THE PYROLYSIS OF POLYCARBONYL COMPOUNDS

II.* SYNTHESIS OF BIPHENYLENES FROM PHTHALIC ANHYDRIDES AND OTHER CARBONYL COMPOUNDS

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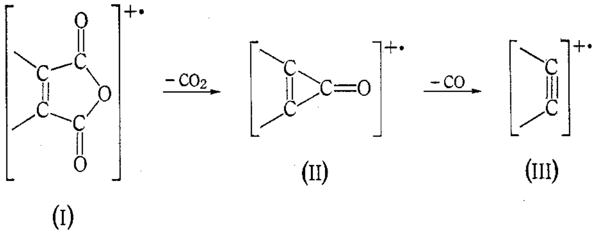
[*Manuscript received August* 22, 1966]

Summary

Pyrolysis of phthalic anhydride or *o*-sulphobenzoic anhydride at 700–1100° and 0·1–10 mm produces benzyne, as shown by the formation of biphenylene and triphenylene. Biphenylene and several polychloro and polymethyl derivatives have been conveniently synthesized by pyrolysis of the corresponding phthalic anhydrides in yields ranging from 3 to 26%. These reactions afford further examples of the parallel between the pyrolytic and mass spectral fragmentations of certain aromatic carbonyl compounds. The yield of biphenylene obtained by pyrolysis of compounds structurally related to phthalic anhydride can be correlated with the instability of the corresponding molecular ions in the mass spectrometer.

Introduction

The primary processes in the mass spectral fragmentation of the cyclic anhydrides maleic anhydride and phthalic anhydride[1] may be represented in partial formulae by the following scheme:



In Part I of this series[2] we showed that the course of the pyrolytic fragmentation of indanetrione closely parallels the mass spectral fragmentation of its molecular ion. Since the partial structure (III) represents the molecular ion of an alkyne or aryne,§

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* Part I, *Aust. J. Chem.*, 1966, **19**, 1045. This paper is also regarded as Part XVII in the series of papers on biphenylenes. For Part XVI see Blatchly, J. M., Gardner, D. V., and McOmie, J. F. W., *J. chem. Soc.*, 1967, in press.

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§ A referee has drawn our attention to a paper[3] which suggests that the ion $[C_6H_4]^{+\cdot}$ may have a linear rather than a cyclic structure. This does not, however, affect the usefulness of the correlation.

[1] Beynon, J. H., "Mass Spectrometry and its Applications to Organic Chemistry." p. 374. (Elsevier: Amsterdam 1960.)

[2] Brown, R. F. C., and Solly, R. K., *Aust. J. Chem.*, 1966, **19**, 1045.

[3] Momigny, J., Brakier, L., and D'Or, L., *Bull. Acad. r. Belg. Cl. Sci.*, 1962, **48**, 1002 (*Chem. Abstr.*, 1963, **59**, 7065*g*).

the extension of this correlation to cyclic anhydrides suggests that these should lose carbon dioxide and carbon monoxide on vigorous pyrolysis to give the corresponding unsaturated species. Indeed the pyrolyses of succinic anhydride to ethylene,[4] of maleic[4] and fluoromaleic[5] anhydrides to acetylene and fluoroacetylene respectively, and of aconitic anhydride[4] to allene and propyne at temperatures in the range 650–900° are well established in the literature. We have now found that arynes can be generated by the pyrolysis of aromatic anhydrides at 700–1100° and 0·1–10 mm (generally 0·1–2·0 mm), and that the pyrolysis of phthalic anhydride itself is a simple method for the preparation of the strained hydrocarbon biphenylene.[6] The generation of benzyne by the pyrolysis of benzene or pyridine solutions of phthalic anhydride at 690° was discovered at about the same time by Fields and Meyerson[7] who were also guided by consideration of the mass spectrum of phthalic anhydride. In their experiments the formation of benzyne was detected by analysis of the products formed by its reaction with the aromatic solvent,[8] a method which we had previously used successfully in our first pyrolyses of indanetrione.[2] Our preliminary communication on the pyrolysis of anhydrides[6] was preceded by that of Cava *et al.*[9] who quite independently discovered the parallel between their mass spectral and pyrolytic fragmentation. By passing the vapour of the anhydride in a stream of nitrogen at 50 mm over a glowing Nichrome coil these workers obtained biphenylene (10–15%) and octachlorobiphenylene (30%) from phthalic and tetrachlorophthalic anhydride respectively. From pyridine-2,3-dicarboxylic anhydride they obtained in low yield β-ethynylacrylonitrile, formed by fission of the expected 2,3-pyridyne intermediate. A closely related fission of a heteroaryne has been observed in the pyrolysis of pyrazine-2,3-dicarboxylic anhydride.[10]

PYROLYSIS OF PHTHALIC ANHYDRIDES, PHTHALIMIDES, AND *o*-SULPHOBENZOIC ANHYDRIDE

The pyrolysis of phthalic anhydride vapour in an unpacked silica tube at 760° and 0·3 mm gave a substantial hydrocarbon fraction with 71% recovery of the starting material as phthalic anhydride and acid. The hydrocarbon fraction contained biphenylene (9% yield), triphenylene (1·5%), and small amounts of naphthalene, biphenyl, and fluorene. Trace amounts only of hydrocarbons in the range C_{14}–C_{17} were present. The yield of biphenylene was raised to 17% at 830° and 0·2 mm, and formation of naphthalene, biphenyl, and fluorene was almost suppressed, so that in the initial separation of the hydrocarbons by chromatography on silica the fraction first eluted by light petroleum was almost pure biphenylene.

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[4] Rice, F. O., and Murphy, M. T., *J. Am. chem. Soc.*, 1942, **64**, 896.

[5] Middleton, W. J., and Sharkey, W. H., *J. Am. chem. Soc.*, 1959, **81**, 803.

[6] Brown, R. F. C., Gardner, D. V., McOmie, J. F. W., and Solly, R. K., *Chem. Commun.*, 1966, 407; and Aust. Provisional Pat. Spec. 61869/65, July 23, 1965.

[7] Fields, E. K., and Meyerson, S., *Chem. Commun.*, 1965, 474.

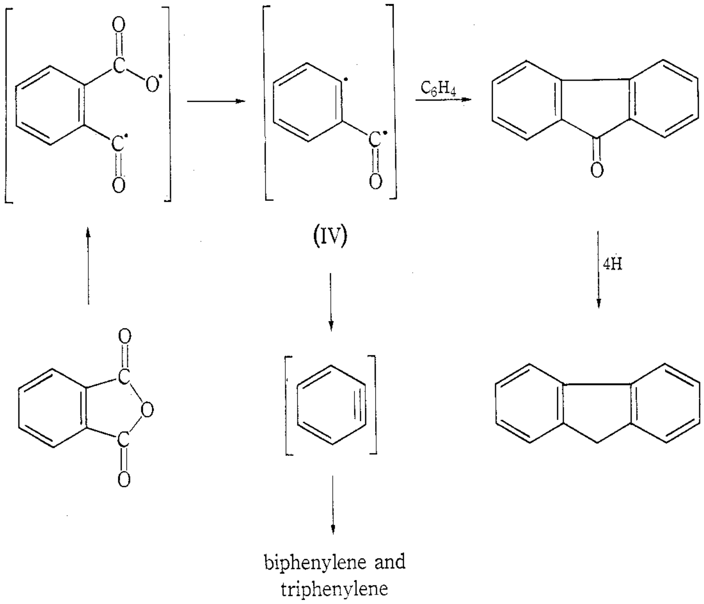
[8] Miller, R. G., and Stiles, M., *J. Am. chem. Soc.*, 1963, **85**, 1789.

[9] Cava, M. P., Mitchell, M. J., De Jongh, D. C., and Van Fossen, R. Y., *Tetrahedron Lett.*, 1966, 2947.

[10] Brown, R. F. C., Crow, W. D., and Solly, R. K., *Chemy Ind.*, 1966, 343.

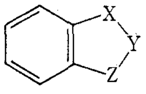
By contrast with the pyrolysis of indanetrione, where the use of a packing of pieces of silica tubing at 600°/0·2 mm gave a high yield of biphenylene (40%),[2] the use of this packing in the pyrolysis of phthalic anhydride at 830°/0·2 mm gave a lower yield of biphenylene (13%), and increased the formation of naphthalene, biphenyl, fluorene, and the C_{14}–C_{18} group of aromatic hydrocarbons. The yield of biphenylene was also reduced (to 3%) and the yield of other hydrocarbons relatively increased by the use of a packed tube at a moderate temperature, 700°, and a higher pressure, 10 mm. Clearly the use of a packing, or of a higher pressure, promotes secondary reactions[2] at the expense of the simple dimerization of benzyne to biphenylene. Pyrolysis of phthalic anhydride at 1100° and 3 mm using a tube packed with porcelain Lessing rings gave only 3·7% yield of biphenylene.

We have not detected the presence of fluorenone, phenanthrenequinone, or anthraquinone in pyrolysates from phthalic anhydride, although the similarity in the composition of the hydrocarbon fractions from indanetrione[2] and from phthalic anhydride led us to expect that these carbonyl compounds might be formed from phthalic anhydride also. Nevertheless, it seems reasonable to explain the formation of fluorene in terms of the stepwise, rather than concerted, loss of carbon dioxide and carbon monoxide from phthalic anhydride to give first an intermediate having the composition of (IV), followed by reaction of this intermediate with benzyne to give fluorenone, and finally reduction of fluorenone to fluorene. Fields and Meyerson[7] have used coupled gas chromatography and mass spectrometry to show the presence of fluorenone in the pyrolysate of a benzene solution of phthalic anhydride, although they propose that fluorenone is formed by reaction of an intermediate equivalent to (IV) with benzene rather than with benzyne. Our preferred scheme is shown below, although it is possible that the intermediates are zwitterions rather than diradicals.

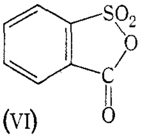


The range of substituents which will survive the high temperatures needed for the pyrolysis of aromatic anhydrides is likely to be rather small, and we are now working to find the practical limits for this new synthesis of biphenylenes. Pyrolysis of 4-chloro-, 4,5-dichloro-, 3,6-dichloro-, 3,4,5,6-tetrachloro-, and 4,5-dimethyl-phthalic anhydride gave 2,6- (or 2,7-) dichloro- (15%), 2,3,6,7-tetrachloro- (6·5%), 1,4,5,8-tetrachloro- (3·8%), octachloro- (26%), and 2,3,6,7-tetramethylbiphenylene (3%) respectively. Octachlorobiphenylene was formed together with hexachlorobenzene (31%, assuming that 3 molecules of anhydride can give 2 molecules of hexachlorobenzene). These yields of biphenylenes compare favourably with those (1–30%) generally obtained by the pyrolysis of mixtures of 2,2′-diiodobiphenyls or biphenylene-2,2′-iodonium iodides with cuprous oxide at 350–400° under atmospheric pressure.[11,12] Pyrolysis of 4-benzyl- and of 4-methoxy-phthalic anhydride gave no trace of biphenylenes.

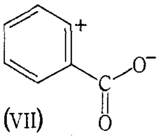
Indanetrione and phthalic anhydride belong to a class of compounds which can be represented by the general structure (V), where X, Y, and Z represent, e.g., –CO–, $-SO_2-$, –O–, –S–, or –NR– groups. Many compounds in this class may be capable of forming benzyne by pyrolytic loss of the stable fragments CO, CO_2, COS, SO_2, or RNCO. However, pyrolysis of *N*-methylphthalimide or phthalimide at 800°/0·05 mm gave no hydrocarbons, and the starting materials were recovered. *o*-Sulphobenzoic anhydride (VI) on pyrolysis at 730°/0·05 mm deposited much carbon on the silica packing, and gave sulphur dioxide and a small hydrocarbon fraction. The major product was *o*-sulphobenzoic acid, presumably formed by reaction of part of the anhydride with water formed by the carbonization of another part. The composition of the hydrocarbon fraction was similar to that obtained from phthalic anhydride at 830°/0·2 mm over a silica packing, and the yield of biphenylene was 5·5%. Fragmentation of *o*-sulphobenzoic anhydride to give benzyne could occur by loss of carbon dioxide and sulphur dioxide, or of carbon monoxide and sulphur trioxide. Sulphur dioxide was collected in the trap, but it is possible that sulphur trioxide if formed would have been reduced to sulphur dioxide in the pyrolysis tube. The mass spectrum of *o*-sulphobenzoic anhydride has been measured by Dr J. H. Beynon; the molecular ion of *m*/*e* 184 (49·5%) undergoes loss of both sulphur dioxide to give an ion of *m*/*e* 120 (34·9%) and of sulphur trioxide to give the ion of *m*/*e* 104 (100%, base peak) which is also the base peak in the spectrum of phthalic anhydride.[1] The presence of the appropriate metastable transitions shows that these daughter ions then lose carbon dioxide and carbon monoxide



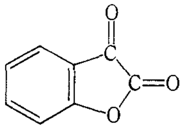
(V)



(VI)



(VII)



(VIII)

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[11] Baker, W., Barton, J. W., and McOmie, J. F. W., *J. chem. Soc.*, 1958, 2658.
[12] Baker, W., McLean, N. J., and McOmie, J. F. W., *J. chem. Soc.*, 1963, 922.

respectively to give the ion of *m/e* 76 corresponding to benzyne. A detailed study of the mass spectrum of *o*-sulphobenzoic anhydride has recently been reported by Fields and Meyerson[13] who investigated the relative importance of the two major paths of fragmentation at different ionizing potentials, and also the relation between the mass spectrum and the products of pyrolysis of a dilute benzene solution at 690°. The major products were biphenyl, naphthalene, and 3,4-benzocoumarin. The formation of the last compound was attributed to the reaction of a zwitterionic intermediate, e.g. (VII), with benzene, and the probable reaction scheme was shown to parallel the most favoured mass spectrometric process in which the first step is loss of sulphur dioxide.

With compounds within the class (V) it is possible to discern a rough correlation between the instability of the parent molecular ion in the mass spectrum and the yield of biphenylene obtained on pyrolysis, as shown in Table 1.

TABLE 1

Compound	Intensity* of $[M]^{+\cdot}$	Yield of Biphenylene	Pyrolytic Conditions
Indanetrione[2]	3%	40%	600°/0·2 mm
Phthalic anhydride[1]	56%	9%	760°/0·3 mm
o-Sulphobenzoic anhydride	55%	5·5%	730°/0·05 mm
N-Methylphthalimide	220%	—	800°/0·05 mm

* Relative to *m/e* 76 = 100%.

Coumarandione (VIII) also belongs to the class of compounds (V), but differs from the isomeric phthalic anhydride in having heterocyclic oxygen in conjugation with the aromatic ring. It has not so far been possible to obtain satisfactory mass spectra of (VIII); Dr Beynon has found that the compound undergoes substantial thermal degradation in both a conventional inlet system and in the direct insertion probe. However, the spectra obtained showed no strong peaks at *m/e* 76,† so that (VIII) would not be expected to be an efficient precursor of biphenylene. Pyrolysis of coumarandione at 600°/0·2 mm gave no biphenylene, and the major products—polysalicylides, xanthone, and 3,4-benzocoumarin—resembled those formed in the pyrolyses of various salicylic and *o*-halobenzoic acid derivatives at much lower temperatures.[14–17] Benzyne may be formed in the high temperature pyrolysis of (VIII), but the reaction sequence lies outside the scope of the present account, and will be considered in a later paper.

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† We are informed by a referee that he has successfully obtained a mass spectrum of this compound using the direct insertion process with a cold source. The ion at *m/e* 76 constituted 4% of the base peak (M—CO) in this spectrum.

[13] Fields, E. K., and Meyerson, S., *Chem. Commun.*, 1966, 275.

[14] Perkin, W. H., *Ber. dt. chem. Ges.*, 1883, **16**, 339.

[15] Baker, W., Ollis, W. D., and Zealley, T. S., *J. chem. Soc.*, 1951, 201.

[16] McNelis, E., *J. org. Chem.*, 1963, **28**, 3188, and references therein.

[17] Beringer, F. M., and Huang, S. J., *J. org. Chem.*, 1964, **29**, 445, 1637.

PYROLYSIS OF DIPHENIC ACID, FLUORENONE, *o*-BROMO- AND *o*-CHLORO-BENZOIC ACID

Pyrolysis of diphenic acid at 850°/0·2–0·4 mm gave mainly fluorenone (21%) together with some biphenylene (4·8%). The formation of fluorenone by pyrolysis of diphenic anhydride was first reported by Graebe and Mensching[18] in 1880. The biphenylene was probably formed directly from diphenic acid or its anhydride rather than from fluorenone, since pyrolysis of fluorenone at 850° and at 1100° gave no isolable amount of biphenylene. When *o*-bromobenzoic acid was pyrolysed at 850° it gave bromobenzene and a trace of biphenylene. Similar pyrolysis of *o*-chlorobenzoic acid gave chlorobenzene but no trace of biphenylene.

EXPERIMENTAL

Melting points are uncorrected. "Light petroleum" refers to the fraction of b.p. 40–60°. Details of spectroscopic equipment and gas chromatographic methods used in this series have been given in Part I.[2]

Pyrolyses of phthalic anhydride, tetrachlorophthalic anhydride, *o*-sulphobenzoic anhydride, and coumarandione were run using the apparatus described in detail in Part I.[2] The solid compounds were sublimed under reduced pressure from a small flask into a silica tube (48 by 2 cm i.d.) heated by an external electric furnace. In some experiments the central 30 cm of the tube was packed with 5-mm lengths of 5 mm i.d./7 mm o.d. silica tubing. The vapour which emerged from the tube was collected in two traps cooled with ice and with liquid air.

Pyrolyses of phthalic anhydride (at 1100°), 4-chloro-, 4,5- and 3,6-dichloro-, and 4,5-dimethyl-phthalic anhydride, diphenic acid, fluorenone, and *o*-bromobenzoic acid were run using a silica tube (35 by 2·6 cm i.d.) in place of the abovementioned one.

Pyrolysis of Phthalic Anhydride

The products and fractions isolated from pyrolyses of phthalic anhydride under four different sets of conditions are shown in Table 2. The methods of separation used differed slightly from experiment to experiment, but the general procedure is shown by the following, which refers to Experiment A of the table.

Phthalic anhydride (5·0 g) was sublimed from a 50-ml flask into the silica pyrolysis tube containing only the silica thermocouple sheath placed concentrically in the heated central 30 cm of the tube. The temperature was maintained at $760° \pm 10°$ and the pressure at $0\cdot3 \pm 0\cdot1$ mm during the time of sublimation (1 hr).

The condensate was washed from the exit tube and ice-cooled trap with methylene chloride. This solvent was evaporated, and the dark oily residue was extracted with light petroleum (3×50 ml). The residue was dissolved in benzene and chromatographed on a column of silica gel (19 by 2 cm). Elution with benzene yielded phthalic anhydride (3·3 g) followed by phthalic acid (0·3 g).

The light petroleum extract was chromatographed on a column of silica gel (22 by 2 cm). Elution with light petroleum gave a hydrocarbon fraction (295 mg) which was separated by gas chromatography on a 2-ft column of Apiezon L (He flow rate 100 ml/min, temperature programme $100 \rightarrow 275°$ at 11°/min) into naphthalene, biphenylene, and fluorene. Small amounts of hydrocarbons of shorter retention time than naphthalene were present, but hydrocarbons of longer retention time than fluorene were present only in trace amounts. Further elution of the same silica gel column with benzene yielded triphenylene (40 mg), shown by gas chromatography to contain only traces of lower hydrocarbons. Hydrocarbons were identified by their melting points and infrared and ultraviolet spectra, as in Part I.[2] Hydrocarbon fractions from C_{14} to C_{18} were identified by gas chromatographic retention times only.

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[18] Graebe, C., and Mensching, C., *Ber. dt. chem. Ges.*, 1880, **13**, 1302.

Phthalic anhydride was not decomposed by pyrolysis in the same apparatus at 500°±10° and 0·15±0·05 mm, while at the other extreme pyrolysis at 1100° and 3·0 mm over Lessing rings, during 3 hr, gave a 3·7% yield of biphenylene.

Pyrolysis of Tetrachlorophthalic Anhydride

The anhydride (5·0 g) was sublimed from a 25-ml flask into the silica pyrolysis tube packed with pieces of silica tubing. The temperature was maintained at 700°±20° and the pressure at 0·2±0·1 mm during the time of sublimation (2·5 hr). The condensate which collected in the exit tube and in the two traps was a dark yellowish green solid (2·69 g) consisting mainly of hexachlorobenzene and octachlorobiphenylene. These could not be cleanly separated by any single process, but a fraction containing mainly hexachlorobenzene was obtained by extraction of the condensate successively with light petroleum (b.p. 60–80°), benzene, and chloroform. Evaporation of these extracts and filtration of a solution of the residue in benzene through silica gel (19 by 2 cm) gave on evaporation a green solid (1·34 g). Gas chromatography of this solid on a 6-in. column of Apiezon L (He flow rate 200 ml/min, temperature programme 100→275° at 11°/min) gave colourless hexachlorobenzene (1·02 g), m.p. and mixed m.p. with an authentic sample 225–227°, and a little octachlorobiphenylene (38 mg).

TABLE 2

	Expt. A	Expt. B	Expt. C	Expt. D
Temperature	760	830	830	700
Pressure (mm)	0·3	0·2	0·2	10
Packing	—	—	silica tubing	silica tubing
Phthalic anhydride (g)	5·0	1·0	1·0	1·0
Time (hr)	1·0	1·2	0·5	1·3
	Yields of Products (mg)*			
Naphthalene	6	traces	8	2
Biphenyl	19		26	18
Biphenylene	240 (9%)	90 (17%)	69 (13%)	17 (3%)
Fluorene	7	—	17	4
C_{14} fraction†	—	—	6	6
C_{15} fraction†	—	—	2	2
C_{16} fraction†	—	—	—	—
C_{17} fraction†	—	—	4	5
C_{18} fraction†			39	15
Triphenylene	40			
Phthalic anhydride	3300	530	—	387
Phthalic acid	300	—	—	—
Unidentified fractions				
(i) no C=O absorption	—	47‡	116	38
(ii) C=O absorption in i.r.	—	—		14§

* Yields of hydrocarbons were estimated by analytical gas chromatography, except where pure triphenylene was isolated.

† Carbon numbers assigned from gas chromatographic retention times.

‡ Orange solid eluted from silica by benzene and containing some higher hydrocarbons.

§ Orange solid having infrared absorption (CS_2) at 1675, 1714, 1740, and 1780 cm^{-1}.

The chloroform-insoluble residue of the original condensate (1·33 g) was recrystallized repeatedly from boiling *o*-dichlorobenzene to give pure octachlorobiphenylene (total yield 0·99 g) as fine yellowish green needles, m.p. 296–298° (lit.[9] 292–294°) (Found: C, 33·9, 34·1. Calc. for $C_{12}Cl_8$: C, 33·7%). λ_{max} ($CHCl_3$) (log ϵ) 269 (infl., 4·34), 279 (4·72), 290 (5·13), 333 (3·22), 352 (3·31), 369 (infl., 3·44), 374 (3·53), 393 (3·56), 424 (3·03), and 453 (2·95) mμ. The mass spectrum showed a group of lines corresponding to the molecular ion, with the ion of lowest *m/e* at 424 ($^{12}C_{12}{}^{35}Cl_8$) and the most intense line at *m/e* 428 corresponding to the chemical molecular weight.

Pyrolysis of 4-Chlorophthalic Anhydride

4-Chlorophthalic anhydride (3·0 g) was sublimed through the pyrolysis tube packed with porcelain Lessing rings at 800° during 1 hr. The pressure gradually rose from 0·1 to 1·5 mm during this time. Chromatography of the crude solid product in hexane on silica gel followed by recrystallization of the first eluates from ethanol gave *2,6-*(or *2,7-*)*dichlorobiphenylene* (278 mg, 15%) as small off-white needles, m.p. 164–166° (sealed tube) (Found: C, 65·45; H, 2·8. $C_{12}H_6Cl_2$ requires C, 65·2; H, 2·7%). λ_{max} (EtOH) (log ϵ) 226sh (3·82), 241sh (4·30), 247 (4·62), 255 (4·83), 348 (3·70), and 367 (3·85) mμ. The infrared spectrum showed a band of medium intensity at 866 cm^{-1} (isolated aromatic hydrogens), a strong band at 830 cm^{-1} (two adjacent hydrogens), and a further strong band at 801 cm^{-1}. The 2,6- rather than the 2,7-orientation seems more likely by analogy with the dimerization of 4-methylbenzyne[19] which gives 2,6-dimethylbiphenylene.

Pyrolysis of 4,5-Dichlorophthalic Anhydride

This was carried out exactly as for the monochloro compound and gave *2,3,6,7-tetrachlorobiphenylene* as needles (6·5%) from benzene, m.p. *c.* 300° with sublimation (Found: C, 49·8; H, 1·4. $C_{12}H_4Cl_4$ requires C, 49·7; H, 1·4%). λ_{max} (EtOH) (log ϵ) 220 (infl., 4·17), 228 (infl., 4·10), 246sh (4·50), 251 (4·85), 261 (5·14), 339sh (3·62), 359 (3·98), and 376 (4·10) mμ. The infrared spectrum showed a strong band at 876 cm^{-1} (isolated aromatic hydrogens).

Pyrolysis of 3,6-Dichlorophthalic Anhydride

The anhydride (4·7 g) was sublimed through the pyrolysis tube packed with porcelain Lessing rings at 795° and *c.* 1 mm during 40 min. The crude product was dissolved in chloroform and stirred with 2N sodium hydroxide at room temperature for 24 hr. Evaporation of the chloroform layer and recrystallization of the residue from hexane (charcoal) gave *1,4,5,8-tetrachlorobiphenylene* (117 mg, 3·8%) as off-white fine needles which sublimed at 246° without melting (Found: C, 49·8; H, 1·5. $C_{12}H_4Cl_4$ requires C, 49·7; H, 1·4%). λ_{max} (EtOH) (log ϵ) 228 (3·65), 234 (3·65), 250sh (3·75), 256sh (3·91), 259 (4·34), 263 (4·30), and 271 (4·74) mμ. The infrared spectrum showed a strong band at 800 cm^{-1} (two adjacent aromatic hydrogens).

Pyrolysis of 4,5-Dimethylphthalic Anhydride

The anhydride (1·44 g) was sublimed through the pyrolysis tube packed with porcelain Lessing rings at 770–790° and 1·5 mm during 20 min. Purification of the product by thick-layer chromatography in hexane on Kieselgel G (E. Merck) followed by recrystallization from ethanol gave 2,3,6,7-tetramethylbiphenylene (26 mg, 3%) as off-white needles, m.p. and mixed m.p. with an authentic sample,[20] 223°.

Pyrolysis of o-*Sulphobenzoic Anhydride*

The anhydride (1·0 g) was sublimed at 0·05±0·02 mm from a 25-ml flask into the silica pyrolysis tube packed with pieces of silica tubing at 730±20° during 1 hr.

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[19] Hart, F. A., and Mann, F. G., *J. chem. Soc.*, 1957, 3939.

[20] Constantine, P. R., Hall, G. E., Harrison, C. R., McOmie, J. F. W., and Searle, R. J. G., *J. chem. Soc.*, 1966, in press.

At the end of the run the second, liquid-air cooled, trap was allowed to warm to room temperature so that the expanding gases passed into a 1-l. flask cooled in a dry ice/acetone bath. The small amount of liquid which collected dissolved completely in aqueous sodium hydroxide (15 ml of 20%), and addition of barium chloride to this solution gave a white precipitate. This dissolved completely in 10N hydrochloric acid with evolution of sulphur dioxide, and no precipitate was obtained on basifying with ammonia, indicating that the sodium hydroxide solution had contained sulphite, but not sulphate, anions.

The condensate remaining in the exit tube and both traps was a dark solid (779 mg). This was extracted with benzene (15 ml) and the benzene-soluble portion was chromatographed on a column of silica gel (18 by 1 cm). Elution with benzene gave a hydrocarbon fraction (36 mg) which was separated by gas chromatography on a 2-ft column of Apiezon L into naphthalene (4 mg), biphenyl (2 mg), biphenylene (23 mg, 5·5%), fluorene (3 mg), and C_{14}–C_{18} hydrocarbons (2·5 mg). Elution of the silica column with chloroform, followed by ethyl acetate, gave a dark gummy solid (591 mg) which, like the original benzene-insoluble solid (111 mg), was very soluble in water. Addition of ethanolic sodium hydroxide to a concentrated aqueous solution of these solids gave a crystalline precipitate of the sodium salt of *o*-sulphobenzoic acid, identified by comparison of its infrared spectrum with that of an authentic sample.

Pyrolysis of Coumarandione

Coumarandione (0·5 g) was sublimed at 0·2±0·1 mm during 6 hr into the silica pyrolysis tube packed with pieces of silica tubing at 600°±20°. The condensate in the exit tube and ice-cooled trap was dissolved in benzene (15 ml) and chromatographed on a column of silica gel (25 by 2 cm). Elution with benzene gave first an oily non-polar fraction (4 mg) which was shown by gas chromatography to contain no biphenylene. This was followed by a pale brown solid fraction (55 mg) containing xanthone and 3,4-benzocoumarin. The latter was heated with a solution of potassium hydroxide (3 g) in 50% aqueous methanol until most of the solid had dissolved. Evaporation of the methanol and extraction with methylene chloride yielded xanthone (14 mg), while acidification of the aqueous layer with 10N hydrochloric acid and re-extraction with methylene chloride gave 3,4-benzocoumarin (35 mg). Further elution of the silica column with benzene gave a second pale brown solid fraction (30 mg) which showed infrared carbonyl absorption at 1760, 1750, 1730, and 1724 cm^{-1}. The infrared spectrum was very similar to that of a 1 : 1 mixture of di- and tri-salicylides, and hydrolysis with 2N sodium hydroxide gave salicylic acid. Elution of the silica column with ethyl acetate yielded a gummy solid (44 mg) which was rechromatographed on silica gel (11 by 1 cm) from chloroform solution. Elution with chloroform gave salicylic acid (14 mg).

The products were identified as follows:

Xanthone.—The crude product was crystallized from ethanol and had m.p. 173–174°, not depressed by admixture with an authentic sample. Infrared and ultraviolet spectra were identical with those of the authentic compound.

3,4-Benzocoumarin.—The crude product was recrystallized from light petroleum (b.p. 60–80°) to give a slightly yellow product, m.p. and mixed m.p. with an authentic sample, 93–94°. Infrared and ultraviolet spectra were identical with those of an authentic sample obtained by peracid oxidation of fluorenone.[21]

Salicylic acid.—The sample obtained from pyrolysis of coumarandione was identified by the infrared spectrum and positive ferric chloride test only. That from hydrolysis of the polysalicylides was recrystallized from water as colourless needles, m.p. and mixed m.p. with an authentic sample, 158–159°.

Pyrolysis of Diphenic Acid

Diphenic acid (1·9 g) was sublimed through the pyrolysis tube, packed with porcelain Lessing rings, at 850° and 0·2–0·4 mm during 2·5 hr. The crude product was extracted with

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[21] Wittig, G., and Pieper, G., *Ber. dt. chem. Ges.*, 1940, **73**, 295.

hexane and the extract was chromatographed on a column of silica gel. Elution with hexane gave biphenylene (57 mg, 4·8%), m.p. 110°. The material which was insoluble in cold hexane (468 mg) was recrystallized from boiling hexane to give fluorenone (280 mg, 21%), m.p. 81–83°.

Pyrolysis of o-*Bromobenzoic Acid*

o-Bromobenzoic acid (5·0 g) was sublimed through the pyrolysis tube, packed with porcelain Lessing rings, at 850° and 0·2–0·4 mm during 3·25 hr. The traps contained a pungent liquid which gave off white fumes. Distillation of this gave bromobenzene, b.p. 155–156°. The solid material in the exit tube was dissolved in chloroform/benzene and chromatographed on silica gel. The presence of a trace of biphenylene was indicated by its R_F value and its characteristic colour reaction when sprayed with 5% ceric sulphate in 20% sulphuric acid.

When the pyrolysis was carried out at 1100° no biphenylene could be detected. Likewise the pyrolysis of *o*-chlorobenzoic acid at 850° gave some chlorobenzene, b.p. 131–132°, but no biphenylene.

ACKNOWLEDGMENTS

The authors wish to thank Dr J. H. Beynon (Dyestuffs Division, Imperial Chemical Industries, England) for the mass spectra of a number of carbonyl compounds; Dr J. L. Occolowitz (Defence Standards Laboratories, Melbourne) for the mass spectrum of octachlorobiphenylene; and Drs R. R. Davies and N. Corby (Dyestuffs Division) for the gift of several substituted phthalic anhydrides.