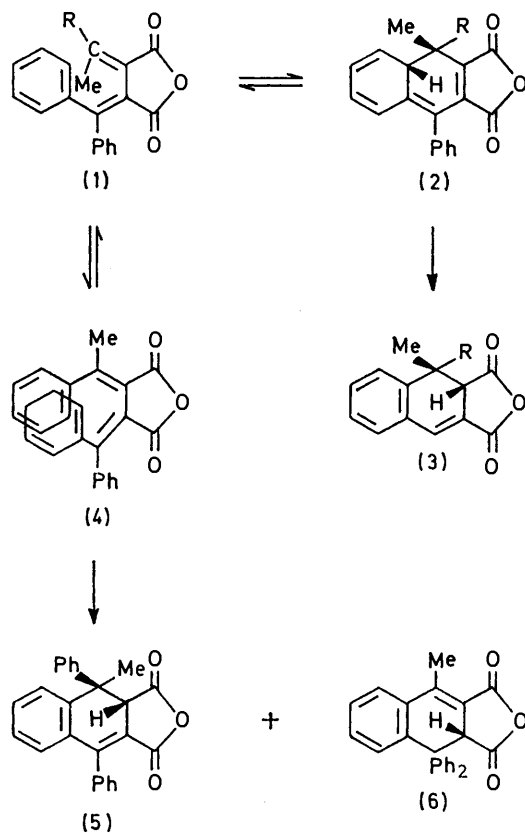


Overcrowded Molecules. Part 17.¹ Thermal Reactions of (α -Phenylethylidene)(substituted methylene)succinic Anhydrides

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The thermal *E*-*Z* isomerisation and electrocyclic reactions of diphenylmethylene-, benzylidene-, and isopropylidene-(α -phenylethylidene)succinic anhydrides and bis-(α -phenylethylidene)succinic anhydrides to yield 1,2-dihydronaphthalene-2,3-dicarboxylic anhydride derivatives are reported. With the exception of the first, these succinic anhydrides undergo competing but reversible sigmatropic rearrangements to yield penta- and hexa-1,3-diene-3,4-dicarboxylic anhydride derivatives.

PREVIOUSLY,² we explained the stereospecific thermal conversion of (*Z*)-2-butylidene(diphenylmethylene)succinic anhydride (1a) into *t*-1-ethyl-1,2-dihydro-1-methyl-4-phenylnaphthalene-2,3-dicarboxylic anhydride



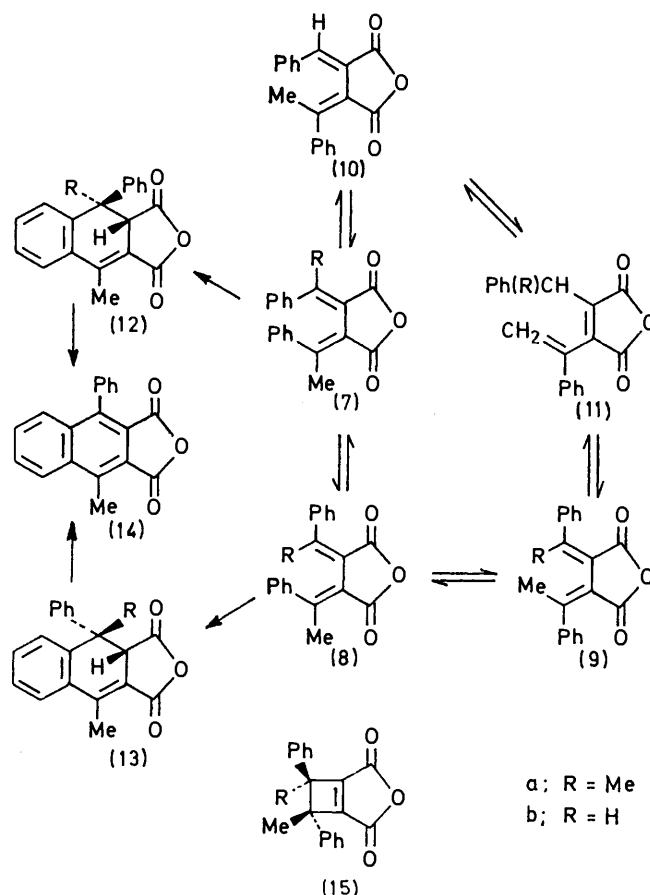
a, R = Et
b, R = Me
c, R = Ph
SCHEME 1

(3a) by disrotatory ring closure to a 1,8a-dihydronaphthalene intermediate (2a) followed by a suprafacial 1,5-hydrogen shift in accord with the Woodward-Hoffmann rule for pericyclic reactions.³ Diphenylmethylene(isopropylidene)succinic anhydride (1b)⁴ undergoes a similar reaction to give 1,1-dimethyl-4-phenyl-1,2-dihydronaphthalene (3b) as the sole product.

We now report analogous new rearrangement reactions of (α -phenylethylidene)(substituted methylene)succinic

anhydrides,⁵ on heating at 180 °C in either *o*-dichlorobenzene or in deuteriochloroform in a sealed n.m.r. tube.

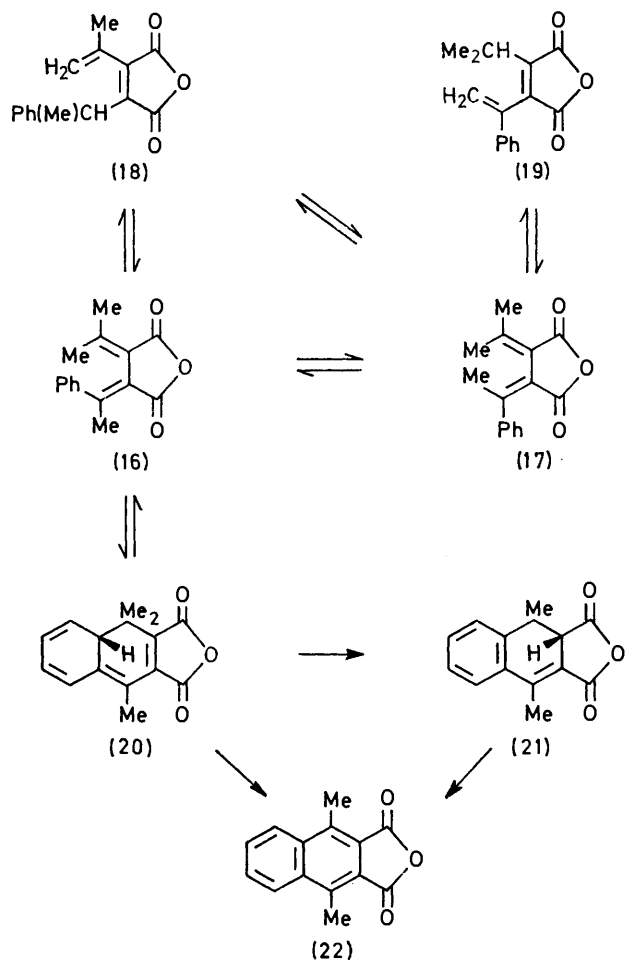
(*Z*)-Diphenylmethylene-(α -phenylethylidene)succinic anhydride (1c) undergoes the above sequence of reactions to yield the 1,2-dihydronaphthalene (3c), and isomerises to the (*E*)-isomer (4) which rearranges in a similar manner to give the dihydronaphthalenes (5) and (6). Compound (5) is not formed in the photorearrangement of the (*E*)-isomer (4);⁶ this undergoes the predicted³ conrotatory ring closure, followed by a thermal suprafacial 1,5-hydrogen shift, to yield the dihydronaphthalenes (3c) and (6) (Scheme 1).



SCHEME 2

Some related fulgides⁴ (substituted bismethylene-succinic anhydrides) undergo thermal 1,5-hydrogen

shifts, presumably by a suprafacial mode, to give derivatives of penta- and hexa-1,3-diene-3,4-dicarboxylic anhydrides (23), a sigmatropic rearrangement not previously recorded for this class of compounds. Competing with geometrical isomerism and reversible sigmatropic rearrangements are the electrocyclic reactions of fulgides and their subsequent 1,5-hydrogen shifts to yield, more slowly but irreversibly, the 1,2-dihydronaphthalenes. The equilibria between isomeric derivatives of fulgide and maleic anhydride are displaced in favour of the dihydronaphthalenes and the fully aromatic compounds derived from them, so that, on prolonged heating, they become the main or sole products of the reaction [Schemes 2 and 3 and Table 1].



SCHEME 3

Because of the thermal interconversion of the (*E,E*)-, (*E,Z*)-, and (*Z,Z*)-bis-(α -phenylethylidene)succinic anhydrides (7a), (8a), and (9a), it was not possible to establish whether the (*E,Z*)-isomer (8a) undergoes the reversible 1,5-hydrogen shift to yield the 2,5-diphenylhexa-1,3-diene-3,4-dicarboxylic anhydride (11a) as well as the rearrangement to the dihydronaphthalene (13a). The (*E,E*)-isomer (7a) gives the dihydronaphthalene (12a) and the (*Z,Z*)-isomer (9a) gives the anhydride (11a). From the variation of product composition with time,

there is no evidence of direct interconversion of (*E,E*)- and (*Z,Z*)-isomers (7a) and (9a) *via* the cyclobutenedicarboxylic anhydride intermediate (15a) [Scheme 2 and Table 1(a)].

Similarly, the isomeric 2-benzylidene-3-(α -phenylethylidene)succinic anhydrides interconvert on heating. The (*2E,3E*)- and (*2Z,3E*)-isomers (7b) and (8b) undergo disrotatory ring closure followed by a 1,5-hydrogen shift to yield the 1,2-dihydronaphthalenes (12b) and (13b), respectively, together with 1-methyl-4-phenyl-naphthalene-2,3-dicarboxylic anhydride (14), the product from dehydrogenation. The (*2E,3Z*)- and/or the (*2Z,3Z*)-isomers (10) and (9b), which cannot undergo the previous reaction to give the dihydronaphthalenes (12b) and (13b), undergo the reversible sigmatropic rearrangement to yield 2,5-diphenylpenta-1,3-diene-3,4-dicarboxylic anhydride (11b). On prolonged heating, the isomeric fulgides, the anhydride (11b), and the dihydronaphthalenes (12b) and (13b) are gradually converted into the fully aromatic compound (14), which is finally obtained in quantitative yield [Scheme 2 and Table 1(b)].

(*Z*)-Isopropylidene-(α -phenylethylidene)succinic anhydride (17) isomerises to the (*E*)-anhydride (16) and can undergo a reversible sigmatropic rearrangement to 2-methyl-5-phenyl- and 5-methyl-2-phenyl-hexa-1,3-diene-3,4-dicarboxylic anhydride (18) and (19). The (*E*)-anhydride (16) cyclises to the intermediate 1,8a-dihydronaphthalene (20) which undergoes an irreversible 1,5-hydrogen shift to give the 1,2-dihydronaphthalene (21) and can give the 2-methyl-5-phenylhexadienedicarboxylic anhydride (18). On heating, all the above products are formed but are gradually converted into the 1,2-dihydronaphthalene (21) and 1,4-dimethylnaphthalene-2,3-dicarboxylic anhydride (22). The latter is presumably formed by elimination of methane from the 1,8a- and 1,2-dihydronaphthalenes (20) and (21) [*cf.* the conversion of (3a) into (14)²] [Scheme 3 and Table 1(c)].

N.m.r. data for the maleic anhydride derivatives (23) are given in Table 2. Rearrangement products were not separated but were identified by comparison of their n.m.r. spectra with those of pure samples isolated from photoreactions (Table 2, ref. 6). Small extraneous absorptions in the n.m.r. spectra of some samples subjected to prolonged heating were not assigned. Product compositions are approximate and were estimated from the integrals of characteristic absorptions of each identified component.

EXPERIMENTAL

The (α -phenylethylidene)(substituted methylene)succinic anhydrides were prepared as described⁵ and samples (50–100 mg) were heated at 180 °C in redistilled *o*-dichlorobenzene (30 ml) or in deuteriochloroform (99.8%; distilled from anhydrous sodium carbonate) (0.5 ml in a sealed n.m.r. tube). *o*-Dichlorobenzene was removed under reduced pressure (0.2 mmHg) at the end of the reaction and replaced by deuteriochloroform (0.5 ml) for n.m.r. studies. The rearrangement reactions were similar for both solvents. N.m.r. spectra were measured with Perkin-Elmer R12 (60

MHz) or R32 (90 MHz) spectrometers (tetramethylsilane as internal standard). Unless stated otherwise, 1,2-dihydronaphthalenes were identified by comparison of their n.m.r.

reduced pressure and the residue was dissolved in water, extracted with ether, and the aqueous layer separated and acidified with 5M-hydrochloric acid. The oily half-ester

TABLE 1

Change in product composition (%) with time on heating (α -phenylethylidene)(substituted methylene)succinic anhydrides at 180 °C in deuteriochloroform

(a) Bis-(α -phenylethylidene)succinic anhydrides						
Time (h)	(<i>E,E</i>) (7a)	(<i>E,Z</i>) (8a)	(<i>Z,Z</i>) (9a)	MA (11a)	1,2-DHN (12a)	1,2-DHN (13a)
0	100					
1.25	50	17		21	12	
5	12	5		40	27	16
10	6			36	38	20
17.25	2			16	55	27
0		100				
0.25	26	32		26	16	
1.25	19	11		42	28	
14.2				12	76	12
20					85	
			100			
0.1		26	42	32		
0.2	6	32	10	52		
0.25	13	29		58		
1.25	15	9		61	6	6
20				23	39	38
(b) Benzylidene-(α -phenylethylidene)succinic anhydrides						
Time (h)	(<i>E,E</i>) (7b)	(2 <i>E</i> ,3 <i>Z</i>) (10)	MA (11b)	1,2-DHNs (12b and 13b)	(14)	
0		100				
1	38	8	54			
4.5	5	2	64	26	2	
7			53	40	7	
17			23	11	66	
23						100
(c) Isopropylidene-(α -Phenylethylidene)succinic anhydrides						
Time (h)	(<i>E</i>) (16)	(<i>Z</i>) (17)	MA (18)	(Ma) (19)	1,2-DHN (21)	(22)
0		100				
2½	60		28	12		
23	29		13	20	33	6
52	15		3	3	55	24

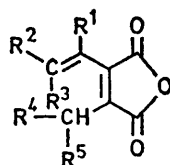
MA, maleic anhydride derivative; DHN, dihydronaphthalene.

spectra with authentic samples (Table 2 and ref. 6). Light petrol refers to the fraction having b.p. 60–80°, and all solvents were dried and distilled before use.

was extracted with ether, the extract dried (MgSO₄) and filtered, and the ether removed. The residual oil was boiled in ethanolic potassium hydroxide (5% w/v) for 2 h. Ethanol

TABLE 2

N.m.r. data for maleic anhydride derivatives



(23)

Compound	R ¹	R ²	R ³	R ⁴	R ⁵	τ values					
						R ¹	R ²	R ³	R ³	R ⁴	H
(11a)	Ph	H	H	Ph	Me		3.98	4.37		8.46d †	6.06q †
(11b)	Ph	H	H	Ph	H		4.08	4.25		6.48	6.48
(18)	Me	H	H	Ph	Me	7.90t *	4.45q *	4.70q *		8.27d †	5.65q †
(19)	Ph	H	H	Me	Me		4.03	4.37	8.78d †	8.78d †	7.27h †

d doublet; t, triplet; q, quartet; h, heptet. * Allylic coupling, J 1 Hz. † Geminal coupling, J 7 Hz.

Diphenylmethylene(isopropylidene)succinic Anhydride (1b). —A mixture of diethyl isopropylidene succinate (53.5 g) and benzophenone (45.5 g) was added dropwise over 30 min to potassium *t*-butoxide [from potassium (11 g)] in *t*-butanol (500 ml) and refluxed for 1 h. *t*-Butanol was removed under

was removed and the residue acidified to afford the diacid (62 g). The diacid in acetyl chloride (200 ml) was refluxed for 1 h. Excess of acetyl chloride was removed and the residual dark oil was crystallised from toluene–light petroleum (1 : 4 v/v), to afford the anhydride (1b) (20.3 g) as

yellow needles, m.p. 167—169° (lit.,⁴ 171.5°), τ 2.4—2.9 (10 H, complex m, ArH), 7.70 (3 H, s, Me *cis* to C=O), and 8.72 (3 H, s, Me *trans* to C=O).

1,1-Dimethyl-4-phenyl-1,2-dihydronaphthalene-2,3-dicarboxylic Anhydride (3b).—The anhydride (1b) (100 mg) after refluxing for 15 h in *o*-dichlorobenzene (30 ml), gave the 1,2-dihydronaphthalene (3b) in 38% yield. A quantitative yield was obtained by irradiation of the anhydride (1b) (300 mg) in toluene (200 ml) at 366 nm for 40 h at 54° using two 125 W mercury discharge lamps with Wood's glass filters. Solvent was removed and the dihydronaphthalene was crystallised from toluene–light petroleum to form needles, m.p. 185—187°, τ 2.3—3.1 (9 H, complex m, ArH), 6.20 (1 H, s, 2-H), 8.10 (3 H, s, Me), and 8.78 (3 H, s, Me) (Found: C, 78.8; H, 5.1. C₂₀H₁₆O₃ requires C, 78.9; H, 5.3%).

Thermal Rearrangement of (Z)-Diphenylmethylene-(α -phenylethylidene)succinic Anhydride (1c).—When the anhydride (1c) was heated for 8 h in *o*-dichlorobenzene or deuteriochloroform, a 7 : 4 : 4 mixture of the 1,2-dihydronaphthalenes (3c), (5), and (6) was obtained. The dihydronaphthalene (5), which has not been reported previously, was not isolated but showed τ 5.31 (1 H, s, 2-H) and 8.27 (3 H, s, Me).

Thermal Reactions of (E,E)-, (E,Z)-, and (Z,Z)-Bis-(α -phenylethylidene)succinic Anhydrides (7a), (8a), and (9a).—Each anhydride (100 mg) was heated in deuteriochloroform in a sealed tube. The change in composition of products with time is shown in Table 1(a). Similar results were obtained when the anhydrides were refluxed in *o*-dichlorobenzene. Double resonance irradiation of the quartets at τ 5.55 (12a) and 6.10 (13a) caused the methyl doublets (J 2.4 Hz, allylic coupling) at 7.25 (12a) and 7.35 (13a) to collapse to singlets.

Thermal Reactions of (2E,3E)- and (2E,3Z)-2-Benzylidene-3-(α -phenylethylidene)succinic Anhydrides (7b) and (10).—

The (2E,3E)-anhydride (7b) (200 mg) in *o*-dichlorobenzene (5 ml) was refluxed for 24 h under nitrogen. On cooling, needles of the 1,2-dihydronaphthalene (12b) (40 mg) separated, m.p. 188—189°, identical (m.p., n.m.r.) with an authentic sample.

Addition of light petroleum to the filtrate caused the dihydronaphthalene (13b) to separate. The compound was crystallised from chloroform–light petroleum, giving needles, m.p. 148—150°, identical (m.p., n.m.r.) with an authentic sample.

The (2E,3Z)-anhydride (10), on heating at 180 °C in deuteriochloroform from which oxygen had not been excluded, gave the rearrangement products shown in Table 1(b), and on prolonged heating (23 h) gave a quantitative yield of 1-methyl-4-phenylnaphthalene-2,3-dicarboxylic anhydride (14).²

Thermal Reactions of (Z)-Isopropylidene-(α -phenylethylidene)succinic Anhydride (16).—When the (Z)-anhydride (16) was heated for 4 h in *o*-dichlorobenzene, the same mixture of products was obtained as on heating in deuteriochloroform at 180 °C [see Table 1(c)].

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