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Reactions of Benzyne-Silver Cation Complex with Substituted Benzenes

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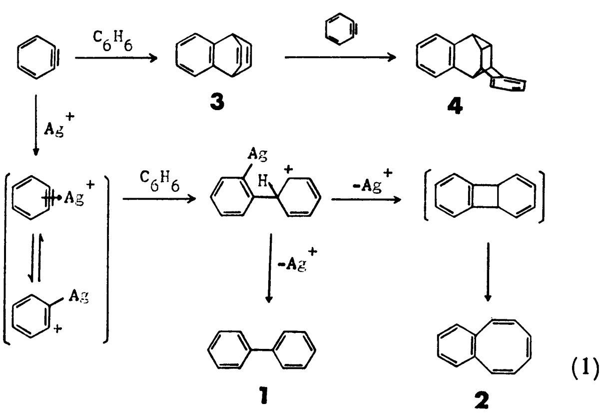
The presence of silver perchlorate changed the products in the reaction of benzyne with substituted benzene (anisole, toluene, chlorobenzene or methyl benzoate) to increase biphenyl and/or benzylidyne trifluoride derivatives by the sacrifice of benzobicyclo[2.2.2]octatriene derivatives. In the case of toluene, *o*-methylbiphenyl (**15**) and 6-methylbenzocyclooctene (**14**) were considered to be formed *via* common intermediate. These results were well explained by an assumption of benzyne-silver cation complex. From competition experiments, it was concluded that benzyne-silver cation complex assumed here had a stronger electrophilicity than benzyne itself.

In the previous paper, we reported the reactions of benzyne with substituted benzenes in the absence of a silver salt to yield benzobicyclo[2.2.2]octatriene derivatives.[1] Stiles *et al.* reported the reaction of benzyne with benzene giving biphenyl (**1**), benzocyclooctene (**2**), benzobicyclo[2.2.2]octatriene (**3**) and one two to one adduct **4**.[2] The addition of Ag^+ in the reaction of benzyne with benzene was reported by Friedman to increase **1** and **2** by the sacrifice of **3**.[3] We also reported that the addition of Hg^+, Hg^{2+}, Sn^{2+}, Co^{2+}, or V^{3+} changed the product distribution in the reaction of benzyne with benzene.[4] Friedman proposed a cationic mechanism of benzyne-silver cation complex to explain the change of the product distribution in the reaction of benzyne with benzene in the presence of a silver salt (Eq. 1).[3] Vedejs *et al.* supported the cationic nature of benzyne-silver cation complex from the result of the reaction of benzyne with cyclooctatetraene in the presence of a silver salt.[5]



(1)

In this paper, we wish to report the products and the relative reactivities of substituted benzenes treated with benzyne in the presence of silver perchlorate and to discuss the nature of benzyne in the presence of silver cation.

Results

The thermolysis of benzenediazonium-2-carboxylate (**6**), prepared from anthranilic acid (**5**), was carried out in an excess of substituted benzene (anisole, toluene, chlorobenzene, methyl benzoate or benzylidyne trifluoride) in the presence of silver perchlorate. The products are shown in Scheme 1 and the product compositions in the typical runs are summarized in Table 1.

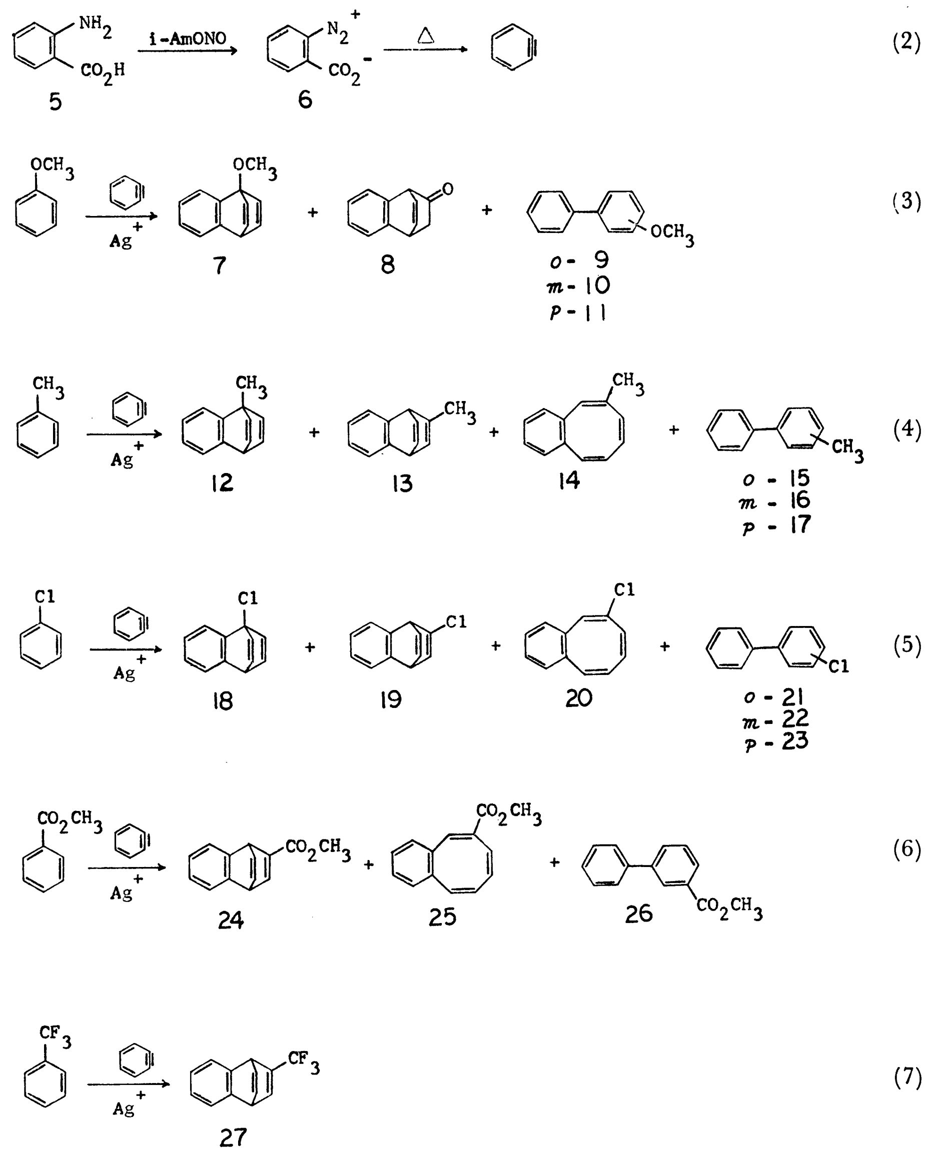
The reaction of benzyne with anisole in the presence of silver perchlorate gave methoxybiphenyls (**9**—**11**), 1-methoxybenzo[2,3]bicyclo[2.2.2]octatriene (**7**) and benzobicyclo[2.2.2]octadienone (**8**) but did not give benzocyclooctene derivatives.

Toluene gave methylbiphenyls (**15**—**17**), 1-methylbenzo[2,3]bicyclo[2.2.2]octatriene (**12**), 2-methylbenzo-[5,6]bicyclo[2.2.2]octatriene (**13**) and hydrocarbon **14**. **14** was a colorless oil and the molecular peak of its mass spectrum was observed at 168 (*m/e*), indicating **14** to be an one to one adduct of benzyne and toluene. IR spectrum of this compound was similar to that of benzocyclooctene (**2**)[6] in the range of 850—650 cm^{-1}. NMR spectrum of **14** in CCl_4 with 100 MHz showed the ratio of aromatic, olefinic and aliphatic protons to be 4: 3: 3. These observations may indicate **14** to be one of methylbenzocyclooctenes. For comparison, NMR spectra of **14** and **2**[7] are shown in Table 2. Only 6-methylbenzocyclooctene can well explain the NMR spectrum of **14**.

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

Substrate (ml)	5(g)	$AgClO_4$ (mg)	Product composition (%)					
Anisole(500)	3	75.0	**7** 10.3	**8** 2.7	**9** 74.5	**10** 1.4	**11** 11.1	
Toluene(170)	3	35.7	**12** 3.3	**13** 7.8	**14** 7.7	**15** 54.3	**16** 18.6	**17** 8.1
Chlorobenzene(200)	1	166	**18** 1.5	**19** 11.1	**20** 68.0	**21** 15.8	**22** 1.0	**23** 2.6
Methyl benzoate(50)	1	115.7	**24** 7.5	**25** 59.6	**26** 32.9			
Benzylidyne trifluoride(50)	1	301	**27** 100					

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



Scheme 1. The products of the reactions of benzyne with substituted benzenes in the presence of silver perchlorate.

The yields of **12**+**13**, **14**, **15**, **16**, and **17** were 2, 4, 31, 10, and 5%, respectively, based on benzyne generated.

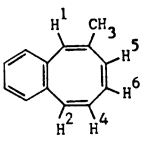
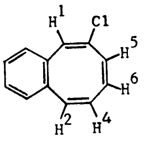
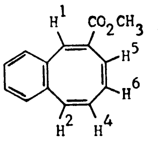
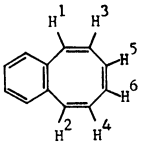
From chlorobenzene, 1-chlorobenzo[2,3]bicyclo[2.2.2]octatriene (**18**), 2-chlorobenzo[5,6]bicyclo[2.2.2]octatriene (**19**), chlorobiphenyls (**21**—**23**) and compound **20** were obtained. On the basis of the NMR spectrum (Table 2), **20** was determined to be 6-chlorobenzocyclooctene.

In the case of methyl benzoate, the decomposition of benzenediazonium-2-carboxylate (**6**) was markedly retarded by silver perchlorate. Heating of a mixture of **6** prepared from 1 g of **5**, 50 ml of methyl benzoate and 115 mg of silver perchlorate at 55 °C for 13 h did not decompose the precipitates of **6** appreciably and additional heating of the mixture at 90 °C for 9 h gave only small amounts of products. Gas chromatographic analysis of the reaction mixture showed the presence of six products, methylbenzo[5,6]bicyclo[2.2.2]octatriene-2-carboxylate (**24**), methyl 3-biphenylcarboxylate (**26**), compound **25**, one undetermined compound, phenyl benzoate and phenyl salicylate.[2] The latter two products were not the products from benzyne and methyl benzoate,[1] and the undetermined compound was not considered to be a one to one adduct of benzyne and methyl benzoate because of its long retention time in gas chromatography. Compound **25** was considered to be benzocyclooctene derivative based on the NMR and IR spectra, and we determined **25** to be methyl 6-benzocyclooctenecarboxylate, tentatively (Table 2).

From benzylidyne trifluoride, only 2-trifluoromethylbenzo[5,6]bicyclo[2.2.2]octatriene (**27**), biphenylene and phenyl benzoate were obtained, but biphenyl or benzocyclooctene derivatives were not obtained.

The effects of the concentration of silver perchlorate on the distributions of the products of biphenyl and/or benzocyclooctene derivatives were examined, in the cases of anisole, toluene and chlorobenzene. The results

Table 2. NMR spectra of **14**,[a] **20**,[a] **25**,[8] and **2**[b]

Compound	Proton	Chemical shift (τ)
 **14**	Aromatic H	2.95—3.3 (m, 4H)
	H^1	3.74 (d, J_{H^1,CH_3}=1.2 Hz, 1H)
	H^2	3.52 (d, J_{H^2,H^4}=11.7 Hz, 1H)
	H^4	4.03 (br d, 1H)
	H^5, H^6	4.24 (br s, 2H)
	CH_3	8.12 (d, 3H)
 **20**	Aromatic H	2.7—3.2 (m, 4H)
	H^1	3.29 (s, 1H)
	H^2	3.40 (d, J_{H^2,H^4}=10.9 Hz, 1H)
	H^4	3.92 (br d, 1H)
	H^5, H^6	4.10 (br s, 2H)
 **25**	Aromatic H	2.7—3.2 (m, 4H)
	H^1	2.30 (s, 1H)
	H^2	3.45 (d, J_{H^2,H^4}=11.6 Hz, 1H)
	H^4, H^5, H^6	3.8—4.15 (m, 3H)
	CH_3	6.21 (s, 3H)
 **2**	H^1, H^2	3.39, 3.51
	H^3, H^4	3.94, 4.06
	H^5, H^6	4.13

a) With 1% TMS as an internal standard in CCl_4, 60 MHz (**14** and **20**) or 100 MHz (**25**). Abbreviations are: s, singlet; d, doublet; m, multiplet; br, broad. b) The values reported in Ref. 7, 100 MHz.

Table 3. The effect of the concentration of silver perchlorate on the distribution of methoxybiphenyls in the reaction of benzyne with anisole

Run	**5** g	Anisole ml	$AgClO_4$/**5** mg/g	Distribution (%)		
				o-(**9**)	*m*-(**10**)	*p*-(**11**)
1	3	500	25	85.7	1.6	12.7
2[a]	1	33	28	86.4	1.3	12.3
3[a]	1	25	47	91.6	0	8.4

a) Result from competition reaction with benzene.

are shown in Tables 3—5.

Competition reactions were carried out to investigate the relative reactivities of benzyne toward substituted benzenes in the presence of silver perchlorate. The relative reactivities were calculated from the amounts of biphenyl and benzocyclooctene derivatives produced, since they were considered to be the products concerned with silver perchlorate (*vide infra*). The results are shown in Table 6.

Discussion

In the presence of silver perchlorate, the reactions of benzyne with anisole, toluene, chlorobenzene and methyl benzoate, as well as benzene,[3] gave predominantly biphenyl and/or benzocyclooctene derivatives, in marked contrast to the results in the absence of silver perchlorate where the main products were benzobicyclo[2.2.2]octatriene derivatives.[1] In the case of benzylidyne trifluoride having a strong electron-withdrawing

Table 4. The effect of the concentration of silver perchlorate on the distribution of methylbiphenyls and 4-methyl-1,2-benzocyclooctene in the reaction of benzyne with toluene

Run	**5** g	Toluene ml	$AgClO_4$/**5** mg/g	Distribution (%)				
				14	*o*-(**15**)	**14**+**15**	*m*-(**16**)	*p*-(**17**)
1	3	170	11.9	8.6	61.3	69.9	20.9	9.3
2[a]	1	100	16.2	16.9	55.0	71.9	19 2	8.9
3	3	500	18.3	27.9	43.4	71.3	19.4	9.4
4	1	200	21	18.8	56.2	75.0	15.1	9.9
5	2	200	27	7.2	62.4	69.6	19.5	10.9
6[a]	1	50	40	9.4	61.2	70.6	20.0	9.4

a) Result from competition reaction with benzene.

Table 5. The effect of the concentration of silver perchlorate on the distribution of chlorobiphenyls and 6-chlorobenzocyclooctene in the reaction of benzyne with chlorobenzene

Run	**5** g	Chlorobenzene ml	$AgClO_4$/**5** mg/g	Distribution (%)				
				20	*o*-(**21**)	**20**+**21**	*m*-(**22**)	*p*-(**23**)
1	1	150	9.1	73.3	25.0	98.3	0	1.7
2	3	400	29	68.4	28.4	96.8	1.1	2.1
3	1	150	53	78.3	18.9	97.2	0.9	1.9
4	1	150	165.3	82.0	18.0	100	0	0
5[a]	1	400	329	77.8	18.0	95.8	1.2	3.0

a) Result from competition reaction with benzene.

TABLE 6. RELATIVE REACTIVITIES OF SUBSTITUTED BENZENES TO BENZENE TOWARD BENZYNE IN THE PRESENCE OF SILVER PERCHLORATE

Substituted benzene	ml	Benzene ml	**5**	$AgClO_4$ mg	k_H/k_R[a)]
$PhOCH_3$	25	100	1	47.3	5.17
$PhOCH_3$	33	99	1	28.0	5.26
$PhCH_3$	100	100	1	16.2	2.39
$PhCH_3$	25	100	1	40.0	3.10
PhCl	400	20	1	329	0.0662
PhCl	200	10	1	166	0.0711

a) Relative reactivity of substituted benzene to benzene.

group, silver perchlorate did not change the product. Thus, it is concluded that silver cation catalyzes the formations of biphenyl and/or benzocyclooctene derivatives in the reactions of benzyne with substituted benzenes, unless the substituent is a strong electron-withdrawing group such as CF_3.

For toluene, the distribution of 6-methylbenzocyclooctene (**14**) and *o*-methylbiphenyl (**15**) was affected by the concentration of silver perchlorate, but the sum of **14** and **15** was almost constant (Table 4). This may indicate that 6-methylbenzocyclooctene and *o*-methylbiphenyl are formed *via* a common intermediate. Similar situation was observed in the distribution of 6-chlorobenzocyclooctene (**20**) and *o*-chlorobiphenyl (**21**) in the case of chlorobenzene (Table 5). These observations can be well explained by benzyne-silver cation complex proposed by Friedman[3)] (Eq. 1). Namely benzyne-silver cation complex attacks ortho position of a substituted benzene(toluene or chlorobenzene) forming the common intermediate **28** and then leaving of silver cation together with carbon–carbon bond formation gives 6-substituted benzocyclooctene (Eq. 9) or leaving of silver cation together with proton transfer gives *o*-substituted biphenyl (Eq. 8). In this mechanism the formation of 5-substituted benzocyclooctene is also possible, but it may be inhibited by the steric effect of a substituent. There is no satisfactory explanation of the effect of the concentration of silver perchlorate on the distribution of **14** and **15**.

Orientations of Benzyne-Silver Cation Complex to Substituted Benzenes. In the case of toluene, both of 6-methylbenzocyclooctene (**14**) and *o*-methylbiphenyl (**15**) should be included in ortho oriented products, since they were considered to be formed *via* the common intermediate. Similar situation was present in 6-chlorobenzocyclooctene (**20**) and *o*-chlorobiphenyl (**21**) from chlorobenzene. Table 7 shows the orientations of benzyne-silver cation complex to anisole, toluene and chlorobenzene, together with those of phenyl cation[8)] and phenyl radical.[9–11)] Obviously, the orientations of benzyne-silver cation complex were mostly ortho and very different from those of phenyl cation and phenyl radical. Therefore, we can not discuss the nature of benzyne-silver cation complex only from the distribution of the products from substituted benzene, although Friedman suggested that the distribution of isomeric methylbiphenyls should reveal the nature of benzyne–silver cation complex.[3)]

TABLE 8. THE RELATIVE REACTIVITIES OF BENZYNE–SILVER CATION COMPLEX TOWARD THE ORTHO POSITIONS OF SUBSTITUTED BENZENES (F_o)

Substituent	OCH_3	CH_3	H	Cl
F_o	16.5	7.6	1	0.247

Relative Reactivities of Benzyne-Silver Cation Complex toward Substituted Benzenes. From Tables 6 and 7, the relative reactivities of benzyne-silver cation complex toward the ortho positions of substituted benzenes (partial rate factor, F_o) were estimated (Table 8).[12)] As is seen, F_o changed about 65-fold with changing substituent from Cl to OCH_3. Hammett plots of log F_o *vs.* σ_p^+ are shown in Fig. 1. A linear relationship was roughly observed between log F_o and σ_p^+, and the reaction constant, ρ, was estimated to be -2.0. A comparison of ρ values for several reactions is made in Table 9. The absolute value of the present ρ is much smaller than that for nitration of substituted benzenes but twice as large as that for cationic phenylation of substituted benzenes and slightly larger than that for 1,4-addition of

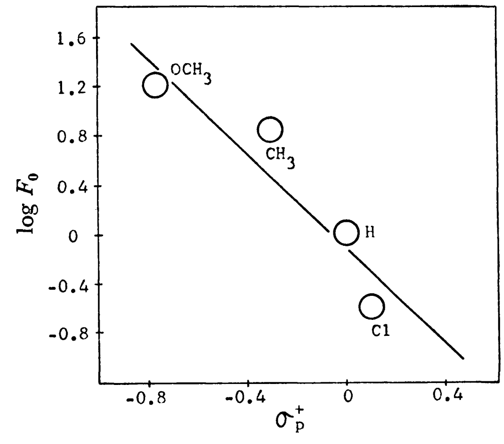


Fig. 1. The Hammett plots for ortho addition reactions of benzyne–silver cation complex to substituted benzenes.

TABLE 7. ORIENTATIONS OF BENZYNE–SILVER CATION COMPLEX, PHENYL CATION AND PHENYL RADICAL

Reagent	$PhOCH_3$			$PhCH_3$			PhCl		
	o	*m*	*p*	*o*	*m*	*p*	*o*	*m*	*p*
Benzyne–Ag^+ (45 °C)[a)]	88	1	11	71	19	10	98	0.5	1.5
$PhN_2^+BF_4^-$ (in DMSO, 40 °C)[b)]	56.4	12.1	31.8	47.3	21.1	31.6	42.8	24.0	27.8
$(PhCO_2)_2$ (80 °C)	67[c)]	28[c)]	5[c)]	66.5[d)]	19.2[d)]	14.3[d)]	50.1[e)]	31.6[e)]	18.3[e)]

a) This work. b) Ref. 8. c) Ref. 9). d) Ref. 10. e) Ref. 11.

TABLE 9. REACTION CONSTANTS FOR SEVERAL REACTIONS OF SUBSTITUTED BENZENES

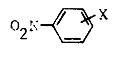
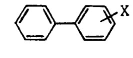
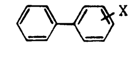
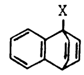
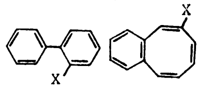
Reagent	Product	Kind of substituent constant	ρ	Reference
HNO_3–H_2SO_4 (in CH_3NO_2 or Ac_2O, 25 °C)		σ^+	−6.53	13
$PhN_2^+BF_4^-$ (40 °C)		σ^+	−1.0	14
$(PhCO_2)_2$ (80 °C)		σ_m	0.05	9, 15
Benzyne (≈45 °C)		σ_p^+	−1.79	1
Benzyne–Ag^+ (≈45 °C)		σ_p^+	−2.0	This work

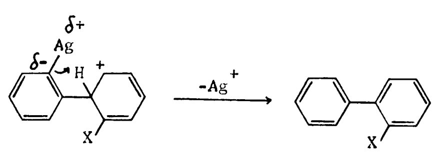
TABLE 10. PERCENTAGES OF THE FORMATIONS OF 6-SUBSTITUTED BENZOCYCLOOCTENE (6-BCOT) AND *o*-SUBSTITUTED BIPHENYL (*o*-BP) IN THE REACTION OF BENZYNE–SILVER CATION COMPLEX WITH SUBSTITUTED BENZENE

Substituent	OCH_3	CH_3	H[a)]	Cl
4-BCOT	0	10—39	29—46[b)]	70—92
o-BP	100	90—61	71—54[c)]	30— 8

a) Refs. 2 and 3. b) Benzocyclooctene (**2**).
c) Biphenyl (**1**).

benzyne to substituted benzenes. Thus, it is concluded that benzyne-silver cation complex has a larger electrophilicity than phenyl cation and benzyne itself. This supports the cationic mechanism proposed by Friedman (Eq. 1).[3)]

Substituent Effect on the Formation of Benzocyclooctene vs. Biphenyl Derivatives. Table 10 shows the percentages of 6-substituted benzocyclooctene (6-BCOT) and *o*-substituted biphenyl (*o*-BP) from the reactions of benzyne–silver cation complex with substituted benzenes, together with those of benzocyclooctene and biphenyl from benzene. Obviously, the formation of 6-BCOT or *o*-BP depends on the electron-donating (or electron-withdrawing) nature of a substituent of a substituted benzene. Namely, anisole having an electron-donating substituent gave exclusively *o*-methoxybiphenyl, while chlorobenzene having an electron-withdrawing substituent gave predominantly 6-chlorobenzocyclooctene. These results can be explained by the following way.



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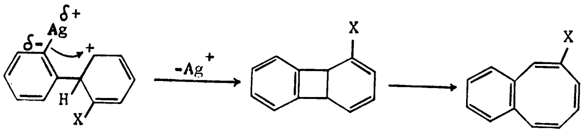
(8)



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(9)

An electron-donating substituent stabilizes the intermediate cyclohexadienyl cation **28** and may reduce the electrophilicity of the cation to the carbon attached to silver. Thus, elimination of silver cation with proton transfer becomes predominant to increase the formation of *o*-substituted biphenyl (Eq. 8). On the other hand, an electron-withdrawing substituent may be reduce the electrophilicity of the cation **28** and elimination of silver cation with cyclization becomes more predominant to increase the formation of 6-substituted benzocyclooctene (Eq. 9). A very strong electron-withdrawing substituent like CF_3 destabilizes the intermediate cyclohexadienyl cation and the cation may not be formed. Thus, the fact that benzylidyne trifluoride did not give biphenyl or benzocyclooctene derivatives could be understood.

Experimental

General Procedure of the Reaction of Benzyne with Substituted Benzene in the Presence of Silver Perchlorate. Benzenediazonium-2-carboxylate (**6**), prepared from 1—3 g of anthranilic acid (**5**) by the method described elsewhere,[1)] was stirred in 25—500 ml of a substituted benzene in the presence of a proper amount of silver perchlorate at about 45 °C. After gas evolution had ceased (20—64 h), the mixture was washed with aq sodium hydrogencarbonate soln and water, and dried on calcium chloride. After removal of the most of substituted benzene, the residue was analyzed by gas chromatography (PEG 20 M, Silicon DC 550).

Reaction of Benzyne with Anisole in the Presence of Silver Perchlorate. After the treatment as described above, gas chromatographic analysis (PEG 20 M, Silicon DC 550) of the concd crude mixture showed the presence of 1-methoxybenzo[2,3]bicyclo[2.2.2]octatriene (**7**), benzobicyclo[2.2.2]octadienone (**8**), methoxybiphenyls (**9**—**11**) and a small amount of phenyl benzoate (6% of the total products). All products were consistent with the authentic samples on the basis of the IR spectra and the retention times on gas chromatography, respectively.

Reaction of Benzyne with Toluene in the Presence of Silver Perchlorate. After the treatment as described above, gas chromatographic analysis (PEG 20 M, Silicon DC 550) of the concd crude mixture revealed the presence of 1-methylbenzo[2,3]bicyclo[2.2.2]octatriene (**12**). 2-methylbenzo[5,6]bicyclo[2.2.2]octatriene (**13**), methylbiphenyls (**15**—**17**) and 4-methyl-1,2-benzocyclooctene (**14**). **14** was isolated by preparative gas chromatography (PEG 20 M) from the distillate of the crude mixture at 57 °C/8 Torr. **14** was a colorless oil: MS, *m*/*e* (rel intensity) 168 (M^+, 92), 167 (49), 165 (28), 153 (100), 152 (50), 141 (21), 128 (44), and 115 (30); IR (neat), 1490, 1430, 830, 790, 760, 725, and 690 cm^{-1}.

Other products were all consistent with the authentic samples on the basis of the IR spectra and the retention times on gas chromatography (PEG 20 M, Silicon DC 550), respectively.

In another experiment using **6** prepared from 2 g (14.6 mmol) of **5**, 200 ml of toluene and 54 mg of silver perchlorate, evolution of 14.4 mmol of gases (N_2 and CO_2, 50% yield of benzyne based on **5** used) was observed. Gas chromatographic analysis of the crude mixture added with weighed diphenylmethane indicated the yields of **12**+**13**, **14**, **15**, **16**, and **17** to be 2, 4, 31, 10, and 5%, respectively, based on benzyne generated.

Reaction of Benzyne with Chlorobenzene in the Presence of Silver Perchlorate. Gas chromatographic analysis (PEG 20 M) of the concd crude mixture indicated the presence of 1-chlorobenzo[2,3]bicyclo[2.2.2]octatriene (**18**), 2-chlorobenzo[5,6]-bicyclo[2.2.2]octatriene (**19**), 6-chlorobenzocyclooctene (**20**) and chlorobiphenyls (**21**—**23**) together with phenyl benzoate (10—20% of the total products). After distillation of the crude mixture at 47—53 °C/3 Torr, **20** was isolated by preparative gas chromatography (PEG 20 M) as a pale yellow oil: n_D^{16} 1.6226; MS, *m/e* (rel intensity) 190 (M+2, 16), 188 (M^+, 47), 154 (28), 153 (100), 152 (58), 151 (36), 150 (14), 128 (11), 127 (14), and 126 (13); IR (neat), 1495, 1100, 830, 795, 770, and 725 cm^{-1}. Calcd for $C_{12}H_9Cl$: C, 76.40; H, 4.81; Cl, 18.79%. Found: C, 76.38; H, 4.74; Cl, 18.52%.

Other products were all consistent with the authentic samples on the basis of the IR spectra and the retention times on gas chromatography (PEG 20 M), respectively.

Reaction of Benzyne with Methyl Benzoate in the Presence of Silver Perchlorate. A mixture of **6** prepared from 1 g of **5**, 116 mg of silver perchlorate and 50 ml of methyl benzoate was heated at 55 °C for 13 h and then 90 °C for 9 h, but only small amount of **6** was decomposed. The most of methyl benzoate was distilled off at 100 °C using 10 cm of packed column and then the residue was dissolved in ether. The ether soln was washed with aq ammonia and sat sodium chloride soln and dried on sodium sulfate, and then concd. Gas chromatographic analysis (Silicon DC 550) of the residue showed six peaks. First three peaks were due to phenyl benzoate (29% of the total products), 2-methoxycarbonylbenzo[5,6]bicyclo-[2.2.2]octatriene (**24**) (3% of the total products) and phenyl salicylate (13% of the total products), in the order of retention time. These products were all consistent with the authentic samples on the basis of the IR spectra and the retention times on gas chromatography (Silicon DC 550), respectively. The fourth peak (22% of the total products) was tentatively determined to be that of methyl 6-benzocyclooctenecarboxylate (**25**) which was isolated by preparative gas chromatography (Silicon DC 550) after column chromatography through silica gel with benzene. **25** was a pale yellow oil: IR (neat), 1715, 1240, 1065, 800, 755, 730, and 710 cm^{-1}. The fifth peak was that of methyl 3-biphenylcarboxylate (**26**) which was consistent with authentic sample on the basis of the IR spectrum and the retention time on gas chromatography. The last peak (20% of the total products) had a 2—3 times longer retention time than the other five peaks. This compd had a IR absorption at 1730 cm^{-1} but the structure was uncertain.

Reaction of Benzyne with Benzylidyne Trifluoride in the Presence of Silver Perchlorate. Reaction of **6** prepared from 1 g of **5**, with 50 ml of benzylidyne trifluoride in the presence of 301 mg of silver perchlorate gave 2-trifluoromethylbenzo[5,6]bicyclo-[2.2.2]octatriene (**27**) (30% of the total products), biphenylene (38% of the total products) and phenyl benzoate (32% of the total products). All products were consistent with authentic samples based on the IR spectra and the retention times on gas chromatography (PEG 20 M, Silicon DC 550).

Competition Reactions of a Series of Substituted Benzenes toward Benzyne in the Presence of Silver Perchlorate. Competition reactions of a series of substituted benzenes toward benzyne in the presence of silver perchlorate were carried out under usual conditions. Relative reactivities of substituted benzenes were estimated from the calibrated gas chromatographic analyses (PEG 20 M, Silicon DC 550) of the crude reaction mixtures. The results are shown in Table 6.

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