Cycloadditions of Benzyne with Cyclic Olefins. Influence of Catalytic Silver[1]

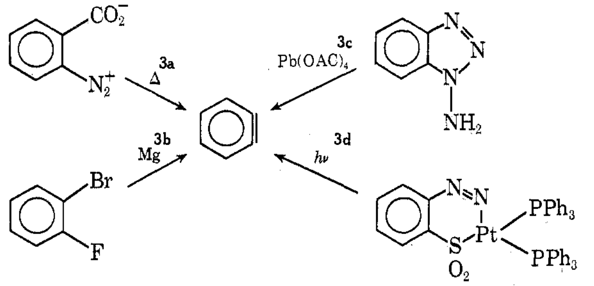
PHILLIP CREWS* AND JOHN BEARD

Division of Natural Sciences, University of California at Santa Cruz, Santa Cruz, California 95060

Received August 8, 1972

The effect of added Ag^+ upon the course of benzyne addition to cyclic and acyclic polyenes is examined. In the presence of catalytic amounts of Ag^+, benzyne reacts with cyclic six- and seven-membered di- and triolefins to give almost exclusive formation of 2 + 4 type products, but with acyclic systems little or no effect is observable on the product compositions. A mechanism is proposed to account for both the catalytic effect and the observed products as a function of olefin type.

There are a variety of methods described in the literature for the preparation of benzyne, and it has been shown that the character of benzyne obtained from rather diverse sources is identical.[2] A sampling of some of the different conditions that can be used to generate benzyne is shown below.[3]

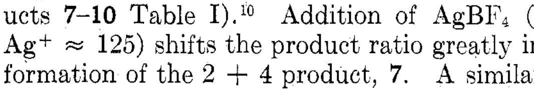


It seems intriguing that, in comparison to the above situation, minute amounts of silver salts[4] or trace metals of unknown origin[5] have been identified as being able to effect significant changes in the product distributions of benzyne additions to olefins. The source of this effect has been uniformly attributed to benzyne capture of Ag^+ giving a complex which is presumed to be far more electrophilic than uncomplexed benzyne.[4-7] If such a proposal is valid it would imply that catalytic effects of this type might be a useful, general feature of cycloaddition reactions.[8]

There is reason to believe that the origin of the Ag^+ catalytic effect might be different than previously proposed. The reaction of benzyne with excess benzene (9.8 mol) gives mainly a 2 + 4 product (benzobarrelene, 85%), but addition of Ag^+ ($\sim 10^{-5}$ mol) reduces the amount of 2 + 4 reaction (55%) while increasing the amounts of other products (benzocyclooctatetraene, 17%; biphenyl, 22%).[4] The previously proposed scheme involving the capture of Ag^+ by benzyne followed by reaction with benzene would imply that benzyne is able to survive more than 10^4 collisions with benzene before colliding with silver;[4] however, this would seem to be an unusual requirement, since benzyne is regarded as being a "hot" electrophile especially in comparison to reactive dienophiles such as maleic anhydride.[9] We feel that a somewhat different scheme provides a more attractive rationale for this effect. Moreover, our preliminary experiments involving benzyne addition to simple cyclic olefins with added Ag^+ indicated that the product types are different than would be predicted by extrapolation from the known benzyne–Ag^+ reactions with benzene and cyclooctatetraene.

Results

We have recently identified the primary influences on the relative partitioning of benzyne among three major paths: 2 + 4, 2 + 2, and ene cycloaddition.[10] Benzyne undergoes concerted 2 + 4 and ene reaction, but stepwise 2 + 2 cycloaddition, and none of these reaction types appear to share a common reaction surface. We have observed that reaction of 1,3-cyclohexadiene (**1**) with benzyne generated from either benzenediazonium 2-carboxylate (**6a**) or 1,2,3-benzothiadiazole 1,1-dioxide (**6b**) yields significant amounts of products from each of these types of reactions (products **7–10** Table I).[10] Addition of $AgBF_4$ (benzyne/Ag^+ ≈ 125) shifts the product ratio greatly in favor of formation of the 2 + 4 product, **7**. A similar trend is observed when **6a** is decomposed in the presence of 1,3-cycloheptadiene (**2**) and 1,3,5-cycloheptatriene (**3**). In the absence of Ag^+ 1,3-cycloheptadiene yields 2 + 4 product **11** (70%) and 2 + 2 product **12** (28%), whereas cycloheptatriene gives no 2 + 4 product **13**, but 2 + 2 product **15** (55%) and ene product **14** (45%).[10] Repeating these reactions in the presence of Ag^+ causes an increase in the relative amounts of 2 + 4 products to 89% from cycloheptadiene and 100% from cycloheptatriene.



	% products	
X	No Ag^+	Ag^+
7 $(CH_2)_2$	48	97
11 $(CH_2)_3$	70	89
13 $CH_2CH{=}CH$	0	100

---

[1] (a) For a preliminary report see P. Crews, M. Loffgren, and D. J. Bertelli, *Tetrahedron Lett.*, 4697 (1971). (b) Support from the UCSC Committee on Research and from the Frederick G. Cottrell Fund of the Research Corp. is gratefully acknowledged.

[2] (a) R. Huisgen and R. Knorr, *Tetrahedron Lett.*, 1017 (1963); (b) B. H. Klanderman and T. R. Criswell, *J. Amer. Chem. Soc.*, **91**, 510 (1969).

[3] (a) L. Friedman and F. M. Logullo, *Org. Syn.*, **48**, 12 (1969); (b) G. Wittig and E. Benz, *Angew. Chem.*, **70**, 166 (1958); (c) C. D. Campbell and C. W. Rees, *Proc. Chem. Soc.*, 296 (1964); (d) T. L. Gilchrist, F. J. Graveling, and C. W. Rees, *Chem. Commun.*, 821 (1968).

[4] L. Friedman, *J. Amer. Chem. Soc.*, **89**, 3071 (1967).

[5] E. Vedejs and R. A. Shepard, *Tetrahedron Lett.*, 1863 (1970); E. Vedejs, *ibid.*, 2633 (1968).

[6] P. Warner, *ibid.*, 723 (1971).

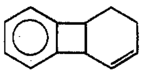
[7] L. A. Paquette, *Chem. Commun.*, 1076 (1971).

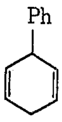
[8] In this regard it was reported in a recent theoretical study of electrophilic additions to olefins that Ag^+ complexation to an olefin should not cause enhanced electrophilic character as judged by the minimal perturbation calculated for the carbon framework of the π complex *vs.* free ethylene: R. D. Bach and H. F. Henneike, *J. Amer. Chem. Soc.*, **92**, 5589 (1970).

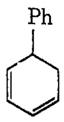
[9] (a) R. W. Hoffmann, "Dehydrobenzyne and Cycloalkynes," Academic Press, New York, N. Y., 1967, p 2; (b) B. H. Klanderman and T. R. Criswell, *J. Org. Chem.*, **34**, 3426 (1969).

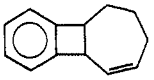
[10] P. Crews and J. Beard, *J. Org. Chem.*, **38**, 522 (1973), and references cited therein.

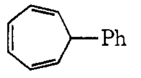
Table I
Reactions of Benzyne with Cyclic Olefins with and without Ag^+

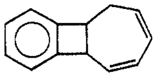

10


8


9


12


14


15

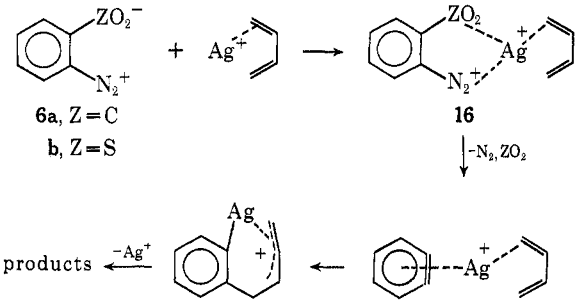
Benzyne precursor	Olefin	Benzyne[a]/ silver	Net yield, %	Relative % products 7	8	9	10
6a	1,3-Cyclohexadiene	*b*	36	48	21	18	13
6a	1,3-Cyclohexadiene	125/1	6	79	8	7	6
6a	1,3-Cyclohexadiene	13/1	2	81	6	7	6
6b	1,3-Cyclohexadiene	*b*	28	51	13	22	14
6b	1,3-Cyclohexadiene	31/1	35	97	0	0	3
				11	Ene	**12**	
6a	1,3-Cycloheptadiene	*b*		70	2	28	
6a	1,3-Cycloheptadiene	16/1		89	1	10	
				13	**14**	**15**	
6a	1,3,5-Cycloheptatriene	*b*	36	0	45	55	
6a	1,3,5-Cycloheptatriene	16/1	20	100			

[a] Ratio based on amount of benzyne precursor used (*i.e.*, anthranilic acid). [b] No silver, results from preceding paper, ref 10.

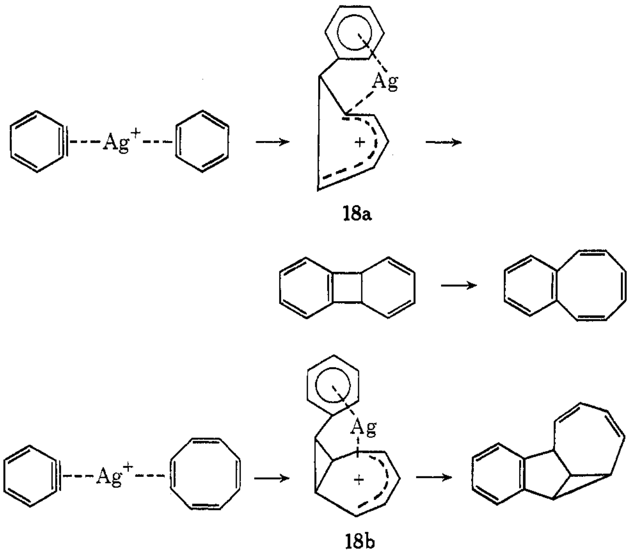
In the above reactions with added Ag^+ we observed the net hydrocarbon yields to be dependent upon the benzyne precursor and/or the amount of Ag^+ used. The net yields from reactions with **6a** are drastically reduced upon addition of Ag^+ (from cyclohexadiene with no silver, net yield 36%; benzyne/$Ag^+ \approx 125$, net yield 6.5%), and, if the amount of Ag^+ added approaches the molar amount of benzyne precursor, no hydrocarbon products are obtained.[11] Alternatively, the reaction with **6b** is homogeneous and the net hydrocarbon yields from reactions with or without silver are almost identical (Table I). This can be taken as an indication that with added Ag^+ increased formation of 2 + 4 products occurs at the expense of ene and 2 + 2 reactions.

Discussion

Rather than assume capture of Ag^+ by benzyne we proposed the scheme below as a rationalization for the Ag^+ catalysis. The major points of this mechanism are a Ag^+–olefin complex which unites with the benzyne precursor **6** to give **16**, which decomposes to the benzyne–olefin complex **17**.[12] To account for the catalytic nature of the Ag^+ effect it must be assumed that the rate of decomposition of **16** and **17** is considerably faster for free **6a** or **6b**.[14] Finally, a stepwise electrophilic attack by the free double bond in the s-cis conformation leads to intermediate **18**, which is identical with that proposed earlier.[4,7]



In a previous publication Paquette pointed out that the seemingly divergent results of Ag^+-promoted benzyne reaction with benzene and cyclooctatetraene could be justified by assuming that intermediates **18a,b** collapse *via* partial bridging of silver to the electropositive terminus of the pentadienyl group followed by ejection of Ag^+ and C–C bond formation as shown below. We find that a similar argument can partially explain our observations with unsaturated six- and seven-membered ring systems. HMO calculations on pentadienyl cation[15] indicate the 1 and 3 positions to be almost equally as electron deficient. If, by analogy to the scheme above, the benzyne–Ag^+–cycloheptatriene complex were to decompose *via* intermediate **18c**, compound **15** would be the final product; however, none of this material is observed. The observed formation of **13** requires partial bonding of Ag^+ to C-3 of the pentadienyl system as in **18d**, followed by collapse to the product.



Extending this reasoning to the case of the 1,3-dienes, it is seen that two kinds of propenyl cation like intermediates are possible, **18e** or **18f**; the ultimate products of these species are different, but only intermediate **18f** can account for the observed increase in 2 + 4 type products, **7** or **11**.

---

(11) Infrared spectra of the product mixtures showed carbonyl absorption indicating lactone functionality (1770 cm^{-1}).

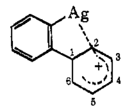
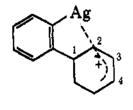
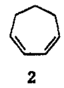
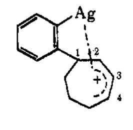
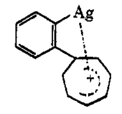
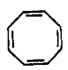
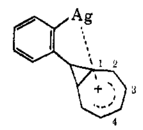
(12) The formation of a species such as **16** can be viewed as being similar to the intermediates that are isolated when **6a** or **6b** are decomposed in the presence of $(Ph_3)_4Pt$.[3d,13]

(13) C. D. Cook and G. S. Jauhal, *J. Amer. Chem. Soc.*, **90**, 1464 (1968).

(14) The catalytic role of Ag^+ in the Arndt–Eistert synthesis might be regarded as a similar situation: J. March, "Advanced Organic Chemistry," McGraw-Hill, New York, N. Y., 1968, p 809.

(15) (a) For pentadienyl cation the following electron densities are calculated: $C_1 = 0.666$, $C_2 = 1.000$, $C_3 = 0.664$. For propenyl cation electron densities are $C_1 = 0.500$; $C_2 = 1.000$.[15b] (b) A. Streitweiser, "Molecular Orbital Theory for Organic Chemistry," Wiley, New York, N. Y., 1961.

TABLE II

		C_b–C_N[a]	
Polyene	Intermediate	$N = 2$	$N = 4$
		3.0	4.1
 1		2.65	3.2
 2		2.7	1.9
 3		2.75	2.2
		2.5	2.6

[a] C_b–C_N distance is measured on a model of the intermediate between the benzene carbon σ bound to silver (C_b) and the carbon of the polyene ring (C_N).

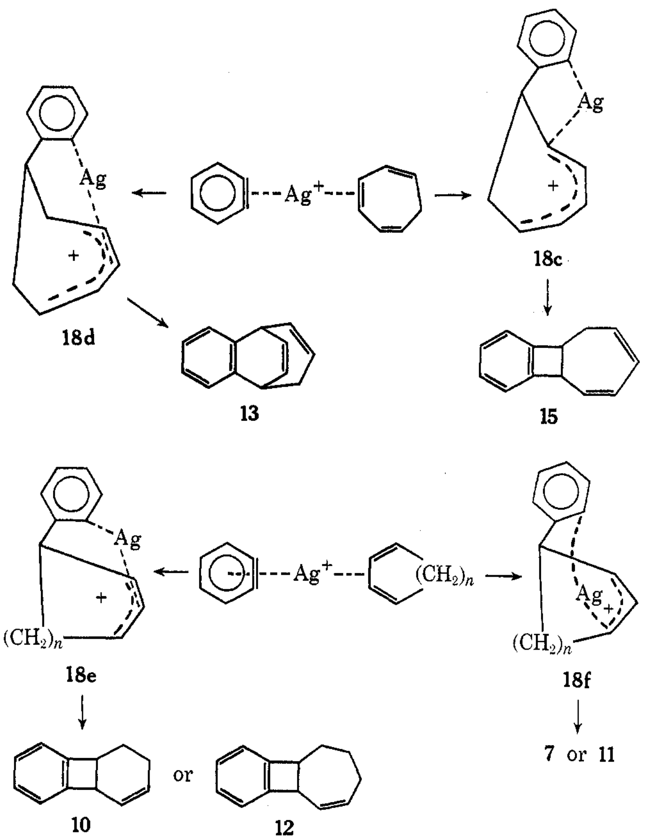
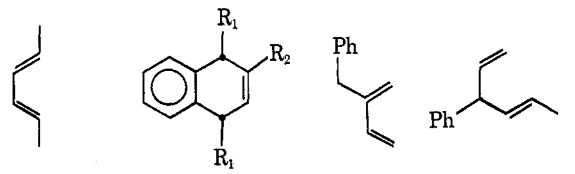


TABLE III

BENZYNE REACTIONS WITH ACYCLIC OLEFINS WITH AND WITHOUT Ag^+



5 **19a**, $R_1 = H$; $R_2 = CH_3$ **b**, $R_1 = CH_3$; $R_2 = H$ **20** **21**

Olefin	Benzyne[a]/ silver	Net yield, %	Relative % products **19a**	**20**	Ref
Isoprene (4)	*b*		41	59[c]	This work
			45	55[d]	
Isoprene (4)	*b*	28	45	55	*e*
Isoprene (4)	46/1		48	52[c]	This work
			49	51[d]	
			19b	**21**	
5	*b*		90	10[c]	This work
5	*b*	74	85	6	16
5	61/1	3	85	4[c]	This work

[a] Ratio based upon the amount of **6a** used. [b] No silver. [c] Product analysis by vpc. [d] Product analysis by nmr. [e] G. Wittig and H. Dürr, *Justus Liebigs Ann. Chem.*, **672**, 55 (1964).

We examined Drieding models of the σ-bonded silver intermediates, anticipating that this approach would offer some input to account for the different selectivity between intermediates observed above. In Table II are compiled the results of measurements of the distances between the benzene carbon σ bound to silver (C_b) and the polyene ring carbon (C_N). Inspection of this table reveals a striking pattern. A choice between the collapse of the two types of intermediates (*i.e.*, bond formation from C_b to either C_2 or C_4) to products seems to be dictated purely on the basis of ring closure by way of the shortest C_b–C_N bond distance. The one exception to this proposal is 1,3-cyclohexadiene, and in this case, since the two C_b–C_N bond distances are fairly close ($\Delta \approx 0.5$ Å), one might expect ring closure to occur *via* the six-membered intermediate derived from **18f** rather than through the more strained four-membered transition state from **18e**.

Two additional facts must be noted concerning the Ag^+-catalyzed benzyne addition to olefins. There is almost *no* change observable on the product distributions when acyclic systems are treated (Table III) with benzyne in the presence or absence of Ag^+. Secondly, the reaction of benzyne with 1,4-*trans*-dimethylbutadiene is observed to be stereospecific (>99%) with and without[16] Ag^+ catalysis. The data from cyclic systems indicates that the Ag^+ effect is not quenched as the diene s-cis chromophore becomes nonplanar,[17] but it would appear that this is not the case for acyclic dienes which have s-trans geometries. Based on the data of Muhs and Weiss, it would seem reasonable to assume that under our experimental conditions the complexing constants between Ag^+ and the cyclic or acyclic dienes are of the same order of magnitude.[18] Consequently, with acyclic dienes the formation of the benzyne–Ag^+–olefin complex **17** is to be expected. If this is a valid assumption, one possible rationalization for the absence of an Ag^+ catalytic effect upon product formation with acyclic dienes is that the σ-bound silver intermediate **18** is not formed (from 1- or 2-methylbutadienes), but instead intermediate **17** dissociates to

---

[16] M. Jones, Jr., and R. H. Levin, *J. Amer. Chem. Soc.*, **91**, 6411 (1969).

[17] Cyclopentatriene has a tub conformation with an angle of 40° between the planes of the double bonds: M. Traetteberg, *ibid.*, **86**, 4265 (1964).

[18] M. A. Muhs and F. T. Weiss, *ibid.*, **84**, 4697 (1962).

give free benzyne which reacts in a normal manner with the large pool of uncomplexed olefin.

Experimental Section

General.—The anthranilic acid was recrystallized from water and allowed to dry before use. The *o*-aminobenzenesulfonic acid was used as received from Aldrich Chemical Co.

Pmr spectra were determined on a JEOL JNM-PS-100 which had Pulse Fourier Transform accessories for proton observation or MH-60 or on a Varian A-56/60 spectrometer. Mass spectral measurements were run on a single-focusing Hitachi Perkin-Elmer RMU-6E instrument, and infrared spectra were run on a Perkin-Elmer 337 instrument.

Gas chromatography conditions follow: A, 20 ft DEGS (30%), 140°, 60 psi; B, 20 ft Carbowax (20%), 180°, 40 psi; C, 8 ft DEGS 140°, 60 psi; D, 8 ft Carbowax (20%), 150°, 35 psi; E, 12 ft Carbowax (20%), 140°, 40 psi. Quantitative yields were obtained by vpc with 3-phenylcyclohexene as a standard.

Benzenediazonium 2-Carboxylate (BDC).—Owing to the explosive nature of this material, preparation and reaction were conducted in a special flask described in ref 10.

BDC–1,3-Cyclohexadiene–Ag$^+$.—A silver–olefin complex of cyclohexadiene was prepared by adding $AgBF_4$ (0.11 g, 5.2 mmol) to cyclohexadiene (12.0 g, 150 mmol) followed by CH_2Cl_2 (50 ml). This mixture was allowed to stand for *ca.* 0.5 hr before use. Benzenediazonium 2-carboxylate from anthranilic acid (9.0 g, 65 mmol) in CH_2Cl_2 (100 ml) was decomposed with the silver–olefin solution by heating in a bath at 50° for 4 hr. At the end of this period the dark brown solution was filtered, washed with water (2 × 100 ml) and saturated bicarbonate (4 × 100 ml), and dried over $MgSO_4$. The solvent was evaporated, leaving a dark liquid; pentane ($\sim$50 ml) was added; and the orange solution was filtered to remove polymeric materials. Evaporation of the solvent gave a red liquid (0.88 g, 6% yield), and vpc analysis, condition A, showed four hydrocarbons (in the relative amounts in Table I) with identical retention times with those of an experiment without Ag$^+$.[10]

This same procedure was repeated exactly except that the amount of $AgBF_4$ (1.0 g, 5.2 mmol) was increased *ca.* tenfold. As before, four hydrocarbon products were observed (Table I), but the yield was greatly reduced (0.2 g, 2%).

Benzothiadiazole (6b)–1,3-Cyclohexadiene–Ag$^+$.—The procedure of Wittig and Hoffman[19] for generating **6b** from *o*-aminobenzenesulfonic acid (1.44 g, 8.7 mmol) was followed. **6b** in CH_2Cl_2 (100 ml) was decomposed without purification at 50° for 4 hr with a silver (0.055 g, 0.28 mmol)–cyclohexadiene (1.9 g, 24 mmol) solution prepared as above. The work-up as described above yielded, after chromatography on neutral alumina (hexane as eluent), a yellow liquid (0.56 g). Vpc analysis, condition A, showed two hydrocarbon products which were identified by retention times (compared to ref 10) and nmr spectra (Table I).

BDC–1,3-Cycloheptadiene–Ag$^+$.—The reaction and work-up of the reaction of benzyne derived from anthranilic acid (3.0 g, 22 mmol) with the silver ($AgBF_4$, 0.3 g, 1.4 mmol)–cycloheptadiene (6.2 g, 66 mmol) complex was carried out by the above procedure. A red liquid was obtained after chromatography on alumina (hexane as eluent). Vpc analysis, condition B, showed four products: 2 + 4 (40 min), 2 + 2 (43 min), ene product (47.5 min), and a final product which was not fully characterized (56 min). A small amount of this last material was vpc collected, and it proved to be a 1:1 adduct based upon the mass spectrum, *m/e* 170 (parent, $C_{13}H_{14}$) and additional fragments at *m/e* 142, 141, 128, 115, and 105. The ir showed only olefinic functionality. It is possible that this material was derived from the 2 + 2 product by a vinylcyclobutane rearrangement. For some similar cases see ref 10, footnotes 19 and 20.

BDC–1,3,5-Cycloheptatriene–Ag$^+$.—The reaction and work-up of the reaction of benzyne derived from anthranilic acid (3.0 g, 22 mmol) with the silver ($AgBF_4$, 0.3 g, 1.4 mmol)–cycloheptatriene (6.0 g, 65.7 mmol) complex were carried out by the above procedure. The work-up as described gave after chromatography on neutral alumina (hexane as eluent) a clear liquid (0.7 g, 21%). Vpc analysis, condition C, showed the material to have a different retention time from that of **14** or **15**. The product was characterized as **13** by spectral data in ref 1a.

BDC and Isoprene.—The reaction and work-up of the reaction of benzyne derived from anthranilic acid (3.0 g, 22 mmol) with isoprene (14.5 g, 66 mmol) was carried out by the above procedure. The work-up described above yielded a yellow liquid after pentane treatment. Product analysis: (a) nmr, **19a** (45%), **20** (55%); (b) vpc, condition D, **19a** (41%), **20** (59%).

BDC–Isoprene–Ag.$^+$—The reaction and work-up of the reaction of benzyne derived from anthranilic acid (3.0 g, 22 mmol) with the silver ($AgClO_4$, 0.1 g, 0.48 mmol)–isoprene (4.5 g, 66 mmol) complex was carried out by the above procedure. The reaction mixture was worked up as described above. Product analysis: (a) pmr, **19a** (49%), **20** (51%); (b) vpc, condition D, **19a** (48%), **20** (52%). A duplicate run with $AgClO_4$ (0.4 g, 1.9 mmol) gave identical results. Another set of duplicate runs with $AgBF_4$ (1.2 or 0.4 g) showed by pmr **19a** ($\sim$46%) and **20** ($\sim$54%).

BDC–*trans,trans*-1,4-Dimethylbutadiene–Ag$^+$.—The reaction and work-up of the reaction of benzyne derived from anthranilic acid (3.0 g, 22 mmol) with the silver ($AgBF_4$, 0.07 g, 0.36 mmol)–dimethylbutadiene (3.0 g, 37 mmol) complex was carried out by the above procedure. The reaction mixture was worked up as described above, and chromatography on alumina (hexane as eluent) yielded a light red liquid (0.43 g). Vpc analysis, condition E, indicated a net hydrocarbon yield of 3% with relative ratios being similar to the report by Jones and Levin (Table III, ref 16) for the same reaction without Ag$^+$. The 2 + 4 product was observed to be pure *cis*-dimethyldihydronaphthalene by pmr observation of the vinyl proton region in Fourier Transform mode (200 pulses) wherein less than 1% of the *trans*-dimethyldihydronaphthalene[20] could be easily seen.

Registry No.—**1**, 592-57-4; **2**, 4054-38-0; **3**, 544-25-2; **4**, 78-79-5; **5**, 5194-51-4; **6a**, 1608-42-0; **6b**, 37150-27-9; Ag$^+$, 14701-21-4; benzyne, 462-80-6.

---

[19] G. Wittig and R. W. Hoffman, *Chem. Ber.*, **95**, 2718 (1962).

[20] Prepared by procedure outlined in ref 16.