Overcrowded Molecules. Part 16.[1] Thermal and Photochemical Reactions of (*E,E*)-Bis(benzylidene)succinic Anhydride

By **Oscar Crescente, Harry G. Heller,** and **Stephen Oliver,** Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth SY23 1NE

Irradiation of (*E,E*)-bis(benzylidene)succinic anhydride in toluene gives 1-phenyl-1,4-dihydronaphthalene-2,3-dicarboxylic anhydride; in the presence of trichloroacetic acid, *cis*- and *trans*-1-phenyl-1,2-dihydronaphthalene-2,3-dicarboxylic anhydrides are also formed; and in the presence of triethylamine, only 1-phenylnaphthalene-2,3-dicarboxylic anhydride and bis(benzyl)maleic anhydride are formed. The last two products are obtained exclusively when (*E,E*)-bis(benzylidene)succinic anhydride is heated in xylene containing triethylamine at 140 °C in *o*-dichlorobenzene at 180 °C, or on heating alone at 180 °C. All the products are presumed to be formed through a 1,8a-dihydronaphthalene intermediate, and bis(benzyl)maleic anhydride *via* rearrangement of (*E*)-benzylidenebenzylsuccinic anhydride. The latter yields (*E,E*)-bis(benzylidene)succinic anhydride, the most sterically hindered of the geometrical isomers, on bromination with *N*-bromosuccinimide followed by dehydrobromination with 2,4,6-trimethylpyridine.

SUCCESSIVE condensation of diethyl succinate with benzaldehyde and *p*-methoxybenzaldehyde gives the same benzylidene-(*p*-methoxybenzylidene)succinic acid as is obtained when the condensations are carried out in the reverse order.[2] Since the bis-(*p*-methoxybenzylidene)succinic acid prepared by a similar procedure gives only one anhydride which has been shown by *X*-ray crystallographic analysis to be the (*E,E*)-isomer (1a; R = OCH₃),[3] it follows that the bis(benzylidene)succinic anhydride, from the condensation of diethyl succinate with benzaldehyde,[4] is also the (*E,E*)-isomer (1a; R = H), and this is confirmed by its n.m.r. spectrum which shows a low-field singlet at τ 2.05[5] attributed to the two olefinic hydrogens deshielded by the carbonyl groups. The stereoselective Stobbe condensation of diethyl succinate with most aromatic aldehydes can be explained by an ' overlap control ' mechanism[6] to give an (*E,E*)-bis(arylmethylene)succinic acid in which severe steric interactions between aryl groups are only introduced when the acid is converted into the anhydride.

It is surprising and unexplained that the most sterically hindered of the three possible geometrical isomers of bis(benzylidene)succinic anhydride (1a; R = H) is the only product which could be isolated when (*E*)-benzylidenebenzylsuccinic anhydride (9a)[2] or bis(benzyl)maleic anhydride (10a)[2] are first brominated with *N*-bromosuccinimide in carbon tetrachloride and then dehydrobrominated using 2,4,6-trimethylpyridine in ether.

In 1904, Stobbe[7] reported that the bis(benzylidene)succinic anhydride, m.p. 203 °C, to which we assign the (*E,E*)-configuration, showed photochromic properties and gave a yellow to orange-red reversible colour change on irradiation and that 1-phenylnaphthalene-2,3-dicarboxylic anhydride (8) was obtained when a solution of the anhydride (1a; R = H) in benzene containing iodine was left in sunlight. His claim that the anhydride (1a; R = H) is thermochromic, undergoing a lemon-yellow to orange-red colour change on heating at 150 °C and reversed on cooling, could not be substantiated by us. Later, he[8] reported that anhydride (1a; R = H) rearranged in sunlight into 1,2- and 1,4-dihydronaphthalene derivatives (1,2- and 1,4-DHN) (5a and/or

6a) and (7) respectively but no supporting evidence for the structural assignment of photoproducts is recorded. The further study by Weinstein and Brattesani[9] provided some i.r. spectra data in support of the structure of the 1,4-DHN (7). In 1968, Santiago and Becker[10] investigated the photochromic properties of (*E,E*)-bis(benzylidene)succinic anhydride (1a; R = H) [to which they incorrectly assigned the (*E,Z*)-configuration (2)] and suggested that the orange-red colour produced on u.v. irradiation was due to photocyclisation of the anhydride (1a; R = H) to yield a 1,8a-DHN intermediate, which gave the naphthalic anhydride (8) in the presence of hydrogen abstractors such as oxygen or iodine.

RESULTS AND DISCUSSION

As part of our programme on the development of thermally stable sensitive photochromic organic compounds, we report our studies on the (*E,E*)-anhydride (1a; R = H). In our earlier publications[6,11] we reported that many phenyl-substituted bis(methylene)succinic anhydrides and *N*-phenylimides undergo thermal disrotatory and photochemical conrotatory ring-closure reactions to yield coloured 1,8a-DHN derivatives, which in turn undergo disrotatory ring opening and 1,5-H shifts in competing thermal processes. We have reported[5] that irradiation at 366 nm of (*E,E*)-bis(benzylidene)-*N*-phenylsuccinimide (1b; R = H) in benzene at 80 °C gives the *trans*-1,2-DHN (6b) and now record that the imide (1b; R = H) on heating at 180 °C in *o*-dichlorobenzene yields the *cis*-1,2-DHN (5b). If a sequence of reactions occurs in accord with the Woodward–Hoffmann rule for pericyclic reactions[12] then these stereospecific reactions are best explained by photochemical or thermal isomerisation of the (*E,E*)-imide (1b; R = H) to the thermodynamically more stable (*E,Z*)-isomer (2b), prior to the electrocyclic and 1,5-H shift reactions as is shown in Scheme 1.

(*E,E*)-Bis(benzylidene)succinic anhydride (1a; R = H) does not undergo a similar series of reactions. When irradiated in benzene at 25 or 80 °C, or in deuteriochloroform at 100 °C, the anhydride (1a; R = H) gives

only the 1,4-DHN (7) and the fully aromatic compound (8). When the anhydride (1a; R = H) is irradiated at 366 nm in deuteriochloroform containing 1% w/v


a; X = O
b; X = NPh

SCHEME 1
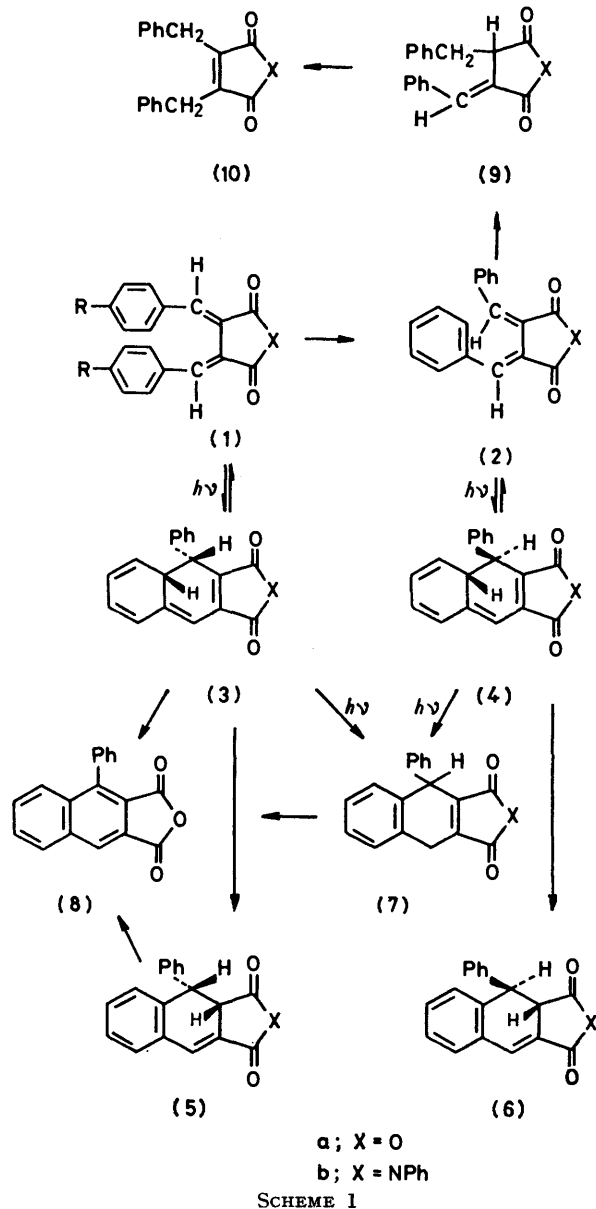
trichloroacetic acid a mixture of cis- and trans-1,2-DHN (5a) and (6a) and 1,4-DHN (7) is obtained. The product composition varies with the amount of acid added and the temperature at which the photoreaction is carried out. Irradiation at 25 °C gave 45% cis-1,2-DHN (5a), 10% trans-1,2-DHN (6a), and 45% 1,4-DHN (7), while at 100 °C under similar conditions, a mixture of 8% cis-1,2-DHN (5a), 82% trans-1,2-DHN (6a), and 10% 1,4-DHN (7) was obtained. The dihydronaphthalenes (5a), (6a), or (7a) in deuteriochloroform containing 1% w/v trichloroacetic acid did not rearrange on heating (4 h) at 100 °C. Percentage compositions are approximate and were determined by measuring the integral of character-

istic peaks in the 90 MHz spectra of the crude photo-products.

The structure and stereochemistry of the cis- and trans-1,2-DHN (5a) and (6a) follow from their n.m.r. spectra which show $J_{1,2}$ 8 and 16 Hz, characteristic of cis (eq–ax) and trans (ax–ax) arrangements of hydrogens at C-1 and C-2 respectively, and $J_{2,4}$ 3 Hz, typical for allylic coupling.[11] The 1,4-DHN (7) shows a doublet at τ 6.02 ($J_{1,4}$ 4.5 Hz) and a triplet at τ 4.82 ($J_{1,4}$ 4.5 Hz), assigned to the hydrogens at C-4 and C-1 respectively. Double-resonance irradiation at τ 4.82 caused the doublet at τ 6.02 to collapse to a singlet. Comparable homo-allylic coupling constants have been reported for related 1,4-DHN derivatives.[13] It would appear that the cis- and trans-1,8a-DHN [(3a) and (4a)], formed by photo-chemical conrotatory ring closure of the (E,E)- and (E,Z)-anhydrides (1a; R = H) and (2a) undergo a more facile photochemical 1,7-H shift than our previously studied phenyl-substituted bis(methylene)succinic anhydrides,[6,11] and that the competing thermal 1,5-H shift reaction is acid-catalysed.

When triethylamine (1% w/v) was added to the (E,E)-anhydride (1a; R = H) in toluene (with the intention of removing acid impurities) the solution turned deep green and on irradiation gradually became colourless and gave, on work-up, naphthalic anhydride (8) and bis(benzyl)-maleic anhydride (10) as the only detectable products. While the (E,E)-anhydride (1a; R = H) is unaffected on heating at 140 °C in xylene, it gives the products (8) and (10a), when triethylamine (1—2% w/v) is added. The same two products are obtained also when the (E,E)-anhydride (1a; R = H) is refluxed in o-dichloro-benzene or heated alone at 180 °C.

We suggest that the (E,E)-anhydride (1a; R = H) undergoes addition of triethylamine to give the green intermediate (11) which cyclises at 140 °C to a 1,8a-DHN (Scheme 2) and that the (E,E)-anhydride (1a; R = H)

(1a; R = H) + NEt₃ ⟶

(11)

(3a) and / or (4a) ⟵

+

NEt₃

SCHEME 2
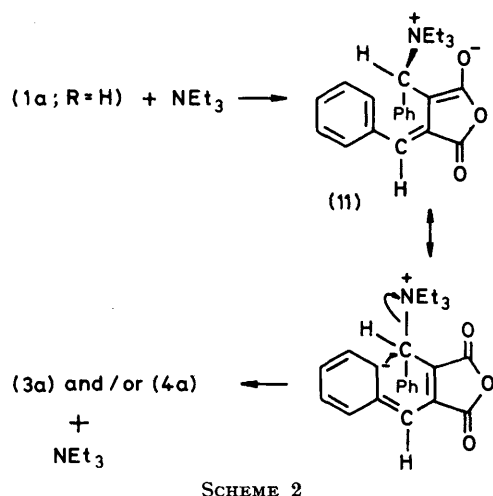
abstracts hydrogen from the 1,8a-DHN thermally or in a base-catalysed photochemical reaction to yield (E)-benzylidenebenzylsuccinic anhydride (9a) which has

been shown to rearrange to the more stable bis(benzyl)-maleic anhydride (10a) under the reaction conditions described. The (E,E)-N-phenylimide (1b; R = H) does not give (E)-benzylidenebenzyl-N-phenylsuccin-imide (9b) or bis(benzyl)-N-phenylmaleimide (10b) under reaction conditions which give rise to bis(benzyl)maleic anhydride (10a). The imide (1b; R = H) in toluene does not show a green colouration on addition of tri-ethylamine but then the imide would be expected to be less susceptible to nucleophilic attack than the anhydride (1a; R = H).

When the isomeric benzylidene(mesitylmethylene)-succinic anhydrides [e.g. the (E,E)-isomer (12)] are heated as a melt at 180 °C, or in xylene containing triethylamine (1% w/v) at 140°, or irradiated (366 nm)

(12)

(13)   (14)

(15)
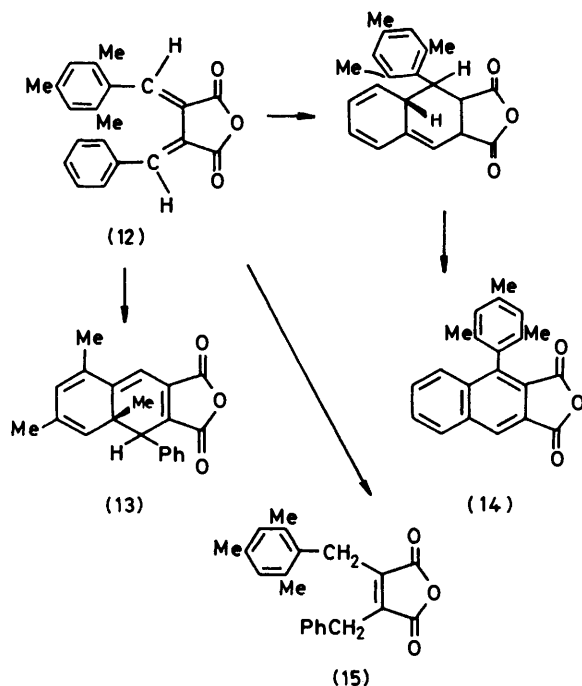
SCHEME 3

in toluene containing triethylamine (1% w/v) at room temperature, E–Z isomerisation occurs and 1-mesityl-naphthalene-2,3-dicarboxylic anhydride (14) and benzyl-(mesitylmethyl)maleic anhydride (15) are formed, presumably as described above (Scheme 3). In marked contrast, on irradiation (366 nm) of the isomeric benzyl-idene(mesitylmethylene)succinic anhydrides in benzene at 54 °C for four weeks, the only observed reactions were photoequilibration of geometrical isomers and photo-cyclisation to the 1,8a-DHN (13).[5] The most likely explanation for the complete absence of photoproducts, analogous to those found on irradiation of bis(benzyl-idene)succinic anhydride (1a; X = O), is exclusive photochemical ring-closure onto the mesityl group.

EXPERIMENTAL

N.m.r. spectra were measured for solutions in deuterio-chloroform with a Perkin-Elmer R32 (90 MHz) spectro-

meter (tetramethylsilane as internal standard). Photo-chemical reactions were carried out for all solvents except deuteriochloroform on 0.1—0.5% solutions 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. Solvent was removed and replaced by deuteriochloroform for n.m.r. studies. Photoreactions in deuteriochloroform were carried out in sealed n.m.r. tubes and exposed to irradiation (366 nm) from a 250-W mercury-vapour discharge lamp (type ME/D) with a filter (type OX1, Chance Pilkington) focused onto the solution. The tube was heated at 100 °C during irradiation by immersion in the vapour of boiling methyl-cyclohexane. Deuteriochloroform (99.8%) and o-dichloro-benzene were boiled with, and distilled from, anhydrous sodium carbonate. Benzene and toluene were dried with sodium wire and distilled from calcium hydride.

(E,E)-Bis(benzylidene)succinic anhydride (1a; R = H).—(E)-Benzylidenebenzylsuccinic anhydride (9a)[2] or bis-(benzyl)maleic anhydride[2] (10a) (1.45 g; 5 mmol) was boiled with N-bromosuccinimide (1.35 g; 5 mmol) in carbon tetrachloride (30 ml) for 2 h. Succinimide was filtered off, solvent removed, and the intractible residual oil stirred (8 h) with 2,4,6-trimethylpyridine (1.27 g; 10 mmol) in ether. The reaction mixture was washed with water, the ether layer separated and dried (MgSO$_4$), and solvent removed. The residue gave the (E,E)-anhydride, m.p. 203 °C, yellow needles [from toluene (55%) yield] and petrol (45% yield)], m.p. 203 °C (lit.,[7] m.p. 203 °C, identical to the (E,E)-anhydride obtained via condensation of benzaldehyde with diethyl succinate in the presence of sodium hydride in toluene.[4, 11]

Rearrangement Reactions of (E,E)-Bis(benzylidene)-N-phenylsuccinimide (1b; R = H).—The imide (100 mg) in deuteriochloroform (0.5 ml) at 100 °C gave, on irradiation, trans-1,2-DHN (6b);[11] when it was heated at 180 °C in the dark it gave the cis-1,2-DHN (5b).[11]

Rearrangement Reactions of (E,E)-Bis(benzylidene)-succinic Anhydride (1a; R = H).—(a) The anhydride (100 mg) in deuteriochloroform at 100 °C, or in benzene at 25 or 80 °C gave, on irradiation, only the 1,4-DHN (7) as colour-less crystals, m.p. 167—170 °C (lit.,[8] 172—175 °C), which oxidises to the naphthalic anhydride (8) on repeated crystal-lisation. N.m.r.; τ 2.5—2.9 (9 H, br, s, ArH), 4.82 (1 H, t, $J_{1,4}$ 4.5 Hz, 1-H), and 6.02 (2 H, d, $J_{1,4}$ 4.5 Hz, 4-H).

(b) Irradiation of the anhydride (100 mg) in deuterio-chloroform containing trichloroacetic acid (1% w/v) at 25 and 100 °C, gave mixtures of cis- and trans-1,2-DHN [(5a) and (6a)] and 1,4-DHN (7) which were not separated. The cis-1,2-DHN (5a) had n.m.r. signals at τ 2.22 (1 H, d, $J_{2,4}$ 2.5 Hz, 4-H), 5.21 (1 H, d, $J_{1,2}$ 8 Hz, 1-H), and 5.65 (1 H, q, $J_{1,2}$ 8 and $J_{2,4}$ 2.5 Hz, 2-H). The trans-1,2-DHN (6a) had n.m.r. signals at τ 2.30 (1 H, d, $J_{2,4}$ 2.5 Hz, 4-H), 5.58 (1 H, d, $J_{1,2}$ 16 Hz, 1-H), and 5.88 (1 H, q, $J_{1,2}$ 16 and $J_{2,4}$ 2.5 Hz).

(c) The anhydride (100 mg) in toluene (100 ml) containing triethylamine (1 g) at 70 °C was irradiated (32 h). Solvent was removed and the residue triturated with light petrol-eum. The insoluble naphthalic anhydride (8) was filtered off, and crystallised from chloroform and petrol to give colourless crystals, m.p. 256 °C (lit.,[14] 255 °C). The light petroleum extract gave bis(benzyl)maleic anhydride (10a) which was identified by comparison of its n.m.r. spectrum with an authentic sample;[2] τ 2.6—3.0 (10 H, m, ArH) and 6.22 (4 H, s, CH$_2$), and characterised as the N-o-amino-

phenylmaleimide, by reaction with *o*-phenylenediamine, golden crystals, m.p. 164 °C (from ethanol), undepressed when admixed with an authentic sample.[2] A similar photoreaction at 25 °C gave the same products.

(*d*) Bis(benzyl)maleic anhydride (10a) was also obtained when the anhydride (1a; R = H) was heated in xylene containing triethylamine (1% w/v) at 140 °C, in *o*-dichlorobenzene at 180 °C, or without solvent at 180 °C.

Rearrangement Reactions of (E,E)-*Benzylidene(mesitylmethylene)succinic Anhydride* (12).—(*a*) The anhydride (12) (50 mg) in xylene (50 ml) containing triethylamine (1% w/v) was refluxed (60 h). Solvent was removed, and the n.m.r. spectrum showed that the product consisted in a mixture of naphthalic anhydride and the maleic anhydride derivatives (14) and (15) respectively, with small amounts of other unidentified materials. The product was extracted with boiling light petroleum (4 × 20 ml) and the combined extracts were evaporated to dryness to give the maleic anhydride (15) as an oil, τ 2.7—2.9, 3.1 (7 H, m, ArH), 6.12 and 6.58 (4 H, 2s, 2 × CH$_2$), 7.69 (3 H, s, *p*-Me), and 7.82 (6 H, s, 2 × *o*-Me), characterised as the *N*-*o*-aminophenylmaleimide,[2] by reaction with *o*-phenylenediamine, golden crystals, m.p. 157—157 °C (from ethanol) (Found: C, 78.8; H, 6.6; N, 6.7. C$_{27}$H$_{26}$O$_2$N$_2$ requires C, 79.0; H, 6.4; N, 6.8%).

The residue consisted mainly of the naphthalic anhydride (14) which showed characteristic resonances at τ 1.35 (1 H, s, 1-H), 7.64 (3 H, s, *p*-CH$_3$), and 8.18 (6 H, s, 2 × *o*-CH$_3$).

(*b*) The anhydride (12) (50 mg) in *o*-dichlorobenzene (30 ml) was refluxed (14 h) at 180 °C. Only *E–Z* isomerisation occurred but when the anhydride (12) (50 mg) was heated (14 h) without solvent it was converted nearly quantitatively into the maleic anhydride (15) and the naphthalic anhydride (14), in the approximate ratio of 3 : 2.

(*c*) The anhydride (12) (60 mg) in toluene (5 ml) containing triethylamine (1% w/v) was irradiated (50 h) at room temperature. The n.m.r. spectrum of the product showed a mixture of gometrical isomers together with the maleic anhydride (15) and the naphthalic anhydride (14).

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