Primary and Secondary Products from Reaction of Benzyne and Benzene at Elevated Temperatures[1]

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Abstract: Pyrolysis of phthalic anhydride in benzene and benzene-d_6 gave a mixture of benzyne-derived C-10 and C-12 hydrocarbons in 40–50% yield based on unrecovered phthalic anhydride. In benzene-d_6, these products consisted of naphthalene-d_4 (80%), biphenyl-d_6 (9%), acenaphthylene-d_4, -d_5, and -d_6 (6%), and acenaphthene-d_6 and -d_7 (5%). In addition, extensive amounts (93% of the total biphenyl) of biphenyl-d_{10} were formed by thermal coupling of benzene-d_6. Biphenylene-d_0 was not detected. Naphthalene is formed by thermal fragmentation of both benzobicyclo[2.2.2]octatriene (1) and benzocyclooctatetraene (2), but acenaphthylene and acenaphthene are formed only by thermal rearrangement of benzocyclooctatetraene. Based on isolated and characterized hydrocarbon products, it is concluded that the major reaction of benzyne with benzene-d_6 is 1,4 addition ($\sim$75%). Intermediate formation of benzocyclooctatetraene-d_6 accounts for approximately 15% of these hydrocarbon products, while the remainder, biphenyl-d_6, is formed via another route. However, there is evidence to suggest that biphenyl-d_6 is not formed by insertion, but it and benzocyclooctatetraene may be derived from a common intermediate.

Recently it was demonstrated that arynes are formed by thermal fragmentation (>500°) of phthalic anhydrides,[2,3,4b] indantrione,[4a] and o-sulfobenzoic anhydride.[4b,5] In the presence of benzene,[2a,4a,5] the benzyne-related products were reported to be mainly biphenyl, naphthalene, and acetylene, along with small amounts of biphenylene[2a,b] and triphenylene.[2a] In the absence of benzene at low pressures, biphenylene[3,4] and triphenylene[4] were reported as major products.

It has been suggested[2,4] that much of the biphenyl arises from an insertion reaction of benzyne with benzene. Naphthalene and acetylene have been presumed[2,4] to be formed by thermal decomposition of benzobicyclo[2.2.2]octatriene (1) (1,4 adduct of benzyne and benzene) and benzocyclooctatetraene (2) (valence-bond tautomer of the 1,2 adduct of benzyne and benzene). The presence of biphenylene and triphenylene have been explained[2,4] by dimerization and trimerization of benzyne, respectively.
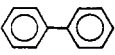
In view of the fact that only trace amounts of biphenyl and benzocyclooctatetraene are formed from the reaction of benzyne (from benzenediazonium-2-carboxylate) with benzene at 45°[6] and that biphenyl is also produced by pyrolysis of benzene alone,[7] a detailed study of the benzyne–benzene reaction at elevated temperatures was undertaken.

Phthalic anhydride (0.1 M) in benzene and benzene-d_6 was pyrolyzed in a fused quartz flow system at 690° (3–5-sec contact time). The products were separated by glpc and identified by infrared, ultraviolet, and mass spectra in addition to retention time. From reactions

in benzene-d_6, the amount of benzyne–benzene-derived biphenyl (d_6) was only 7.4% of the total biphenyl (d_6 and d_{10}) obtained.[8] Thus, most of the biphenyl observed in these reactions is a result of benzene coupling.[7] The isolation of naphthalene-d_4 is consistent with its formation from either 1-d_6 or 2-d_6.

Two other major products, in addition to naphthalene and biphenyl, were observed from reactions conducted in benzene-d_0 (and benzene-d_6). The first was not separable from biphenylene (glpc) and had the same molecular weight (m/e 152) while the second had a molecular weight of 154. These were found to be acenaphthylene and acenaphthene, respectively, on the basis of glpc and infrared, ultraviolet, and mass spectral data. Acenaphthylene was found to be contaminated ($\sim$3.5%) with what could have been biphenylene as determined by ultraviolet spectrometry (absorption at 248 mμ). However, there was no mass spectral evidence for biphenylene-d_0 (by dimerization of benzyne) from reactions carried out in benzene-d_6. The results of these experiments are summarized in Table I. The

Table I. Pyrolysis of Phthalic Anhydride at 690° in Benzene

Solvent	Yield,[a]	Hydrocarbon composition, %			
C_6D_6	48	80	9.1[c]	6.0	5.0
C_6H_6	41[d]	81	9.4[d]	5.2	3.9

[a] Benzyne-derived products, based on unrecovered phthalic anhydride. [b] Benzyne derived. [c] Biphenyl-d_5 -d_6, -d_7, and -d_8 are assumed to be derived from benzyne. [d] Calculated, assuming a naphthalene:biphenyl ratio equal to that in C_6D_6.

extent of deuteration of the acenaphthylene (mainly d_4, d_5, and d_6) and acenaphthene (mainly d_6 and d_7) obtained from the reactions in benzene-d_6 clearly indicated

(1) (a) Taken from the Ph.D. Thesis of D. F. Lindow, Case Institute of Technology, 1968. (b) Support from the Case Research Fund is gratefully acknowledged.

(2) (a) E. K. Fields and S. Meyerson, Chem. Commun., 474 (1965); (b) J. Org. Chem., 31, 3307 (1966); (c) Chem. Commun., 708 (1966).

(3) M. P. Cava, M. J. Mitchell, D. C. DeJongh, and R. Y. Van Fossen, Tetrahedron Letters, 2947 (1966).

(4) (a) R. F. C. Brown and R. K. Solly, Australian J. Chem., 19, 1045 (1966); (b) R. F. C. Brown, D. V. Gardner, J. F. W. McOmie, and R. K. Solly, ibid., 20, 139 (1967).

(5) S. Meyerson and E. K. Fields, Chem. Commun., 275 (1966).

(6) L. Friedman, J. Am. Chem. Soc., 89, 3071 (1967).

(7) G. M. Badger, Progr. Phys. Org. Chem., 3, 1 (1966).

(8) It was assumed that biphenyl-d_5, -d_6, -d_7, and -d_8 (Table II) were derived from benzyne while biphenyl-d_9 and -d_{10} were nonbenzyne products.

Table II. Deuterium Content of Products from Pyrolyses Conducted in Benzene-d_6

Precursor	Products	Deuterium composition, mole %										
		d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}
Phthalic anhydride												
	Naphthalene	0.27	0.22	0.31	1.31	58.73	28.38	8.03	1.48	1.28		
	Biphenyl			0.10	0.06	0.06	0.50	4.46	1.79	0.61	3.93	88.51
	Acenaphthylene				1.4	16.4	41.5	26.2	9.3	5.2		
	Acenaphthene						10.1	39.3	35.6	11.8	2.2	1.0
Phthalic anhydride (protium-contaminated C$_6$D$_6$)												
	Naphthalene	1.0	0.4	0.4	2.7	86.1	8.5	0.6	0.1	0.2		
	Biphenyl					0.3	4.2	3.3	0.2	0.2	5.7	86.2
Benzobicyclo[2.2.2]octatriene												
	Naphthalene	34.84	32.99	18.72	8.12	3.02	1.08	0.53	0.32	0.40		
	Biphenyl	0.09	0.07	0.11	0.09	0.07	0.06	0.16	0.08	0.48	7.24	91.55
Benzocyclooctatetraene												
	Naphthalene	43.04	32.25	15.10	5.67	2.17	0.73	0.43	0.22	0.40		
	Biphenyl	0.34	0.89	0.41	0.16	0.09	0.45	0.32	0.09	0.47	8.16	88.62
	Acenaphthylene	26.71	30.13	22.54	12.29	5.23	2.05	0.76	0.27			
	Acenaphthene	21.52	39.91	24.21	9.79	2.86	1.21	0.49				
Acenaphthene												
	Acenaphthylene	34.53	32.96	19.48	8.56	3.16	0.89	0.42				
	Acenaphthene	59.70	29.74	8.08	1.97	0.38	0.09	0.05				

that these compounds are benzene–benzyne-derived products.

When pyrolyses are conducted in deuterated benzene, protium–deuterium exchange occurs.[9,10] While the amount of exchange occurring with benzene-d_6 at 690° is appreciable, it does not cause much difficulty since most of the material is the parent compound and its analog containing one more deuterium atom. The mass spectral data (corrected for natural isotopic abundance) for all pyrolyses carried out in benzene-d_6 are given in Table II.

In addition to the four benzyne-derived products, it might be expected[7] that the isomeric terphenyls (by coupling of benzene and biphenyl), isomeric phenyl-naphthalenes and fluoranthene (by coupling of benzene with naphthalene) would also be found in these reaction mixtures. Peaks corresponding to each of these compounds and fluorenone[2a] were observed by glpc analysis. Mass spectral data confirmed the assignments of fluorenone, terphenyl, phenylnaphthalene, and fluoranthene. In addition a peak m/e 178 corresponding to anthracene was observed. This left only four extremely minor peaks or shoulders unidentified.

In order to elucidate the mechanism(s) of formation of biphenyl,[11] acenaphthylene, and acenaphthene, benzobicyclo[2.2.2]octatriene[12,13a] was pyrolyzed in a sealed tube and under the conditions of phthalic anhydride pyrolysis. It was anticipated that this 1,4 benzyne-benzene adduct might be the common precursor to naphthalene (via retro Diels–Alder reaction), biphenyl[11] (cleavage of bond a), acenaphthene (cleavage of bond b, followed by ring closure), and acenaphthylene (by de-
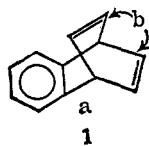
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(9) E. K. Fields and S. Meyerson, *J. Am. Chem. Soc.*, **88**, 21 (1966).
(10) D. F. Lindow and L. Friedman, *ibid.*, **89**, 1271 (1967).
(11) Formed by the reaction of benzyne with benzene.
(12) R. G. Miller and M. Stiles, *ibid.*, **85**, 1798 (1963).
(13) Conveniently prepared by decomposition of benzenediazonium-2-carboxylate in benzene:[6,12] (a) in the absence of silver ion; (b) in the presence of silver ion. See Experimental Section.

hydrogenation of acenaphthene). However, irrespective of the mode of thermal decomposition, the only products were naphthalene and acetylene.

Although benzocyclooctatetraene[12,13b,14] was only formed in trace amounts from the reaction of benzyne with benzene at 45°,[6] its thermal behavior was studied to determine if it is a precursor of the aforementioned hydrocarbons. Pyrolysis of **2** in benzene-d_6 at 690° gave naphthalene, acenaphthylene, acenaphthene, and only biphenyl-d_{10}[14b,c] (Table III).

Table III. Pyrolysis of Benzobicyclo[2.2.2]octatriene and Benzocyclooctatetraene in Benzene-d_6 at 690°

Substrate	Hydrocarbon composition, %			
	⬡⬡	C$_6$H$_5$C$_6$H$_5$	(acenaphthylene)	(acenaphthene)
Benzobicyclo-[2.2.2]octatriene	100	0	0	0
Benzocyclo-octatetraene	41	0	40	19

Acenaphthylene was not converted to acenaphthene under the reaction conditions, but acenaphthene was partially converted (~30%) to acenaphthylene. This means that at least part of the acenaphthylene was formed by pyrolysis of acenaphthene.[15,16] An attractive over-all reaction scheme is outlined in Figure 1.

(14) (a) G. Wittig, H. Eggers, and P. Duffner, *Ann.*, **619**, 10 (1958). (b) Naphthalene and 1-vinylnaphthalene have been reported as major by-products in the formation of benzocyclooctatetraene from pyrolysis of 7-acetoxy-3,4-benzo-1,3,5-cyclooctatriene at 500°.[14a] A minor peak (~2%), which might have been vinylnaphthalene, was observed on glpc analysis of the pyrolysate from benzocyclooctatetraene and benzene-d_6. A minor peak, with the same retention time, however, was obtained from the acenaphthene pyrolysate.
(15) For other examples see: (a) A. Behr and W. A. vanDorp, *Ber.*, **6**, 735 (1873); (b) *Ann.*, **172**, 263 (1874); (c) M. Blumenthal, *Ber.*, **7**, 1092 (1874); (d) K. Dziewonski and G. Rapalski, *ibid.*, **45**, 2491 (1912).
(16) A common intermediate, such as **3** or **4**, may account for both acenaphthene and part of the acenaphthylene.
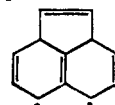
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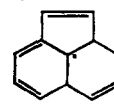
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Thus at elevated temperatures, based on the isolated and characterized hydrocarbon products (48%), the major reaction of benzyne with benzene is 1,4 addition to give **1**.[17] This was determined by comparing the sum of acenaphthene and acenaphthylene formed relative to that of naphthalene (Table III). The ratio of **1** to **2** is calculated to be between 4 and 5 (Figure 1). Biphenyl[11] formation *via* benzyne insertion or an equivalent process is only a minor (9.1%) reaction pathway under these conditions.

The absence of biphenylene (by dimerization of benzyne) is not surprising since other reactions of benzyne are possible.[4] Since triphenylene has been shown to be formed by vapor phase pyrolysis of biphenylene,[10] the formation of triphenylene is not expected in these reactions.

Inasmuch as biphenyl and benzocyclooctatetraene only arise from benzyne and benzene at 45° in the presence of silver ion,[6,12] it is worthwhile to speculate as to their mode of formation at elevated temperatures. It is conceivable that surface catalysis (on fused quartz chips, etc.) or some other mechanism(s) characteristic of pyrolytic reactions occurs. However, it is possible that at high temperatures, where benzyne might be expected to be less selective, these are normal benzyne products.

The simplest explanation is, of course, that benzocyclooctatetraene arises *via* 1,2 cycloaddition of benzyne to benzene followed by valence bond isomerization and biphenyl arises *via* an insertion reaction of benzyne with benzene. It is suggested that the term insertion be used only to described a bimolecular concerted process. Thus, an insertion reaction of benzyne with benzene would require that biphenyl is formed by benzyne coupling to benzene with concerted abstraction of hydrogen (*i.e.*, a four-center reaction). A more liberal definition might also include a stepwise process, but the net effect is still that both the phenyl group and the hydrogen must come from the same benzene molecule. Fortunately, pertinent data (Table II) were obtained by pyrolysis of phthalic anhydride in inadvertently contaminated (with a nonbenzene protium source)[18] benzene-d_6. The naphthalene was mainly d_4 which is consistent with a cycloaddition reaction to benzene-d_6. As expected[19a] the amount of more highly deuterated species was diminished but the relative amount of d_3 species was essentially unchanged.[19b] On the other hand, biphenyl isolated from phthalic anhydride pyrolysis with impure benzene-d_6[18] showed a marked increase in the relative amount of biphenyl-d_5 at the expense of biphenyl-d_6 and -d_7 species. Thus, there is no doubt that most, if not all, of the biphenyl[11] is formed by some process other than insertion as defined above.
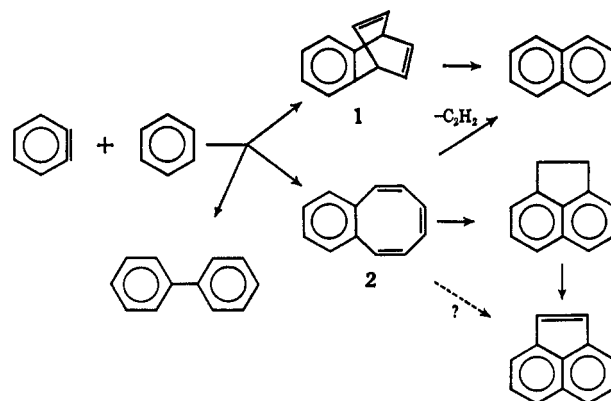

Figure 1.

A reasonable alternative to insertion is that the bonds to the phenyl group and the hydrogen are formed at different times; this allows them to come from either the same benzene molecule or different benzene molecules. It is interesting to note that a catalytic benzyne mechanism similar to that proposed to account for benzocyclooctatetraene and biphenyl in the presence of silver ion[6] provides for initial formation of a carbon–carbon bond. Any positive site, such as might be found on quartz, could serve as the catalyst. Since there are other conceivable ways (both benzyne and nonbenzyne) which are consistent with the data and allow nonconcerted formation of the carbon–carbon and carbon–hydrogen bonds, further speculation along these lines is unwarranted.

On the other hand there are two conceivable routes to biphenyl which can be eliminated. The first possibility is that benzyne is reduced to benzene.[20,21] If aryne reduction (or the equivalent process) followed by coupling were a major pathway to biphenyl[11] in pyrolysis of phthalic anhydride in benzene-d_6, the biphenyl[11] would contain appreciably more d_7 than d_6. Since the amount of biphenyl-d_7 (Table II) is best explained by protium–deuterium exchange, reduction is not a major process in the phthalic anhydride–benzene system.

While **5** is almost certainly an intermediate in the formation of benzocyclooctatetraene, it is also a possible intermediate in the formation biphenyl[11] as outlined in Figure 2. Reaction of benzyne with benzene-d_6 at 45° gives only undeuterated biphenylene.[6] At elevated temperatures, although biphenylene may have been detected by ultraviolet spectrometry, no evidence for undeuterated biphenylene was detected by mass spectrometry. However, biphenylene-d_4 is indistinguishable from acenaphthylene-d_4 by both glpc and mass spectrometry. The major product from pyrolysis of

(17) 1,4 Addition was postulated as the predominant reaction of benzyne (from the pyrolysis of phthalic anhydride) with the isomeric dichlorobenzenes: S. Meyerson and E. K. Fields, *Chem. Ind.* (London), 1230 (1966).

(18) Contaminated with tetrahydrofuran and/or its pyrolysis products.

(19) (a) There is no question that the H–D exchange is primarily intermolecular since biphenylene and its pyrolysis products show the same level of exchange and the use of a nonbenzene protium source as a contaminant lowers the level of exchange.[22] Pyrolysis of naphthalene (0.015 M) in contaminated benzene-d_6 gave 86.4% d_0, 11.5% d_1, 1.1% d_2, and 0.9% d_3 which is about the same level of exchange observed when naphthalene is a product (Table II). (b) This effect was also observed in triphenylene, isolated from the pyrolysis of biphenylene with contaminated benzene-d_6.[18]

(20) Decomposition of phthalic anhydride in pyridine[2b] and thiophene[2c] is reported to give large amounts of unsymmetrical biaryls. In the pyrolysis of pyromellitic anhydride and mellophanic anhydride in pyridine,[2b] much of the product composition (~50%) is reported to be phenylpyridine, naphthalene, and quinoline. These products can only be explained by reduction of arynes (hydrogenation) or a nonaryne process involving sequential loss of CO_2 and CO as well as abstraction of hydrogen by the intermediates. In the pyrolysis of phthalic anhydride in thiophene,[2c] benzene was reported as one of the products.

(21) The formation of naphthalene from pyrolysis of benzyne precursors in the absence of benzene[4] is best explained by reduction of benzyne to benzene which subsequently reacts with benzyne to give **1** and **2**. We have observed the products of reduction of arynes in vapor phase pyrolysis of triptycenes (unpublished work).
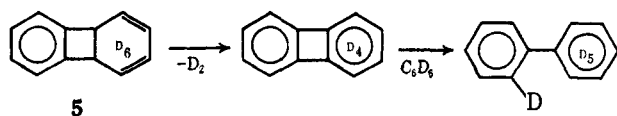
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Figure 2.

biphenylene-d_4 would be expected to be biphenyl-d_6.[10,22] If the amount of biphenyl-d_4 (relative to d_5 and d_6) from pyrolysis of phthalic anhydride and contaminated benzene-d_6 (Table II) is compared to the amount of biphenyl-d_0 (relative to d_1 and d_2) from pyrolysis of biphenylene in the same benzene-d_6,[22] it appears unlikely that the mechanism outlined in Figure 2 is important. However, there is no reason why minute quantities of biphenylene-d_4 could not be produced from **5** since biphenylene would have some stability at 690°.[10,22,23]

Thus, it is apparent that benzocyclooctatetraene is formed via either concerted 1,2 cycloaddition of benzyne to benzene or a stepwise process resulting in the same intermediate, **5**. There are also apparently two possible routes to biphenyl,[11] initial formation of either a carbon–carbon bond or a carbon–hydrogen bond. It is clear, however, that insertion, as defined, is not a major path to biphenyl,[11] formation. At 45°, at the expense of the normal benzyne–benzene products, the amount of both benzocyclooctatetraene and biphenyl increases with increasing silver ion concentration;[6] therefore, it may be argued that a common intermediate is involved. By analogy, the possibility of a common intermediate, similar to that proposed for silver catalysis,[6] is also attractive at elevated temperatures. In addition, even at 45° in the absence of silver ion, catalysis by glass could account for the trace amounts of benzocyclooctatetraene and biphenyl.[6] Although these arguments provide a case in favor of the catalytic mechanism, it is certainly not strong enough to rule out the possibility of separate mechanisms for the formation of benzocyclooctatetraene and biphenyl.[11]

Experimental Section

General. The purity of the solvents was the same as in the previous paper.[22] Pyrolysis and analysis techniques were identical with those previously described[22] except that the pyrolysis temperature was 690°. Isothermal glpc (135°) was conducted on a 10-ft, SE 30 silicone rubber on Chromosorb W column with a Matronic 500 gas chromatograph.

Benzocyclooctatetraene. Isoamyl nitrite (125 ml) was added to a magnetically stirred solution of anthranilic acid (68.5 g, 0.5 mol) and trifluoroacetic acid[24] (0.75 g) in tetrahydrofuran (750 ml) contained in a 2-l. beaker cooled in a dish containing about 150 g of crushed ice. The resultant mixture was stirred and allowed to warm to room temperature over a period of 1.3 hr. The off-white benzenediazonium-2-carboxylate[25] was collected [Caution][26] on a polyethylene Büchner funnel, washed with cold tetrahydrofuran

until the washings were colorless, and washed four times with cold benzene. The still-moist benzenediazonium-2-carboxylate was slurried with benzene [Caution][27] and added to a 12-l. flask containing 9.75 l. of benzene and 1.04 g (5 mmol) of silver perchlorate[6] agitated by mechanical stirring. The temperature was maintained at 45° for 24 hr by means of a heating mantle and a thermocap relay (Niagara Electron Laboratories). The reaction mixture was concentrated to 800 ml by distillation through a short Vigreux volume and filtered to remove 10.5 g of insoluble material. The filtrate was concentrated with a rotary vacuum evaporator and the residue was steam distilled[28] to obtain a light yellow oil. The steam distillate was extracted with petroleum ether, and the extract was concentrated to 100 ml and dried over anhydrous potassium carbonate. In addition to biphenyl, the solution contained benzocyclooctatetraene and benzobicyclo[2.2.2]octatriene in a ratio of 12.5:1 (glpc).[6] Finely powdered (mortar and pestle) silver nitrate (15 g) and distilled water (0.3 ml)[29] were added to the petroleum ether solution, and the mixture was magnetically stirred[30] for 1 hr. Glpc showed that benzocyclooctatetraene and benzobicyclo[2.2.2]octatriene were almost entirely removed from the solution. The solid mixture (19.48 g) of silver nitrate and hydrocarbon complex was collected on a Büchner funnel and washed with petroleum ether. The complex was decomposed by adding it to concentrated aqueous ammonia (30 ml). Distilled water (30 ml) was added to the mixture, and the product was extracted with petroleum ether. The extract was dried over anhydrous potassium carbonate. Removal of the solvent with a rotary vacuum evaporator afforded 4.16 g (5.4% based on anthranilic acid) of crude benzocyclooctatetraene (mp 44–47.5°). Glpc showed that this crude product contained 6.1% benzobicyclo[2.2.2]octatriene. One recrystallization from a methanol (60 ml)–water (8 ml) mixture gave 2.31 g of 99.5% pure (glpc) benzocyclooctatetraene (light yellowish white plates, mp 49–50°). Evaporation of some of the mother liquor and recrystallization afforded another 1.19 g of product (mp 49–50°, 99.7% pure). Ultraviolet[12] and infrared[14a] spectra agreed with those reported previously.

Benzobicyclo[2.2.2]octatriene. Anthranilic acid (68.5 g, 0.50 mol) was diazotized as above and decomposed in 10.25 l. of silver-free benzene in a 12-l. flask fitted with a mechanical stirrer and a thermocap relay so that the temperature was maintained at 45° for 24 hr. The reaction mixture was concentrated to 800 ml by distillation and filtered to remove 1 g of insoluble material. The filtrate was concentrated on a rotary vacuum evaporator and the residue was steam distilled[28] to obtain a light yellow oil which solidified upon cooling. The steam distillate was extracted with petroleum ether and the extract was concentrated to 100 ml and dried over anhydrous potassium carbonate. The solution contained mainly benzobicyclo[2.2.2]octatriene with a small amount of biphenylene and traces of biphenyl and benzocyclooctatetraene (glpc). Finely powdered (mortar and pestle) silver nitrate (25 g) and distilled water (0.5 ml)[29,31] were added to the petroleum ether solution, and the mixture was magnetically stirred[29] for 1 hr. An additional 10 g of powdered silver nitrate and 0.2 ml of distilled water[31] were added and stirred for 1 hr after the first batch had been collected on a Büchner funnel. Glpc showed that about 99% of the benzobicyclo[2.2.2]octatriene was removed. The solid was collected on a Büchner funnel and the combined solids (41.81 g) were added to concentrated aqueous ammonia (50 ml). An equal volume of distilled water was added to the mixture, and the product was extracted with petroleum ether. The extract was dried over anhydrous potassium carbonate. Removal of the solvent with a rotary vacuum evaporator afforded 6.69 g (8.7% based on anthranilic acid) of crude benzobicyclo[2.2.2]octatriene (white needles, mp 64.5–66.5°). Glpc showed that this crude product contained

(22) L. Friedman and D. F. Lindow, *J. Am. Chem. Soc.*, **90**, 2324 (1968).

(23) An extremely small peak corresponding to triphenylene was observed (glpc), and a peak corresponding to o-terphenyl was larger than would be expected. In the absence of further proof of structure, this identification is tenuous.

(24) Trifluoroacetic acid may be conveniently handled as a solution in tetrahydrofuran.

(25) Procedure developed by F. M. Logullo, Ph.D. Thesis, Case Institute of Technology, 1965.

(26) Benzenediazonium-2-carboxylate is extremely sensitive to shock, heat, and friction. It is especially explosive when very dry. The danger of explosion is greatly lessened by keeping the solid moist with solvent. Polyethylene spatulas and Bücher funnels should be used to decrease the possibility of friction-initiated detonation. Benzenediazonium-2-carboxylate can be conveniently discarded by dissolving in water.

(27) In order to minimize danger during transfer of large amounts of benzenediazonium-2-carboxylate the moist solid is washed from the Büchner funnel by using a wash bottle of benzene. Approximately 500 ml of benzene is needed to make a safe transfer on this scale.

(28) Sodium hydroxide (20 g) should be added to the distilling flask to increase the efficiency of the steam distillation by dissolving the tars.

(29) A 50% aqueous solution of silver nitrate was not as effective because a distribution equilibrium was established. Anhydrous silver nitrate was completely ineffective.

(30) A florence or round-bottomed flask should be used so that the magnetic stirbar makes good contact with the solid. If efficient stirring is not maintained lumps are formed which decrease the effective surface of the silver nitrate.

(31) Two 10-g portions of silver nitrate (each with 0.2 ml of distilled water) are sufficient if the flask is shaped so that the magnetic stirbar makes contact with the solid.

0.4% benzocyclooctatetraene. One recrystallization of 96.3% pure benzobicyclo[2.2.2]octatriene[32] (0.85 g) from a methanol (30 ml)–water (10 ml) mixture gave 0.53 g of pure (glpc) benzobicyclo-[2.2.2]octatriene (white needles, mp 65.6–66.5°). The ultraviolet and infrared spectra agreed with those reported previously.[12]

Pyrolysis of Phthalic Anhydride. Reagent grade phthalic anhydride (0.08 to 0.09 M in benzene or benzene-d_6) was pyrolyzed at 690° (3–5-sec contact time) to give 35–45% recovered phthalic anhydride. Phthalic anhydride was removed from the pyrolysate by washing with 10% aqueous sodium hydroxide. The following results were obtained for a typical run in benzene. In order of retention time, naphthalene (100),[33] biphenyl (358), acenaphthylene (6.3), and acenaphthene (4.7) were identified by infrared, ultraviolet, and mass spectra. In addition, the following products were tentatively identified by retention time: fluorenone (0.9),[34] o-terphenyl (1.5), 1-phenylnaphthalene (2.8), 2-phenylnaphthalene (1.4), and a poorly resolved peak containing fluoranthrene, m-terphenyl, and p-terphenyl (total, 3.9). Of the five other extremely small peaks and shoulders, four were unidentified and the fifth may have been triphenylene. Mass spectral data confirmed the assignments of fluorenone, terphenyl, phenylnaphthalene, and fluoranthene. In addition a peak, m/e 178, corresponding to anthracene was observed.

Pyrolysis of Benzocyclooctatetraene. A 0.098 M solution of benzocyclooctatetraene in benzene-d_6 was passed through the flow system under the usual pyrolysis conditions. In order of retention time the products were naphthalene (40),[33] biphenyl-d_{10}, an unknown (2), acenaphthylene (39), and acenaphthene (19). Benzo-

cyclooctatetraene was not recovered. Ultraviolet spectra and low-voltage mass spectrometry confirmed the identity of the products. The biphenyl was contaminated with only trace amounts of d_5–d_7 species. Pyrolysis of benzocyclooctatetraene (4 mg) in an evacuated sealed tube for 2 hr at 352–370° produced a complex mixture which was not investigated further.

Pyrolysis of Benzobicyclo[2.2.2]octatriene. A 0.091 M solution of benzobicyclo[2.2.2]octatriene in benzene-d_6 was passed through the flow system under the usual pyrolytic conditions. The products were only naphthalene and biphenyl (containing only trace amounts of d_5–d_7 species) as analyzed by glpc and low-voltage mass spectrometry. Benzobicyclo[2.2.2]octatriene was not recovered. Pyrolysis of benzobicyclo[2.2.2]octatriene (7 mg) in an evacuated sealed tube[12] at 352–370° for 2 hr afforded essentially pure naphthalene.

Pyrolysis of Acenaphthylene. A 0.097 M solution of commercial acenaphthylene (14.5% acenaphthene, 85.5% acenaphthylene) in benzene-d_6 was passed through the flow system under the usual pyrolysis conditions. In addition to biphenyl-d_{10}, the pyrolysate contained a mixture of 10.5% acenaphthene and 89.8% acenaphthylene.

Pyrolysis of Acenaphthene. A 0.100 M solution of pure acenaphthene in benzene-d_6 was passed through the flow system under the usual pyrolytic conditions. In addition to biphenyl-d_{10}, the pyrolysate contained a mixture of 69% recovered acenaphthene and 29% acenaphthylene confirmed by ultraviolet spectra and low-voltage mass spectrometry. Two minor peaks were also observed. These products had retention times corresponding to naphthalene (0.6%) and the unknown (1.4%) from the pyrolysis of benzocyclooctatetraene.

(32) A sample from another run which was contaminated with 3.7% benzocyclooctatetraene.
(33) Glpc, relative number of moles.
(34) Peak area relative to naphthalene (100).

Photoisomerization of Substituted Acrylic[1] Acids and Acrylamides to β-Lactones and β-Lactams

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Abstract: Irradiation of cis-α-phenylcinnamic acid in the presence of tetramethylethylene in degassed ether gives trans-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane. The mechanistic path of the reaction is shown to involve initial isomerization of cis-α-phenylcinnamic acid to the trans- and cis-β-lactones. The cis-β-lactone is isolated in 79% yield. Irradiation of the cis-β-lactone in the presence of tetramethylethylene gives trans-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (85%). Irradiation of either trans- or cis-stilbene in tetramethylethylene gives trans-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (95 and 93%, respectively). The photoisomerization of α,β-disubstituted acrylic acids to β-lactones is shown to be quite general when one substituent is phenyl. A qualitative study of the effect of para substituents in the α- and β-phenyl rings of cis-α-phenylcinnamic acid has revealed a striking dependence on the nature of the substituent. In the α-phenyl group electron-donating substituents facilitate reaction and electron-withdrawing substituents retard reaction. In the β-phenyl ring the substituent effect is reversed. Irradiation of cis-α-phenylcinnamamide and cis-α-phenylcinnamanilide in degassed benzene gives in each case the cis- and trans-β-lactams.

As one aspect of our study of the photocycloaddition reactions of compounds of the type $C_6H_5CH=CXY$,[2] we attempted to add tetramethylethylene to cis-α-phenylcinnamic acid. In this case, the reaction

took a different course and led to a general investigation of the photochemistry of substituted acrylic acids and amides.

Irradiation of cis-α-phenylcinnamic acid (1) in the presence of tetramethylethylene in degassed solution[3]

(1) Photochemical Transformations. XXII. A preliminary account of this work has been published: O. L. Chapman and W. R. Adams, *J. Am. Chem. Soc.*, **89**, 4243 (1967).
(2) O. L. Chapman, A. A. Griswold, E. Hoganson, G. Lenz, and J. Reasoner, *J. Pure Appl. Chem.*, **9**, 585 (1964); O. L. Chapman, Abstracts, 20th National Organic Chemistry Symposium of the American Chemical Society, Burlington, Vt., June 18–22, 1967, p 111.

(3) Irradiations of cis-α-phenylcinnamic acid in the presence of iodine[4a] and cis-α-phenylcinnamamide in the presence of oxygen[4b] give the corresponding phenanthrene derivatives in good yield. Oxidative cyclization of 3,4-dihydroxycinnamic acid to 6,7-dihydroxycoumarin has also been observed.[4c] These oxidative cyclizations have been