Overcrowded Molecules. Part VII.[1] Thermal and Photochemical Reactions of Photochromic (E)- and (Z)-Benzylidene(diphenylmethylene)-succinic Anhydrides and Imides

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The photochromic (E)- and (Z)-benzylidene(diphenylmethylene)succinic anhydrides and imides undergo reversible photochemical conrotatory ring closure reactions to form 1,8a-dihydronaphthalene intermediates, which ring open by a disrotatory mode yielding (Z)- and (E)-isomers, respectively, and rearrange to 1,2-dihydronaphthalene derivatives in two competing thermal processes. Product distribution depends on the temperature at which the photochemical reaction is carried out. The stereoselective Stobbe condensation of succinic esters with aromatic aldehydes is explained by Zimmerman's ' overlap control ' mechanism.

WE have introduced the name ' fulgimides ' [2] for the novel class of photochromic compounds obtained by substitution of hydrogen in dimethylenesuccinimide, by analogy with the name ' fulgides ' assigned to derivatives of dimethylenesuccinic anhydride.[3] These imides are prepared by heating fulgides with primary aromatic amines in benzene and cyclising the resulting succinamic acids with acetyl chloride. From our studies on ester, anhydride, and imide derivatives prepared through the Stobbe condensation of aromatic aldehydes with succinic esters, we find that they usually have a *trans* arrangement of aryl and carbonyl groups.

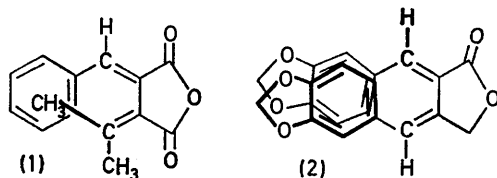N.m.r. studies on arylmethylene(diphenylmethylene)-succinic anhydrides and imides show that for compounds in the E-configuration the olefinic absorption appears as a rule at 0·7—1·0 p.p.m. to lower field than for compounds in the corresponding Z-configuration, owing to the deshielding effect of the carbonyl group in the first case and the shielding effect of the aryl group in the second. (E)-Arylmethyleneisopropylidenesuccinic anhydrides [e.g. (1)], prepared by Stobbe condensation of aromatic aldehydes with diethyl isopropylidenesuccinate, show deshielding of the olefinic hydrogen atom and one of the methyl groups by the carbonyl groups, and shielding of the other methyl group by the aryl group (see Table 1). In Taiwanin A (2), the olefinic protons give signals at τ 2·53 and 3·32, demonstrating the effect of an absence of the deshielding influence of a carbonyl group

[1] Part VI, H. G. Heller and K. Salisbury, *J. Chem. Soc. (C),* 1970, 1977.

[2] R. J. Hart, H. G. Heller, and K. Salisbury, *Chem. Comm.,* 1968, 1627; B.P. 14,327/1968.

[3] H. Stobbe, *Ber.,* 1905, **38**, 3673; *Annalen,* 1906, **349**, 333.

on one of them.[4] Assignment of stereochemistry by n.m.r. spectroscopy is supported by X-ray crystallographic studies on the isomeric bis-*p*-methoxybenzylidenesuccinic anhydrides[5] and earlier studies.[6,7] The

(1)   (2)

ready assignment of stereochemistry is evident from the characteristic spectra of (E)- and (Z)-benzylidene(diphenylmethylene)succinic anhydrides (7a) and (8a) which
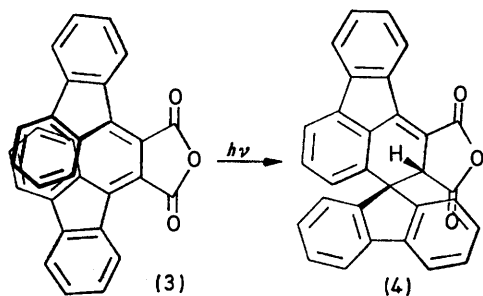
TABLE 1

N.m.r. data (τ values) for arylmethyleneisopropylidene-succinic anhydrides

Aryl	=CH	CH$_3$	CH$_3$
(E)-Phenyl [a]	2·28	7·52	8·38
(Z)-Phenyl	>2·4	7·42	7·60
(E)-Mesityl	2·28	7·64	8·82
(Z)-Mesityl	2·65	<7·7	<7·7
(E)-Cumyl [a]	2·28	7·49	8·29
(E)-*p*-Nitrophenyl	2·29	7·52	8·40
(E)-α-Naphthyl	1·71	7·60	8·73

[a] H. Stobbe, *Ber.*, 1905, **38**, 3893.   [b] H. Stobbe, *Ber.*, 1906, **39**, 292.

show olefinic absorptions at τ 2·38 and 3·15 respectively and shielding of the aromatic protons in the E-isomer. In our opinion, the stereochemistry of many bisarylmethylenesuccinic anhydrides reported[4,8-10] and implied in formulation by others[11] is incorrect.

The explanation[8-10] that (E,E)-bisarylmethylenesuccinic anhydrides are not formed because of severe

(3)   (4)

steric interactions between aryl groups is untenable since bisdiphenylmethylenesuccinic anhydride[12] (7c) and bis-fluorenylidenesuccinic anhydride (3)[13] are stable high-melting crystalline compounds, readily synthesised *via* the Stobbe condensation.

[4] G. A. Swoboda, K. T. Wang, and B. Weinstein, *J. Chem. Soc. (C)*, 1967, 161; *Chem. Comm.*, 1965, 592.

[5] M. D. Cohen, H. W. Kaufmann, D. Sinnreich, and G. M. J. Schmidt, *J. Chem. Soc. (B)*, 1970, 1035.

[6] H. G. Heller and B. Swinney, *J. Chem. Soc. (C)*, 1967, 1024.

[7] K. Freudenberg and T. Kempermann, *Annalen*, 1957, **602**, 184.

[8] G. Brunow and H. Tylli, *Acta Chem. Scand.*, 1968, **22**, 590.

[9] D. P. Chakraborty, T. Sleigh, R. Stevenson, G. A. Swoboda, and B. Weinstein, *J. Org. Chem.*, 1966, **31**, 3342.

[10] S. H. Harper, A. D. Kemp, and J. Tannock, *J. Chem. Soc. (C)*, 1970, 626.

The stereoselectivity of the Stobbe condensation involving aromatic aldehydes can be explained by a mechanism involving ' overlap control,' analogous to that proposed by Zimmerman[14] to account for the stereoselectivity of carbanionoid reactions, *e.g.* Perkin and Darzens reactions. In the Stobbe condensation, the intermediate (5)[15] is stabilised by delocalisation of negative charge on to the oxygen atom of the ester carbonyl
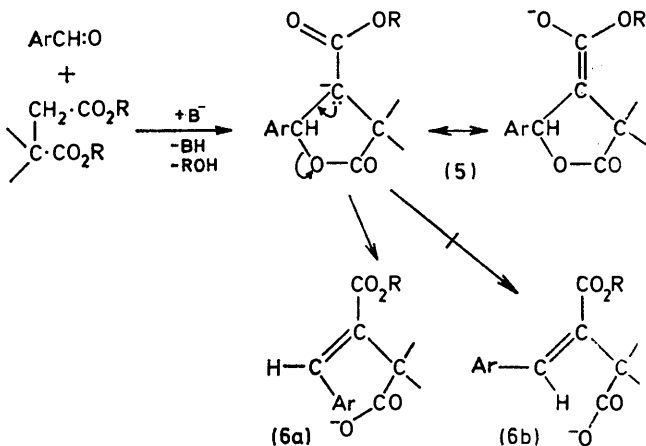
group. This delocalisation imposes a conformational restriction about the C(1)–C(2) bond, maximum overlap of orbitals occurring only when the ester carbonyl group and the C(1)–C(2) bond are coplanar. Dreiding models indicate that there is less steric resistance to coplanarity in the transition state (5) ⟶ (6a) than in (5) ⟶ (6b), in which interaction between ethoxy- and aryl groups occurs. Hence the reaction (5) ⟶ (6a) is preferred (see Scheme 1).

When bisdiphenylmethylene-N-phenylsuccinimide (7d) in benzene, hexane, or chloroform was exposed to radiation of wavelength 366 nm, the colour of the solution changed rapidly from yellow to orange-red. The colour change could be reversed thermally or by exposure to a tungsten filament lamp. On prolonged irradiation at 366 nm, the solution became colourless and a quantitative yield of 1,2-dihydro-1,1,4,N-tetraphenylnapthalene-2,3-dicarboximide (11d) was obtained. We suggest that the red colouration is due to the 1,8a-dihydronaphthalene intermediate (9d), formed by electrocyclic ring closure of the dimethylenesuccinimide, that photochemical or thermal ring-opening of the C(1)–C(8a) bond occurs readily to regenerate a succinimide derivative and that the 1,2-dihydronaphthalene derivative (11d) is formed by a suprafacial 1,5-shift of a hydrogen atom in the 1,8a-dihydronaphthalene intermediate (9d).[2] A similar

[11] S. M. Abdel-Wahhab and N. R. El-Rayyes, *J. Chem. Soc. (C)*, 1971, 3171; 1968, 867.

[12] C. F. Koelsch and H. J. Richter, *J. Org. Chem.*, 1939, **3**, 473.

[13] S. Goldschmidt, R. Riedle, and A. Reichardt, *Annalen*, 1957, **604**, 121.

[14] H. E. Zimmerman, L. Ahramjian, L. Singer, and B. S. Thyagarajan, *J. Amer Chem. Soc.*, 1959, **81**, 108, 2086; 1960, **82**, 5459.

[15] W. S. Johnson, A. McCloskey, and D. A. Dunnigam, *J. Amer. Chem. Soc.*, 1950, **72**, 514.

mechanism for the photochemical rearrangement reactions of other sterically hindered s-cis-butadienes has been put forward.[16] Santiago and Becker [17] reported
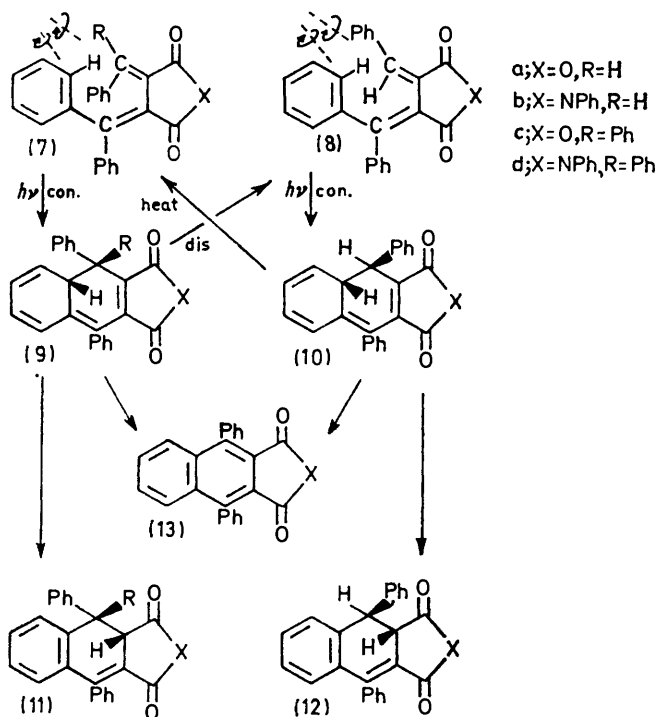
that no naphthalene derivative could be isolated after prolonged irradiation of bisdiphenylmethylenesuccinic anhydride (7c). We find that this succinic anhydride derivative undergoes ready photorearrangement to 1,2-dihydro-1,1,4-triphenylnaphthalene-2,3-dicarboxylic anhydride (11c). Bisfluorenylidenesuccinic anhydride (3) undergoes a similar reaction to give 2,3-dihydrofluoranthene-3-spiro-9'-fluorene-1,2-dicarboxylic anhydride (4).

(E)-Benzylidene(diphenylmethylene)succinic anhydride (7a) and (E)-benzylidene(diphenylmethylene)-N-phenylsuccinimide (7b) can be converted into their corresponding Z-isomers (8a and b) by photoisomerisation with an Hanovia 1 l photoreactor. However, on irradiation at 366 nm EZ-isomerisation does not occur.*

On irradiation at 366 nm, the (E)- and (Z)-benzylidene-(diphenylmethylene)-N-phenylsuccinimides (7b) and (8b) undergo conrotatory electrocyclic ring closure in accord with the Woodward–Hoffmann selection rules [18] to yield red (Z)- and (E)-1,8a-dihydronaphthalene intermediates (9b) and (10b), respectively, which undergo two competing thermal reactions: disrotatory ring opening to give the isomeric succinimide derivatives, or a 1,5-hydrogen shift to give the (Z)- and (E)-1,2-dihydro-

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* This has been established by irradiating a benzene solution of the (E)-succinimide derivative (7b) of known concentration at 366 nm, determining the concentration of 1,8a-dihydronaphthalene intermediate (9b) produced, demonstrating that this intermediate is converted quantitatively into the 1,2-dihydronaphthalene derivative (11b) at 18°, and showing spectroscopically that the remaining succinimide derivative is pure E-isomer. These studies will be reported in a later paper.

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naphthalene derivatives (11b) and (12b), respectively. As the rates of these two competing reactions vary with temperature, there is a dramatic change in product distribution depending on the temperature at which the initial photochemical reaction is carried out. (E)- and (Z)-Benzylidene(diphenylmethylene)succinic anhydrides (7a) and (8a) undergo similar reactions. Control experiments showed that the (E)- and (Z)-succinic anhydride and succinimide derivatives were thermally stable at 140° but that thermal rearrangement occurred on heating at 180° in o-dichlorobenzene. In each case, high yields of the (Z)-1,2-dihydronaphthalene derivatives (11a and b) were obtained. We suggest that the (Z)-succinic anhydride derivative (8a) and (Z)-succinimide derivative (8b) undergo a disrotatory electrocyclic ring closure followed by a 1,5-hydrogen shift in accord with the selection rules,[18] but that the severely overcrowded and thermodynamically less stable (E)-succinic anhydride derivative (7a) and (E)-succinimide derivative (7b) isomerise at 180° to Z-isomers (8a and b) and that ring closure occurs predominantly through the Z-isomers (see Table 2).

The stereochemistry of the (Z)- and (E)-1,2-dihydronaphthalene derivatives follows from n.m.r. studies. (Z)-1,2-Dihydronaphthalene derivatives (11a and b) have an axial–equatorial arrangement of methine hydrogen atoms, accounting for the observed J value of 7·5 Hz. In the E-isomers (12a and b), there is an axial–axial arrangement of methine hydrogen atoms and a J value of 15 Hz is observed. The equatorial hydrogen atom at

TABLE 2

Product composition from thermal and photochemical reactions of (E)- and (Z)-benzylidene(diphenylmethylene)succinic anhydrides and -N-phenylsuccinimides

Reactant	Reaction conditions; solvent	Product composition (%)					
(7a)	366 nm, 18°; benzene	(11a)	95	(12a)	5	(13a)	0
	366 nm, 140°; xylene		80		20		0
	180°; o-dichlorobenzene		65		15		20
(7b)	366 nm, 18°; benzene	(11b)	95	(12b)	0	(13b)	5
	366 nm, 140°; xylene		65		30		5
	180°, o-dichlorobenzene		80		0		20
(8a)	366 nm, 18°; benzene	(11a)	90	(12a)	5	(13a)	5
	366 nm, 140°; xylene		0		100		0
	180°; o-dichlorobenzene		80		0		20
(8b)	366 nm, 18°; benzene	(11b)	60	(12b)	0	(13b)	40
	366 nm, 140°; xylene		10		85		5
	180°; o-dichlorobenzene		70		0		30

C-1 in the Z-isomers is deshielded by the carbonyl group and gives a signal at lower field than the corresponding axial hydrogen atom at C-1 in the E-isomers.

EXPERIMENTAL

U.v. spectra were measured for solutions in chloroform with a Unicam SP 500 spectrometer: n.m.r. spectra were

[16] H. G. Heller and K. Salisbury, J. Chem. Soc. (C), 1970, 399, 873.

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

[18] R. Hoffmann and R. B. Woodward, Accounts Chem. Res., 1968, 1, 17; ' The Conservation of Orbital Symmetry,' Academic Press, New York, 1970.

obtained for solutions in deuteriochloroform with a Perkin-Elmer R12 (60 MHz) spectrometer (tetramethylsilane as internal standard). Solvents used in photochemical reactions were carefully purified before use and reactions were carried out under oxygen-free conditions. Oxygen-free nitrogen was prepared by bubbling 'white-spot' nitrogen through Fieser's solution,[19] then through concentrated sulphuric acid to dry the gas, and then passing through a column (3 ft) of copper wool in a copper tube (0·75 in diam.) heated at 300°, followed by a glass spiral immersed in ice. Photochemical reactions were carried out for 0·3% w/v solutions in benzene or xylene and thermal reactions in boiling o-dichlorobenzene, under nitrogen. For photoreactions using 366 nm radiation, an assembly of four 125 W mercury discharge lamps (A.E.I. Lamp and Lighting Co., Leicester) with Wood's glass filters was used. Other photochemical reactions were carried out in a 1 1 Hanovia photoreactor consisting of a medium-pressure mercury discharge lamp contained in a quartz thimble and quartz cooling jacket immersed in a 1 1 flask filled with a solution of the reactant. Product distributions were determined by n.m.r. studies, i.e. by measuring the areas under characteristic peaks of spectra of crude reaction products after removal of solvent. Products were separated by column chromatography on silica gel with benzene as eluant.

Bisdiphenylmethylene-N-*phenylsuccinimide* (7d).—2,3-Bis-diphenylmethylene-N-phenylsuccinamic acid (0·4 g), m.p. 228—230° [from bisdiphenylmethylenesuccinic anhydride[12] (0·4 g) and aniline (0·1 g) in benzene (50 ml) after boiling for 12 h)] was dissolved in acetyl chloride (10 ml) and left at room temperature for 24 h. Acetyl chloride was removed and the residue crystallised from acetic acid giving bisdiphenylmethylene-N-*phenylsuccinimide* (0·35 g), orange crystals, m.p. 285° (Found: C, 85·6; H, 5·05. $C_{36}H_{25}NO_2$ requires C, 85·9; H, 5·0%), $\lambda_{max.}$ 316 and 363 nm (log ε 4·25 and 3·65).

1,2-*Dihydro*-1,1,4-*triphenylnaphthalene*-2,3-*dicarboxylic Anhydride* (11c).—Obtained in 88% yield from photorearrangement of bisdiphenylmethylenesuccinic anhydride (7c) in benzene at 366 nm, the *anhydride* (11c) formed crystals (from acetic acid), m.p. 219—220°, (Found: C, 83·8; H, 4·6. $C_{30}H_{20}O_3$ requires C, 84·1; H, 4·7%), $\lambda_{max.}$ 313 nm (log ε 3·83), τ 2·3—3·3 (19H, complex m, aromatic protons) and 4·90 (1H, s, 2-proton).

2,3-*Dihydrofluoranthene*-3-*spiro*-9'-*fluorene*-1,2-*dicarboxylic Anhydride* (4).—Bisfluorenylidenesuccinic anhydride[13] (3) (1 g) in benzene (1 1) was irradiated in the Hanovia photoreactor until the solution turned from dark red to yellow (4 h). Solvent was removed and the residue crystallised from acetic acid to give golden *needles*, which decomposed slowly above 240°. The yellow crystals gave an intense blue solution in acetone (Found: C, 84·5; H, 3·85. $C_{30}H_{16}O_3$ requires C, 84·9; H, 3·8%), $\lambda_{max.}$ 271 and 355 nm (log ε 4·74 and 4·05), τ 1·3 (1H, q, 10-proton, deshielded by carbonyl), 2·0—3·7 (14H, complex m, aromatic protons), 4·85 (1H, s, 2-proton).

(Z)-*Benzylidene*(*diphenylmethylene*)*succinic Anhydride* (8a).—(E)-Benzylidene(diphenylmethylene)succinic anhydride[20] (7a) (2 g) in benzene (1 1) was irradiated (10 h) in the Hanovia photoreactor. The solvent was removed and the residue chromatographed. The first yellow band gave (Z)-benzylidene(diphenylmethylene)succinic anhydride as

bright orange needles (from acetic acid), m.p. 192° (Found: C, 82·2; H, 4·6. $C_{24}H_{16}O_3$ requires C, 81·8; H, 4·6%), $\lambda_{max.}$ 303 and 395 nm (log ε 4·08 and 4·18), τ 2·2—2·8 (15H, complex m, aromatic protons) and 3·15 (1H, s, olefinic proton).

N-Phenylsuccinimide derivatives were prepared by boiling equimolar proportions of succinic anhydride derivatives and aniline in benzene. In each case the solvent was removed and the residual succinamic acid boiled with acetyl chloride until evolution of hydrogen chloride ceased. Acetyl chloride was distilled off and the residue crystallised from acetic acid unless otherwise stated.

(E)-*Benzylidene*(*diphenylmethylene*)-N-*phenylsuccinimide* (7b) formed yellow plates, m.p. 239—240° (Found: C, 79·2; H, 5·2; N, 2·85. $C_{30}H_{21}NO_2,CH_3\cdot CO_2H$ requires C, 78·8; H, 5·15; N, 2·85%), $\lambda_{max.}$ 302 and 379 nm (log ε 4·42 and 4·05), τ 2·40 (1H, s, olefinic proton) and 2·56—3·05 (20H, complex m, aromatic protons).

(Z)-*Benzylidene*(*diphenylmethylene*)-N-*phenylsuccinimide* (8b), prepared in the same way as (Z)-benzylidene(diphenylmethylene)succinic anhydride, formed yellow plates [from petroleum (b.p. 100—120°)], m.p. 185·5—186° (Found: C, 84·3; H, 4·95; N, 3·1. $C_{30}H_{21}NO_2$ requires C, 84·3; H, 4·95; N, 3·3%), $\lambda_{max.}$ 281sh and 376 nm (log ε 4·25 and 4·19), τ 2·30—2·80 (20H, complex m, aromatic protons) and 3·19 (1H, s, olefinic proton).

1,4-Diphenylnaphthalene-2,3-dicarboxylic anhydride (13a) formed needles (from benzene), m.p. 272—273° (lit.,[21] 273—275°).

1,4,N-*Triphenylnaphthalene*-2,3-*dicarboximide* (13b) formed needles (from acetic acid), m.p. 295—296° (Found: C, 84·6; H, 4·75. $C_{24}H_{15}NO_2$ requires C, 84·7; H, 4·5%), $\lambda_{max.}$ (CHCl₃) 267, 355, and 370 nm (log ε 4·61, 3·65, and 3·70).

(Z)-1,2-*Dihydro*-1,4-*diphenylnaphthalene*-2,3-*dicarboxylic anhydride* (11a) formed needles [from petroleum (b.p. 100—120°)], m.p. 166—168° (Found: C, 81·8; H, 4·55. $C_{24}H_{16}O_3$ requires C, 81·8; H, 4·6%), $\lambda_{max.}$ 3·15 nm (log ε 4·07), τ 2·40—2·80 (14H, complex m, aromatic protons), 5·18 (1H, d, $J_{1,2}$ 7·5 Hz, 1-proton), and 5·54 (1H, d, $J_{1,2}$ 7·5 Hz, 2-proton).

(E)-1,2-*Dihydro*-1,4-*diphenylnaphthalene*-2,3-*dicarboxylic anhydride* (12a) formed needles (from acetic acid), m.p. 189—190° (Found: C, 81·4; H, 4·6. $C_{24}H_{16}O_3$ requires C, 81·8; H, 4·55%), $\lambda_{max.}$ 315 nm (log ε 3·96), τ 2·20—3·20 (14H, complex m, aromatic protons), 5·4 (1H, d, $J_{1,2}$ 16 Hz, 1-proton), and 5·66 (1H, d, $J_{1,2}$ 16 Hz, 2-proton).

(Z)-1,2-Dihydro-1,4,N-triphenylnaphthalene-2,3-dicarboximide (11b) formed needles (from acetic acid), m.p. 205—206° (lit.,[21] 210—214°) (Found: C, 84·2; H, 4·86. Calc. for $C_{30}H_{21}NO_2$: C, 84·3; H, 4·95%), $\lambda_{max.}$ 315 nm (log ε 4·17), τ 2·40—3·1 (19H, complex m, aromatic protons), 5·14 (1H, d, $J_{1,2}$ 7·0 Hz, 1-proton), and 5·72 (1H, d, $J_{1,2}$ 7·0 Hz, 2-proton).

(E)-1,2-*Dihydro*-1,4,N-*triphenylnaphthalene*-2,3-*dicarboximide* (12b) formed needles (from ethanol), m.p. 229—230° (Found: C, 84·4; H, 4·9; N, 3·4. $C_{30}H_{21}NO_2$ requires C, 84·3; H, 4·95; N, 3·3%), $\lambda_{max.}$ 311 nm (log ε 4·14), τ 2·10—3·29 (19H, complex m, aromatic protons), 5·41 (1H, d, $J_{1,2}$ 15 Hz, 1-proton), and 5·85 (1H, d, $J_{1,2}$ 15 Hz, 2-proton).

[19] L. F. Fieser, *J. Amer. Chem. Soc.*, 1924, **24**, 2639.
[20] H. Stobbe, *Ber.*, 1904, **37**, 2656.

[21] G. Quinkert, K. Opitz, W. W. Wiersdorff, and M. Finke, *Annalen*, 1966, **693**, 44.