Benzocyclobutenes. Part 4.[1] Synthesis of Benzocyclobutene-1,2-diones by Pyrolytic Methods

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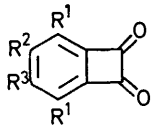
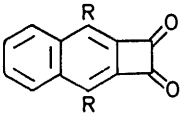
Oxidation of the cyclic hydrazides prepared from phthalic anhydrides in the presence of anthracene gives the corresponding Diels–Alder adducts which, on flash vacuum pyrolysis, give benzocyclobutene-1,2-dione (BBD) and its 4-chloro, 3,6- and 4,5-dichloro, 4,5-dibromo, and 4,5-dimethyl derivatives in 75—98% yield. Cyclobuta[*b*]- and cyclobuta[*a*]-naphthalene-1,2-dione as well as cyclobuta[*b*]- and cyclobuta[*a*]-pyridine-1,2-dione have been prepared similarly; the last three of these diones are very unstable. Cyclobuta[*b*]naphthalene-1,2-dione has also been made by pyrolysis of benz[*f*]indene-1,2,3-trione. Attempts to make thiophen and furan analogues of BBD from appropriate anthracene adducts failed as did attempts to make tetrachloro- and tetrabromo-derivatives of BBD by the pyrolysis of tetrahalogenophthalimidosulphoximides.

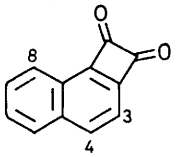
BENZOCYCLOBUTENE-1,2-DIONE (1) (BBD) is a useful intermediate for the synthesis of 1,2-disubstituted benzocyclobutenes [2] and of thiophen- [3] and 1,4-diaza-analogues [4] of biphenylene. It has been made from 1,2-dibromobenzocyclobutene *via* the 1,2-dinitrate [5] and *via* the 1,1,2,2-tetrabromide; [5] by the hydrolysis of 2,2-dibromobenzocyclobuten-1-one; [6] by the vapour phase pyrolysis of indene-1,2,3-trione,[7] of the Diels–Alder adducts of phthalazine-1,4-dione with cyclopentadiene [8] and with indene,[8] and by similar pyrolysis of *SS*-



(1) $R^1 = R^2 = R^3 = H$
(2) $R^1 = R^3 = H, R^2 = Cl$
(3) $R^2 = R^3 = H, R^1 = Cl$
(4) $R^1 = H, R^2 = R^3 = Cl$
(5) $R^1 = H, R^2 = R^3 = Br$
(6) $R^1 = H, R^2 = R^3 = Me$



(7) R = Ph
(8) R = H



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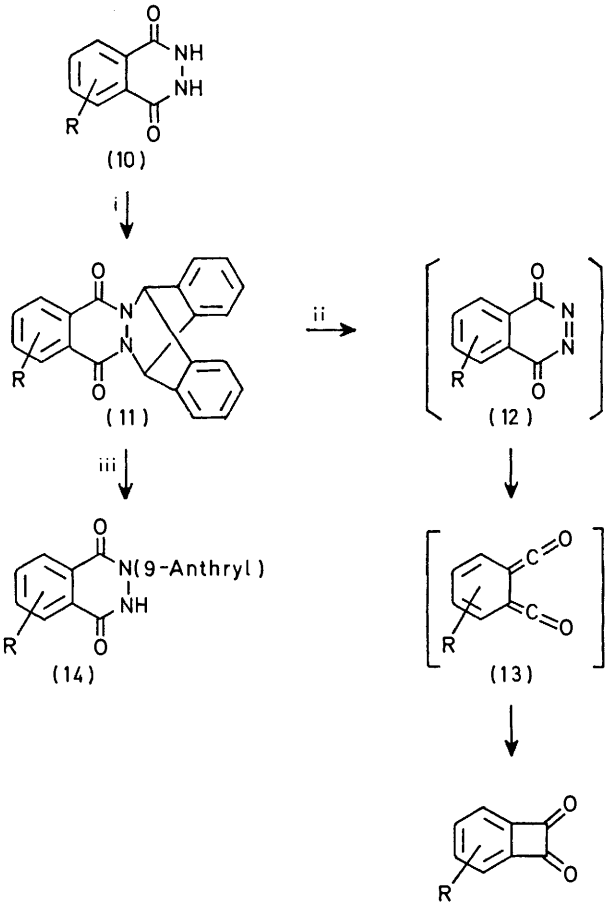
dimethyl-(and -diphenyl)-*N*-phthalimidosulphoximide [9] and of 3-benzoyloxyphthalide; [10] by the oxidation of *N*-aminophthalimide; [11] from diethyl cyclohex-4-ene-1,2-dicarboxylate; [12] and from cyclo-octa-1,5-diene.[13] Substituted benzocyclobutenediones would be of interest by themselves as well as being versatile intermediates. As mentioned in our preliminary communication [14] only two such compounds had been made at the outset of our work, namely, 3,8-diphenylcyclobuta[*b*]naphthalene-1,2-dione (7) [15] and 3,4,5,6-tetrachlorobenzocyclobutenedione.[16] Since then, the 3-methoxy-, 3-methoxymethoxy-, and (by hydrolysis of the latter) 3-hydroxy-derivatives of BBD have been made [17] by our method and the following derivatives have been made by a variety of other methods: 3-amino,[18] 3,6-dibromo-4,5-dichloro,[19] 4,5-dichloro-3,6-dimethyl,[19] and 3,4,5,6-tetrafluoro.[20]

Benzocyclobutene-1,2-diones.—As a general route to these diones the flash vacuum pyrolysis of Diels–Alder adducts of phthalazine-1,4-diones (12) appeared attractive to us both because of the availability of substituted precursors and the reasonably low pyrolysis temperature used. Rees *et al.*[8] had found that pyrolysis of the cyclopentadiene and indene adducts of phthalazine-1,4-dione



SCHEME Reagents: i, $Pb(OAc)_4$–Anthracene; ii, Pyrolysis; iii, Pyrolysis or H^+

(12; R = H) at 500 °C gave BBD in 88 and 64% yields respectively. However, in our apparatus these adducts gave much lower yields of BBD so we turned our attention to the anthracene adduct (11; R = H), which had been made (but not pyrolysed) by Clement.[21]

This proved very satisfactory: at 450 °C it gave an almost quantitative yield of BBD; at 300 °C there was no reaction; at 400 °C it gave BBD (18%) and unchanged adduct (74%) and at 800 °C the adduct yielded biphenylene in 23% yield.

Various substituted phthalic anhydrides were converted into 2,3-dihydrophthalazine-1,4-diones (10) which, on oxidation with lead tetra-acetate in the presence of anthracene, gave the respective Diels–Alder adducts (11) as shown in the Scheme. These were pyrolysed at 450 °C and 0.01 mmHg and gave the following new derivatives of BBD in 75—98% yield: 4-chloro (2), 3,6-dichloro (3), 4,5-dichloro (4), 4,5-dibromo (5), and 4,5-dimethyl (6). We have similarly made 4-methoxy- and 4,5-dimethoxy-BBD and thence the corresponding hydroxy-compounds: these are discussed in the following paper.[22] All of the symmetrically disubstituted adducts (11) gave the corresponding benzo- or naphtho-[*b*]cyclobutenediones and so did some of the monosubstituted compounds. However, when the unsymmetrical anthracene adducts (11) derived from 4-benzyl-, 4-bromo-, and 4-nitro-phthalic anhydride were pyrolysed they did not give the desired diones but, instead, isomerised and gave 9-substituted anthracenes (14), identified by their analyses, spectroscopic data, and by their preparation *via* the known acid-catalysed rearrangement of the adducts.[21] There are two possible isomers of each of the three anthracenes (14; R = $PhCH_2$, Br, and NO_2) and the melting points (Table 4) suggest that some of the products obtained by thermal or acid-catalysed isomerisation were mixtures but they could not be separated by chromatography. The anthracenes of type (14) were stable in our apparatus up to 800 °C, therefore can not be intermediates in the formation of the benzocyclobutenediones. We consider it unlikely that the thermal isomerisation of adducts (14; R = CH_2, Br, and NO_2) was caused by acid catalysis on the surface of the pyrolysis tube since this was cleaned with organic solvents or, when necessary, with a commercial scouring powder (alkaline) followed by washing with water and acetone.

Although the yields were very good in two of the steps of our BBD synthesis, namely the preparation of the cyclic hydrazides (10) and the pyrolysis of the adducts (11), the formation of the anthracene adducts often gave low yields (see Table 2). Ideally the oxidation of the

TABLE 1

Substituted 2,3-dihydrophthalazine-1,4-diones (10) and hetero-analogue

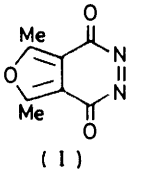
Substituent(s)	Solvent [a]	Yield (%)	M.p. (°C)	Analysis C [b]	H [b]	N [b]	C [c]	H [c]	N [c]
6-Benzyl [d]	Acetic acid	90	276—277	70.9	4.8	11.1	71.4	4.8	11.1
6,7-Dibromo	Acetic acid	94	>350	29.8	1.8	8.5	30.0	1.3	8.6
6,7-Dimethyl	Ethanol	78	>350	62.4	5.2	14.6	63.2	5.3	14.7
Dichloro-thiophen (23)	Acetic acid	32	315 (decomp.)	30.2	1.0		30.4	0.8	

[a] For preparation. [b] Found (%). [c] Required (%). [d] Recrystallised from nitrobenzene.

TABLE 2

Anthracene adducts of phthalazine-1,4-diones

Substituent(s) [a] or azo-compound	Solvent [b]	Yield (%)	M.p. (°C)	Analysis C [c]	H [c]	N [c]	C [d]	H [d]	N [d]
6-Benzyl	CCl_4	65	214—216	81.5	5.3	6.1	81.3	4.7	6.5
6-Bromo	CH_2Cl_2–light petroleum	32	267—268 (decomp.)	63.4	3.4	6.5	63.3	3.1	6.7
6-Chloro	CH_2Cl_2–light petroleum	40	266—268 (decomp.)	70.9	3.6	7.5	70.9	3.5	7.5
6,7-Dibromo	CH_2Cl_2–light petroleum	41	>350	53.9	2.6	5.6	53.2	2.4	5.7
5,8-Dichloro	CH_3OH	28	287—289 (decomp.)	65.1	3.2	6.9	64.9	3.0	6.9
6,7-Dichloro	CCl_4	19	>350	64.7	3.2	6.8	64.9	3.0	6.9
6,7-Dimethyl	CH_2Cl_2–light petroleum	34	310—311 (decomp.)	78.4	4.9	7.5	78.7	5.0	7.7
5-Nitro	C_2H_5OH	13	273—274 (decomp.)	68.6	3.7		68.9	3.4	
6-Nitro	CH_3OH	85	259—260	69.1	3.7		68.9	3.4	
Benzo[*f*]	$PhCH_3$	61	295—300 (decomp.)	80.0	4.3	7.0	80.4	4.2	7.2
Benzo[*g*]	CH_2Cl_2–light petroleum	89	308—309 (decomp.)	80.3	4.2	7.2	80.4	4.2	7.2
(I)	CH_2Cl_2–light petroleum	4	120—125 (decomp.)	(M^+ 356.116)			(M 356.116)		
(II)	CH_2Cl_2–light petroleum	8	319—320 (decomp.)	58.0	2.6	6.7	58.1	2.4	6.8
(III)	CH_2Cl_2–light petroleum	23	275—277 (decomp.)	74.2	4.0	12.2	74.3	3.9	12.4
(IV)	C_6H_6	23	277—278 (decomp.)	74.2	4.0	12.3	74.3	3.9	12.4



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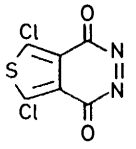

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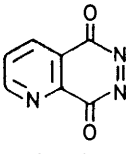

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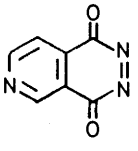


(IV)

[a] Position of substituent in phthalazine-1,4-dione. [b] For recrystallisation. [c] Found (%). [d] Required (%).

cyclic hydrazide (10) should be carried out in homogeneous solution but we were unable to find a solvent which would dissolve the lead tetra-acetate, cyclic hydrazide, and anthracene; we found the best compromise to be dichloromethane. We, therefore, studied some substituted anthracenes, in place of anthracene itself, in the hope that they would be more soluble in dichloromethane and/or more reactive. When the parent hydrazide (10; R = H) was oxidised in the presence of 2-methyl-, 9-methyl-, 9,10-dimethyl-, 9-chloro-10-methyl-, or 9,10-dichloro-anthracene it gave the corresponding adducts in 40, 40, 68, 30, and 0% yields respectively compared with 40—50% when anthracene was used (we were unable to get the 71% reported by Clement [21]). Pyrolysis of the adduct with 2-methylanthracene proceeded normally at 500 °C and gave BBD (50%) but similar pyrolysis of the other adducts regenerated the cyclic hydrazide in 29%, 60% (90 at 700 °C), and low yield respectively. The adduct with 9-methylanthracene, on treatment with acid, isomerised to the 10-methylanthranyl analogue of compound (14; R = H).

TABLE 3

Other Diels–Alder adducts with phthalazine-1,4-diones

'Diene'	Phthalazine-1,4-dione	Yield (%)	M.p. (°C)	Analyses C [a]	H [a]	N [a]	C [b]	H [b]	N [b]
2-Methyl-A [h]	parent	40 [c]	255—259 (decomp.)	79.0	5.0	7.7	78.4	4.6	8.0
9-Methyl-A	parent	40 [c]	197—199 (decomp.)	78.6	4.5		78.4	4.6	
9,10-Dimethyl-A	parent	68 [d]	230 (decomp.)	78.4	5.1	7.4	78.7	5.0	7.7
9-Chloro-10-methyl-A	parent	30 [e]	275 (decomp.)	71.0	4.2	7.0	71.4	3.9	7.3
9-Methyl-A	(III)	41 [f,g]	200—202 (decomp.)			11.8			11.9
9-Methyl-A	(IV)	34 [f]	185—187	75.1	4.7		74.8	4.3	
Cyclopentadiene	(III)	57 [c]	223—225 (decomp.) [Lit.,[26] 220 (decomp.)]	63.4	4.1	18.3	63.4	4.0	18.5
Indene	(III)	63 [c,f]	[229—231 (decomp.)]	69.6	4.1	14.8	69.3	4.0	15.2

[a] Found (%). [b] Required (%). [c] Recrystallised from CH_2Cl_2–light petroleum. [d] Recrystallised from EtOH. [e] Recrystallised from Me_2SO–H_2O. [f] Possibly a mixture of two isomers. [g] Recrystallised from $CHCl_3$. [h] A = anthracene.

The dibenzobiphenylene was also obtained (60%) by pyrolysis of the anthracene adduct at 650 °C. The electrochemistry and e.s.r. spectrum of dione (8) have been measured by Rieke *et al.*[25]

When the isomeric adduct, made from the cyclic hydrazide of naphthalene-1,2-dicarboxylic acid, was pyrolysed at 500 °C it gave the angular dione (9) in 5—20% yield. This poor yield was mainly due to thermal decomposition of the adduct before it sublimed. The yield was raised to 20% by mixing the adduct with four times its weight of anthracene and using a slightly lower temperature to sublime the mixture into the pyrolysis tube. Like its linear isomer (8) the angular dione (9) was thermally unstable. It melted at 192—193 °C but after further heating from 195 °C it turned red and solidified to red needles which melted slowly at 270 °C with decomposition. The dione (9) is also very light sensitive. When first made it was pale yellow but on exposure to sunlight it immediately turned green, but reverted to the yellow form if kept in the dark for a few minutes or by heating to 40 °C. This photochromic behaviour could be repeated several times but eventually the compound was converted into a yellow photodimer. Photodimerisation of BBD itself is known to occur *via* the bisketen (13) [23] and it is probable that the photolability of the angular dione (9) is related to the relative stability of

TABLE 4

2-Substituted-2,3-dihydrophthalazine-1,4-diones

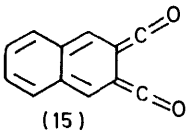
Substituents	Action of acid Yield (%)	Action of acid M.p. (°C)	Pyrolysis Yield (%)	Pyrolysis M.p. (°C)	Analysis C [a]	H [a]	N [a]	C [b]	H [b]	N [b]
2-(9-Anthryl)-6- or -7-benzyl [c]	49	285—295	29	288—295	81.6	4.6		81.3	4.7	
2-(9-Anthryl)-6- or -7-bromo [d]	72	324—325 (decomp.)	35	324—325 (decomp.)	63.4	3.2	6.7	63.3	3.1	6.7
2-(9-Anthryl)-6- or -7-nitro [e]	48	336—338 (decomp.)	74	336—338 (decomp.)	69.4	3.6	10.6	68.9	3.4	11.0
2-(10-Methyl-9-anthryl) [f]	44	330 (decomp.)			77.9	4.3		78.4	4.6	

[a] Found (%). [b] Required (%). [c] $\nu_{max.}$ 3 033, 1 628, and 1 570br cm^{-1}. [d] $\nu_{max.}$ 3 033, 1 623, 1 575, and 1 557 cm^{-1}. [e] $\nu_{max.}$ 3 033, 1 642, and 1 590br cm^{-1}. [f] $\nu_{max.}$ 3 080, 1 635, 1 590, and 1 560 cm^{-1}.

Naphtho-analogues of BBD.—Pyrolysis of the anthracene adduct derived from the cyclic hydrazide of naphthalene-2,3-dicarboxylic acid gave cyclobuta[*b*]-naphthalene-1,2-dione (8) (as yellow needles), which was stable at room temperature when protected from strong light. The compound did not melt sharply but on rapid heating melted at *ca.* 250—255 °C to give a red liquid which, on further heating, solidified to red needles. The mass spectrum of this red product corresponded to a dimer. This thermal instability is in contrast to the very stable parent (1), although this does dimerise photochemically.[23]

Cyclobuta[*b*]naphthalene-1,2-dione (8) was also formed by the pyrolysis of benz[*f*]indene-1,2,3-trione,[24] the products at 600 °C being the dione (8) (17%), dibenzo-[*b*,*h*]biphenylene (8%), and unchanged trione (30%).

the bis-keten (16) whereas the light-stable linear dione (8) would have to give the much less stable bis-keten (15) *cf.* the relative stabilities of 1,2-naphthoquinone > 1,2-benzoquinone ≫ 2,3-naphthoquinone. An attempt to trap the bis-keten (15) by heating the linear dione (8)



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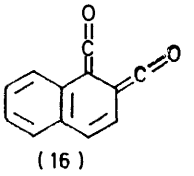

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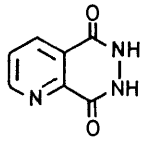
with *N*-phenylmaleimide in triethyleneglycol dimethyl ether at 240 °C for 5 h was unsuccessful.

Heterocyclic Analogues of BBD.—Shortly after the publication of Rees' note [8] on the pyrolysis of cyclopentadiene and indene adducts of phthalazine-1,4-dione we prepared the corresponding adducts starting from pyridine-2,3-dicarboxylic anhydride *via* the hydrazide (17). Pyrolysis of the indene adduct at 650 °C resulted in complete decomposition while at 500 °C no reaction occurred. However, pyrolysis of the cyclopentadiene adduct (18) at 500—525 °C gave a 2% yield of a mixture of unchanged adduct and a yellow crystalline solid which, on exposure to air, rapidly turned black. A solution of the mixture in dichloromethane had $\nu_{max.}$ 1 880w, 1 822s, 1 790s, and 1 773m cm^{-1} in the carbonyl region which is similar to that of BBD itself namely $\nu_{max.}$ (CH_2Cl_2) 1 853w, 1 807s, 1 779s, and 1 763m cm^{-1}. Pyrolysis of the anthracene adduct corresponding to (18) at 450 °C also gave traces of the yellow ketonic material but the 9-methylanthracene adduct corresponding to (18) underwent extensive decomposition at 215—220 °C even before it sublimed into the tube kept at



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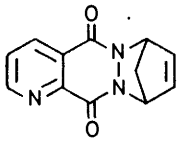

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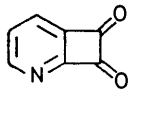

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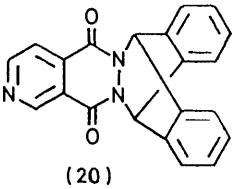

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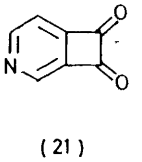

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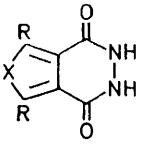


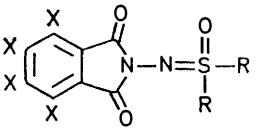
(22) X = O, R = Me
(23) X = S, R = Cl

500 °C; the only identifiable products were 9-methylanthracene and hyrazide (17).

Starting from the pyridine-3,4-dicarboxylic anhydride we prepared the anthracene (20) and 9-methylanthracene adducts. Pyrolysis of the adduct (20) at 450—475 °C gave a mixture of anthracene and a pale yellow crystalline solid, which darkened rapidly in air. The infrared spectrum, measured as quickly as possible after opening the pyrolysis apparatus, showed $\nu_{max.}$ (CH_2CH_2) at 1 876w, 1 818m, 1 783s, and 1 770s cm^{-1}. We consider that the infrared spectra provide strong evidence that we have prepared the diones (19) and (21) but that they are too labile to be isolated in a pure state. Independently, Jones and Jones [26] prepared the cyclopentadiene adduct (18) and its isomer starting from pyridine-2,3- and -3,4-dicarboxylic anhydrides respectively, but pyrolysis of these adducts was unsuccessful.

We also prepared the known furan [27] and new thiophen cyclic hydrazides (22) and (23) respectively but oxidation of them in the presence of anthracene by the general method gave disappointing low yields of the anthracene adducts (Table 2). Pyrolysis of the anthracene adduct derived from the thiophen (23) at 450 °C resulted in profound decomposition and anthracene was the only recognisable product. We obtained insufficient of the anthracene adduct corresponding to the furan (22) for pyrolysis studies.

Study of Other Routes to Substituted Benzocyclobutene-1,2-diones.—The oxidation of the 5-amino cyclic hydrazide (10; R = 5-NH_2) by t-butyl hypochlorite has been reported [18] to give 3-aminobenzocyclobutene-1,2-dione in 70% yield but, despite many attempts, we were



(24) X = H, R = Me
(25) X = H, R = Ph
(26) X = Cl, R = Me
(27) X = Cl, R = Ph
(28) X = Br, R = Me
(29) X = Br, R = Ph

unable to oxidise either the parent hydrazide (10; R = H) to BBD or the cyclic hydrazide from napththalene-2,3-dicarboxylic acid to the naphtho-dione (8). In both cases mixtures of products were obtained, none of which reacted with 2,4-dinitrophenylhydrazine, whereas BBD and its derivatives rapidly give the corresponding 2,4-dinitrophenylhydrazones. The oxidation of the cyclic hydrazide (10; R = H) has been studied by Kealy and he, too, failed to obtain any BBD.[28]

Vapour-phase pyrolysis of the dimethylsulphoximide (24) has been found to give BBD (35%) and phthalimide (48%) while similar pyrolysis of the diphenyl analogue (25) gave BBD in 68% yield.[29] We prepared the dimethyl- and diphenyl-sulphoximides from *N*-aminotetrachloro- and *N*-aminotetrabromo-phthalimide but pyrolysis of these four compounds [(26)—(29)] did not give the desired tetrahalogenodiones, the only recognisable product being the tetrahalogenophthalimides.

EXPERIMENTAL

Unless otherwise stated the following conditions apply. I.r. and u.v. spectra were measured for Nujol mulls and for

solutions in 95% ethanol respectively. N.m.r. spectra were recorded on a Varian HA-100 spectrometer for solutions in deuteriochloroform. T.l.c. was carried out on Kieselgel G (Merck). Wet-column chromatography was carried out on silica gel M.F.C. (Hopkins and Williams) or on aluminium oxide, Brockman activity II (BDH Chemicals Ltd.) and dry-column chromatography [30] on silica gel M.F.C. deactivated with 15% (w/w) water. Light petroleum refers to the fraction of b.p. 60—80 °C.

Sources of Phthalic Acids and Heterocyclic Analogues.—3- and 4-Nitro-, 3,4,5,6-tetrabromo-, and 3,4,5,6-tetrachlorophthalic acid and also pyridine-2,3- and -3,4-dicarboxylic acid were obtained commercially. 4,5-Dimethylphthalic acid,[31] 2,5-dimethylfuran-3,4-dicarboxylic acid,[32] and 2,5-dichlorothiophen-3,4-dicarboxylic acid [33] were made by literature methods. 4,5-Dibromophthalic acid was prepared in 77% yield by oxidation of 4,5-dibromo-*o*-xylene by the same method as for 4-bromophthalic acid (see below).

4-Bromophthalic Acid.—A mixture of 4-bromo-*o*-xylene (5 g) and a solution of potassium hydroxide (1 g) in water (10 ml) was stirred while a solution of potassium permanganate (15 g) in water (300 ml) was added dropwise over 3 h. During the following 2 h solid potassium permanganate (9 g) was added in portions. After a total of 7 h, ethanol was added to reduce unchanged potassium permanganate and the solution was filtered. The filtrate was acidified with conc. hydrochloric acid, concentrated to *ca.* 50 ml, and then extracted with ether (3 × 100 ml). The extract yielded a sticky solid which, on drying under vacuum, gave 4-bromophthalic acid (4.4 g, 67%), m.p. 170—172 °C (lit.,[34] 170.5 °C).

General Procedure for the Preparation of Phthalic Anhydrides.—The substituted phthalic acid was dissolved in the minimum volume of hot redistilled acetic anhydride and the solution was heated under reflux for 4 h. On cooling, crystals of the required anhydride usually formed but, if not, the acetic anhydride was removed under reduced pressure and the residue recrystallised from dichloromethane–light petroleum.

General Procedure for the Preparation of Substituted 2,3-Dihydrophthalazine-1,4-diones.—An excess of 64% aqueous hydrazine hydrate was added to a solution of the substituted phthalic anhydride in ethanol or acetic acid and the solution was refluxed for 30 min. The solution was cooled and the solid collected, washed with methanol, and then dissolved in 10% aqueous sodium hydroxide. The resulting yellow solution was filtered and the filtrate was acidified with concentrated hydrochloric acid giving the pure dione. Details of new compounds are given in Table 1.

General Procedure for the Preparation of Diels–Alder Adducts of Phthalazine-1,4-diones.—To a stirred mixture of the 2,3-dihydrophthalazine-1,4-dione (0.01 mol) and anthracene (0.01 mol) in dichloromethane (50 ml) was added lead tetra-acetate (1.2 × 0.01 mol) in small portions during 2 h at room temperature. After being stirred for 2 h more the mixture was filtered and the filtrate concentrated. The residue was chromatographed on a column of alumina with carbon tetrachloride as eluant until no more anthracene was eluted. Further elution with the same solvent gave the adduct.

The same procedure was used for the adducts with substituted anthracenes except that a solution of lead tetra-acetate (1.2 × 0.01 mol) in dichloromethane (20 ml) was added dropwise instead of adding the solid reagent. Details of new compounds are given in Tables 2 and 3.

Acid-catalysed Rearrangement of Anthracene–phthalazinedione Adducts.—The following is a typical example. The anthracene adduct of 6-bromophthalazine-1,4-dione (500 mg) in acetic acid (10 ml) and concentrated hydrochloric acid (1 ml) was refluxed for 1 h. On cooling, the product (362 mg, 72%) crystallised as needles. See Table 4 for further data on this and other compounds prepared similarly.

General Method for Pyrolysis of Diels–Alder Adducts.—The apparatus consisted of a horizontal silica tube (35 × 1 cm internal diameter) heated by an external electric furnace (Gallenkamp) with a built-in thermocouple giving temperature readings on a dial.

The adduct (50–350 mg) was sublimed from a small flask at *ca.* 200 °C into the pyrolysis tube kept at 450 °C and 0.01 mmHg pressure during 2 h. The products which emerged from the tube were collected partly in the exit tube and partly in two traps cooled in liquid nitrogen. The products were extracted with dichloromethane and purified by chromatography on silica gel in dichloromethane giving anthracene followed by the substituted benzocyclobutene-1,2-dione or other products.

Properties of Substituted Benzocyclobutene-1,2-diones.—(Substituent or compound, yield, m.p. *etc.* Solvent for crystallisation was always cyclohexane). *4-Chloro* (94%), yellow plates, m.p. 93—95 °C (Found: M^+, 165.983 and 167.980. $C_8H_3{}^{35}ClO_2$ and $C_8H_2{}^{37}ClO_2$ require M, 165.982 and 167.979), $\nu_{max.}$ 1 820w, 1 775vs br, 1 740m, 1 142s, and 738s cm^{-1}, $\lambda_{max.}$ 240, 258sh, 296, and 303 nm (log ε 4.16, 3.54, 3.68, and 3.69), τ 1.96 (H-3, d), 2.00 (H-6, q), and 2.28 (H-5, m), $J_{3,5}$ 1.6, $J_{3,6}$ 0.8, and $J_{5,6}$ Hz. *3,6-Dichloro* (92%), yellow plates, m.p. 178—180 °C (Found: M^+, 199.945 and 201.941. $C_8H_2{}^{35}Cl_2O_2$ and $C_8H_2{}^{35}Cl^{37}ClO_2$ require 199.943 and 201.940), $\nu_{max.}$ 1 760vs br, 1 175s, 1 123vs, and 863s cm^{-1}, $\lambda_{max.}$ 247, 258sh, 296, and 303 nm (log ε 4.43, 3.52, 3.80, and 3.85), τ 2.38 (H-4, H-5, s). *4,5-Dichloro* (92%), yellow needles, m.p. 182—183 °C (Found: C, 47.8; H, 0.9; Cl, 35.5. $C_8H_2Cl_2O_2$ requires C, 47.8; H, 1.0; Cl, 35.3%), $\nu_{max.}$ 1 775vs br, 1 165s cm^{-1}, τ 1.92 (H-3, H-6, s). *4,5-Dibromo* (75%), yellow needles, m.p. 182—183 °C (Found: C, 33.2; H, 0.8. $C_8H_2Br_2O_2$ requires C, 33.1; H, 0.9%), $\nu_{max.}$ 1 750vs br, 900s, 743s cm^{-1}, $\lambda_{max.}$ 248, 270sh, 310sh, 322, and 332 (log ε 4.51, 3.67, 3.64, 3.88, and 3.92), τ 1.64 (H-3, H-6, s). *4,5-Dimethyl* (80%), yellow needles, m.p. 187—188 °C (Found: C, 75.1; H, 5.4. $C_{10}H_8O_2$ requires C, 75.0; H, 5.0%), $\nu_{max.}$ 1 788vs, 1 765vs, 1 740s, and 1 121s cm^{-1}, $\lambda_{max.}$ 237, 262sh, 306, and 316 nm (log ε 4.07, 3.20, 3.33, and 3.35), τ 2.20 (H-3, H-4) and 7.52 (Me). *Cyclobuta[b]naphthalene-1,2-dione* (8) (71%), yellow needles, for m.p. behaviour see Discussion, M^+, 182; (Found: C, 79.7; H, 3.8. $C_{12}H_6O_2$ requires C, 79.1; H, 3.3%), $\nu_{max.}$ 1 770vs br, 1 117s, 1 101s, 955w, 925w, 907m, and 765m cm^{-1}, $\lambda_{max.}$ 236, 271, 340sh, 348sh, and 359 nm (log ε 3.92, 4.97, 4.30, 4.42, and 4.56), τ 1.46 (H-3, H-8, s), 1.85 (H-4, H-7, q), and 2.18 (H-5, H-6, q).

Pyrolysis of Benz[f]indene-1,2,3-trione.—The trione [24] was sublimed at 170 ± 10 °C and 0.01 mmHg through a silica tube (43 × 1 cm internal diameter). At 500 °C no reaction occurred. The trione (100 mg) was pyrolysed at 600 °C during 3 h. The pyrolysate was extracted with dichloromethane leaving a residue (30 mg, 30%) of unchanged trione. The filtrate was chromatographed on a dry column of deactivated silica gel and the material from the yellow bands was sublimed, giving dibenzo[*b,h*]biphenylene (5 mg, 8%) [35] and cyclobuta[*b*]naphthalene-1,2-dione (8) (15 mg, 17%).

Pyrolysis of the Anthracene Adduct of Benzo[f]*phthalazine-1,4-dione*.—(*a*) Pyrolysis of the adduct at 500 °C gave a mixture which was separated by preparative t.l.c. *in the dark*. The ketonic fraction was sublimed at 90—100 °C and 0.01 mmHg and gave *cyclobuta*[a]*naphthalene-1,2-dione* (9) (5%) as a yellow solid, m.p. 192 °C (decomp.) which was photolabile (see Discussion) Found: M^+, 182.037. $C_{12}H_6O_2$ requires M, 182.037), $\nu_{max.}$ 1 830w br, 1 785vs, 1 770vs, 1 750vs, 1 620m, 1 201m, 1 140m, 1 055m, 840m, 825m, and 770m cm^{-1}, $\lambda_{max.}$ 224, 265sh, 312, 330, and 340 nm (log ε 4.14, 4.53, 3.63, 3.56, and 3.64).

(*b*) The anthracene adduct (100 mg) was well mixed with anthracene (400 mg) and was pyrolysed at 500 °C during 1.5 h. The pyrolysate was chromatographed on a dry column of silica gel. Elution with light petroleum removed anthracene. The remaining bands on the column were separated by t.l.c. followed by sublimation and gave the naphthalenedione (9) (10 mg, 20%).

Pyrolysis of the Cyclopentadiene Adduct (18).—The adduct was sublimed at 220—225 °C and 0.01 mmHg through the tube kept at 500—525 °C. The pyrolysate consisted of unchanged adduct and a yellow solid which is described in the Discussion.

Pyrolysis of the Anthracene Adduct corresponding to (18).—The adduct (300 mg) was pyrolysed at 450 °C by the general method. The pyrolysate condensed in the exit tube in four distinct regions. In order of decreasing volatility the regions contained anthracene, the yellow solid thought to be the dione (19), $\nu_{max.}$ 1 880m, 1 821s, 1 794s, and 1 776s cm^{-1}, the hydrazide (17), and the 2- or 3-(9-anthryl) derivative of hydrazide (17), $\nu_{max.}$ 3 060w, 1 648m, 1 570s, and 1 555s cm^{-1} [*cf.* compound (14; R = H), $\nu_{max.}$ 3 060w, 1 640m, 1 590s, 1 570s, and 1 550s cm^{-1}].

Pyrolysis of the Anthracene Adduct (20).—The adduct was pyrolysed at 450—475 °C by the general method. The pale yellow pyrolysate consisted mainly of anthracene plus a yellow solid thought to be the dione (21) (see Discussion).

SS-*Dimethyl*-N-*tetrachlorophthalimidosulphoximide* (26).—Lead tetra-acetate (5.0 g) was added in small portions to a stirred suspension of *N*-aminotetrachlorophthalimide [36] (3.0 g) in anhydrous dimethyl sulphoxide (10 ml) during 10 min. After 10 min more the mixture was poured into ether (300 ml) and the resulting precipitate was collected. It was extracted with boiling dichloromethane and yielded the *dimethyl sulphoxide* (26) (3.2 g, 85%) as needles, m.p. 279—280 °C (from dichloromethane) (Found: C, 31.9; H, 1.6. $C_{10}H_6Cl_4N_2O_3S$ requires C, 32.0; H, 1.7%), $\nu_{max.}$ 1 790m and 1 730vs cm^{-1}; *m/e* for largest isotope peaks (no parent peak), 300(2%), 285(7), 270(2), 242(100), 214(51), 78(36), and 62(186).

SS-*Diphenyl*-N-*tetrachlorophthalimidosulphoximide* (27).—Prepared as for the preceding compound, the *diphenylsulphoximide* (81%) formed off-white plates, m.p. 255—256 °C (from dichloromethane) (Found: C, 48.0; H, 2.0; Cl, 28.3; N, 5.6. $C_{20}H_{10}Cl_4N_2O_3S$ requires C, 48.4; H, 2.0; Cl, 28.4; N, 5.6%), $\nu_{max.}$ 1 795m, 1 725br vs, 1 605w, and 1 580w cm^{-1}; *m/e* for largest isotope peaks (no parent peak), 300 (106%), 285 (52), 270 (32), 242 (100), 214 (61), 202 (29), and 186 (112) (intensities relative to $ArCO^+$ peak).

N-*Benzylideneaminotetrabromophthalimide*.—Benzaldehyde (4 ml) was added to a solution of *N*-aminotetrabromophthalimide [37] (1 g) in boiling acetic acid (100 ml) and the mixture was refluxed for 30 min. On cooling, the solution gave the *benzylidene derivative* (1 g, 84%) as off-white needles, m.p. 274—275 °C (from ethanol) (Found: C, 32.35; H, 1.3; Br, 56.7. $C_{15}H_6Br_4N_2O_2$ requires C, 31.8; H, 1.1; Br, 56.5%).

SS-*Dimethyl*-N-*tetrabromophthalimidosulphoximide* (28).—Made as above for the chloro-analogue, the *bromo-compound* (87%) formed plates, m.p. 265—268 °C (from dichloromethane) (Found: C, 21.8; H, 1.0; N, 5.2. $C_{10}H_6Br_4N_2O_3S$ requires C, 21.7; H, 1.1; N, 5.1%), $\nu_{max.}$ 1 770w and 1 712 br vs cm^{-1}; *m/e* for largest isotope peaks (no parent peak) 478(6%), 463(25), 448(4), 420(100), 392(35), 78(162), and 62(305).

SS-*Diphenyl*-N-*tetrabromophthalimidosulphoximide* (29).—Made as above for the chloro-analogue, the *bromo-compound* (59%) formed plates, m.p. 262 °C (from dichloromethane) (Found: C, 35.1; H, 1.4; Br, 47.3; N, 4.3. $C_{20}H_{10}Br_4N_2O_3S$ requires C, 35.4; H, 1.5; Br, 47.2; N, 4.1%), $\nu_{max.}$ 1 785w, 1 730br vs, and 1 680w cm^{-1}; *m/e* for largest isotope peaks (no parent peak), 478(26%), 463(70), 420(100), 392(41), 202(600), and 186(2 460).

Pyrolysis of Tetrahalogenosulphoximides.—All four sulphoximides were sublimed at *ca.* 200 °C and 0.01 mmHg into a silica tube (43 × 1 cm internal diameter). At 400 °C the main product was the unchanged sulphoximide. At 500 to 550 °C reaction occurred to give mixtures which were separated in dichloromethane by t.l.c. The products were unchanged sulphoximide, the tetrahalophthalimide, and a small amount of yellow compound which did not react with 2,4-dinitrophenylhydrazine nor did it have a mass spectrum compatible with the dione or with an octahalogenobiphenylene.

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REFERENCES

[1] Part 3, A. J. Boulton and J. F. W. McOmie, *J. Chem. Soc.*, 1965, 2549.
[2] M. P. Cava, R. J. Pohl, and M. J. Mitchell, *J. Amer. Chem. Soc.*, 1963, **85**, 2080; M. P. Cava and R. P. Stein, *J. Org. Chem.*, 1966, **31**, 1866.
[3] P. J. Garratt and K. P. C. Volhardt, *J. Amer. Chem. Soc.*, 1972, **94**, 7087.
[4] J. W. Barton, M. C. Goodland, K. J. Gould, J. Hadley, and J. F. W. McOmie, *Tetrahedron*, 1978, **34**, 495; J. W. Barton, M. C. Goodland, K. J. Gould, J. F. W. McOmie, W. R. Mound, and S. A. Saleh, *Tetrahedron*, 1979, **35**, 241.
[5] M. P. Cava, D. R. Napier, and R. J. Pohl, *J. Amer. Chem. Soc.*, 1963, **85**, 2076.
[6] M. P. Cava, D. Mangold, and K. Muth, *J. Org. Chem.*, 1964, **29**, 2947.
[7] R. F. C. Brown and R. K. Solly, *Austral. J. Chem.*, 1966, **19**, 1045; P. R. Buckland and J. F. W. McOmie, *Tetrahedron*, 1977, **33**, 1797.
[8] D. L. Forster, T. L. Gilchrist, C. W. Rees, and E. Stanton, *Chem. Comm.*, 1971, 695.
[9] T. L. Gilchrist, C. W. Rees, and E. Stanton, *Chem. Comm.*, 1971, 801.
[10] R. F. C. Brown, F. W. Eastwood, and G. L. McMullen, *J.C.S. Chem. Comm.*, 1975, 328.
[11] L. Hoesch and A. S. Dreiding, *Helv. Chim. Acta*, 1975, **58**, 980.
[12] T. R. Kowar and E. Le Goff, *Synthesis*, 1973, 212.
[13] T. R. Kowar and E. Le Goff, *J. Org. Chem.*, 1976, **41**, 3760.
[14] J. F. W. McOmie and D. H. Perry, *J.C.S. Chem. Comm.*, 1973, 248.
[15] M. P. Cava and B. Hwang, *Tetrahedron Letters*, 1965, 2297.
[16] A. Roedig, G. Bonse, R. Helm, and R. Kohlhaupt, *Chem. Ber.*, 1971, **104**, 3378.
[17] M. E. Jung and J. A. Lowe, *J. Org. Chem.*, 1977, **42**, 2371.
[18] J. Nikokavouras, A. Perry, and G. Vassilopoulos, *Israel J. Chem.*, 1972, **10**, 19.

[19] A. Roedig, B. Heinrich, and V. Kimmel, *Liebigs Annalen*, 1975, 1195.
[20] V. E. Platonov, T. V. Senchenko, and G. G. Yakobson, *Zhur. Org. Khim.*, 1976, **12**, 816 (*Chem. Abs.*, 1976, **85**, 20910e).
[21] R. A. Clement, *J. Org. Chem.*, 1962, **27**, 1115.
[22] R. B. Jansen, J. F. W. McOmie, and D. H. Perry following paper.
[23] R. F. C. Brown and R. K. Solly, *Tetrahedron Letters*, 1966, 169; H. A. Staab and J. Ipaktschi, *Chem. Ber.*, 1968, **101**, 1457.
[24] D. W. Jones and R. L. Wife, *J.C.S. Perkin I*, 1972, 2722.
[25] R. D. Rieke, C. K. White, L. D. Rhyne, M. S. Gordon, J. F. W. McOmie, and N. P. Hacker, *J. Amer. Chem. Soc.*, 1977, **99**, 5387.
[26] G. Jones and R. K. Jones, *J.C.S. Perkin I*, 1973, 26.
[27] R. G. Jones, *J. Amer. Chem. Soc.*, 1956, **78**, 159.
[28] T. J. Kealy, *J. Amer. Chem. Soc.*, 1962, **84**, 966.
[29] D. J. Anderson, D. C. Horwell, E. Stanton, T. L. Gilchrist, and C. W. Rees, *J.C.S. Perkin I*, 1972, 1317.
[30] B. Loev and M. M. Goodman, *Chem. and Ind.*, 1967, 2026.
[31] P.-Y. Blanc, *Helv. Chim. Acta*, 1961, **44**, 1.
[32] H. Gilman and R. R. Burtner, *Rec. Trav. chim.*, 1932, **51**, 667.
[33] B. E. Ayres, S. W. Longworth, and J. F. W. McOmie, *Tetrahedron*, 1975, **31**, 1755.
[34] H. N. Stephens, *J. Amer. Chem. Soc.*, 1921, **43**, 1950.
[35] J. W. Barton and S. A. Jones, *J. Chem. Soc.* (*C*), 1967, 1276.
[36] H. D. K. Drew and F. H. Pearman, *J. Chem. Soc.*, 1937, 26.
[37] W. B. Ligett, R. D. Closson, and C. N. Wolf, U.S.P. 2,657,169/1953 (*Chem. Abs.*, 1954, **48**, 942).