p. 195—196° (Found: C, 82.15; H, 4.95; N, 3.55%), $\lambda_{max.}$ 310 nm (log ε 4.26), τ 2.20—3.15 (15 H, complex m, ArH and 4-H), 5.6 (1 H, d, $J_{1,2}$ 15 Hz, 1-H), and 6.0 (1 H, q, $J_{1,2}$ 15, $J_{2,4}$ 2—4 Hz, 2-H) together with 1,N-diphenylnaphthalene-2,3-dicarboximide. The latter could be obtained in quantitative yield by irradiation of the dihydronaphthalenes (3a) and (5a) in the presence of oxygen.

(E,E)-*Benzylidene(mesitylmethylene)succinic anhydride* (1c; X = O) in deuteriochloroform (0.6 ml) was irradiated at 54 °C. The colour of the solution changed from yellow to deep red and an equilibrium mixture of (E,E)-, (E,Z)-, and (Z,E)-isomers was reached within 30 h which showed methyl absorptions at τ 7.62, 7.72, 7.82, and 8.11, the relative intensities of which remained unaltered when the solution was irradiated further for 4 weeks. A similar result was obtained for the corresponding imide (1c; X = NPh). The isomers could not be separated by fractional crystallisation or chromatography.

A solution of (E)-2-isopropylidene-3-(β-naphthylmethylene)-N-phenylsuccinimide (7b; X = NPh) (60 mg) in deuteriochloroform (0.6 ml) was irradiated for 340 h. The n.m.r. spectrum showed the presence of a 60 : 40 mixture of E- and Z-imides (7b and 8b; X = NPh), as also observed after irradiation for 24 h. Irradiation of the E-imide (0.4 g) in benzene (200 ml) at 54 °C for 24 h gave the same photostationary state and no by-products were detected by n.m.r. spectroscopy. Fraction crystallisation of the mixture from chloroform and petroleum gave (Z)-2-*isopropylidene-3-(β-naphthylmethylene)-N-phenylsuccinimide* (8b; X = NPh) as pale yellow needles, m.p. 191—192° (Found: C, 81.7; H, 5.4; N, 4.0. $C_{24}H_{19}NO_2$ requires C, 81.6; H, 5.4; N, 4.0%),

$\lambda_{max.}$ 278 and 349 nm (log ε 4.34 and 4.27). The following Z-isomers were obtained from the corresponding E-compounds by an analogous procedure: (Z)-2-*isopropylidene*-3-(α-*naphthylmethylene*)-N-*phenylsuccinimide* (8a; X = NPh), yellow plates, m.p. 165° (Found: C, 81.1; H, 5.4; N, 4.05), $\lambda_{max.}$ 356 nm (log ε 4.07); (Z)-2-*isopropylidene*-3-(β-*naphthyl-methylene*)*succinic anhydride* (8b; X = O), yellow prisms, m.p. 182—183° (Found: C, 77.3; H, 5.0. $C_{18}H_{14}O_3$ requires C, 77.7; H, 5.0%), $\lambda_{max.}$ 280 and 349 nm (log ε 4.07 and 4.17); (Z)-2-*isopropylidene*-3-(α-*naphthylmethylene*)*succinic anhydride* (8a; X = O), yellow needles, m.p. 194—199° (Found: C, 78.2; H, 5.1%), $\lambda_{max.}$ (EtOH) 284 and 344 nm (log ε 3.81 and 3.73).

cis-1,2-*Dihydro*-1-(β-*naphthyl*)*naphthalene*-2,3-*dicarboxylic anhydride* (3b) was obtained in quantitative yield on irradiation of the (E,E)-anhydride (1b) (60 mg) in benzene (80 ml) within 24 h, as plates (from benzene), m.p. 203—204° (Found: C, 80.9; H, 4.7. $C_{22}H_{14}O_3$ requires C, 81.0; H, 4.3%), $\lambda_{max.}$ 268, 290, and 306 nm (log ε 3.96, 4.06, and 4.08), 2.24 (1 H, d, $J_{2,4}$ 2.5 Hz, 4-H), 2.35—2.97 (11 H, complex m, ArH), 5.13 (1 H, d $J_{1,2cis}$ 8.5 Hz, 1-H), and 5.65 (1H, q, $J_{2,4}$ 2.5, $J_{1,2cis}$ 8.5 Hz, 2-H).

(E,E)-3,3'-*Di-isopropylidene*-NN'-*diphenyl*-2,2'-(*naphthal-ene*-2,6-*diyldimethylidyne*)*disuccinimide* (14).—Potassium t-butoxide (5.5 g, 0.04 mol) was added to a solution of diethyl isopropylidenesuccinate (19 g, 0.09 mol) and naphthalene-2,6-dicarbaldehyde [12] (4 g, 0.02 mol) in t-butyl alcohol (100 ml) under reflux. Work-up by the usual procedure, after 40 min, gave a brown oil (9 g) from which the bis-half-ester (13; R^1 = H, R^2 = Et) (1 g) was obtained as a solid after trituration with chloroform–petroleum. Hydrolysis of the residual brown oil gave the (E,E)-tetra-acid (6.8 g) (13; R^1 = R^2 = H) as a pale yellow solid after trituration with benzene. This acid (1 g) was treated with an excess of diazomethane in ether to give the *tetraester* (13; R^1 = R^2 = Me), as plates from benzene–petroleum, m.p. 133—134° (Found: C, 69.45; H, 6.2%; M^+, 520.2. $C_{30}H_{32}O_8$ requires

C, 69.2; H, 6.2%; M, 520.56), $\lambda_{max.}$ (hexane) 236, 279, and 340 nm (log ε 4.45, 4.49, and 4.53). The tetra-acid (5 g) with acetyl chloride (100 ml) gave a dark red solid, presumed to be the dianhydride, insoluble in acetone, chloroform, ethanol, xylene, ethyl acetate, and other organic solvents. The bis-half-ester (13; R^1 = H, R^2 = Et) (1 g) in ether was boiled with ethereal anilinomagnesium iodide in excess for 20 min. The mixture was cooled and acidified, the ether was removed and the disuccinamic acid was extracted with chloroform. The extract was dried ($MgSO_4$), filtered, and evaporated and the residual oil was boiled (2 h) with acetyl chloride (30 ml). Acetyl chloride was removed and the residue in benzene chromatographed on neutral alumina (Woelm W200) with benzene–petroleum (1 : 1) as eluant. The *bis-imide* (14) (0.23 g) was obtained as yellow plates (frombe nzene–petroleum), m.p. 268.5—270° (Found: C, 79.1; H, 5.3; N, 4.6%; M^+, 578. $C_{38}H_{30}N_2O_4$ requires C, 78.9; H, 5.2, N, 4.8%; M, 578), $\lambda_{max.}$ (benzene) 283 and 385 nm (log ε 4.50 and 4.52), τ 2.00—2.60 (18 H, complex m, olefinic and ArH), 7.50 (6 H, s, two Me *cis* to C=O), and 8.38 (6 H, s, two Me *trans* to C=O).

The bis-imide (14) (60 mg) was irradiated in deuterio-chloroform. The photostationary state of 33% (E,E)- and 67% (E,Z)-isomer [(14) and (15)] was attained within 24 h. No other photorearrangement products were detected by n.m.r. spectroscopy after prolonged irradiation.

[12] P. W. Storms and P. R. Taussig, *J. Chem. and Eng. Data,* 1966, **11**, 272.