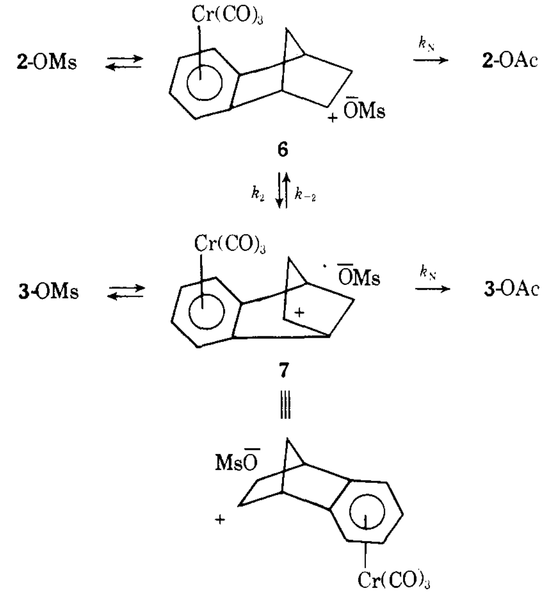
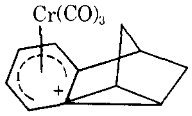
noncomplexed *exo*-2-benzonorbornenyl derivatives.[10] The 24,100/90.5 = 266 times rate enhancement of **3**-OMs relative to **2**-OMs indicates that *the endo-tricarbonylchromium provides an additional driving force over that due to the ring itself.*[11] We are unable to estimate the extent to which the additional rate enhancement is attributable to a steric effect, but the preferential formation of the more hindered and less stable product (**3**-OAc) clearly implies that electronic factors are important.

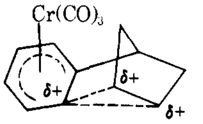
These data confirm that the metal moiety exhibits a strong tendency to precede[3] the ring during the migration and to stabilize that intermediate (**7**) in which the positive charge is concentrated in the vicinity of the metal;[12] *cf.* Scheme II.[13] Pseudosymmetric cationic intermediates such as **8** are excluded as are diastereomeric structures which by rapid equilibration achieve such symmetry prior to attack by acetate.[14]

Scheme II





8a



8b

We cannot distinguish between direct metal bridging[15] or σ–π type homoconjugation[16] as the mode of stabilization of **7**, for either interpretation would appear to be compatible with our data.[17,18]

Acknowledgment. We are indebted to the Directorate of Chemical Sciences of the Air Force Office of Scientific Research (Grant No. 991-67) for their generous support of this work, and to Professor E. L. Amma and his group for the single-crystal X-ray diffraction study of **2**-OAc.[5]

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(10) (a) P. D. Bartlett and W. P. Giddings, *J. Amer. Chem. Soc.*, **82**, 1240 (1960); (b) W. P. Giddings and J. Dirlam, *ibid.*, **85**, 3900 (1963); (c) D. V. Braddon, G. A. Wiley, J. Dirlam, and S. Winstein, *ibid.*, **90**, 1901 (1968), and references cited therein; (d) H. Tanida, H. Ishitobi, T. Irie, and T. Tsushimi, *ibid.*, 90, 4512 (1968).

(11) This compares favorably with the factor of 280 observed by Wells and Trahanovsky[7] for the hydrolysis of 3-OBs in 70% acetone at 80° and implies that a major portion of the observed enhancement of 3-OMs relative to 5-OMs, 24,100/0.24 = 100,000, may be due to some type of metal participation.

(12) Although we represent 6 and 7 as charge localized for convenience and simplicity, we do not intend to imply that delocalization may not be substantial, especially in the latter case.

(13) If in fact more 3-OAc is produced from 2-OMs than from 3-OMs, 7 clearly cannot be the only intermediate which yields 3-OAc. It may be that the nucleophile prefers to attack that site of positive charge in the diastereomeric tight ion pairs 6 and 7 which is least shielded by the methanesulfonate counterion.

(14) *I.e.*, the following condition cannot obtain: $k_2 \approx k_{-2} \gg (k_N + k_N')$.

(15) (a) J. H. Richards and E. A. Hill, *J. Amer. Chem. Soc.*, **81**, 3484 (1959); **83**, 3840, 4216 (1961); (b) M. Cais, *Organometal. Chem. Rev.*, **1**, 435 (1966).

(16) (a) T. G. Traylor and J. C. Ware, *Tetrahedron Lett.*, 1295 (1965); *J. Amer. Chem. Soc.*, **89**, 2304 (1967); (b) J. A. Mangravite and T. G. Traylor, *Tetrahedron Lett.*, 4461 (1967); (c) W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, **92**, 829 (1970).

(17) Implicit in the concept of σ–π type homoconjugation,[16a] though perhaps not explicity stated in the case of cationic intermediates, is the expectation that in a π-complexed "bridged" intermediate, *cf.* ref 6, Charts IX and XI, the "inside" bridging bond adjacent to the metal will be more rapidly broken by an attacking nucleophile than the "outside" one,[19] hence even a pseudosymmetric structure such as **8a** or **8b** could be expected to react with acetate in an asymmetric fashion.

(18) *Cf.* M. J. Nugent, R. Kummer, and J. H. Richards, *J. Amer. Chem. Soc.*, **91**, 6141 (1969), for a similar conclusion in the ferrocene series.

(19) Private communication from T. G. Traylor to the senior author dated July 7, 1967.

(20) NSF Trainee, 1968–1970.

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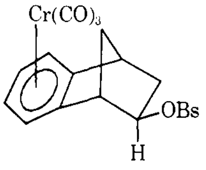
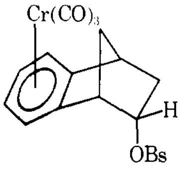
Arene–Metal Complexes. III. Solvolysis of the anti-exo-2, anti-endo-2, and syn-exo-2 Isomers of (Benzonorbornen-2-yl)tricarbonylchromium *p*-Bromobenzenesulfonates[1]

Sir:

There are four possible isomers of (benzonorbornen-2-yl)tricarbonylchromium *p*-bromobenzenesulfonates, anti-exo-2 (**1**), anti-endo-2 (**2**), syn-exo-2 (**3**), and syn-endo-2 (**4**). We now report the solvolysis study of the first three isomers. Attempts to synthesize the fourth isomer have met with failure, undoubtedly because of the severe steric interactions of the *syn*-tricarbonylchromium and the endo-2 substituent that would exist.



1



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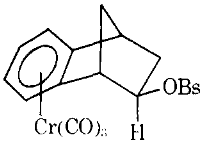

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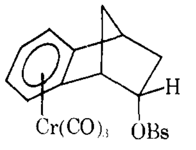

4

The *anti*-tricarbonylchromium complex of benzonorbornen-2-*exo*-yl acetate was prepared and reduced

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(1) (a) II: D. K. Wells and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, **91**, 5871 (1969). (b) This work was partially supported by Public Health Service Grant No. GM 13799 from the National Institute of General Medical Sciences and Grant No. 5261-AC from the Petroleum Research Fund administered by the American Chemical Society. We thank these organizations for their support. (c) Based on work by D. K. W. in partial fulfillment of the requirements for the Ph.D. degree at Iowa State University.

to the alcohol which was converted to **1**. The anti complex of benzonorbornen-2-*endo*-ol was prepared and converted to **2**. The syn complex of benzonorbornadiene was prepared and treated with diborane and oxidized to give the alcohol which was converted to **3**.

The nmr and mass spectra of the three isomers confirm their structures and differences in their spectra and melting points show that they are three distinct isomers. The assigned stereochemistry of these isomers is reasonable based on their synthesis but was confirmed by a detailed analysis of the nmr spectra of these and related complexes. The stereochemistry of the anti-exo-2 acetate has been determined by X-ray diffraction.[2] Bly and Strickland[3] have determined the stereochemistry of the three complexed alcohols by chemically interrelating them to the anti-exo-2 acetate. The physical constants of these alcohols that were obtained by Bly and Strickland agree very well with our measurements. The very good agreement between the results of Bly and Strickland's[3] solvolysis study of the methanesulfonates of these alcohols and the results of our study confirms the stereochemistry of our *p*-bromobenzenesulfonates.

In Table I the titrimetric rate constants of solvolysis of free and complexed benzonorbornen-2-yl *p*-bromobenzenesulfonates in 70% aqueous acetone are presented. Solvolysis products were determined by nmr analysis. Solvolysis of *syn*-*exo*-2-*p*-bromobenzenesulfonate (**3**) through 10 half-lives gave 92% syn-exo-2 alcohol. Product studies of the other two isomers were complicated by the fact that the complexes decomposed during the long reaction times under these conditions. Solvolysis of *anti*-*exo*-2-*p*-bromobenzenesulfonate (**1**) for 10 half-lives gave 30% complexed products, which were composed of approximately equal amounts of the anti-exo-2 and the syn-exo-2 alcohols, and 70% uncomplexed exo-2 alcohol. Only uncomplexed *exo*-2-benzonorbornenol was observed after three half-lives of solvolysis of *anti*-*endo*-2-*p*-bromobenzenesulfonate (**3**). Since no complexed products were isolated from the solvolysis of the anti-endo-2 isomer, the observed solvolysis rate constant may be that of the uncomplexed *p*-bromobenzenesulfonate, not the complexed material.

Table I. Rates of Solvolysis of Free and Complexed Benzonorbornen-2-yl *p*-Bromobenzenesulfonates in 70% Aqueous Acetone

p-Bromobenzenesulfonate	Temp, °C	10^4k, sec^{-1}	Rel rates, 80°
exo-Norbornen-2-yl	40.9	2.4	5800[a]
	60.0	21	
	80.0	140	
endo-Norbornen-2-yl	80.0	0.024	(1.0)[a]
	100.0	0.19	
	120.2	1.2	
anti-Tricarbonylchromium	80.0	0.33	14
exo-Norbornen-2-yl (**1**)	100.0	3.9	
anti-Tricarbonylchromium	80.0	0.016	0.67
endo-Norbornen-2-yl (**2**)	100.0	0.065	
syn-Tricarbonylchromium	60.0	26	3900
exo-Norbornen-2-yl (**3**)	80.0	94	

[a] An exo/endo rate ratio of 15,000 in acetic acid at 25° was obtained by H. C. Brown and G. L. Tritle, *J. Amer. Chem. Soc.*, **88**, 1320 (1966).

Anti complexation by the tricarbonyl group retards the solvolysis rate of *exo*-2-*p*-bromobenzenesulfonate be a factor of 400. Using a ρ of -3.26 for the solvolysis of benzene-substituted benzonorbornen-2-*exo*-yl *p*-bromobenzenesulfonates[4] and a σ of 0.83 for the tricarbonylchromium moiety, which was determined from the pK_a of (phenylacetic acid)tricarbonylchromium,[5] the calculated rate constant for solvolysis of *anti*-*exo*-2-*p*-bromobenzenesulfonate is 2.14×10^{-3} sec^{-1}, which agrees very well with the observed 2.41×10^{-3} sec^{-1}. These results are consistent with direct participation of the benzene ring of benzonorbornen-2-yl systems in the solvolysis of exo derivatives[6] and indicate that the π electrons of the complex are less available for stabilization of an adjacent positive center than those of the uncomplexed compound. The rate of solvolysis of *syn*-*exo*-2-*p*-bromobenzenesulfonate (**3**) is about 300 times faster than that of the anti isomer **1** and is about equal to that of the uncomplexed *exo*-2-*p*-bromobenzenesulfonate. Thus, a special cation-stabilizing effect of the *syn*-tricarbonylchromium group is required since if no special effect existed, then the *syn*-tricarbonylchromium group should retard the solvolysis rate of the *exo*-2-*p*-bromobenzenesulfonate by exerting an electron-withdrawing inductive effect, and inhibiting direct interaction of the arene π system with the positive center.

Steric acceleration by the *syn*-tricarbonylchromium moiety could be offered as an explanation for its rate-enhancing ability since the 2-carbon goes from an sp^3 to an sp^2 state of hybridization during ionization. However, competitive hydrogenation experiments using palladium in acetic acid show that the relative rates of hydrogenation of the double bond of the uncomplexed and the *anti*- and *syn*-tricarbonylchromium complexes of benzonorbornadiene are 7, 3, and 1, respectively. Since the hydrogen should be added to the double bond from the exo side[7] in all cases, and the 2- and 3-carbon atoms are changed from sp^2 to sp^3 states of hybridization, these hydrogenation rates give no indication of a large steric interaction between the *syn*-tricarbonylchromium moiety and the endo-2 and endo-3 hydrogen atoms.

It has been established that cations attached to the complexed phenyl ring are stabilized by the tricarbonylchromium group.[1a,8] For example, (benzyl cation)tricarbonylchromium is thermodynamically slightly more stable than the benzhydryl cation.[8b] Two mechanisms can be proposed for this stabilization which are based

---

(2) Personal communication from H. Lüth, I. F. Taylor, Jr., and E. L. Amma, whom we thank for making their results available to us prior to publication.

(3) (a) R. S. Bly and R. C. Strickland, Abstracts, 159th National Meeting of the American Chemical Society, Houston, Tex., Feb 1970, ORGN-133; (b) R. S. Bly and R. C. Strickland, *J. Amer. Chem. Soc.*, **92**, 7459 (1970). We thank these authors for making their results available to us prior to publication.

(4) H. Tanida, H. Ishitobi, T. Irie, and T. Tsushima, *ibid.*, **91**, 4512 (1969).

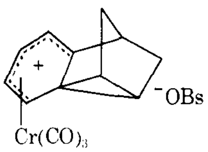
(5) B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1969).

(6) (a) P. D. Bartlett and W. P. Giddings, *J. Amer. Chem. Soc.*, **82**, 1240 (1960); (b) W. P. Giddings and J. Dirlam, *ibid.*, **85**, 3900 (1963); (c) H. Tanida, K. Tori, and K. Kitahonoki, *ibid.*, **89**, 3212 (1967); (d) H. C. Brown and G. L. Tritle, *ibid.*, **90**, 2689 (1968).

(7) K. Tori, K. Aono, Y. Hata, R. Muneyoki, T. Tsuji, and H. Tanida, *Tetrahedron Lett.*, 9 (1966).

(8) (a) J. D. Holmes, D. A. K. Jones, and R. Pettit, *J. Organometal. Chem.*, 4, 324 (1965); (b) W. S. Trahanovsky and D. K. Wells, *J. Amer. Chem. Soc.*, 91, 5870 (1969).

on those offered to explain the unusual stability of ferrocenylcarbinyl cations,[3] the "hyperconjugation"[9a,b] and the "direct interaction"[9c,d] mechanisms. Two similar mechanisms can be proposed for the stabilization of homobenzylic cations which would account for the rapid rate of solvolysis of the syn-exo-2 isomer. If



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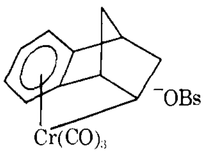

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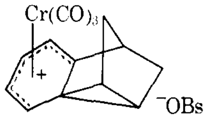

7

the "homoconjugation" mechanism operates, which is analogous to the hyperconjugation mechanism, resonance structure **5** would be relatively stable and an important contributor to the structure of the transition state. However, if the direct interaction mechanism operates, structure **6** would be stable and important. The relatively slow rate of solvolysis of the anti-exo-2 isomer indicates that resonance structure **7** of its transition state is not unusually stable. Therefore we prefer to accept the direct interaction mechanism to explain the rate enhancement of the syn-exo-2 isomer rather than the homoconjugation mechanism which requires that the π electrons on the side of the metal atom are much more available to adjacent cations than the π electrons on the opposite side of the metal atom. However, our data do not exclude the latter possibility and an explanation for the greater availability of the π electrons on the side of the metal atom than those on the opposite side has been offered.[10]

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(9) (a) T. G. Traylor and J. C. Ware, *J. Amer. Chem. Soc.*, **89**, 2304 (1967); (b) W. Hanstein, H. J. Berwin, and R. G. Traylor, *ibid.*, **92**, 829 (1970); (c) M. Cais, *Organometal. Chem. Rev.*, **1**, 435 (1966), and references cited therein; (d) M. J. Nugent, R. E. Carter, and J. H. Richards, *ibid.*, **91**, 6145 (1969).

(10) J. A. Mangravite and T. G. Traylor, *Tetrahedron Lett.*, 4461 (1967).

(11) (a) American Chemical Society Petroleum Research Fund Graduate Fellow, 1968–1969; (b) Alfred P. Sloan Research Fellow, 1970–1972.

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Evidence for a Radical Mechanism of Aromatic "Nucleophilic" Substitution[1]

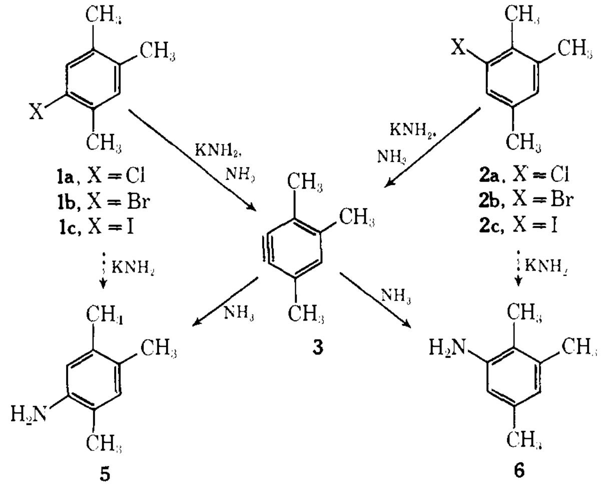
Sir:

According to the aryne mechanism,[2] the reactions of 5- and 6-halopseudocumenes (**1** and **2**, respectively) with KNH_2 in liquid ammonia should proceed *via* the same aryne intermediate (**3**) and form 5- and 6-pseudocumidine (**5** and **6**, respectively) in identical proportions. Neither the identity of the halogen nor its location (5 or 6 position) should affect the product ratio.

These expectations are fulfilled insofar as reactions of bromo compounds **1b** and **2b** and chloro compounds **1a** and **2a** are concerned. With KNH_2 in NH_3, these afford **5** and **6** in high yield and with a **6**:**5** product ratio varying from 1.45 to 1.55. This variation is within experimental error. However, from iodo compounds **1c** and **2c**, the **6**:**5** product ratios were 0.63 and 5.86, respectively (with 0.29 *M* KNH_2). Pseudocumene (**4**) was formed in significant amounts as a by-product in reactions of **1c** and **2c**.

The fact that each of the iodo substrates forms some cine-substitution product indicates that each reacts in part *via* the aryne mechanism. However, the wide divergences of the pseudocumidine **6**:**5** ratio from the "aryne ratio" of about 1.5 demonstrate that some other mechanism also plays a major role. Inasmuch as the divergences are both in the direction of retention of the original orientation, the additional mechanism must be a nonrearranging one.

Scheme I



It is unlikely that the nonrearranging pathway is straightforward aromatic nucleophilic substitution, such as encountered in reactions of *o*- and *p*-halonitrobenzenes[3] and often symbolized SNAr. Aryl iodides generally are somewhat *less* reactive in SNAr reactions than their chloro or bromo analogs, whereas they are generally *more* reactive than the corresponding chlorides in aryne formation and only slightly less reactive than the corresponding bromides.[4] Thus, a change of the halogen from chlorine to iodine would be expected strongly to favor the aryne mechanism in competition with SNAr, while a change from bromine to iodine might slightly favor or slightly disfavor it.

Evidence in Table I indicates the nonrearranging mechanism to be radical in character. This table also gives details on experiments mentioned above. When the reaction of **1c** or **2c** is carried out in the presence of 2-methyl-2-nitrosopropane[5] or tetraphenylhydrazine, both of which are radical-trapping agents (the latter *via* dissociation into diphenylamino radicals[6] or *via* radical displacement on nitrogen), the **6**:**5** pseudocumidine ratio is in both cases shifted toward the "aryne ratio." A shift in the same direction is realized

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(1) Support from the National Science Foundation is gratefully acknowledged.

(2) J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, *J. Amer. Chem. Soc.*, **78**, 601 (1956).

(3) J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 273 (1951); J. F. Bunnett, *Quart. Rev., Chem. Soc.*, **12**, 1 (1958).

(4) F. W. Bergstrom, R. E. Wright, C. Chandler, and W. A. Gilkey, *J. Org. Chem.*, **1**, 170 (1936); J. F. Bunnett and F. J. Kearley, *ibid.*, in press.

(5) M. J. Perkins, P. Ward, and A. Horsfield, *J. Chem. Soc. B*, 395 (1970).

(6) W. E. Bachmann, "Organic Chemistry," 2nd ed, H. Gilman, Ed., Wiley, New York, N. Y., 1943, p 616.