Reactions of Benzyne with Substituted Benzenes

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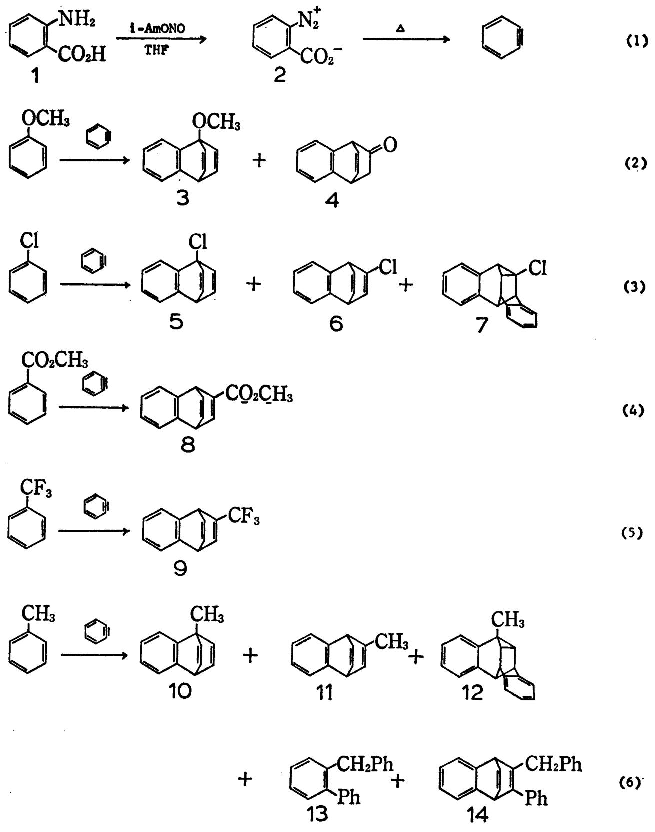
The reactions of benzyne with substituted benzenes(anisole, chlorobenzene, methyl benzoate, benzylidyne trifluoride and toluene) giving the Diels-Alder adducts were investigated, where two positionally isomeric adducts were possible, *i.e.*, a geminal-para adduct (1,4-adduct with respect to the substituent) and an ortho-meta adduct (2,5-adduct). From the competition reactions, relative reactivities of benzyne to substituted benzenes were estimated for the 1,4-addition and 2,5-addition. Markedly different substituent effects were observed. For the 1,4-addition, large negative ρ value (-1.79) was observed, but for the 2,5-addition, substituent effect was small. From benzyne and toluene, *o*-benzylbiphenyl (**13**) and 2-benzyl-3-phenylbenzo[5,6]bicyclo[2.2.2]octatriene (**14**) were obtained as the successive "ene" products together with the normal Diels-Alder adducts.

Reactions of halogenated benzynes with substituted benzenes were studied well where the Diels-Alder adducts were obtained in good yield.[1] But the reactions of benzyne with substituted benzenes have been scarcely studied probably because of the low reactivity. Only the reactions of benzyne, generated from the thermolysis of benzenediazonium-2-carboxylate, with benzene[2,3] and some alkylbenzenes[4] and that, generated from the pyrolysis of phthalic anhydride, with *o*-dichlorobenzene[5] have been reported. Stiles reported that the reaction of benzyne with benzene gave three one to one adducts, biphenyl, benzocyclooctene and benzobicyclo[2.2.2]octatriene, together with a two to one adduct **15**.[2] Friedman, however, showed that the former two products were formed only in the presence of a catalytic amount of silver cation and their formations were reduced to near zero in the reaction where the starting benzenediazonium-2-carboxylate was prepared from anthranilic acid(**1**) and pentyl nitrite in the absence of a silver salt.[3,6] We also reported that the addition of several metal salts changed the products of the reaction of benzyne with benzene.[7]

In this paper we report the products and the relative reactivities of substituted benzenes treated with benzyne, generated from benzenediazonium-2-carboxylate, in the absence of a metal salt.



Scheme 1. The products of the reactions of benzyne with substituted benzenes.[9]

Results

The thermolysis of benzenediazonium-2-carboxylate (**2**) was carried out in a substituted benzene(anisole, chlorobenzene, methyl benzoate, benzylidyne trifluoride or toluene). The products are shown in Scheme 1 and their compositions are listed in Table 1.[8]

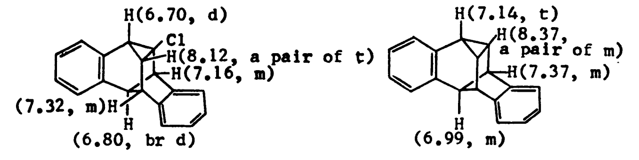
Table 1. The product compositions of the reactions of benzyne with substituted benzenes[a]

Substrate (ml)	1 (g)	Product compositions (%)				
Anisole	10	**3**	**4**			
(500)		82.9	17.1			
Chlorobenzene	3	**5**	**6**	**7**		
(500)		17.8	44.4	37.8		
Methyl benzoate	3	**8**				
(225)		≈100				
Benzylidyne	3	**9**				
trifluoride (75)		≈100				
Toluene	3	**10**	**11**	**12**	**13**	**14**
(500)		13.9	28.4	4.1	37.1	16.5

a) The product compositions were determined by means of gas chromatography (PEG 20M and Silicon DC 550 columns) and/or NMR spectroscopy.

The reaction of benzyne with anisole gave 1-methoxybenzo[2,3]bicyclo[2.2.2]octatriene(**3**) and benzobicyclo[2.2.2]octadienone(**4**) in 25(32) and 6(8)% yields, respectively, on the basis of anthranilic acid used (yields in the parentheses were based on benzyne generated).[10] **4** was determined on the basis of its IR spectrum identical with that reported in literature[11] in every detail.

Chlorobenzene gave 1-chlorobenzo[2,3]bicyclo[2.2.2]octatriene(**5**), 2-chlorobenzo[5,6]bicyclo[2.2.2]octatriene (**6**) and compound **7** together with biphenylene(19% of the total products)[9] and phenyl benzoate



7 **15**

Fig. 1. H^1 NMR spectra of **7** and **15** (τ-value). Abbreviations are: d, doublet; t, triplet; m, multiplet; br, broad.

(4% of the total products).[9] The molecular peak of mass spectrum of **7** was observed at 264 (*m*/*e*) with relative intensity 12, indicating that **7** was the two to one adduct of benzyne and chlorobenzene. The 60 MHz NMR spectrum of **7** in CCl_4 consisted of aromatic absorptions as a multiplet at 2.55—3.05 τ (8H) and aliphatic absorptions at 6.70 τ(doublet, 1H), 6.80 τ(broad doublet, 1H), 7.16 τ(multiplet, 1H), 7.32 τ(multiplet, 1H), and 8.12 τ(a pair of triplet, 1H). No olefinic proton was observed. The 60 MHz spin-decoupling experiments showed that the original signal at 8.12 τ was coupled with the signal at 6.70 τ with *J* value of 7.2 Hz and also coupled with the signal at 6.80 τ with *J* value of 1.8 Hz. The NMR spectrum of **7** compared with that of unsubstituted compound **15**[2b] is shown in Fig. 1. Observed NMR spectrum of **7** was fully interpreted on the basis of the assigned structure.

Methyl benzoate gave 2-methoxycarbonylbenzo[5,6]-bicyclo[2.2.2]octatriene (**8**), biphenylene and phenyl benzoate. No 1-substituted benzobicyclo[2.2.2]octatriene was obtained in a detectable amount.

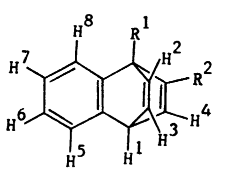
From benzylidyne trifluoride, 2-trifluoromethylbenzo-[5,6]bicyclo[2.2.2]octatriene (**9**), biphenylene and phenyl benzoate were obtained.

From toluene, three products, 1-methylbenzo[2,3]-bicyclo[2.2.2]octatriene (**10**), 2-methylbenzo[5,6]bicyclo[2.2.2]octatriene (**11**) and *o*-benzylbiphenyl (**13**) were obtained as was reported elswhere.[4] In addition, unknown compounds **12** and **14** were obtained. Structure of **12** was tentatively determined as shown in Scheme 1 on the basis of NMR spectrum which consisted of the signals at 8.95 τ(singlet), 7.4 τ(broad singlet), and 7.0 τ(broad singlet). The molecular peak of the mass spectrum of **14** was observed at 320 (*m*/*e*) indicating **14** to be the three to one adduct of benzyne and toluene. Its NMR spectrum showed the olefinic multiplet at 3.06—3.25 τ(2H) and aliphatic signals at 4.99 τ (doublet of doublet, 1H), 5.50 τ (doublet of doublet, 1H), and 6.40 τ (AB quartet, 2H). According to the decoupling experiment, no appreciable coupling was observed between the signals at 4.99 and 5.50 τ. The most probable structure of **14** and NMR assignment are shown in Fig. 2.

The NMR spectra of other benzobicyclo[2.2.2]octatriene derivatives are summarized in Table 2.

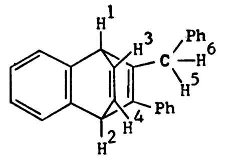
Competition reactions were carried out to estimate the relative reactivities of benzyne toward substituted benzenes. In each run, 0.5 g of anthranilic acid and 20—30 g of substituted benzenes were used. Results are shown in Table 3.

TABLE 2. ^1H NMR SPECTRA OF BENZOBICYCLO[2.2.2]OCTATRIENE DERIVATIVES[a]



Compounds	R^1	R^2	τ-value									
			R^1	H^1	R^2	H^2	H^3	H^4	H^5	H^6	H^7	H^8
3	OCH_3	H	6.25 (s)	5.35 (tt)	2.95—3.45 (m)							2.65—2.83 (m)
5	Cl	H	—	5.21 (m)	2.90—3.40 (m)							2.40—2.60 (m)
6	H	Cl	5.13—5.45 (m)		—	2.75—3.25 (m)		3.76 (m)	2.75—3.25 (m)			
8	H	CO_2CH_3	4.50—4.73 (m)	4.95—5.24 (m)	6.30 (s)	2.65—3.40 (m)		3.27 (dd)	2.65—3.40 (m)			
9	H	CF_3	4.95—5.23 (m)		—	2.65—3.25 (m)						
10	CH_3	H	8.04 (s)	5.26 (m)	3.58 (dd)		2.80—3.30 (m)					
11	H	CH_3	5.46—5.72 (m)	5.24—5.46 (m)	8.12 (m)	2.85—3.35 (m)		3.65—3.90 (m)	2.85—3.35 (m)			

a) With 1% TMS as an internal standard, 5—10% in CCl_4, 60 MHz. Abbreviations are: s, singlet; d, doublet; dd, doublet of doublet; tt, triplet of triplet; m, multiplet.



Aromatic H: 2.65—3.06 τ (m, 14H)
H^3, H^4: 3.06—3.25 τ (m, 2H)
H^2: 4.99 τ (dd, 1H), J_{H^2,H^4}=5.4 Hz, J_{H^2,H^3}=2.8 Hz
H^1: 5.50 τ(dd, 1H), J_{H^1,H^3}=5.4 Hz, J_{H^1,H^4}=2.6 Hz
H^5, H^6: 6.40 τ (center, AB quartet, 2H), J_{H^5,H^6}=16.5 Hz

Fig. 2. The NMR spectrum of **14**. With 1% TMS as an internal standard, 10% in CCl_4, 60 MHz. Abbreviations are: dd, doublet of doublet; m, multiplet.

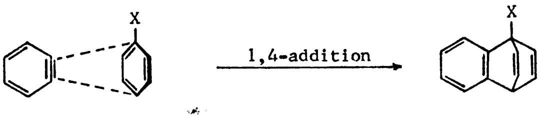
Table 3. Competition reactions of a series of substituted benzene toward benzyne[a]

Run	Substrate (g)	Ratio of products derived from two substrates	k_R/k_H[b]
1	Benzene (30)	1	1
	Anisole (20)	3.82	7.93
2	Benzene (25)	1	1
	Toluene (25)	3.61	4.25
3	Benzene (20)	1	1
	Chlorobenzene (30)	0.862	0.794
4	Benzene (20)	1	1
	Benzylidyne trifluoride (30)	0.466	0.580
5[c]	Chlorobenzene (20)	1	0.794
	Methyl benzoate (30)	1.45	0.993

a) The products from benzene were benzobicyclo[2.2.2]-octatriene (**16**) and **15**. b) Relative reactivities of substituted benzenes to benzene. c) Product compositions derived from chlorobenzene were slightly changed from those shown in Table 1 to **5**, 6.1% and **6**+**7**, 93.9%. The cause of these differences was not clear but it may be due to solvent effect.

Discussion

Regioselectivity of the Diels-Alder Addition. The reaction of benzyne with substituted benzene gave the Diels-Alder adducts[12] where two positional isomers were possible, a geminal-para adduct(1,4-addition; Eq. 7) and an ortho-meta adduct(2,5-addition; Eq. 8) with respect to a substituent.



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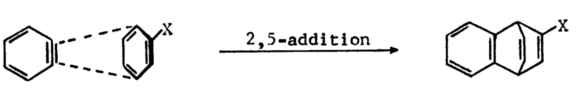

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Table 4. The isomer compositions of the Diels-Alder adducts (%)

Substrate	1,4-Adduct	2,5-Adduct
Anisole	82.9	17.1
Toluene	28.6	71.4
Chlorobenzene	17.8	82.2
Methyl benzoate	≈0	≈100
Benzylidene trifluoride	≈0	≈100

Table 5. The relative reactivities of benzyne toward substituted benzenes with respect to 1,4-addition and 2,5-addition[a]

Substituent	OCH_3	CH_3	H	Cl	CO_2CH_3	CF_3
1,4-Addition	19.1	2.32	1	0.436	≈0	≈0
2,5-Addition	2.36	2.90	1	0.973	1.49	0.870

a) Statistical factors are corrected.

The isomer compositions are shown in Table 4.[13] As shown in the table, the predominant product was systematically changed from the 1,4-adduct for anisole to the 2,5-adduct for methyl benzoate or benzylidyne trifluoride depending on the electron-donating(withdrawing) property of substituent.[14] If the steric factor alone is important, it should reduce the amount of the 1,4-adduct relative to the 2,5-adduct.[15] But our results indicated that the regioselectivity of the Diels-Alder addition could not be so simply explained as only the steric repulsion in the transition state was important (*vide infra*).

The Relative Reactivities of Benzyne toward Substituted Benzenes. The relative reactivities of benzyne toward substituted benzenes were estimated from the competition experiments. In Table 5, the relative reactivities of benzyne toward substituted benzenes with respect to 1,4-addition and 2,5-addition are shown. The reactivity of 1,4-addition changed more than 40-fold with changing a substituent, while that of 2,5-addition changed only 3.5-fold. Hammett plots of the relative reactivities of 1,4-addition and 2,5-addition of benzyne toward substituted benzenes are shown in Figs. 3 and 4, respectively. For 1,4-addition, the plot of the logarithms of the relative reactivities *vs.* σ_p^+ gave a straight line and the reaction constant, ρ, was estimated to be −1.79. A comparison of ρ values for several reactions is made in Table 6. As is seen, the absolute value of the present ρ is much smaller than that for the nitration of substituted benzenes but slightly larger than that for cationic phenylation of substituted benzenes.[19] This fact indicates that some positive charge may be induced in benzyne in the transition state of 1,4-addition.

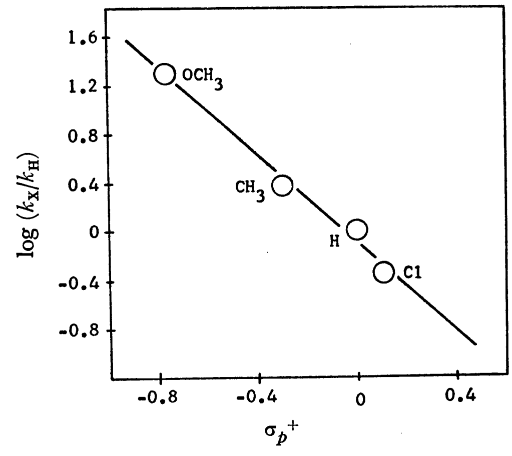


Fig. 3. Hammett plots for 1,4-addition.

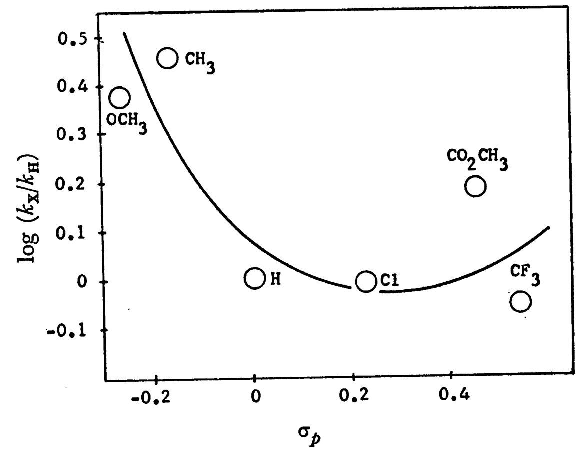
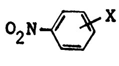
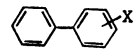
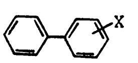
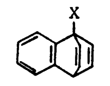


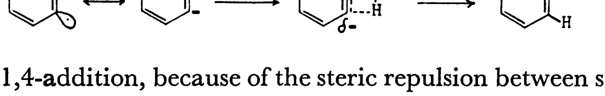
Fig. 4. Hammett plots for 2,5-addition.

TABLE 6. REACTION CONSTANTS FOR SEVERAL REACTIONS OF SUBSTITUTED BENZENES

Reagent	Product	Kind of substituent constant	ρ	Reference
HNO_3–H_2SO_4 (in CH_3NO_2 or Ac_2O, 25 °C)		σ^+	−6.53	16
$PhN_2^+BF_4^-$ (40 °C)		σ^+	−1.0	17
$(PhCO_2)_2$ (80 °C)		σ_m	0.05	18
Benzyne (≈45 °C)		σ_p^+	−1.79	this work

To a marked contrast, for 2,5-addition, no clear correlation was observed between logarithms of the relative reactivities and σ_p, although some electrophilic nature of benzyne may be seen from Fig. 4. And present substituent effect seems to be similar to that of the radical decomposition of symmetrically disubstituted benzoyl peroxide.[20]

A possible explanation of these results can be made by a concerted mechanism of benzyne with substituted benzenes. Most stable electronic state of benzyne is considered to be a nonbonding diradical.[21] But benzyne is also considered to be strongly polarized in the transition state of the reactions with the nucleophiles[22] as shown for the case of alcohol (Eq. 9). In the transition state of 1,4-addition, because of the steric repulsion between substituent of substituted benzene and hydrogen of benzyne, two bond formations may be unequal. Therefore, the charges are induced in benzyne in the transition state as shown in Fig. 5 and the large substituent effect is observed. On the contrary, for 2,5-addition, this steric repulsion can be negligible, and two bond formations may be equal. Therefore, relatively small charges are induced in benzyne in the transition state (Fig. 5) and the substituent effect appears small. This mechanism also explains the substituent effect of 2,5-addition to be similar to those of the radical reactions. Radical or cationic two step mechanism can neither explain both substituent effects of 1,4- and 2,5-additions satisfactorily at the same time, nor explain no formation of 1,2-adduct(benzocyclooctene derivative).



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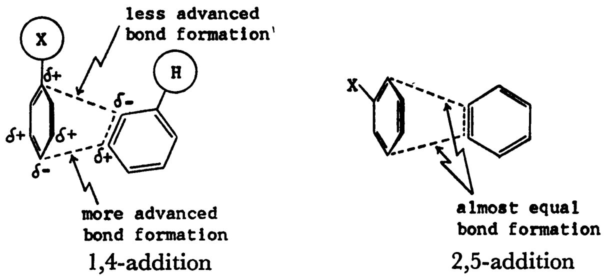
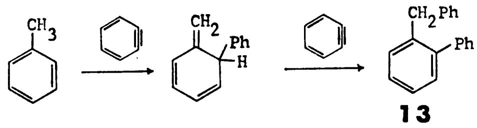


Fig. 5. Unequal bond formations of 1,4-addition and almost equal bond formations of 2,5-addition in the transition states.

Double "Ene" Reaction of Benzyne with Toluene. Toluene gave, together with the normal Diels-Alder adducts, the abnormal products *o*-benzylbiphenyl (**13**) and 2-benzyl-3-phenylbenzo[5,6]bicyclo[2.2.2]octatriene (**14**). The formation of **13** was explained by the successive "ene" reactions of two benzyne molecules to one toluene molecule[4] as shown in Eq. 10. The formation of **14** can be also explained by the successive "ene" reactions of two benzyne molecules to one molecule of **11** (Eq. 11).[23] The fact that intermediates proposed here could not be isolated may be due to the fast second "ene" reactions. The reactions of halogenated benzynes with toluene gave exclusively the Diels-Alder adducts.[1] Thus, there is a remarkable difference between benzyne and halogenated benzyne.



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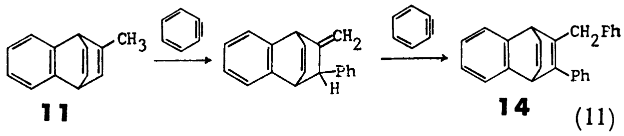

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Experimental

Benzenediazonium-2-carboxylate (2). Benzenediazonium-2-carboxylate (**2**) was prepared by the Friedman's method.[3] To a stirring soln of 3 g of anthranilic acid (**1**) in 20 ml of tetrahydrofuran (THF) in the presence of a catalytic amount of trichloroacetic acid was added dropwise 5 g of isopentyl nitrite. The mixture was stirred for 1 h and then cooled with ice bath. After the pale yellow solid of **2** was precipitated, upper liquid was carefully pipetted out, and immediately cold THF was added to the ppt. The mixture was stirred for a moment and kept standing with external cooling until the ppt was settled. Then, the upper THF layer was again removed from the ppt this procedure was repeated until the THF layer became practically colorless (3—4 times). Then the ppt was similarly washed with dichloromethane twice to remove THF.[10] The ppt, benzenediazonium-2-carboxylate (**2**), thus obtained was used directly for the reaction.

General Procedure of the Reaction of Benzyne with a Substituted Benzene. A mixture of benzenediazonium-2-carboxylate (**2**), prepared from 3—10 g of anthranilic acid (**1**), and 75—500 ml of a substituted benzene was stirred at about 45 °C. After gas evolution had ceased (20—48 h), the mixture was washed with aq sodium hydrogencarbonate soln and water, dried and then concd. The residue was analyzed by gas chromatography (Silicon DC 550, PEG 20M and Golay column of silicon oil). After distillation of the mixture, products were separated by preparative gas chromatography and identified by means of their IR, NMR, and mass spectra.

Reaction of Benzyne with Anisole. Anisole used for the reaction was dried on sodium. Gas chromatographic analysis of the concd crude mixture showed the presence of two products, 1-methoxybenzo[2,3]bicyclo[2.2.2]octatriene (**3**) and benzobicyclo[2.2.2]octadienone (**4**). Distillation of the concd crude mixture at 55—66 °C/0.7 Torr afforded the mixture of **3** and **4**. They were separated by preparative gas chromatography (PEG 20 M). **3** was a colorless oil, n_D^{16} 1.5840; MS, *m*/*e* (rel intensity) 184 (M^+, 90), 169 (100), 158 (24), 141 (87), 115 (84), and 94 (37); IR (neat), 1330, 1080, 1015, 860, 745, 695, and 680 cm^{-1}. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57%. Found: C, 84.52; H, 6.82%.

4 was the known compd and its IR spectrum was completely consistent with the reported one.[11]

Gas evolution was measured in the reaction of **2**, prepared from 1 g (7.30 mmol) of **1**, with 200 ml of anisole at 48 °C for 9 h, which amounted to 268 ml on water at 16.2 °C, indicating that 5.62 mmol of benzyne to be generated (77% based on **1** used). Gas chromatographic analysis of the crude mixture calibrated with the weighed internal standard (biphenyl) showed that the yields of **3** and **4** were 25 (32) and 6 (8)%, respectively based on **1** used (yields in the parentheses were based on benzyne generated).

Reaction of Benzyne with Chlorobenzene. The concd crude mixture was analyzed by gas chromatography on PEG 20 M which revealed the presence of 1-chlorobenzo[2,3]bicyclo[2.2.2]octatriene (**5**), 2-chlorobenzo[5,6]bicyclo[2.2.2]octatriene (**6**) and a compd **7** together with phenyl benzoate (4% of the total products), biphenylene (19% of the total products) and a small amount of ester not yet characterized. The distillate of the mixture at 70—73 °C/7 Torr consisted of **5**, **6**, biphenylene and phenyl benzoate. Isolations of **5** and **6** were carried out by preparative gas chromatography. **5** was obtained as white crystals, mp 47—48 °C, from ether; MS, *m*/*e* (rel intensity) 190 (M+2, 12), 188 (M^+, 35), 162 (14), 154 (18), 153 (100), 152 (39), 151 (19), 127 (16), and 126 (10); IR (neat), 1450, 1320, 990, 830, 750, and 685 cm^{-1}. Calcd for $C_{12}H_9Cl$: C, 76.40; H, 4.81; Cl, 18.79%. Found: C, 76.24; H, 5.08; Cl, 18.59%.

6 was obtained as white crystals, mp 47 °C, from ether; MS, *m*/*e* (rel intensity) 190 (M+2, 17), 188 (M^+, 41), 154 (27), 153 (100), 152 (100), 151 (27), 128 (14), 127 (18), and 126 (13); IR (neat), 1460, 1305, 1005, 820, 810, 750, and 710 cm^{-1}. Calcd for $C_{12}H_9Cl$: C, 76.40; H, 4.81; Cl, 18.79%. Found: C, 76.20; H, 4.77; Cl, 18.58%.

The distillate of the mixture at 116—130 °C/0.9 Torr afforded **7** which was further purified through a column of silica gel (eluted with petroleum ether) and with recrystallization from hexane, mp 128 °C; MS, *m*/*e* (rel intensity) 266 (M+2, 4), 264 (M^+, 12), 230 (23), 229 (100), 228 (53), 227 (13), 226 (23), 114 (24), 113 (18), 102 (12), and 101 (14); IR (neat), 1490, 1460, 1290, 1250, and 750 cm^{-1}. Calcd for $C_{18}H_{13}Cl$: C, 81.66; H, 4.95; Cl, 13.39%. Found: C, 81.95; H, 5.13; Cl, 13.67%.

Reaction of Benzyne with Methyl Benzoate. Gas chromatographic analysis (Silicon DC 550) of the concd crude mixture showed the presence of 2-methoxycarbonylbenzo[5,6]bicyclo[2.2.2]octatriene (**8**) together with biphenylene (21% of the total products) and phenyl benzoate (25% of the total products). Distilled **8** at 82—90 °C/4 Torr was further purified by preparative gas chromatography, followed by recrystallization from hexane, mp 63.5 °C; MS, *m*/*e* (rel intensity) 212 (M^+, 58), 169 (12), 154 (20), 153 (100), 152 (70), 151 (19), 128 (20), and 127 (20); IR (neat), 1700, 1240, 1200, 1060, 725, and 690 cm^{-1}. Calcd for $C_{14}H_{12}O_2$: C, 79.23; H, 5.70; O, 15.08%. Found: C, 78.94; H, 5.62; O, 14.79%.

Reaction of Benzyne with Benzotrifluoride. Gas chromatographic analysis (PEG 20 M) of the concd crude mixture showed the presence of 2-trifluoromethylbenzo[5,6]bicyclo[2.2.2]octatriene (**9**) together with biphenylene (45% of the total products) and phenyl benzoate (18% of the total products). Preparative gas chromatography of the distillate at 64—67 °C/3 Torr afforded **9** as a colorless oil, n_D^{16} 1.5092; MS, *m*/*e* (rel intensity) 222 (M^+, 100), 201 (17), 196 (16), 154 (31), 153 (95), 152 (76), 151 (28), 146 (22), 128 (44), and 127 (19); IR (neat), 1465, 1340, 1260, 1150, 1110, 1015, 740, and 685 cm^{-1}. Calcd for $C_{13}H_9F_3$: C, 70.27; H, 4.08; F, 25.65%. Found: C, 70.81; H, 4.35; F, 25.27%.

Reaction of Benzyne with Toluene. The mixture of **2**, prepared from 3 g of **1**, and 500 ml of toluene in 500 ml of dichloromethane was refluxed for 2 days. After usual workup, gas chromatographic analysis (PEG 20 M) of the concd crude mixture showed the presence of 1-methylbenzo[2,3]bicyclo[2.2.2]octatriene (**10**), 2-methylbenzo[5,6]bicyclo[2.2.2]octatriene (**11**), small amounts of biphenylene (9% of the total products) and phenyl benzoate (4% of the total products), together with *o*-benzylbiphenyl (**13**) and **12**. The distillate at 68—69 °C/17 Torr consisted of **10** and **11** which were separated by preparative gas chromatography. **10** and **11** were reported elsewhere but their properties were not described.[4] **10** was a colorless oil; MS, *m*/*e* (rel intensity) 168 (M^+, 96), 167 (68), 165 (36), 153 (100), 152 (49), 149 (81), 141 (45), 128 (73), and 115 (41); IR (neat), 1460, 1445, 1330, 1010, 920, 740, 700, and 680 cm^{-1}. **11** was a colorless oil; MS, *m*/*e* (rel intensity) 168 (M^+, 100), 167 (71), 155 (38), 153 (97), 152 (54), 149 (62), 141 (45), 128 (85), and 115 (84); IR (neat), 1460, 1310, 805, 735, and 670 cm^{-1}.

The distillate at 64—74 °C/8 Torr consisted of biphenylene, phenyl benzoate and small amounts of **10** and **11**.

The distillate at 70—110 °C/0.8 Torr consisted of **12**, **13**, and **14** in a ratio of 1 : 9 : 4. The mixture was chromatographed through a column of silica gel. Elution with hexane gave a mixture of **12** and **13**. **13** was purified by recrystallization from carbon tetrachloride, melted at 54—55 °C (lit,[24] 54—56 °C). Although **12** was not purified, its structure was tentatively determined on the basis of the NMR spectrum of the mixture of **12** and **13** (**12** was isolated satisfactorily neither by gas chromatography nor by column chromatography). Further elution with a mixture of hexane and benzene gave **14**, recrystallized from hexane; mp 69—71 °C; MS, *m*/*e* (rel intensity) 320 (M^+, 41), 229 (100), 228 (25), 129 (37), 128 (98), 116 (40), 115 (40), and 105 (28); IR (neat), 1460, 1450, 740, and 690 cm^{-1}. Calcd for $C_{25}H_{20}$: C, 93.71; H, 6.29%. Found: C, 93.53; H, 6.07%.

Even if dichloromethane as a solvent was not used, the products and product composition were scarcely changed.

Competition Reactions of a Series of Substituted Benzenes toward Benzyne. Competition reactions of a series of substituted benzenes toward benzyne were carried out using **2**, prepared from 0.5 g of **1**, and the following combinations of substituted benzenes: A) benzene 25 g, toluene 25 g; B) benzene 30 g, anisole 20 g; C) benzene 20 g, chlorobenzene 30 g; D) benzene 20 g, benzylidyne trifluoride 30 g; E) chlorobenzene 20 g, methyl benzoate 30 g. Relative reactivities were estimated from the calibrated gas chromatographic analysis and/or NMR analysis of the crude mixtures.

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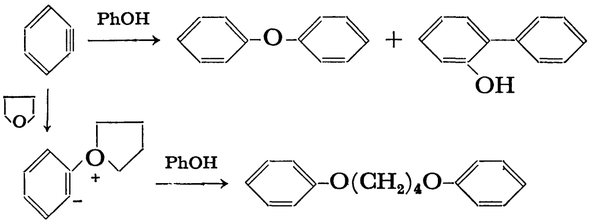
8) The products **10**, **11**, and **13** from toluene were already reported by L. Friedman, see Ref. 4.

9) In each case except anisole, biphenylene (9—45% of the total products) and phenyl benzoate (4—25% of the total products) were obtained. But obviously they are not the reaction products of benzyne with substituted benzenes.

10) Anisole distilled on sodium metal was used. In a run where anisole distilled on phosphorus pentoxide was used, diphenyl ether and *o*-hydroxybiphenyl were obtained together with **3** and **4**, and in the presence of tetrahydrofuran, 1,4-diphenoxybutane was also obtained. These products seem to be formed from phenol as follows.



Wolthuis *et al.* reported that from benzyne, tetrahydrofuran and water, 1,4-diphenoxybutane was also obtained. See, E. Wolthuis, B. Bouma, J. Modderman, and L. Sytsma, *Tetrahedron Lett.*, **1970**, 407.

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12) In the presence of a silver salt, the reactions of benzyne with substituted benzenes gave mainly biphenyl and/or benzocyclooctene derivatives. See, I. Tabushi, H. Yamada, Z. Yoshida, and R. Oda, *Bull. Chem. Soc. Jpn.*, **50**, 291 (1977).

13) As for toluene, the product **14** was included in 2,5-adduct and the product **12** was included in 1,4-adduct. Similarly for chlorobenzene, the product **7** was included in 2,5-adduct.

14) For anisole and toluene, the results of benzyne were very similar to those of halogenated benzynes. For example, in the case of tetrafluorobenzyne, 86% of 1,4-adduct and 14% of 2,5-adduct from anisole, and 23% of 1,4-adduct and 77% of 2,5-adduct from toluene were obtained. See Ref. 1a.

15) Actually the ratios of 1,4-adducts to 2,4-adducts in reactions of tetrahalogenated benzynes with *t*-butylbenzene were reported to be markedly affected by the bulkiness of halogens. See Ref. 1i.

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23) There is a some possibility of the formation of **14** by the cycloaddition of benzyne to **13**. But, under the experimental condition, that possibility may be small, because the concentration of **13** was much lower than that of toluene and the reactivity of benzyne toward **13** is estimated to be similar to that toward toluene from the result of the substituent effect.

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