Preparation of 9-Anthryl Isocyanate Dimer from 9-Aminoanthracene Photodimer.—Phosgene (500 mg) was passed into a stirred solution of 9-aminoanthracene photodimer (300 mg) in 50 ml of dry toluene (distilled from phosphorus pentoxide) and left at room temperature for 23 hr. The solution was then refluxed under reduced pressure for 1 hr to remove unreacted phosgene. The white solid was collected by suction filtration. This compound was the 9-aminoanthracene dimer hydrochloride salt (300 mg, 85% yield, mp >250° dec). The infrared spectrum showed peaks at 3.6, 6.2, and 6.6 μ (1516 cm^{-1}). A small amount of this compound was made basic with aqueous ammonia, and the resulting white precipitate was collected by suction filtration and dried under reduced pressure. The infrared spectrum of the product was superimposable on that of the photodimer of 9-aminoanthracene.

Evaporation of the filtrate from the toluene solution under reduced pressure and trituration of the residue in boiling hexane gave 9-anthryl isocyanate dimer (30 mg, 8.9% yield, mp 188–189° dec). The infrared spectrum was superimposable on that of the photodimer of 9-anthryl isocyanate and that of 9-anthryl isocyanate dimer prepared from the photodimer of 9-anthroic acid.

Registry No.—1a, 22037-98-5; 1a hydrochloride, 22003-71-0; 1b, 22003-72-1; 1e, 22003-73-2; 1f, 22003-74-3.

Acknowledgment.—This research was supported by a grant from the National Science Foundation (GP-6740).

Reactions of Phthalic Anhydride with Biphenyl at 700°

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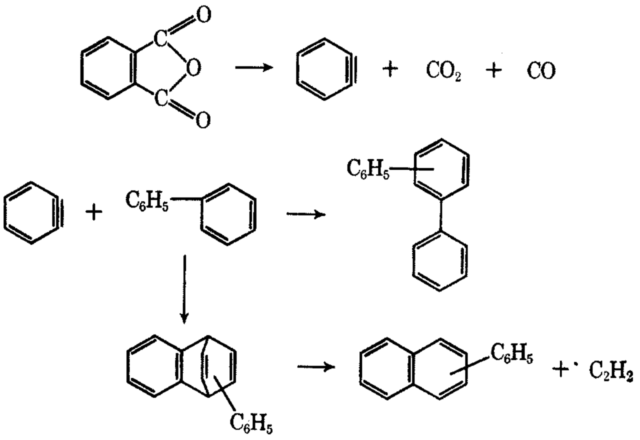
Received April 11, 1969

Phthalic anhydride at 700° loses carbon dioxide and carbon monoxide to give benzyne; in the presence of benzene it yields biphenyl by insertion and naphthalene by 1,2 and 1,4 addition and subsequent loss of acetylene.[1] With biphenyl, phthalic anhydride should give 1- and 2-phenylnaphthalene and the three terphenyls as the major products (Scheme I).

Scheme I



To test this prediction and to determine the relative yields of the insertion and addition products as well as isomer distribution, we allowed a mixture of phthalic anhydride and biphenyl to react at 700° and obtained the products shown in Table I.

Table I

Products from the Reaction of Phthalic Anhydride with Biphenyl[a]

Product	Relative concentration[b]
Anthracene, phenanthrene	24
Phenylnaphthalene	36
Terphenyl	100
Binaphthyl	20
Naphthylbiphenyl	18
Quaterphenyl	73
Quinquephenyl	14
Sexiphenyl	4

[a] Conditions: 0.02 mol of phthalic anhydride, 0.1 mol of biphenyl; 700°; contact time, 35 sec; N_2, 10 cc/min; total weight of products, 4.55 g. [b] Relative intensity in the low-voltage (7.5 V uncorrected) mass spectrum on the basis terphenyl = 100.

Phenylnaphthalene and terphenyls were indeed formed as major products. Gas chromatographic analysis gave the yields and isomer distributions shown in Table II.

Table II

Product	Yield, mol %	Isomer, %
Phenylnaphthalene	16.7	1, 27
		2, 73
Terphenyl	40.6	*ortho*, 8
		meta, 57
		para, 35

On the basis of other studies,[2] we had assumed that little or no terphenyl would arise from biphenyl alone,[3] and, for confirmation, we pyrolyzed biphenyl at 700° with the results shown in Table III. Evidently biphenyl gives terphenyl at high temperatures, and about as much as quaterphenyl, contrary to previous

Table III

Products from Biphenyl[a]

Products	Relative concentrations[b]	
Benzene[c]	28	25
Terphenyl	116	71
Quaterphenyl	100	100
Quinquephenyl	2	3
Sexiphenyl		0.5

[a] Conditions: 0.1 mol biphenyl; 700°; N_2, 10 cc/min; contact time, 7.5 sec (1.2% conversion) and 37 sec (6.6% conversion), respectively. [b] Relative intensity in the low-voltage mass spectrum normalized to quaterphenyl = 100. [c] Owing to work-up procedure, most benzene was lost before analysis. The figures merely serve to indicate that benzene was a product of the reaction.

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(1) E. K. Fields and S. Meyerson, *Advan. Phys. Org. Chem.*, **6**, 1 (1968).

(2) K. L. Hall and F. A. Elder, *J. Chem. Phys.*, **31**, 1420 (1959); J. G. Burr, J. M. Scarborough, and R. H. Shudde, *J. Phys. Chem.*, **64**, 1359 (1960); M. Hellmann, National Bureau of Standards Report 5255, U. S. Government Printing Office, Washington, D. C., April 1957.

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

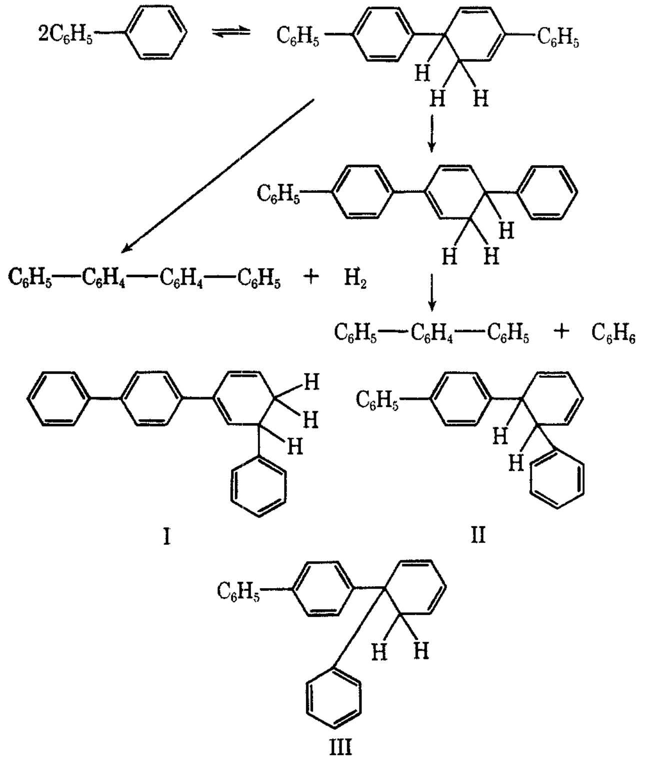
TABLE IV

REACTION PRODUCTS FROM LABELED PHTHALIC ANHYDRIDE AND BIPHENYL[a]

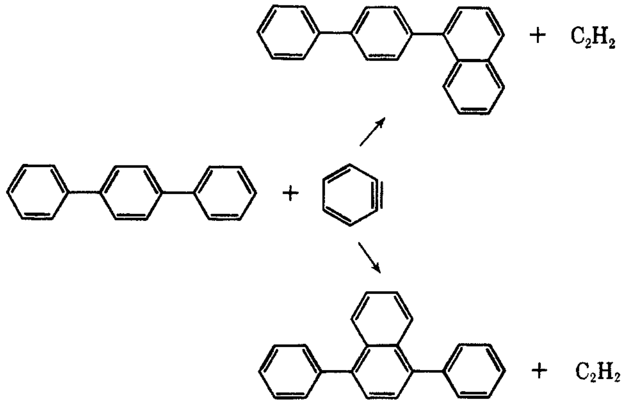
Product	Phthalic anhydride and biphenyl-d_{10}[b]			Phthalic anhydride-d_4[c] and biphenyl		
	Isotopic distribution, %[d]		Total relative concentration[e]	Isotopic distribution, %[d]		Total relative concentration[e]
Phenylnaphthalenes	d_7	10	46	d_2	11	50
	d_8	29		d_3	28	
	d_9	29		d_4	42	
	d_{10}	16				
	d_{11}	7				
Terphenyls	d_6	6	100	d_0	62	100
	d_7	6		d_1	14	
	d_{10}	6		d_2	7	
	d_{12}	6		d_3	6	
	d_{13}	21		d_4	7	
	d_{14}	43				
$C_{22}H_{16}$ (naphthylbiphenyls and diphenylnaphthalenes)	d_{10}	5	24	d_0	8	17
	d_{12}	19		d_1	8	
	d_{13}	19		d_2	13	
	d_{14}	18		d_3	25	
	d_{15}	5		d_4	25	
	d_{16}	5		d_5	8	
				d_6	8	
Quaterphenyls	d_{16}	10	64	d_0	61	79
	d_{17}	26		d_1	17	
	d_{18}	42		d_2	6	

[a] Conditions: mol ratio of phthalic anhydride to biphenyl, 1:5; 700°; N_2, 20 cc/min; contact time, 21.5 sec. [b] Isotopic composition: 0.4% d_8, 8.5% d_9, 91.1% d_{10}. [c] Isotopic composition: 5.7% d_3, 94.3% d_4. [d] Derived from low-voltage mass spectrum. Isotopic species comprising less than 5% of the yield of any one product are omitted as probably due to isotopic impurities in the reagents and thermal protium–deuterium scrambling. [e] Summed relative intensity for each chemical species in the low-voltage spectrum, normalized to terphenyl = 100.

SCHEME II



SCHEME III



assumptions.[4] This is perhaps not surprising. Phenylcyclohexadiene has been proposed as an intermediate in the pyrolysis of benzene to biphenyl;[3] a similar intermediate derived from biphenyl might be expected to have isomeric structures such as I, II, and III among others (Scheme II).

Such structures appear set up to form terphenyl by loss of benzene as readily as quaterphenyl by loss of hydrogen.

To find how much terphenyl forms by benzyne insertion and by biphenyl pyrolysis alone in the reaction of biphenyl with phthalic anhydride, we allowed mixtures of one labeled and one unlabeled reagent to react at 700°, with the results shown in Table IV.

The low-voltage mass spectra were clear and relatively easy to interpret with no overlapping of molecular weights between chemical species. The products of mol wt 280–296 most likely include diphenylnaphthalenes as well as naphthylbiphenyls (Scheme III). Statistically as well as sterically, naphthylbiphenyls should constitute the major portion. Most of the terphenyl, about 70% average for the two reactions, comes entirely from biphenyl; at least 12% arises by benzyne insertion. Surprisingly, some 6–12% of the

(4) T. Gaeumann and J. M. Rayraux, *Helv. Chim. Acta*, **45**, 1563 (1962), heated biphenyl and biphenyl-d_{10} at 438–472° for 2–200 hr (2 × 10^2–10^4 as long as in our pyrolyses), and found evidence for the reaction C_6H_5-$C_6H_5 \rightleftharpoons 2C_6H_5\cdot$.

terphenyl in the reaction of biphenyl-d_{10} seems to contain one benzene ring derived from biphenyl and two from phthalic anhydride. In the reaction of phthalic anhydride-d_4 with unlabeled biphenyl a small amount of terphenyl, about 3% of the total, contains 6 and 7 deuterium atoms and thus may be formed in the same fashion.

Almost all phenylnaphthalene comes *via* benzyne addition to biphenyl. Naphthylbiphenyl similarly should arise from benzyne and terphenyl. Terphenyl-d_{13} and -d_{14} would be expected to give $C_{22}(H + D)_{16}$ containing 12 deuterium atoms as well as 13 and 14, as a result of intramolecular scrambling in the 1,4 adduct before it loses acetylene; however, as the first column in Table IV shows, there was an appreciable amount of d_{15} and d_{16} species as well. Correspondingly, terphenyl-d_0 with benzyne-d_4 gave not only the expected d_3 and d_4 species, but also an appreciable amount of the d_0 and d_1. In both reactions these species suggest hydrogen transfer from biphenyl to benzyne and formation of phenylbenzyne (Scheme IV), paralleling the formation of thiophyne from thiophene and benzyne.[5]

SCHEME IV

The ratios of addition to insertion products in the reaction of benzyne with biphenyl-d_{10} and benzyne-d_4 with biphenyl in this study were 5.1 and 3.8, respectively.[6] Although benzyne in solution reacts as a dienophile,[7] the ratio of addition to insertion products in the reactions of benzyne from phthalic anhydride with different reagents varies over a wide range.[8] See Table V.

TABLE V

Reagent	Ratio, addition to insertion products
Benzene-d_6	7.0
Naphthalene	3.4
Phenanthrene	2.4
Hexafluorobenzene	0.21
Hexachlorobenzene[a]	
Hexamethylbenzene[a]	
Pyridine	1.9
Thiophene	1.5
Thianaphthene	2.5
Dibenzothiophene	2.0

[a] All addition, no insertion product.

From the table, the factors influencing benzyne addition *vs.* insertion are not clear. We are examining the reactions of phthalic anhydride with additional aromatic and heterocyclic compounds at 700°.

Experimental Section

Reactions were run in a Vycor tube filled with Vycor beads, in an electric furnace maintained at 700 ± 1° under pure dry nitrogen. Phthalic anhydride and biphenyl were separately sublimed from heated bulbs and swept by nitrogen through a Y junction into the heated tube. The vapors were condensed in a bulb at −10°. The condensate was distilled to recover unreacted material and the residue was analyzed.

Analyses were performed with a Consolidated Model 21-103 mass spectrometer with the inlet system at 250°; with a directly coupled gas chromatograph–mass spectrometer combination[9] also employing a 21-103 instrument with an electron multiplier in place of the Faraday-cup detector; and by 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.

The reagents and standards for gas chromatography were purchased from Aldrich Chemicals and used as received. Where purity was critical, the reagent was analyzed and, if necessary, purified by distillation, crystallization, and gas chromatography. Biphenyl-d_{10} was prepared from biphenyl, deuterium oxide, and platinum in a shaking bomb at 185°.[10] Phthalic anhydride-d_4 was prepared by oxidation of naphthalene-d_8 (from naphthalene, deuterium oxide, and platinum at 185°[9]) with calcium permanganate[11] in 45% yield.

Registry No.—Phthalic anhydride, 85-44-9; biphenyl, 92-52-4.

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[5] E. K. Fields and S. Meyerson, "Organosulfur Chemistry," M. J. Jannsen, Ed., Interscience Publishing Co., New York, N. Y., 1967, p 143.

[6] Because of the shorter contact time used to minimize thermal scrambling, some of the products listed in Table I such as anthracene, phenanthrene, and binaphthyl were formed in concentrations too low to list as significant in Table IV. This omission may introduce some error into the addition to insertion ratios; however, they are consistent with the figures in the last table, and demonstrate a marked preference for addition over insertion, except in the reaction with hexafluorobenzene.

[7] G. Wittig, *Angew. Chem.*, **69**, 245 (1957); T. G. Corbett and A. N. Porter, *Aust. J. Chem.*, **18**, 781 (1965); W. L. Dilling, *Tetrahedron Lett.*, 939 (1966).

[8] E. K. Fields and S. Meyerson, unpublished data.

[9] 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).

[10] G. E. Calf and J. L. Garnett, *Aust. J. Chem.*, **21**, 1221 (1968), and references cited therein.

[11] F. Ullmann and B. Uzbacher, *Ber.*, **36**, 1797 (1903).

Thiols and Sulfides from Xanthogenic Acid Ester

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Received March 6, 1969

Previous work on the preparation of thiol from xanthogenic acid ester (I) was carried out with a water-soluble thiol such as thioglycolic acid.[1] Although Maneli[2] obtained the derivatives of thiocarbaminic acid ester and thiol on the reaction of I with amine such as liquid ammonia, monoethanolamine, or pyrolidine, little attention was paid to this reaction as a convenient synthetic method for thiols. Furthermore, any attempt to prepare sulfides through the reaction of alkyl chlorides with thiols or I in the presence of ethylenediamine had not been tried. In this paper, it has been demonstrated that even water-insoluble I decomposes under mild conditions in ethylenediamine to afford thiols in good yield, and that the reaction of I or thiol with alkyl chlorides in ethylenediamine affords sulfides directly.

This procedure, as well as the thiuronium salt method has given good results with a wide variety of halides.

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[1] E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. I, Chemical Publishing Co., Inc., New York, N. Y., 1958, p 31.

[2] E. Maneli, *Chem. Abstr.*, **49**, 186 (1955).