The Reactivity of Benzyne toward Anthracene Systems

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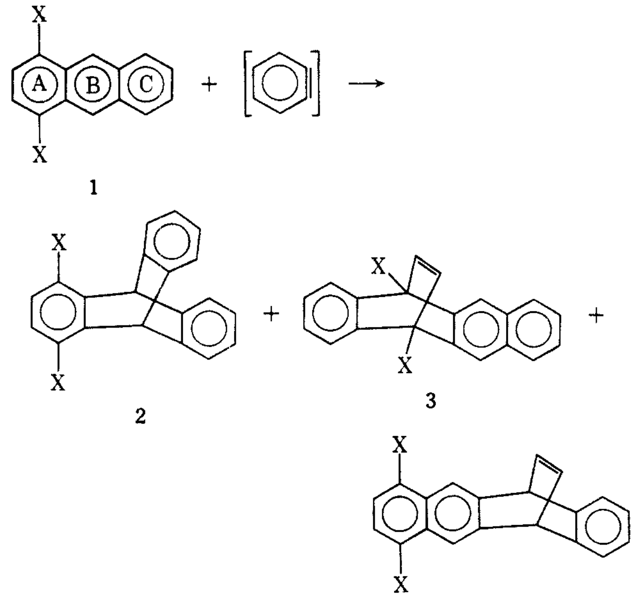
Benzyne reacts with anthracenes to form Diels–Alder adducts with both the center and end rings of anthracene systems. The nature and position of the substituents markedly influence the relative amounts of center- and end-ring adducts formed; the electrophilic nature of benzyne and its steric requirements have been elucidated. The relative reactivities of a number of substituted anthracenes toward benzyne have been measured by a series of competition experiments. These relative reactivities generally parallel those of anthracenes toward maleic anhydride; however, some significant exceptions have been noted. Calculations of the partial relative rate factors for benzyne addition to the center and end rings of substituted anthracenes can be made from the relative reactivity and center- to end-ring adduct ratio data. In general, substituents in one ring do not affect the reactivity of the other ring toward benzyne, but 9,10-diphenylanthracene represents a noteworthy exception.

The reaction of benzyne with anthracene systems is of interest because of the types and relative amounts of the various products formed. In addition, information can be gained about the relative reactivities of substituted anthracenes toward benzyne, and knowledge can be obtained about the reactivity and nature of benzyne itself. This paper will deal with these subjects.

In a preliminary report,[1] we have shown that not only does benzyne react in a Diels–Alder fashion with the B ring (center ring) of anthracenes (**1**) to produce triptycenes (**2**), but that A-ring (end-ring) adducts, 5,12-dihydro-5,12-ethenonaphthacenes (**3**), can also be characterized. We have now shown that, for an anthracene with end-ring substituents, the C-ring adduct (**4**) can be detected as well as the A-ring and B-ring adducts. The relative amounts of the various types of products formed depend upon the substituents in the anthracene system. Table I shows the anthracenes studied in this work and the center- to end-ring adduct ratios which were observed, and Table II gives the physical data for the adducts. In these studies, benzyne was generated from anthranilic acid diazotized *in situ* by the procedure of Friedman and Logullo[2] or by their propylene oxide modification.[3]



The anthracene–benzyne adducts were best characterized by nmr and/or mass spectral molecular weights and cracking patterns. All but one of the B-ring adducts and five representative A-ring adducts (**3g**, **3h**, **3j**, **3l**, and **3m**) were isolated in sufficient quantities to allow the usual complete characterization. Furthermore, the unambiguous assignment of the 4 + 2, rather than 2 + 2, cycloadduct structure to the A-ring adducts was made by a combination of uv and nmr comparisons of the adduct and its dihydrogenated product, as described previously[1] for anthracenes **1h** and **1j**. For 1,4-dimethylanthracene, **1e**, assignments of the A-ring and C-ring adducts were made from a combination of vpc, nmr, and mass spectral data. The C-ring adduct of 1,4-dimethoxyanthracene, **1g**, could not be detected and probably underwent further reaction with benzyne.[4]

A detailed consideration of the B/A ring (center- to end-ring) adduct ratios observed for the anthracenes studied reveals interesting trends. In general, electron-donating substituents on a ring increase the relative proportion of adduct formation from that ring, and similarly, electron-withdrawing substituents decrease the relative reactivity of the substituted rings. Thus,

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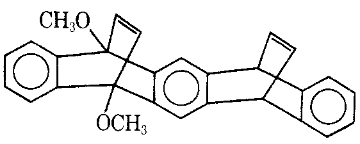
[1] B. H. Klanderman, *J. Amer. Chem. Soc.*, **87**, 4649 (1965).

[2] L. Friedman and F. M. Logullo, *ibid.*, **85**, 1549 (1963).

[3] F. M. Logullo, Ph.D. Dissertation, Case Institute of Technology, 1965.

[4] A study of the products formed in the reaction of 1,4-dimethoxyanthracene, **1g**, with benzyne revealed two high retention-time zones in the vpc data. These minor-component (less than 1%) zones were trapped and had mass spectral *m/e* parent molecular ion peaks at 390 (adduct plus benzyne) and fragmentation patterns which were very similar to each other and to that of **3g** for the methyl group–oxygen cleavages. Therefore, these adducts most likely are the isomeric adducts **5** and **6**, which would result from the reaction of benzyne with the A-ring adduct, **3g**, rather than with the B-ring adduct, **2g**. Adducts **5** and **6** could also arise from the reaction of benzyne with the C-ring adduct, **4g**. Indeed, the methoxy-substituted ring of the C-ring adduct would probably be more reactive than the C ring of 1,4-dimethoxyanthracene toward benzyne, and consequently the fact that no C-ring adduct could be detected for **1g** seems reasonable.



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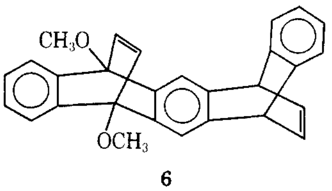

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TABLE I

REACTIVITY DATA FOR THE REACTION OF BENZYNE WITH ANTHRACENE SYSTEMS

	Anthracene substrate	B ring/A ring[a,b]	Rel reactivity[c] with benzyne	Rel reactivity[d] with maleic anhydride	$K_{9,10}$[e]	$K_{1,4}$[b,e]
1a	9,10-Dimethylanthracene	~200	19.2	220	19.2	0.05
1b	9-Methylanthracene	~70	4.0	17.0	4.0	0.03
1c	9,10-Dimethoxyanthracene	28	2.7	0.30	2.7	0.05
1d	9,10-Bis(acetoxymethyl)anthracene		2.7			
1e	1,4-Dimethylanthracene	13.0	1.4		1.3	0.10
1f	2,6-Dimethylanthracene	14.0	1.4		1.4	0.05
1g	1,4-Dimethoxyanthracene	2.5	1.2		0.86	0.34
1h	Anthracene	30	1.0	1.0	1.0	0.02
1i	9-Phenylanthracene	35	1.0	0.076	1.0	0.01
1j	9-Cyanoanthracene	3.7	0.44	0.007	0.39	0.05
1k	9-Nitroanthracene	4.3	0.29	0.009	0.26	0.03
1l	9,10-Diphenylanthracene	0.08	0.20		0.03	0.17
1m	9,10-Dicyanoanthracene	1.0	0.15		0.10	0.05

[a] The *observed* B/A ratios are recorded. Except for **1e** and **1g**, the actual B/A reactivity ratio is twice the observed ratio. [b] The B/C reactivity ratio for **1e** is ~70 and $K_{5,8}$ is 0.02. [c] The relative reactivities are related to anthracene, and all substituted anthracenes were compared directly with anthracene except for **1k**, which was compared experimentally with **1e**. [d] The relative reactivities for maleic anhydride, corrected for comparison with anthracene as unity, are recorded in ref 8. [e] The partial rate factors were calculated from the B/A ratio and relative reactivity with benzyne data, and correction for the number of A rings was made where necessary.

methyl groups favor adduct formation with rings so substituted and cyano and nitro groups have the reverse effect. Compare **1h** as a reference with **1a**, **1b**, **1e**, **1f**, **1j**, **1k**, and **1m**. Note that the two methyl groups on the same ring in **1e** have about the same effect as the additive effect of the two methyl groups of **1f**. (The B/A ratios in the table represent observed ratios, and there are two A rings for **1f**.)

The effects of the methoxy and phenyl groups are not as straightforward. Substitution of two methoxy groups on the center ring, as in **1c**, gives no significant change in the B/A ratio (compared with anthracene); however, substitution of two methoxy groups on an end ring, as in **1g**, leads to a very pronounced effect. These results can be explained by the fact that the *peri* hydrogens in **1c** inhibit coplanarity of the methoxy groups with the anthracene ring system, so that the inductive electron-withdrawing effect counterbalances the reduced resonance (conjugative) electron-releasing effect of the methoxy groups. In **1g**, the methoxy group can be coplanar with the aromatic ring, and electron-donating effects predominate. The one phenyl group of **1i** shows the same behavior as the two methoxy groups of **1c** as far as the B/A ratio is concerned. With two phenyl groups on the center ring, as in **1l**, a very pronounced steric effect produces an unusually low B/A ratio. Similarly, maleic anhydride and dimethyl acetylenedicarboxylate, both less reactive than benzyne, have been reported to react only with the end rings of **1l**.[5-7]

The B/A ratio data therefore support the electrophilic nature of benzyne and agree with the relative yield data for the reaction of benzyne with substituted tetraphenylcyclopentadienones.[8] Further quantitative data concerning this matter and further clarification of the effects of substituents on each ring can be gained from a consideration of the relative reactivities of anthracene systems toward benzyne.

The relative reactivities of a number of substituted anthracenes were determined by a series of competition experiments in which equivalent amounts of anthracene and a substituted anthracene were allowed to compete simultaneously for benzyne generated from a limited quantity of 2-carboxybenzenediazonium chloride and propylene oxide.[3] The quantities of anthracene and substituted anthracene were determined by vapor-phase chromatographic techniques before and after reaction with benzyne, and relative reactivities were calculated in the standard manner. Table I shows the results.

The electrophilic nature of benzyne is again confirmed by the general trend of the results, which show that electron-donating substituents enhance and electron-withdrawing substituents lower the reactivity of anthracenes toward benzyne. A comparison with the order of reactivity of anthracenes toward maleic anhydride[9] shows that the general trend is similar but that benzyne is much less selective, and that there are some discrepancies in the exact order of reactivity (Table I). The most significant discrepancies are anthracenes **1c** and **1i**, both of which have substituents, methoxy and phenyl, which are inductively electron withdrawing and conjugatively electron donating, and which cannot be coplanar with the ring system. In the case of benzyne, the electron-withdrawing effects may be less significant than for maleic anhydride, but a smaller sensitivity of benzyne to steric effects could account for the observed order of reactivity. The relatively high reactivity of anthracene **1d** with benzyne further shows a small sensitivity to steric effects, and thus the bifunctional triptycene **2d** can readily be prepared in good yield for use in polymer studies.[10]

A similar mechanism has been assumed for the Diels–Alder reactions of benzyne and maleic anhydride with all of the anthracenes studied, but the geometry of approach may differ. Thus, benzyne should approach

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(5) I. Gillet, *Bull. Soc. Chim. Fr.*, **17**, 1141 (1950).

(6) J. W. Cook and L. Hunter, *J. Chem. Soc.*, 4109 (1953).

(7) J. Rigaudy and N. K. Cuong, *Compt. Rend.*, **253**, 1705 (1961).

(8) F. M. Beringer and S. J. Huang, *J. Org. Chem.*, **29**, 445 (1964).

(9) J. Sauer, D. Lang, and A. Mielert, *Angew. Chem. Intern. Ed. Engl.*, **1**, 268 (1962).

(10) B. H. Klanderman and J. W. H. Faber, *J. Polymer Sci.*, *A-1*, **6**, 2955 (1968).

the anthracene system perpendicularly to the plane of the anthracene ring system because the reacting orbitals of benzyne are in the plane of the benzyne ring. However, maleic anhydride would approach with its ring parallel to the anthracene ring system because the reacting orbitals of maleic anhydride are perpendicular to the plane of the maleic anhydride ring. The different steric requirements for the approach of benzyne and maleic anhydride would then be detected for their reactions with anthracenes **1c** and **1i**, which contain methoxy and phenyl groups at the 9 and/or 10 positions. The steric requirements of these groups, which cannot readily be coplanar with the anthracene ring system (at the 9 and 10 positions), would tend to inhibit the approach of benzyne less than that of maleic anhydride.

A more detailed analysis of relative reactivities of anthracenes toward benzyne can be made by a calculation of the partial relative rate factors for the center and end rings of the various anthracene systems. These values, tabulated in Table I, are readily obtained from the B/A ratios and relative reactivity data for the anthracene systems as a whole.

Considering first the relative reactivities of unsubstituted end rings (all compounds except **1e**–**1g**), we see that with one exception, **1l**, the relative reactivity of the end ring (A ring or C ring) is reasonably constant (within the range of experimental error) regardless of the substituents on the center ring. Thus, the primary effect of a substituent is to activate or deactivate the ring containing the substituent, as can be seen for the A rings of **1e**–**1g**. Note that the effect of the two methyl groups in **1e** is double that for one methyl group in each end ring of **1f**.

The unusually large relative rate factor for the end rings of **1l** is most interesting, especially in comparison with the value for **1i**. A possible explanation of this anomaly may be that the phenyl groups of **1l** complex sufficiently with the benzyne to allow more reaction to occur with the end rings, while at the same time benzyne is sterically prevented from attacking the center ring to a large extent. The extreme steric difference between **1i** and **1l** has already been pointed out.

The relative reactivities of the center rings parallel those of the anthracene systems as a whole, except for the cases where high A-ring reactivity has been noted (**1g** and **1l**). The relative effects of the methyl and methoxy groups have already been discussed for the system as a whole and for the rings on which they are substituted. There may be a small activating effect for methyl groups on adjacent rings (**1e** and **1f** *vs.* **1h**) and an opposite effect for methoxy groups (**1g** *vs.* **1h**).

An examination of the anthracenes studied shows that 1,4-dimethoxyanthracene (**1g**) has a high relative reactivity with benzyne and also gives a relatively high percentage of A-ring adduct. The methoxy groups are relatively inert; and, therefore, **1g** serves as a good diagnostic tool in testing for the equivalency of benzyne generated under various conditions.[11]

In conclusion, the reactivity studies of benzyne toward anthracenes give a quantitative measure of the highly reactive, relatively unselective electrophilic nature of benzyne, and the small steric requirements of benzyne have been elucidated. The fact that diphenylanthracene (**1l**) forms any B-ring adduct at all supports these conclusions.

Nmr Results.—The rigid adducts formed in these studies represent systems in which interesting chemical shifts for the bridgehead protons and methyl groups are observed in the nmr spectra. Considering first A-ring adducts **3h**, **3j**, **3m**, and **3l**, the bridgehead proton peaks are shifted downfield by the *peri* cyano groups from τ 4.82 to 4.26 but upfield by the *peri* phenyl groups to τ 5.00. For B-ring adducts **2h**, **2b**, **2i**, **2j**, and **2k**, no significant effect is transmitted between bridgehead positions; however, both *peri* methyl and methoxy groups shift the bridgehead proton absorptions downfield, *e.g.*, from τ 4.57 for **2h** to τ 4.38 for **2e** and τ 4.10 for **2g**.

The bridgehead methyl proton absorptions for **2a**, **2b**, and **3e** are shifted downfield to τ 7.60, 7.61, and 7.82, respectively, compared with the methyl proton absorption at τ 8.75 for ethylbenzene. Similarly, the bridgehead methoxy proton absorptions for **2c** and **3g** are shifted downfield to τ 5.72 and 5.98, respectively, compared with the methoxy proton absorption at τ 6.21, 6.06, and 6.22 for **2g**, **1g**, and anisole, respectively.

All these shifts can be explained by aromatic ring-current effects or proximities induced by the rigid systems.

Experimental Section

Nmr spectra were determined with a Varian A-60 spectrophotometer using tetramethylsilane as an internal reference; mass spectra were obtained by using a Consolidated Electrodynamics Model 21-110B mass spectrometer; and vpc analyses were obtained with a F & M (Hewlett-Packard) Model 720 dual-column, programmed-temperature gas chromatograph equipped with 2-, 4-, and 6-ft silicon rubber and Apiezon columns.

2-Carboxybenzenediazonium Chloride.[3]—Isopentyl nitrite (20 ml) was added to a magnetically stirred solution of anthranilic acid (10.95 g, 80 mmol) and concentrated hydrochloric acid (8 ml) in absolute ethanol (120 ml) contained in a 400-ml beaker in an ice bath. The mixture was stirred for 10 min, ether (120 ml) was added, and stirring was continued for 5 min. The crystals were suction-filtered (polyethylene funnel) and washed on the filter with ether to give 11.9–13.4 g (80–90%) of air-dried salt.

Hazard Note.—Quantitative shock-sensitivity tests show that 2-carboxybenzenediazonium chloride is more sensitive to shock than was originally observed.[3] *Caution should be exercised in the handling of this compound.*

Characterization of Products.—The center- and end-ring anthracene–benzyne adducts (**2** and **3**) were isolated from the reactions of anthracenes **1g**, **1h**, **1j**, **1l**, and **1m** (5–50 g) with benzyne generated from anthranilic acid diazotized *in situ*[2] or from 2-carboxybenzenediazonium chloride and propylene oxide.[3] In some cases, unreacted anthracenes were removed by the reaction with maleic anhydride in refluxing xylene followed by aqueous alkaline extractions. Often, the major adduct precipitated during concentration of the reaction mixture. The isolation of minor components was effected by column chromatographic techniques utilizing Florisil, acid-washed alumina, and/or neutralized alumina packed in petroleum ether (bp 35–60°) and eluted with petroleum ether and/or mixtures of petroleum ether and benzene or methylene chloride. As many as four chromatographic separations of long duration were needed to isolate some of the components. Final recrystallizations were usually accomplished by the use of benzene, cyclohexane, heptane, or benzene–heptane mixtures. The physical data for the isolated adducts are tabulated in Table II.

For the other anthracenes studied, the major (center-ring) adducts (**2**) were fully characterized except for **2f**, which was readily characterized by the use of the nmr data obtained on the reaction mixture in which the starting anthracene was essentially

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[11] B. H. Klanderman and T. R. Criswell, *J. Amer. Chem. Soc.*, **91**, 510 (1969).

TABLE II

PHYSICAL DATA FOR BENZYNE–ANTHRACENE ADDUCTS

Product[a]	Mp, °C[b]	Nmr max, τ (multiplicity, no. of protons)[c]	Rel vpc t_R[d] Substrate	Rel vpc t_R[d] Adduct
2a	330–332[e]	2.53–3.09 (m, 12), 7.60 (s, 6)	2.7	5.7
3a				7.2
2b	255–257[f]	2.52–3.17 (m, 12), 4.60 (s, 1), 7.61 (s, 3)	1.5	3.6
3b				5.1
2c[g]	192–194	2.30–3.08 (m, 12), 5.72 (s, 6)	2.3	8.2
3c				4.5
2d[g]	281–283	2.54–3.07 (m, 12), 4.30 (s, 4), 7.80 (s, 6)		
2e	249–251[h]	2.55–3.18 (m, 8), 3.33 (s, 2), 4.38 (s, 2), 7.58 (s, 6)	1.9	4.0
3e		2.37–3.11 (m, 10), 3.40 (s, 2), 7.82 (s, 6)		6.5
4e				7.5
2f		2.57–3.30 (m, 10), 4.71 (s, 2), 7.80 (s, 6)	1.8	4.1
3f				5.7
2g[g]	239–241	2.48–3.12 (m, 8), 3.51 (s, 2), 4.10 (s, 2), 6.21 (s, 6)	3.5	6.2
3g[g]	156–158	2.15–3.05 (m, 12), 5.98 (s, 6)		9.8
2h	253–254[i]	2.50–3.10 (m, 12), 4.57 (s, 2)	1.0	2.7
3h[g]	145–146	2.23–3.14 (m, 12), 4.82 (m, 2)		4.0
2i[g]	270–272	1.71–2.06 (m, 2), 2.17–3.24 (m, 15), 4.59 (s, 1)	5.1	11.0
3i				23.0
2j[g]	292–294[j]	2.19–3.02 (m, 12), 4.54 (s, 1)	2.3	4.4
3j	221–222	1.86–3.07 (m, 11), 4.33 (m, 1), 4.77 (m, 1)		8.8
2k	240–242[k]	2.18–3.06 (m, 12), 4.60 (s, 1)	2.5	6.1
3k				8.8
2l[g]	281–283	1.75–3.25 (m, 22)	13.0	36.0
3l[g]	300–301	2.35–3.22 (m, 20), 5.00 (m, 2)		26.0
2m[g]	300–302	2.14–2.89 (m, 12)	3.5	4.5
3m[g]	275–276	1.80–3.00 (m, 10), 4.26 (m, 2)		5.4

[a] The numerical portion of each product designation refers to the type of adduct and the letter portion refers to the appropriate anthracene substrate. [b] The melting points are uncorrected and are given for adducts which were isolated. [c] All nmr spectra were measured in deuteriochloroform except for that of **3l**, which was determined in deuterated dimethyl sulfoxide. [d] The relative vpc retention times are compared with anthracene as unity. The substrate refers to the starting anthracene used to obtain the corresponding adducts. These data were obtained from a combination of the vpc data for competition experiments and B/A ratio studies using different columns and temperatures for vpc analyses ranging from 225 to 300°, and therefore the data are subject to significant error (up to 10%). [e] Lit. mp 329–330° [W. Theilacker, U. Berger-Brose, and H.-K. Beyer, *Chem. Ber.*, **93**, 1958 (1960)], 332–337.5° [P. DeKoe, A. J. Van-Bennekom, and J. Coops, *Rec. Trav. Chim. Pays-Bas*, **82**, 1051 (1963)]. [f] Lit. mp 253–254° (Theilacker reference from footnote *e*). [g] Satisfactory microanalytical data were obtained for this new compound. [h] Lit. mp 253–255.5° [T. H. Regan and J. B. Miller, *J. Org. Chem.*, **32**, 2789 (1967)]. [i] Lit. mp 254.8–255.2° [P. D. Bartlett, M. J. Ryan, and S. G. Cohen, *J. Amer. Chem. Soc.*, **64**, 2649 (1942)]. [j] Lit. mp 205° (Theilacker reference from footnote *e*) [E. C. Kornfeld, P. Barney, J. Blankley, and W. Faul, *J. Med. Chem.*, **8**, 342 (1965)]; satisfactory microanalytical data were also obtained for this compound because of the large discrepancy of the melting point value compared with one literature value. [k] Lit. mp 241–243° (Theilacker reference from footnote *e*), 246–248.5° (Kornfeld reference from footnote *j*).

completely converted to products. Table II gives the appropriate data.

The minor (end-ring) adducts **3a**, **3b**, **3c**, **3f**, **3i**, and **3k** were characterized by a combination of vpc and mass spectral techniques, and the relevant data are found in Table II. These adducts were isolated as trapped vpc zones, and these zones were the only observable zones, other than the respective center-ring adducts, with retention times greater than the respective starting anthracenes. The mass spectral data support the assigned structures and are in keeping with the mass spectral data for the fully characterized adducts. See next section for details.

Adducts **3e** and **4e** were chracterized by vpc, nmr, and mass spectral techniques. Two minor vpc zones were collected which had *m/e* parent molecular ion peaks at 282 in the mass spectra. The material with the shorter vpc retention time had a mass spectral fragmentation pattern more characteristic of a compound with bridgehead (aliphatic) methyl groups rather than aromatic methyl groups. Furthermore, this zone had 5.5 times the area of the other zone, and in the nmr spectrum of the product mixture, a small peak at τ 7.82 (*cf.* τ 7.67 for **2a**) was observed as the only absorption other than the τ 7.58 peak for **2e** in the τ 7.0–8.0 region (τ 7.32 for **1e** methyl protons). Therefore, the shorter retention-time vpc zone is **3e** and the other minor zone is **4e**. The mass spectral cracking patterns further confirm these assignments (see below). The ratio of the 282 (M) and 267 (M − CH_3) peaks substantiate the aliphatic bridgehead methyl groups or **3e** and the aromatic methyl groups for **4e**. Furthermore, only in the mass spectrum of **4e** was a significant peak at 256 (M − C_2H_2) found; this fragmentation substantiates the etheno bridge of **4e**. Normally, the M − C_2H_2 fragmentation of end-ring adducts is not seen because functional group cleavages occur more readily. (Note the 228 peak for **3h**.)

Mass Spectral Data for Benzyne–Anthracene Adducts.—The significant high-mass peaks [*m/e* (relative intensity)] are recorded for all adducts.

2a: 282(67), 267(100), 266(9), 265(15), 263(6), 253(22), 252(70); **3a**: 282(68), 267(100), 266(11), 265(16), 263(6), 253(45), 252(68); **2b**: 268(67), 267(8), 265(7), 253(100), 252(52), 250(9), 239(6); **3b**: 268(74), 267(16), 265(11), 253(100), 252(50), 250(9), 239(6); **2c**: 314(100), 299(92), 283(42), 282(29), 269(21), 268(32), 267(42), 252(34), 239(66), 237(16); **3c**: 314(100), 299(88), 283(37), 282(22), 269(17), 268(27), 267(34), 252(32), 239(49), 237(17); **2e**: 282(94), 281(12), 267(100), 266(24), 265(30), 263(14), 253(12), 252(40); **3e**: 282(69), 281(13), 267(100), 266(20), 265(25), 263(9), 253(10), 252(43); **4e**: 282(100), 281(22), 267(87), 266(28), 265(28), 263(6), 256(8), 253(10), 252(26); **2f**: 282(100), 281(23), 267(96), 266(25), 265(23), 263(9), 252(32); **3f**: 282(100), 281(24), 267(97), 266(27), 265(23), 263(11), 252(33); **2g**: 314(100), 299(8), 283(79), 268(24), 252(17), 239(31); **3g**: 314(83), 299(100), 283(58), 268(17), 239(33); **2h**: 254(96), 253(100), 252(46), 250(13), 239(4), 226(5); **3h**: 254(100), 253(86), 252(46), 250(7), 239(3), 228(11), 226(11); **2i**: 330(100), 329(33), 253(28), 252(33); **3i**: 330(100), 329(40), 253(51), 252(82); **2j**: 279(100), 278(74), 277(29), 275(7), 264(9), 253(14), 252(26), 251(9), 250(13); **3j**: 279(100), 278(71), 277(35), 275(7), 264(2), 253(14), 252(19), 251(9), 250(9); **2k**: 299(64), 282(6), 269(8), 268(8), 267(7), 253(100), 252(92), 251(13), 250(31); **3k**: 299(56), 282(5), 269(33), 268(28), 267(11), 253(100), 252(89), 251(11), 250(25); **2l**: 406(67), 405(17), 329(100), 328(100), 327(33), 326(29), 252(17); **3l**: 406(100), 405(26), 380(2), 329(53), 328(21), 327(16), 326(16), 252(5); **2m**: 304(100), 303(43), 302(13), 278(49), 277(63); **3m**: 304(100), 303(50), 302(21), 278(14), 277(18).

Hydrogenation of 3h and 3j.—Hydrogenations were carried out using the internal method for the Brown[2] hydrogenation apparatus.[12] To a 250-ml flask were added absolute ethanol (20 ml), decolorizing carbon (0.5 g), and 0.2 *M* chloroplatinic acid in ethanol (0.5 ml). By the use of a hypodermic syringe, 1.00 *M* sodium borohydride in ethanol (3.0 ml) was added, followed 1 min later by glacial acetic acid (2.5 ml). Then a solution of **3h** or **3j** (100 mg) in ethanol (100 ml) was added and the hydrogenation mixture was stirred for 6 hr at room temperature. The reaction mixture was filtered, the carbon was washed with methylene chloride, and the solvents were removed from the filtrate. The residue was treated with methylene chloride and dilute sodium bicarbonate solution, the organic layer was dried with sodium sulfate, and the solvent was removed. The residue was recrystallized from heptane or benzene–heptane.

5,12-Dihydro-5,12-ethanonaphthacene had mp 169–171°; nmr ($CDCl_3$) τ 2.15–3.01 (m, 10), 5.61 (m, 2), and 8.22 (m, 4); mass spectrum *m/e* 256 (molecular ion peak).

Anal. Calcd for $C_{20}H_{16}$: C, 93.7; H, 6.3. Found: C, 93.4; H, 6.6.

6-Cyano-5,12-dihydro-5,12-ethanonaphthacene had mp 170–171°; nmr ($CDCl_3$) τ 1.80–2.96 (m, 9), 5.08 (m, 1), 5.59 (m, 1), and 8.22 (m, 4); mass spectrum *m/e* 281 (molecular ion peak).

Anal. Calcd for $C_{21}H_{15}N$: C, 89.6; H, 5.4; N, 5.0. Found: C, 89.3; H, 5.5; N, 4.9.

Center-Ring Adduct *vs.* End-Ring Adduct (B/A) Ratio Experiments.—Reactions were carried out at 70° for 3–5 hr with 2 mmol of an anthracene, 4–8 mmol of 2-carboxybenzenediazonium chloride,[3,13] 40 ml of stock solvent solution (19:1 v/v 1,2-dichloroethane–propylene oxide), and an internal standard where applicable. Internal standards were employed when direct comparisons between reaction mixtures and mixtures of authentic adducts **2** and **3** could be made. See the next section for procedural details.

Vpc analyses were made on the worked-up reaction mixtures. For isolated pairs of adducts where thermal-conductivity differences could be calculated, the differences ranged from 0 to 15%. For the other pairs of adducts, the thermal conductivities of a given pair were assumed to be the same.

Competition Experiments.—Anthracene (356 mg, 2.00 mmol), a substituted anthracene (2.00 mmol), and an internal standard (octadecane, docosane, tetracosane, or octacosane) for vpc analysis were placed in a 100-ml one-neck flask equipped with a reflux condenser and a magnetic stirring bar operated by a water-driven magnetic stirrer. A solvent stock solution (20 ml), prepared by adding 1,2-dichloroethane (1520 ml) to propylene oxide (80 ml), was added to the flask, which was then placed in a constant-temperature bath at 70 ± 1°. A small aliquot was removed when complete solution was achieved.

Solid 2-carboxybenzenediazonium chloride (368 mg, 2.00 mmol) was added to the reaction mixture, and an additional 20 ml of the stock solvent solution, which had been maintained at 70°, was added. The heterogeneous reaction mixture was rapidly stirred for 3 hr, during which time it changed to a red-brown solution.

An equal volume of water was added to quench the reaction, and the organic layer was dried with magnesium sulfate and concentrated in preparation for vpc analysis.

For each competition experiment, vpc comparisons were made between the amounts of anthracenes in the reaction mixture prior to and subsequent to the reaction with 2-carboxybenzenediazonium chloride. The average value of triplicate vpc determinations was used in each case.

The relative reactivities were calculated using the expression

$$\log[(X)/(X_0)]/\log[(Y)/(Y_0)] = k_{X/Y}$$

where (X) and (Y) refer to final concentrations of substituted anthracene and anthracene, respectively, and (X_0) and (Y_0) refer to initial concentrations.

Registry No.—Benzyne, 462-80-6; **2a**, 15254-35-0; **2b**, 793-39-5; **2c**, 21372-89-4; **2d**, 21372-90-7; **2e**, 17417-17-3; **2f**, 21372-92-9; **2g**, 21372-93-0; **2h**, 477-75-8; **2i**, 20466-07-3; **2j**, 1092-87-1; **2k**, 797-67-1; **2l**, 21372-98-5; **2m**, 4044-52-4; **3a**, 21373-00-2; **3b**, 21373-01-3; **3c**, 21373-02-4; **3e**, 21373-03-5; **3f**, 21373-04-6; **3g**, 21373-05-7; **3h**, 4044-73-9; **3i**, 21373-07-9; **3j**, 4044-74-0; **3k**, 21373-09-1; **3l**, 21373-10-4; **3m**, 4044-75-1; **4e**, 21373-12-6; 5,12-dihydro-5,12-ethanonaphthacene, 10117-59-6; 6-cyano-5,12-dihydro-5,12-ethanonapthacene, 21373-14-8.

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[13] Enough 2-carboxybenzenediazonium chloride was added such that essentially all starting anthracene was converted into products. The more unreactive anthracenes necessitated a larger excess of benzyne precursor.

Azides and Amines from Grignard Reagents and Tosyl Azide

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Grignard reagents react with tosyl azide to form salts of tosyltriazenes, which can be reduced to amines by Raney nickel alloy and aqueous base. Fragmentation of the triazene salts to form aryl or alkyl azides takes place best in aqueous sodium pyrophosphate at 0–20°. Yields are moderate to good with aromatic reagents, poor with aliphatic. *o*-Tolyl and *o*-*t*-butylphenyl Grignard reagents react with tosyl azide under some conditions to give the azobenzene and toluenesulfonamide instead.

The traditional methods for converting organic halides to amines or azides involve displacement reactions with ammonia, metal amides, or metal azides, and thus are unsatisfactory or fail altogether with unreactive halides, including most aryl halides. Grignard reagents react with a variety of nitrogenous reagents to give products in which the aryl or alkyl group of a Grignard reagent has become attached to a nitrogen atom (chloramine,[2] alkoxyamines,[3] nitrosyl chloride,[4] and alkyl nitrates[5]), providing potential alternative routes to amines and azides. Some instances of preparative utility have been reported, but none of these

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[1] From the doctoral dissertations of L. B. Bruner, 1957, and C. D. Rowe, 1968.

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