Arynes by Pyrolysis of Acid Anhydrides

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Nine aromatic and two heterocyclic anhydrides were pyrolyzed in admixture with pyridine under standardized conditions. Each anhydride lost carbon dioxide and carbon monoxide to give the corresponding aryne. This was demonstrated by the formation of products of insertion and of 1,2 and 1,4 addition, followed by rearomatization with loss of hydrogen cyanide or acetylene.

With the discovery of benzyne formation by pyrolysis of phthalic anhydride,[1] a new field was opened for the investigation of aryne reactions at high temperatures. Our first concern was to determine the generality of aryne formation from aromatic acid anhydrides. Such syntheses could be of considerable significance because of the enormous quantities of aromatic mono- and polyanhydrides available from petroleum aromatics by oxidation.

Accordingly, nine aromatic and two heterocyclic anhydrides were pyrolyzed in admixture with pyridine under standardized—although not necessarily optimum—conditions, and the relative amounts of aryne or hetaryne produced were determined by analysis of the reaction products. Although benzene as reactant would have given far fewer products and isomers, it had the disadvantage of pyrolyzing to bi- and terphenyl, and there appeared no easy way to distinguish the products formed by benzene pyrolysis from those formed by aryne insertion. An attempt to use deuterated benzene for this purpose led to results difficult to interpret because of scrambling of protium and deuterium.[2]

The products were identified in all cases by mass spectrometry, and in some by gas chromatography or by directly coupled gas chromatography–mass spectrometry. Because measuring spectra of chromatographic effluent on the fly requires that the entire relevant mass range be scanned in a few seconds, the quality of such spectra is somewhat impaired. In some cases where a critical component could not be unequivocally distinguished from a possible isomer by the spectrum alone, the identification was completed by comparison of its retention time with those of authentic samples. Results so obtained gave us sufficient confidence to assign structures to products identified solely by parent peak masses at low voltage. Relative intensities of the parent peaks of components in a spectrum measured at reduced ionizing voltage (7.5 v, uncorrected) were taken as a first approximation to relative concentrations.[3,4a]

(1) E. K. Fields and S. Meyerson, *Chem. Commun.*, 474 (1965).

(2) E. K. Fields and S. Meyerson, *J. Am. Chem. Soc.*, **88**, 21 (1966).

(3) Sensitivity, *i.e.*, the proportionality factor between parent-peak intensity and concentration, differs from one compound to another. However, closely related compounds have roughly equal sensitivities at the ionizing voltage employed in our work.[4a] In any case, the use of relative intensities is perfectly valid for intercomparison of concentration ratios of identical components in separate samples[4b] within the limits of reproducibility of the low-voltage data.

(4) (a) G. F. Crable, G. L. Kearns, and M. S. Norris, *Anal. Chem.*, **32**, 13 (1960); (b) S. Meyerson and E. K. Fields, *Chem. Commun.*, 275 (1966).

Experimental Section

Pyrolyses were run in a Vycor tube filled with Vycor beads heated in an electric furnace maintained at 690 ± 2° under dry nitrogen. After each run the tube was thoroughly cleaned and all carbon removed. Frequent check runs were made with new tubes and beads.

For anhydrides soluble in pyridine, the solution was dropped in the tube at a predetermined rate to give a contact time of 20 ± 2 sec. For anhydrides insoluble or only slightly soluble in pyridine, the anhydride was volatilized from a bulb maintained at 10° above its boiling point in a stream of nitrogen containing the pyridine into the pyrolysis tube. Products were condensed in a chilled bulb.

Analyses were performed with a Consolidated Model 21-103c mass spectrometer with the inlet system at 250°; with a directly coupled gas chromatograph–mass spectrometer[5] also employing a 21-103c instrument with an electron multiplier in place of the Faraday-cup detector; and with gas chromatography on a column of polyethylene glycol sebacate on Chromosorb W. Mass spectra were measured at the conventional 70 ionizing v and at low voltage, 7.5 v, uncorrected. For the low-voltage measurements, the repellers were maintained at an average potential of 3 v, the exact values being selected to give maximum sensitivity.

In a typical experiment, a solution of 1.48 g (0.01 mole) of phthalic anhydride in 8.05 ml (0.1 mole) of pyridine was pyrolyzed at 690° in dry, high-purity nitrogen flowing at the rate of 0.1 ft³/hr. Contact time was 20.2 sec. The products were distilled to recover 6.34 ml of pyridine. The distillation residue weighed 2.12 g, of which 0.06 g was removed for analysis by mass spectrometry. The remainder was dissolved in ether and separated into nitrogen bases (1.44 g) and hydrocarbons (0.62 g) by extraction with dilute hydrochloric acid. Analysis by gas chromatography, by comparison of retention times with authentic samples, gave the results shown in Table I.

TABLE I

GAS CHROMATOGRAPHIC ANALYSIS

Compounds	Area %
Hydrocarbons	
Naphthalene	93
Higher boiling hydrocarbons	7
Nitrogen bases	
Quinoline	4.0
Isoquinoline	<0.1
2-Phenylpyridine	23.9
3-Phenylpyridine[a]	13.4
4-Phenylpyridine	3.3
Dipyridyl isomers	42.4
Unknowns	12.9

[a] Deduced from its retention time.

Analysis of the exit gases by mass spectrometry gave these results (nitrogen-free basis; carbon monoxide confirmed in a similar run under helium): carbon dioxide, 45.6; carbon mon-

(5) R. S. Gohlke, *Anal. Chem.*, **31**, 535 (1959); L. P. Lindeman and J. L. Annis, *ibid.*, **32**, 1742 (1960); J. T. Watson and K. Biemann, *ibid.*, **36**, 1135 (1964).

TABLE II
INSERTION AND ADDITION REACTION PRODUCTS OF ARYNES WITH PYRIDINE

Anhydride	Yield[a]	Insertion	Relative amount[b]	Addition	Relative amount[b]
Phthalic	95	Phenylpyridine	100	Naphthalene	167
				Quinoline	25
Tetrachlorophthalic	17.5	Tetrachlorophenylpyridine	3	Tetrachloronaphthalene	24
Tetraphenylphthalic	10	Tetraphenylphenylpyridine	51	Tetraphenylnaphthalene	36
				Tetraphenylquinoline	0.9
Trimellitic	52	Phenylpyridine	18	Naphthalene	4
		Carboxyphenylpyridine	37	Quinoline	2
				Naphthoic acid	1
Pyromellitic	88	Phenylpyridine	22	Naphthalene	29
		Phenylenedipyridine	14	Quinoline	3
		Naphthylpyridine	6	Anthracene	11
				Benzoquinoline	1
				Pyridylquinoline	5
Mellophanic	47	Phenylpyridine	29	Naphthalene	29
		Phenylenedipyridine	14	Quinoline	3
		Naphthylpyridine	28	Phenanthrene	23
				Benzoquinoline	5
				Pyridylquinoline	1
Benzophenonetetracarboxylic dianhydride	82	Pyridylbenzophenone	36	Phenylnaphthyl ketone	20
		Dipyridylbenzophenone	13	Dinaphthyl ketone	2
				Naphthylpyridylphenyl ketone	12
1,8-Naphthalic	12	Naphthylpyridine	27		...
Naphthalene-2,3-dicarboxylic	66	Naphthylpyridine	250	Anthracene	155
				Benzoquinoline	5
Quinolinic	7	Pyridylquinoline	2	Quinoline	12
		Dipyridyl	c		
	14[d]	Phenylpyridine	7	Quinoline	4
Pyrazine-2,3-dicarboxylic	1.1[d]	Phenylpyrazine	5		...

[a] Of total insertion and addition products. See Experimental Section. [b] Relative intensities of parent peaks in the low voltage mass spectra. The intensities are all relative to a value of 100 assigned to dipyridyl. [c] See text. [d] With benzene.

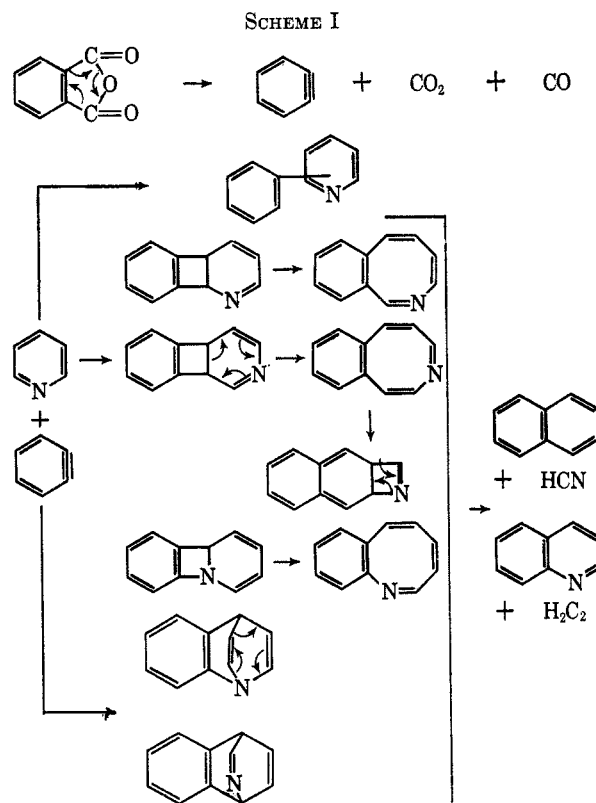oxide, 45.4; hydrogen cyanide, 1.8; acetylene, 0.4; hydrogen, 6.8; all values in mole per cent.

Yields were calculated on the basis of aromatic anhydride. For example, 0.01 mole of phthalic anhydride with excess pyridine theoretically should give a total of 0.01 mole of the products of insertion and addition: naphthalene, quinoline, isoquinoline, and phenylpyridines. The total weight of all products of the reaction, coupled with the approximate relative concentrations, as shown in Table II, gave an estimated 0.0095 mole of products.

Discussion of Results

The reactions of this study involved insertion of the aryne, as well as 1,2 and 1,4 addition followed by rearomatization[1] (Scheme I).

Detection of the aryne dimer and trimer, equivalent to biphenylene and triphenylene from benzyne, was not deemed a necessary criterion for aryne production. There exist little or no data on the thermal stability and reactivity of biphenylene species at elevated temperatures. Thus, although biphenylene was unequivocally identified as a product in the pyrolysis of phthalic anhydride in benzene,[1] and a species of mole wt 252, presumably binaphthylene, was detected among the pyrolysis products of both naphthalene anhydrides, biphenylene alone above 375° has been reported to give tetraphenylene quantitatively.[6]

Table II shows the relative amounts of insertion and addition products formed from the various anhydrides. To ascertain that none of the products arose from pyridine itself, pyridine was pyrolyzed under the identical conditions. It gave a 2.2% yield of products, of which

(6) D. F. Lindow, L. Friedman, and A. H. Seity, Division of Organic Chemistry Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 28–31, 1966, Paper No. 111.

SCHEME I

dipyridyl was 96.2%, terpyridyl, 2.7%, and unidentified, 1.1%.

From the addition reactions of phthalic anhydride with pyridine, naphthalene was formed in much greater quantity than quinoline; isoquinoline was either totally

absent or present in only minute amounts. These facts indicated (a) if there were much 1,2 addition of benzyne, it occurred predominantly at the 1,2 and 3,4 atoms in pyridine; (b) 1,4 addition took place at carbon atoms in preference to a nitrogen and a carbon atom. Studies with other systems indicate thus far that arynes have a decided preference for 1,4 over 1,2 addition.[7]

Elimination of hydrogen cyanide was favored over that of acetylene in the rearomatization step. The ratio of hydrogen cyanide to acetylene in the exit gases was not identical with that predicted from the analysis of the less volatile products; this was probably due to secondary pyrolytic transformations of both gases under the reaction conditions. Such transformations were found in separate pyrolyses of hydrogen cyanide and acetylene alone.

Tetrachlorophthalic anhydride gave a relatively low yield of products derived from tetrachlorobenzyne. The pyrolysis tube was badly carbonized; evidently extensive decomposition of the anhydride, the aryne, or the chlorinated products had occurred. Tetrabromophthalic anhydride gave a lower yield of products. These are not listed in the table because none of them retained all four bromine atoms and could be definitely ascribed to reactions of tetrabromobenzyne, although tribromo- and dibromonaphthalene were present in appreciable amounts. Tetraphenylphthalic anhydride also gave low yields of products of the reaction of tetraphenylbenzyne with pyridine. This was not because of the stability of the anhydride and its reluctance to form the aryne, but rather because the aryne preferred to stabilize itself intramolecularly. The behavior of tetraphenylphthalic anhydride will be the subject of a separate publication.

Trimellitic anhydride yielded products derived both from benzyne and carboxybenzyne. Decarboxylation at 690° should be extensive, and this compound then would react like phthalic anhydride. Under the circumstances, the survival of appreciable amounts of carboxybenzyne derivatives was surprising. The 4-methyl ester of trimellitic anhydride is being studied as a stable source of carboxybenzyne methyl ester.
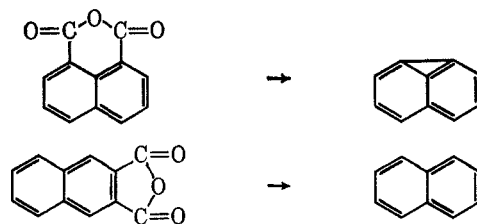
Pyromellitic and mellophanic dianhydrides gave similar product distributions, derived from a presumed benzodiyne. The reactions possibly took place in a stepwise, rather than in a concerted fashion. These arynes evidently have a strong tendency to abstract hydrogen, as shown by formation of appreciable amounts of phenylpyridine, naphthalene, and quinoline. Products of both insertion and addition in the same molecule were also formed (naphthylpyridine, pyridylquinoline). This was also true of another dianhydride, benzophenone-3,3',4,4'-tetracarboxylic acid dianhydride. The latter gave dinaphthyl ketone (the product of diaddition), dipyridylbenzophenone (the product of diinsertion), and naphthyl pyridylphenyl ketone (the product of addition plus insertion).

An attempt was made to convert mellitic anhydride, the simplest aromatic trianhydride, to benzotriyne. It reacted with pyridine, but apparently the products totally decomposed; the only compounds isolated were those derived from pyridine itself. Because of its extremely low solubility, volatility, and decomposition

(7) S. Meyerson and E. K. Fields, *Chem. Ind.* (London), 1230 (1966).
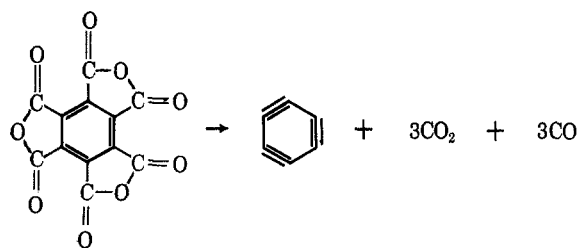
temperature, mellitic anhydride is being studied by the use of special techniques.

The yield of products from 1,8-naphthalic anhydride was low, partly because of the thermal stability of the anhydride. At 690° with 20-sec contact time, 50% was recovered unchanged. Its behavior contrasted markedly with that of naphthalene-2,3-dicarboxylic anhydride, reflecting the greater difficulty of forming perinaphthalyne as against 2,3-naphthalyne. Azafluor-

anthene should result from perinaphthalyne and pyridine by addition, but only the insertion product formed. This contrasted with the low temperature reaction of benzene with perinaphthalyne (from the oxidation of amino-1,8-naphthatriazole with lead tetraacetate) to give fluoranthene.[8]

Quinolinic anhydride gave the products of pyridyne addition and insertion, quinoline and pyridylquinoline. Naphthyridene may have been present at a concentration too low to detect. The major insertion product, dipyridyl, was also formed by pyrolysis of pyridine itself. To demonstrate clearly the insertion products of 2,3-pyridyne, quinolinic anhydride was also pyrolyzed in benzene to give the products shown in Table II.

Pyrazine-2,3-dicarboxylic anhydride gave no products of the reaction of the corresponding hetaryne with pyridine; however, it gave a small but definite amount of phenylpyrazine with benzene, establishing the formation of pyrazyne. This anhydride is readily converted by ring opening and rearrangement to succinonitrile.[9]

Pyrolysis of aromatic and heterocyclic anhydrides is a general method of forming arynes and hetarynes. Thus, this reaction closely parallels the behavior of the anhydrides in the mass spectrometer[1] where in every instance the parent ion[10] loses carbon dioxide and carbon monoxide. Because products in addition to those from 1,2 and 1,4 addition and insertion always formed, more detailed investigations, involving a large number of reagents and emphasizing the use of labeled compounds, are in progress.

(8) C. W. Rees and R. C. Storr, *Chem. Commun.* 193 (1965).

(9) R. F. C. Brown, N. D. Crow, and R. K. Solly, *Chem. Ind.* (London), 343 (1966).

(10) For additional examples of such parallel behavior, see ref 4b and E. K. Fields and S. Meyerson, *J. Am. Chem. Soc.*, **88**, 2836 (1966).