and Turner.[14] This accounts for 5% of the original perester carbonyl.

The nonvolatile products remaining after removing the chlorobenzene under vacuum were found by infrared and nmr spectroscopy to consist mainly of an acid. A comparison of the area of the hydroxyl proton at τ −2.2 to the area of the aromatic protons indicated the acid was present to the extent of 70%. Several extractions of the nonvolatile products (0.603 g) in ether with 10% sodium carbonate followed by acidification gave component 2 (0.370 g), an acid, mp 128.5–131°. It was identified as 8-(phenylthio)-1-naphthoic acid by comparison with an authentic sample by infrared spectroscopy and mixture melting point. The amount of this acid isolated accounts for 60% of the perester carbonyl (70% by nmr).

Attempts to resolve the remaining deep red tarry residue (0.233 g) by column chromatography on Florisil and alumina were unsuccessful. Evidence for products containing a phenyl ester group, which could have resulted from phenyl migration, was specifically sought in the infrared spectra of various chromatographic fractions, but none was observed (lack of absorption near 1730 cm^{-1}).

Products of the Decomposition of *t*-Butyl *o*-(Phenylthiomethyl)perbenzoate. A. Volatile Products. The perester (0.184 g, 0.585 mmole) was dissolved in chlorobenzene (0.5 ml), degassed, and heated at 110° for 19.2 hr. The volatile products were found to consist of acetone (28%) and *t*-butyl alcohol (65%), as the major products accounting for 93% of the original *t*-butyl group of the perester.

B. Nonvolatile Products. The nmr spectrum of this decomposition mixture, after removal of volatiles, consisted of the following peaks: a singlet a τ −0.6, a multiplet in the aromatic region 2–3, a singlet at 3.3, and a singlet at 5.5, with the relative areas of 1.0, 21, 1.5, and 2.0, respectively. The infrared spectrum of this mixture had a strong absorption at 1775 and a medium one near 1700 cm^{-1}.

Component 1 was identified as 2-carboxybenzyl phenyl sulfide by comparison with its known infrared and nmr spectra. Extraction of the decomposition mixture with aqueous sodium carbonate removed the peaks assigned to component 1 in the spectra of the decomposition mixture. Component 1 accounts for 33% of the original perester carbonyl.

Component 2 was left after the extraction with sodium carbonate. It was identified as 3-(phenylthio)phthalide on the basis of the following spectral evidence. The infrared spectrum has a strong absorption at 1775 cm^{-1}, and no OH absorption. The nmr spectrum has peaks at τ 2.0–2.8, a singlet at 3.3, and a small amount of absorption at 8.4–9.3 (presumably from products containing *t*-butyl residues; these peaks were not present in all spectra), with relative areas of 9.0, 0.82, and 2.6, respectively.

In order to isolate component 2, the perester (1.2 g) in 8.0 ml of chlorobenzene was heated at 110° for 46 hr. After evaporation of solvent, the residue was dissolved in ether and extracted with sodium carbonate. Removal of ether left 0.48 g of a light yellow solid (51% of perester carbonyl), mp 95–97° after recrystallization from ether–pentane. The instability of this compound was suggested by the smell of thiophenol observed in all recrystallizations. The infrared and nmr spectra were the same as those obtained above. From these data component 2 was identified as 3-(phenylthio)phthalide, and accounted for 50–65% of the perester carbonyl.

Anal. Calcd for $C_{14}H_{10}O_2S$: C, 69.39; H, 4.16. Found: C, 68.49; H, 4.46, with a small residue not burned.

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Pyrolysis of Chlorobenzene

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Abstract: The reaction products of chlorobenzene with benzyne—from pyrolysis of phthalic anhydride—were naphthalene, chloronaphthalene, and chlorodiphenyl. Chlorobenzene alone also gave small, but definite, amounts of naphthalene and chloronaphthalene. Benzyne was evidently formed from chlorobenzene by intramolecular dehydrochlorination at elevated temperatures.

Previous investigations have found diphenyl, 4-chlorodiphenyl, 4,4′-dichlorodiphenyl, and some *p*-terphenyl as the products of pyrolysis of chlorobenzene.[1,2] On the basis of a kinetic study at 770–850° and 12 torr, in which the main products were hydrogen, hydrogen chloride, and 4,4′-dichlorodiphenyl, a chain mechanism was proposed in which chlorine atoms and chlorophenyl radicals were the chain carriers.[2]

We are presently engaged in studying the high-temperature reactions of benzyne, generated by pyrolysis of phthalic anhydride, with aromatic compounds. Benzene gives naphthalene and biphenyl;[3] chlorobenzene should give chlorodiphenyls by insertion and naphthalene and chloronaphthalenes by 1,2 and 1,4 addition and rearomatization with respective loss of chloroacetylene and acetylene.

To test this prediction, phthalic anhydride was pyrolyzed in admixture with chlorobenzene at 690°. The major products and their relative intensities in a low-voltage mass spectrum, analyzed by mass spectrometry, were: naphthalene, 3.5; chloronaphthalenes, 30.0; chlorodiphenyls, 34.6; and dichlorodiphenyls, 100.0. The postulated products from insertion and addition of benzyne were therefore indeed formed. In addition, a small amount of biphenylene, 1.2 on the same scale, resulted.

However, pyrolysis of chlorobenzene alone under identical conditions, for comparison, gave some rather surprising results. Among the products, analyzed in the same way, were: naphthalene, 0.3; chloro-

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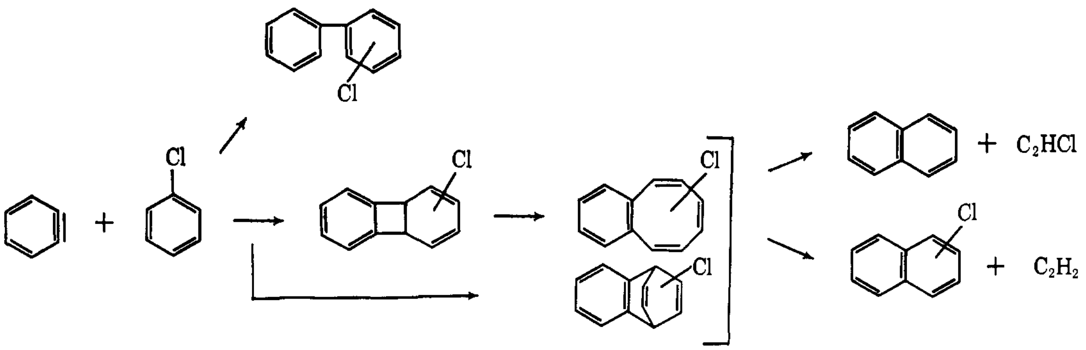
[1] J. G. Kramers, *Ann.*, **189**, 135 (1877).

[2] C. F. Cullis and J. E. Manton, *Trans. Faraday Soc.*, **54**, 381 (1958).

[3] E. K. Fields and S. Meyerson, *Chem. Commun.* (London), 474 (1965).



naphthalenes, 0.1; chlorodiphenyls, 23.6; and dichlorodiphenyls, 100.0. The formation of naphthalene and chloronaphthalenes by pyrolysis of chlorobenzene has not been previously reported, and represents a reaction sequence unaccounted for by a simple chain reaction. These products are most readily explained by loss of hydrogen chloride from chlorobenzene to yield benzyne, which then reacts with chlorobenzene in the manner already described.

The formation of benzyne from chlorobenzene at 690° is further substantiated by the presence of a small amount, 0.5 on the same scale, of biphenylene among the products. The high-temperature behavior of chlorobenzene thus parallels somewhat its behavior at ordinary temperatures in the presence of strong bases.[4] Here, however, both *o*-halophenyl anion and benzyne are formed in a large excess of nucleophile, with which they undergo rapid reaction to yield products.

The concentration and total amount of chlorodiphenyls from the phthalic anhydride pyrolysis was appreciably greater than from chlorobenzene alone, as would be expected from the insertion reaction. Nevertheless, the major reaction of benzyne with chlorobenzene appears to be addition, in contrast to its reaction with benzene, where insertion predominates.[5] The products from chlorobenzene-2-*d* and from other aromatic halides upon pyrolysis are under investigation.

Experimental Section

Phthalic anhydride was sublimed from commercial material. Chlorobenzene was dried and distilled; analysis by gas chromatography and mass spectrometry showed no impurities. A solution of 1.48 g (0.01 mole) of phthalic anhydride in 50.6 g (0.45 mole) of chlorobenzene was pyrolyzed at 690° with a residence time of 24 sec in a Vycor tube filled with Vycor beads under high-purity dry nitrogen flowing at a steady rate of 60 ml/hr. The products remaining after distillation of unreacted chlorobenzene (5.9 g) were identified by mass spectrometry.[6] Independent confirmation of the products reported here was obtained by direct-coupled gas chromatography-mass spectrometry, in which the spectra of the separated components in the column effluent furnished unequivocal identification.[7] Relative intensities of parent peaks of the major components, measured at reduced ionizing voltage (7.5 v, uncorrected), were taken as a first approximation to relative concentrations.[8,9]

Chlorobenzene (50.6 g, 0.45 mole) was pyrolyzed alone, in an unused tube and beads, under nitrogen flowing at the same rate and giving the same contact time. The residue, after removal of chlorobenzene, weighed 4.0 g.

Duplicate pyrolyses of chlorobenzene alone and chlorobenzene with phthalic anhydride checked the total yields of products and their relative amounts within 3%.

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[4] H. Heaney, *Chem. Rev.*, **62**, 81 (1962).

[5] Similar results were obtained from the pyrolysis of indanetrione in chlorobenzene: R. F. C. Brown and R. K. Solly, *Chem. Ind.* (London), 181 (1965).

[6] Spectra were measured with 70-v electrons on a Consolidated Model 21-103C instrument with the inlet system at 250°.

[7] 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).

[8] Low-voltage sensitivities are probably equal within a factor of about 2.[7] Assuming that this factor is unity, therefore, introduces errors into the analysis of a given sample. Nonetheless, results so obtained are entirely valid for intercomparison of concentration ratios in separate samples.

[9] G. F. Crable, G. L. Kearns, and M. S. Norris, *Anal. Chem.*, **32**, 13 (1960).