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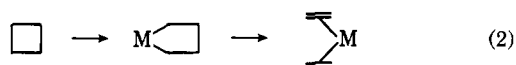
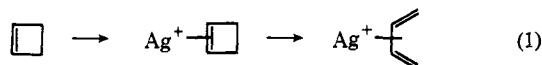
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On the Mechanism of Metal-Catalyzed Rearrangement of Strained Cyclobutane and Cyclobutene Derivatives

Sir:

We have previously reported that silver ions can effect the disrotatory ring opening of certain cyclobutene systems to yield derivatives of butadiene, and it was suggested that the mechanism of this reaction involves insertion of the silver ion into the double bond to form the silver-olefin π complex followed by a concerted disrotatory ring opening process to form the corresponding silver complex of butadiene (eq 1).¹ In the absence of silver ions such a concerted reaction is of course forbidden and arguments attempting to describe how such metal-catalyzed reactions may occur, within the framework of the Woodward-Hoffmann concepts of orbital symmetry conservation, have been given.¹



Recently this interpretation has been brought into question on the basis of the seemingly related ring-opening reactions of certain strained cyclobutane derivatives with various rhodium catalysts to yield diolefin systems.^{2,3} In essence it has been suggested that for these latter reactions the overall process is not concerted⁴ but involves initial insertion of the metal atom into a σ bond to yield a dialkylmetal derivative followed by conversion to the diolefin (eq 2).⁵ It is implied that similar insertion into the carbon-carbon σ bond, rather than the π bond, is involved in the cyclobutene-butadiene conversions mentioned above (eq 3).

In the reaction of cubane with norbornadienerhodium chloride $[\text{Rh}(\text{NOR})\text{Cl}]_2$, leading to the formation of tricyclooctadiene, it has been suggested that the

(1) W. Merk and R. Pettit, *J. Amer. Chem. Soc.*, **89**, 4788 (1967); R. Pettit, H. Sugahara, J. Wristers, and W. Merk, *Discuss. Faraday Soc.*, **47**, 71 (1969).

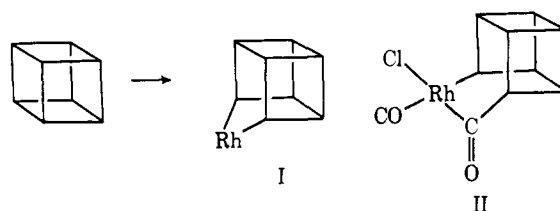
(2) L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, **92**, 3515 (1970).

(3) T. J. Katz and S. A. Cereface, *ibid.*, **91**, 2405 (1969).

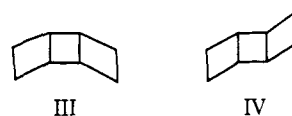
(4) The catalyzed conversion of quadricyclane to norbornadiene by rhodium complexes had been considered to be a concerted process [F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, **89**, 2184 (1967)].

(5) The interesting question as to whether the second step of eq 2 involves a concerted process or not has not been discussed.

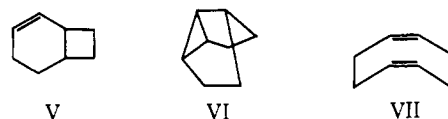
σ -bonded rhodium complex I is involved as an intermediate; taken as support of this scheme is the fact that when $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ is used as the metal source, the acylmetal complex II can actually be isolated.²



In the present study we have investigated the behavior of *syn*- and *anti*-tricyclooctane (III and IV, respectively), with AgBF_4 , $[\text{Rh}(\text{NOR})\text{Cl}]_2$, and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$. The systems III and IV bear obvious interesting steric relationships to the cubane molecule, and the results have a bearing both on the cyclobutene-butadiene conversion and the reactions of fully saturated hydrocarbons with these metal systems.



No reaction of *anti*-tricyclooctane (IV) is observed after 5 days of heating with equimolar amounts of AgBF_4 in acetone (0.25 M solutions) at 56°. Under identical conditions the *syn* isomer III is completely converted in approximately 1 min to a mixture of bicyclooctene (V), tetrahydrosemibullvalene (VI), and 1,5-cyclooctadiene (VII) in the ratio of 18:80:2, respectively.⁷



Similar behavior is seen in the reactions of the isomeric tricyclooctanes with $[\text{Rh}(\text{NOR})\text{Cl}]_2$, whereas the *syn* isomer III reacts completely within 3 hr in benzene at 63° to produce a mixture of the hydrocarbons V, VI, and VII in a ratio of 70:2:28, respectively;⁸ the *anti* isomer IV under similar conditions is completely unaffected after 20 hr.

On the other hand, $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ reacts with both the *syn*- and *anti*-tricyclooctanes under similar conditions to yield acylrhodium complexes presumably of the type II observed in the reaction with cubane.⁹

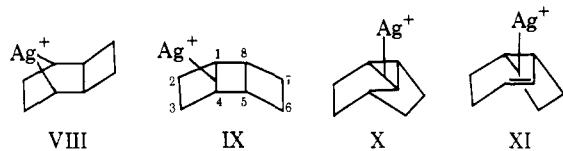
(6) It is significant that *anti*-tricyclo[4.2.0.0^{2,5}]oct-3-ene on the other hand reacts readily with AgBF_4 at room temperature to yield bicyclo[4.2.0]octa-2,4-diene.

(7) According to the nmr spectrum and vpc analysis of the total reaction product there were no other materials produced in the reaction. The three components can be separated by preparative vpc. We thank Professor H. E. Zimmerman for providing us with the nmr and ir spectra of authentic samples of tetrahydrosemibullvalene. The reaction leading to tetrahydrosemibullvalene is analogous to that observed by W. G. Dauben and coworkers (*Tetrahedron Lett.*, 787 (1970)) and by L. A. Paquette and J. C. Stowell (*J. Amer. Chem. Soc.*, **92**, 2584 (1970)). The cage-like nature of the starting materials used by these workers, however, precluded reactions leading to products analogous to V.

(8) In this experiment the concentrations of *syn* isomer and the rhodium complex were 1.0 and 0.1 M, respectively. Similarly, the reaction of the *syn* isomer proceeds completely in the presence of only catalytic amounts of Ag^+ .

(9) The reactions were run in CHCl_3 containing equimolar amounts of hydrocarbon and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$. The *syn* isomer reacted faster by approximately one order of magnitude in rate and yielded a red crystalline acyl-rhodium complex displaying a strong carbonyl absorption at

Since $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ reacts with both the *syn*- and the *anti*-tricyclooctanes, steric effects alone are not responsible for the lack of reactivity of AgBF_4 and $[\text{Rh}(\text{NOR})\text{Cl}]_2$ with the anti isomer. Also, in view of the notorious ease of decomposition of silver alkyls,¹⁰ it would seem that if such an insertion to form the dialkylsilver complex VIII were to occur then some decomposition of the anti isomer should have been observed. It is therefore unlikely that σ -bonded metal systems are being formed in the attempted reaction of AgBF_4 with the anti isomer IV. Nor is it necessary to invoke σ -bonded silver intermediates analogous to VIII to account for the reactivity of the *syn* isomer III with AgBF_4 . At the outset such a scheme holds little attraction for it would involve silver in a formal oxidation state of +3. One alternative explanation is that the silver ion interacts with the strained σ bond to give the system IX in which a three-center bond is



involved rather than two discrete Ag-C bonds. In IX it is proposed that the bonding involves both forward coordination and back-donation type interactions between the C-C σ bonding and antibonding orbitals and the atomic orbitals of silver in a manner exactly analogous to that proposed for C-C π bond interactions with silver ion,¹¹ and, as in the case of silver π type complexes, much of the total bonding involves carbon-carbon orbital interaction. The system IX is not considered to be an intermediate; concerted migration of the trans carbon atom 6 to carbon 4 leading to X, or to carbon atom 1, leading to the bicyclooctene complex XI, or concerted rearrangement to the cyclooctadiene-Ag⁺ complex, could occur. Ejection of silver ion from these latter three systems leads to the products observed. The formation of the products V, VI, and VII each represents in the absence of the metal a forbidden reaction in a concerted process according to the Woodward-Hoffmann rules. The role of the silver atom in "allowing" these reactions to occur is most readily seen in the reaction leading to cyclooctadiene; the argument based on orbital symmetry considerations for the conversion of IX to the silver complex of 1,5-cyclooctadiene is exactly the same as used earlier for the silver-catalyzed conversion of cyclobutene to butadiene.¹ Because of the lack of symmetry elements, the reactions leading to X and XI are less amenable to orbital symmetry considerations. The role that the silver ion plays in allowing these reactions to occur with low activation barriers is possibly related to its ability to form multicentered interactions with three carbon atoms during the reaction path; such interactions would be analogous, for example, to those existing in stable π -allylic metal systems.¹²

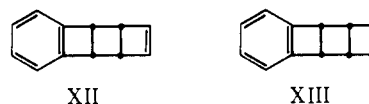
1720 cm^{-1} (cf. ref 2). The anti isomer gave products which also contained strong absorption in 1735- cm^{-1} region. The structures of these complexes are under further investigation.

(10) See, for example, C. D. M. Beverivizk, G. J. M. van Derkerk, A. J. Lensink, and J. G. Noltes, *Organometal. Chem. Rev., Sect. A*, 5, 218 (1970).

(11) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

We propose that in the interaction of metal systems with strained saturated hydrocarbons the initial attack is generally *via* metal-carbon bond interactions analogous to IX. Whether this system then proceeds to the fully inserted σ -bonded dialkylmetal complex or, as with those metals whose alkyl derivatives are not stable, in some other direction such as rearrangement, will depend on the nature of the metal and its other accompanying ligands as well as the nature of the organic substrate. Thus $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ may well react with both *syn*- and *anti*-tricyclooctanes to form alkylrhodium complexes prior to formation of the observed acylrhodium products; on the other hand, the silver complex of the anti isomer analogous to IX cannot readily react due to the high energy of silver alkyls and the relative high energy of rearranged products such as *trans,trans*-1,5-cyclooctadiene. However, because of the favorable geometry, the corresponding Ag⁺ complex derived from the *syn* isomer IX is able to rearrange to less strained species.

Concerning the metal-catalyzed cyclobutene-butadiene interconversion, it is also improbable that complete insertion of Ag⁺ into the σ bond is occurring (eq 3). However, there remains the possibility that the concerted rearrangement involves attack of the metal ion on the σ bond first in a manner analogous to IX, rather than the π bond as in eq 1. The clearest indications that at least one metal proceeds *via* initial π bond attack are seen in the reactions of AgBF_4 and bicyclooctadienenickel $[\text{Ni}(\text{COD})_2]$ with *syn*-benzotricyclooctadiene XII and *syn*-benzotricyclooctene XIII. AgBF_4 reacts with both hydrocarbons at comparable



rates to produce, *via* the *o*-xylylene intermediates, benzocyclooctatetraene and benzocyclooctatriene, respectively.¹ $\text{Ni}(\text{COD})_2$, however, reacts with the olefin systems XII to generate benzocyclooctatetraene, but under the same conditions, no isomerization of XIII occurs.¹⁴ If in the isomerization of the olefin XII with nickel the initial attack were to proceed *via* one of the strained bridging σ bonds, there would be no reason why similar isomerization should not occur with XIII. Thus in the case of $\text{Ni}(\text{COD})_2$ at least, the attack is *via* initial interaction with the π system. It seems most probable that this is also true for Ag⁺.

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(12) Dewar in an alternative way of viewing concerted reactions does not consider individual orbital symmetries but considers whether the transition state for a reaction is aromatic (low energy) or anti-aromatic (high energy).¹³ Extension of this approach would also account for the metal catalysis observed here; it is known that normally high-energy species, *e.g.*, cyclobutadiene and the allyl system, can form stable complexes with metals. The gain in bonding energy upon complexation to a metal could lower the energy of an otherwise high-energy transition state, *e.g.*, the cyclobutadiene type molecular orbital system seen in the disrotatory ring opening of cyclobutene to butadiene, and thus render a "forbidden" reaction to become "allowed."

(13) (a) M. J. S. Dewar, *Tetrahedron, Suppl.*, No. 8, 75 (1966); (b) M. J. S. Dewar, *Angew. Chem., Int. Ed. Engl.*, in press.

(14) Thus after allowing a solution in benzene (8 ml) of 0.3 mmol each of XII and XIII and 1.4 mmol of $\text{Ni}(\text{COD})_2$ to stand at 25° for 3.5 hr, there is observed complete isomerization of XII to benzocyclooctatetraene, while no reaction of XIII is apparent from the nmr spectrum.

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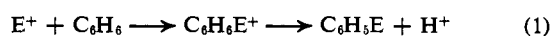
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Electrophilic Aromatic Substitution Reactions. An Ion Cyclotron Resonance Study

Sir:

We have observed that ions to which electrophilic behavior in solution is ascribed form ionic complexes with benzene at relatively low pressures (ca. 4×10^{-5} Torr) at 30 eV in patterns reminiscent of the first step of textbook mechanisms for electrophilic substitution (eq 1).¹ The first step of this process can be



approximated in an ion-molecule reaction involving attack of a nucleophile on benzene, frequently in the form of the transfer of the electrophile from a Lewis base to benzene, a process conveniently studied by ion cyclotron resonance (icr) spectrometry.²

We find through the icr technique that benzene (10^{-5} Torr) can be nitrated by a variety of reagents ($2-4 \times 10^{-5}$ Torr). As possible reagents for the nitration of benzene at these pressures, we have examined NO_2 itself as well as selected ions formed in the icr chemistry of alkyl nitrates (eq 2 and 3).³ The



origin of the m/e 130 ion ($C_6D_6NO_2^+$) formed in a mixture of C_6D_6 and NO_2 is found through ion cyclotron double resonance (icdr) not to correspond to the product of electrophilic substitution, for its primary precursor is the linear⁴ $C_6D_6^+ \cdot$ not NO_2^+ (eq 4).⁵ However, icdr studies on mixtures of C_6D_6 with CH_3ONO_2 or $C_2H_5ONO_2$ show that here the m/e 130 ion is formed not from



$C_6D_6^+ \cdot$ but, to a substantial degree, from $H_2NO_3^+$ (m/e 64), $CH_2ONO_2^+$ (m/e 76), or $CH_3CHONO_2^+$ (m/e 90). The protonated esters are also able to nitrate benzene. These processes correspond to the first step of eq 1, electrophilic addition.

A further ion-molecule product of these systems is $C_6D_6O^+ \cdot$ (m/e 100), whose origin is principally the m/e 46 ion, NO_2^+ . If the structure of $C_6D_6O^+ \cdot$ is that of phenol, this electrophilic substitution (eq 5) may be

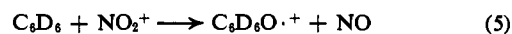
(1) For a recent review, see E. Berliner, *Progr. Phys. Org. Chem.*, **2**, 253 (1964).

(2) For a description of the technique see (a) J. M. S. Henis, *J. Amer. Chem. Soc.*, **90**, 844 (1968); (b) J. L. Beauchamp, L. R. Anders, and J. D. Baldeschwieler, *ibid.*, **89**, 4569 (1967).

(3) P. Kriemler and S. E. Buttrill, Jr., *ibid.*, **92**, 1123 (1970).

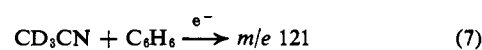
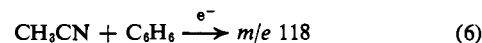
(4) Cf. J. Momigny, L. Brakier, and L. D'Or, *Bull. Cl. Sci. Acad. Roy. Belg.*, **48**, 1002 (1962).

(5) This m/e 130 peak is weak ($<1\%$ of the intensity of the m/e 84 peak) under conditions where the m/e 130 peak in the $C_6D_6-CH_3ONO_2$ and $C_6D_6-C_2H_5ONO_2$ systems is much larger; it must be collision stabilized, and the process is not important under these conditions.

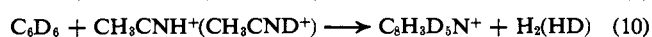
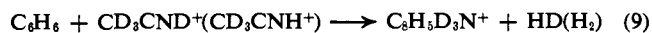


analogous to the probable first step in the formation of nitrophenols upon irradiation of mixtures of benzene and NO_2 .^{6,7} No information on its structure, as with most ions, is readily available, however.

In a search for other possible electrophilic substitution, mixtures of deuterated and undeuterated acetonitrile and benzene (eq 6-8) under conditions

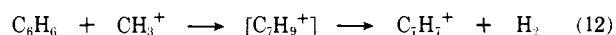
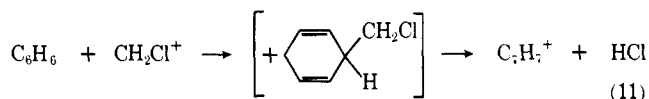


similar to those above produce an ion which corresponds (in mass) to that expected ($C_6H_6CH_2CN^+$) from cyanomethylation. However, icdr shows that this electrophilic addition is not a simple attack of cyanomethyl cation, CH_2CN^+ , on benzene, for the attacking species is protonated acetonitrile, CH_3CNH^+ .^{8,9} The reaction therefore could correspond to a Hoesch synthesis¹⁰ at its first step involving benzene, and the gaseous ionic products correspond to loss of a hydrogen atom from benzene and the NH hydrogen from CH_3CNH^+ in the collision complex (eq 9 and 10),



perhaps in a four-center process to yield $C_6H_5 \cdot C=N^+CH_3$.

A third electrophilic reaction system, methyl chloride and benzene, also includes reactions corresponding to the addition step of electrophilic aromatic substitution; in each case the required expulsion of a neutral molecule masks the electrophilic attack, for no simple addition product is observed at our pressures. One pathway is analogous to the Blanc chloromethylation reaction,¹¹ for the final product is formed from attack of CH_2Cl^+ on benzene (eq 11). Another pathway corresponds to the Friedel-Crafts reaction¹² at first, but again the gaseous ionic and solution routes separate after the initial attack of the electrophile on benzene (eq 12). Equation 11 is exothermic by 59 or



52 kcal/mol if $C_7H_7^+$ is benzyl or tropylium;¹³ eq 12

(6) W. Kemula and A. Grabowska, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **8**, 517 (1960).

(7) Note also the thermolysis of nitrobenzene: E. K. Fields and S. Meyerson, *Accounts Chem. Res.*, **2**, 273 (1969).

(8) CH_3CNH^+ is found in the ion-molecule chemistry of acetonitrile: G. A. Gray, *J. Amer. Chem. Soc.*, **90**, 2177 (1968).

(9) Icdr also indicates that $C_6H_6CH_2CN^+$ is also produced by an additional pathway, attack of $C_6H_5^+$.

(10) K. Hoesch, *Chem. Ber.*, **48**, 1122 (1915).

(11) G. Blanc, *Bull. Soc. Chim. Fr.*, **33**, 313 (1923).

(12) C. Friedel and J. M. Crafts, *Compt. Rend.*, **84**, 1292, 1450 (1877).

(13) In unimolecular decompositions, $C_7H_7^+$ which decomposes is tropylium.¹⁴ In high-pressure chemical ionization studies of toluene,¹⁵ formation by $C_7H_7^+$ by hydrogen abstraction does not involve randomization before abstraction. We see no further fragmentation of $C_7H_7^+$.

(14) (a) H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York,