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REACTIONS OF 4-NITROPHTHALIC ANHYDRIDE

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Arynes are formed by the decomposition of aromatic dicarboxylic anhydrides at 700°.[1] Aryl radicals are formed by the dissociation of aromatic nitro compounds at 600°.[2] Ergo, arynyl free radicals may be formed by the pyrolysis of aromatic dicarboxylic anhydrides substituted with nitro groups. The postulated decomposition reactions may, of course, occur in discrete steps and, further, may be separated in the total reaction sequence by bond-making processes with other molecules in the system. Nonetheless, extrapolation from the reactions of the monofunctional species furnishes a working hypothesis for those of the difunctional ones.

To test this hypothesis, we heated 7.05 g. (0.073 mole) of 4-nitrophthalic anhydride in 310 ml. (3.5 moles) of benzene at 650° for 32 seconds under nitrogen in a flow apparatus.[3] The major products of the 23 g. total were biphenyl, terphenyl, and phenylnaphthalene, together with small amounts of phenylphthalic anhydride, terphenyldicarboxylic anhydride, and quaterphenyl. The mechanisms by which these products were formed were clarified by reacting 4-nitrophthalic anhydride with benzene-$\underline{d}_6$ under identical conditions. Isotopic distributions of the major products are shown in Table I.

Nearly all the biphenyl came from benzene-$\underline{d}_6$ alone; its relatively large proportion among the products was a result of the high benzene-to-nitrophthalic anhydride mole ratio, necessitated by the low solubility of the anhydride. Phenylnaphthalenes, almost all -$\underline{d}_9$, -$\underline{d}_{10}$, and -$\underline{d}_{11}$, were evidently derived from two molecules of benzene-$\underline{d}_6$ and one of nitrophthalic anhydride, as were terphenyl-$\underline{d}_{11}$ and -$\underline{d}_{12}$. Phenylnaphthalene and terphenyl species are most simply accounted for by arylation coupled with 1,4 addition and insertion, respectively, of a benzynyl free radical (II):

TABLE I

ISOTOPIC DISTRIBUTIONS OF MAJOR COMPONENTS[a]

Chemical Species	Molecular Weight	Number of D Atoms	Isotopic Distribution, %	Summed Relative Intensity[b]
Biphenyl	158	4	0.5	100
	159	5	0.5	
	160	6	1.0	
	161	7	3.4	
	162	8	3.8	
	163	9	10.4	
	164	10	80.2	
Terphenyl	237	7	1	14.1
	238	8	2	
	239	9	3	
	240	10	6	
	241	11	20	
	242	12	25	
	243	13	16	
	244	14	27	
Phenyl-naphthalene	212	8	5	7.7
	213	9	31	
	214	10	40	
	215	11	19	
	216	12	5	

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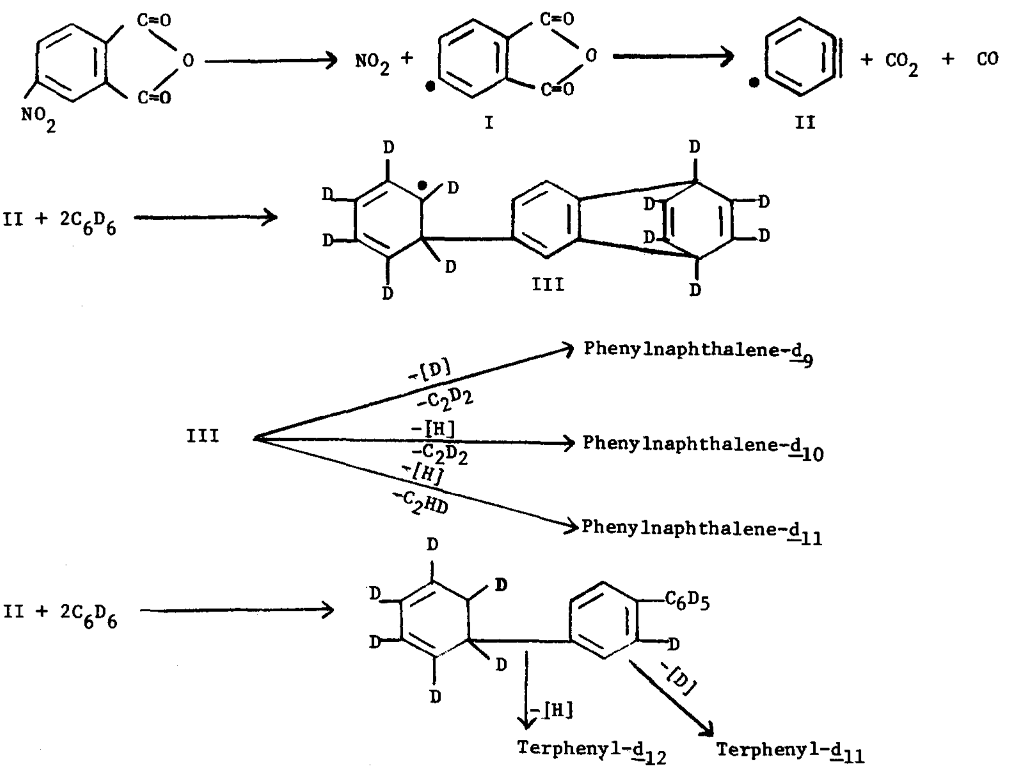
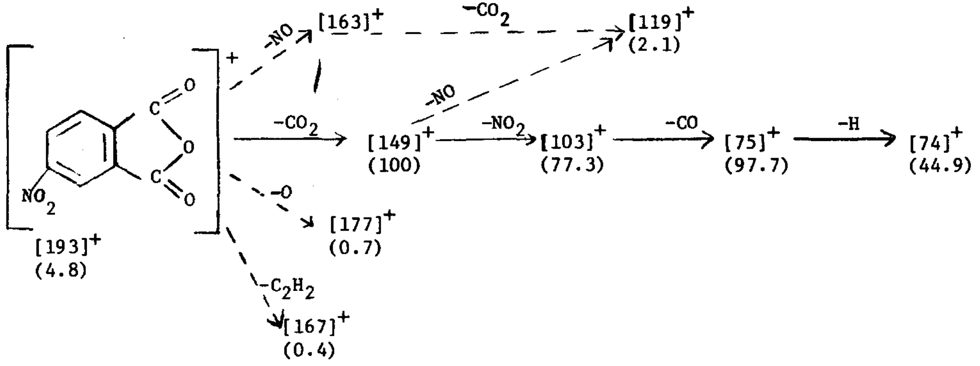
a) Determined by mass-spectral analysis at low voltage (7.5 v, nominal) on a Consolidated model 21-103 mass spectrometer.

b) Relative intensity of molecular ions summed for each chemical species.



Many aromatic compounds exhibit parallel behavior under electron impact in the mass spectrometer and thermally.[1,2] The mass spectrum of 4-nitrophthalic anhydride suggests this decomposition scheme in which solid arrows denote processes supported by metastable peaks:



Relative intensities of the ions, shown in parentheses, show that the major decomposition path consists of successive loss of CO_2, NO_2, CO and H. The ion of mass 75, the second most abundant in the spectrum has the elemental composition of benzynyl and may be visualized tentatively as having the benzynyl structure, differing from that of benzynyl free radical only by virtue of the charge.

The reactions of 4-nitrophthalic anhydride with pyridine and with thiophene at 650° furnish additional evidence for benzynyl free radical -- or, again, the equivalent succession of reactive intermediates. Pyridine gave pyridylnaphthalene and dipyridylbenzene; thiophene gave thienylnaphthalene, thienylbenzothiophene, and dithienylbenzene. These products are the heterocyclic equivalents of the aromatic hydrocarbons produced from 4-nitrophthalic anhydride and benzene, and are most readily accounted for by reaction of benzynyl free radical (II) with two molecules of pyridine or thiophene.

Small amounts of aryl or heteroaryl anhydrides among the products show that the decomposition of 4-nitrophthalic anhydride is, at least in part, stepwise rather than concerted.

We are presently studying additional high-temperature reactions of 4-nitrophthalic anhydride, as well as reactions of 3-nitrophthalic anhydride and 3-nitro-1,8-naphthalic anhydride under similar conditions. The most abundant ion in the mass spectrum of 3-nitrophthalic anhydride and the second most abundant in that of 3-nitro-1,8-naphthalic anhydride, like the second most abundant in that of 4-nitrophthalic anhydride, have masses corresponding to loss of the elements of CO_2, CO and NO_2. The spectra thus suggest that these anhydrides at high temperatures will also give products that would be expected from reactions of the corresponding arynyl free radicals.

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