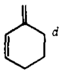
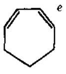
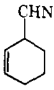
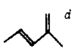
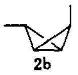
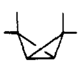
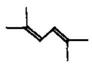
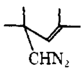
metal and the carbene species formally derived from the diazoalkane. Therefore, reaction of diazo*alkene* of general structure III with Ag(I) and Pd(II) will provide useful information as to whether intermediates I and II are indeed involved in metal-catalyzed rearrangements of bicyclobutanes.

We prepared diazoalkenes **1**-III, **2**-III, and **3**-III corresponding to bicyclobutanes **1**, **2**, and **3** and examined the product distribution of metal-catalyzed reactions of these compounds. The results are summarized in Table I. Product distributions obtained from a pair of bicyclobutane and diazoalkene with Pd(II) were exactly the same or similar in all the cases. These results strongly suggest that both reactions proceed through the same or similar intermediates, expressed in I, and that migration of the hydrogen or vinyl groups to the presumably somewhat positively charged carbenoid center (C-1) (before or after departure of the metal) leads to the type 1 and type 2 products, respectively.[1a,1b]

Table I. Product Distribution (%) of Metal-Catalyzed Reaction[a]

Compd	$PdCl_2(C_6H_5CN)_2$[b]			$AgClO_4$[c]		
 **1**	 **4** (90)[d]			 **5** (97)[e]		
 **1**-III	**4** (95)			**4** (95)		
 **2a**	 **6** (37)	 **7** (16)	 **8** (47)[d]	**6** (78)	**7** (22)	**8** (0)[c]
 **2b**	**6** (51)	**7** (24)	**8** (24)[d]	**6** (5)	**7** (95)	**8** (0)[e]
 CHN_2 **2**-III	**6** (26)	**7** (14)	**8** (60)	**6** (17)	**7** (38)	**8** (45)
 **3**	 **9** (95)			**9** (90)		
 CHN_2 **3**-III	**9** (90)			**9** (90)		

[a] The yields described herein are the average based on the integration of glpc peaks using cyclohexane as reference. [b] Bicyclobutanes (0.2 *M*) with a catalytic amount of $PdCl_2(C_6H_5CN)_2$ in chloroform at 25°. [c] Bicyclobutanes (0.3 *M*) with $AgClO_4$ (0.1 *M*) in benzene at 25°. [d] Reference 1b. [e] Reference 1d.

In sharp contrast to Pd(II), in the presence of Ag(I), bicyclobutanes and the corresponding diazo compounds behaved in a dramatically different manner in the following two cases. While compound **1** was rearranged exclusively to compound **5**, **1**-III gave compound **4**, but none of **5**. We found earlier[1d,5] that **2a** and **2b** underwent stereoselective isomerization to provide *trans,trans*- and *cis,trans*-hexa-2,4-dienes (**6** and **7**), respectively, and that 2-methylpentadiene (**8**) was absent in the product. However, the main product of **2**-III was **8** and the stereoselectivity (**6** and **7**) was decreased to a large extent.

In spite of the recent proposal[1c] that carbenoid Ag(I) (II) is an intermediate in nearly all the Ag(I)-catalyzed reactions of bicyclobutanes including **1**, we do not believe that there has been presented compelling evidence to demand such a species intervening in all these reactions. Rather, *if* the earlier proposal by Kirmse for the mechanism of diazoalkane–metal reactions is applicable to the present case, then the intermediacy of II is excluded in one case (compound **1**) and not mainly responsible for the formation of the major products in another case (**2a** and **2b**). This reasoning leads us to consider seriously an alternative mechanism. The type 2 product could also arise from a pathway not involving a carbenoid but rather the heterolytic cleavage of the C-1,2 bond followed by a cyclopropylcarbinyl–allylcarbinyl-type rearrangement.[1b] The similarity of Ag(I)-catalyzed reactions to the carbonium type rearrangements was implied earlier by inspecting the structures of starting material and products, and was indicated in the investigation of other systems.[6,7] In the following communication, we elaborate on this particular aspect of the Ag(I)–bicyclobutane rearrangement.[8]

Acknowledgment. We are grateful to the National Research Council of Canada for financial support.

---

(5) L. A. Paquette, S. E. Wilson, and R. P. Henzel, *J. Amer. Chem. Soc.*, **93**, 1288 (1971).

(6) J. E. Byrd, L. Cassar, P. E. Eaton, and J. Halpern, *Chem. Commun.*, 40 (1971); K. L. Kaizer, R. F. Child, and P. M. Maitlis, *J. Amer. Chem. Soc.*, **93**, 1270 (1971).

(7) Compound 3 and 3-III provided the same product, **9**. While **3**-III very likely proceeded through II followed by the vinyl migration, **3** may have undergone a carbonium ion type rearrangement, at least as probably as a carbenoid (II) type reaction. Experimental evidence to provide a clear distinction between the two pathways in the case of **3** is not available at present. For further discussion, see ref 8.

(8) M. Sakai, H. H. Westberg, H. Yamaguchi, and S. Masamune, *ibid.*, **93**, 4611 (1971).

M. Sakai, S. Masamune*
Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada

Received June 7, 1971

Silver(I)-Catalyzed Rearrangement of Bicyclobutanes. Some Aspects of the Mechanism. II[1]

Sir:

We wish to present evidence which sheds light on the initial and ensuing stage of the silver(I)-catalyzed rearrangement of bicyclobutane.[2]

That the initial attack of Ag(I) on the bicyclobutane system very likely involves a one-bond rupture rather than a simultaneous two-bond cleavage has been supported by the following experiments using tricyclo-$[4.1.0.0^{2,7}]$heptane (**1**) as an example. Treatment of **1** (0.4 *M*) in methanol with silver perchlorate (0.1 *M*) in the presence of a trace of sodium methoxide (5×10^{-3}) provided in more than 90% yield a 94:6 mixture of *cis*- and *trans*-methoxybicyclo[4.1.0]heptanes (**2a** and

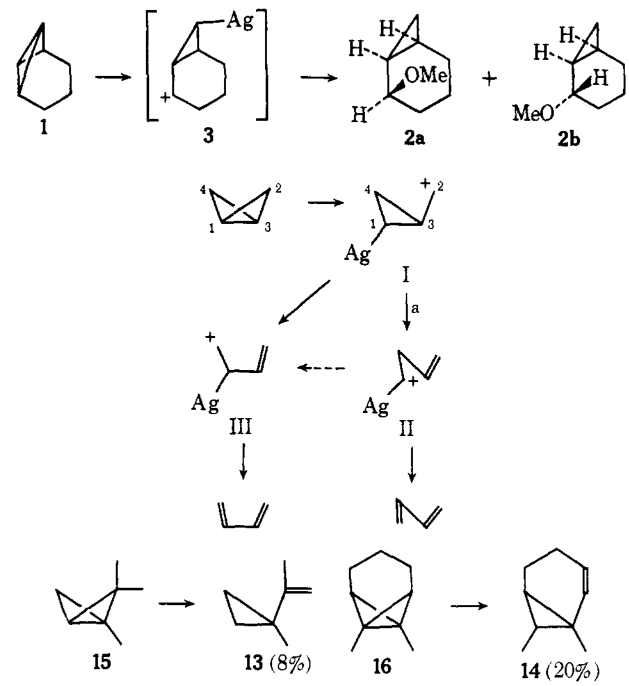
---

(1) Part I: M. Sakai and S. Masamune, *J. Amer. Chem. Soc.*, **93**, 4610 (1971).

(2) For the recent literature, see (a) L. A. Paquette, R. P. Henzel, and S. E. Wilson, *ibid.*, **93**, 2335 (1971); (b) M. Sakai, H. Yamaguchi, H. H. Westberg, and S. Masamune, *ibid.*, **93**, 1043 (1971), and references therein.

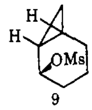
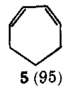
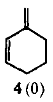
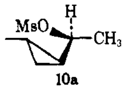
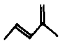
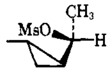
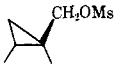
2b) within 2 min. In order to eliminate the possibility that this reaction was effected by a proton instead of Ag(I), we performed a control experiment.[3] With ammonium perchlorate and a trace of sodium methoxide, **1** was recovered unchanged, at least in 75% yield after 20 hr.[4] These results strongly indicate that the initial intermediate in the Ag(I)–bicyclobutane reaction in an aprotic solvent such as benzene would possess the structure shown in **3** and use of methanol effects interception of **3**,[5] Ag(I) being ejected, a well-known protonolysis (see Scheme I).

Scheme I



Next we have considered, as a likely fate of the intermediate of general structure I, a cyclopropyl–allylcarbinyl rearrangement which results in cleavage of either the C-1,3 or C-3,4 bond. If C-1,3 is preferred (route a), then I is converted into a carbenoid–Ag(I) complex II.[1,2a] That this may not always be the case has already been discussed.[1] We have directed attention to the similarity of the Ag(I)-catalyzed reaction and the carbonium-type rearrangement and have examined the product distribution of the elimination reaction of cyclopropylcarbinyl mesylates in benzene, using pyridine or 1,5-diazabicyclo[4.3.0]non-5-ene. The mesylate group is placed at the carbonium center of I and since silver is ejected as Ag(I) from the reaction system, H^+B serves to simulate the collapse of I. The results are summarized in Table I.[6] The product distributions of the two different reactions, Ag(I)–bicyclobutanes and the elimination reaction of cyclopropylcarbinyl mesylates, are remarkably similar. Compound **9** was converted exclusively into **5**, and not into **4**.[7] *exo,exo*-2,4-Dimethylbicyclobutane[7] and mesylate (**10a**) provided mainly *trans,trans*-dimethylhexa-2,4-diene (**6**) while the endo,exo isomer (bicyclobutane) and **10b** both gave *trans,cis*-hexadiene (**7**).[2b] The two sets of starting materials are stereochemically interrelated through intermediate I (see the stereochemistry of **2a**). Further, compounds **11** and **12** provided the type 1 product[1] only, strongly indicating the preference of C-1,3 bond cleavage in both reactions. It is reasonable to assume that the bond cleavage of I occurs in such a way as to produce the more substituted carbonium ion which in turn ejects Ag(I) or H^+ to complete the reaction.

Table I. Product Distribution of the Elimination Reaction of Mesylates

Compd	Reagent	Product (%)[d]		
 9	*a, b*	 **5** (95)	 **4** (0)	Unknown (5)
 **10a**	*a, b*	 **6** (75)	 **7** (20)	 **8** (0)
 **10b**	*a, b*	**6** (8)	**7** (86)	**8** (0)
 **11**	*c*	**8** (95)		
 **12**	*b*	**8** (95)		

[a] 2 equiv of pyridine at 70°. [b] 2 equiv of 1,5-diazabicyclo[4.3.0]-non-5-ene. [c] Bicyclobutane (0.3 *M*) with $AgClO_4$ (0.1 *M*) in benzene at 25°. [d] Determined by glpc using cyclohexane as reference.

The proposal of intermediate I offers a distinct advantage for rationalizing the formation of rather uncommon products reported earlier.[2a] Two vinylcyclopropanes (**13** and **14**) were obtained as minor products from 1,2,2-trimethylbicyclobutane (**15**) and 1,7-dimethyltricyclo[4.1.0.$0^{2,7}$]heptane (**16**).[8] Collapse of the

---

(3) The extreme acid sensitivity of bicyclobutane is well known [K. B. Wiberg and G. Szeimies, *J. Amer. Chem. Soc.*, **92**, 571 (1970) and ref 2b (footnote 4)]. Acid-catalyzed conversion of **1** in methanol was reported to afford a 4:1 mixture of **2a** and **2b** (also confirmed by us). With $PdCl_2(C_6H_5CN)_2$ the ratio was 88:12. A variation in product distribution caused by different catalysts (*e.g.*, H^+ and Ag(I)) shows that a ring of **1** was opened by Ag(I) but not by a trace of acid adventitiously present in the reaction mixture.

(4) Silver hydroxide ($K_b = 1.15 \times 10^{-4}$) is a stronger base than ammonium hydroxide ($K_b = 1.79 \times 10^{-5}$) [J. W. Mellow, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. III, Longmans, London, 1923, p 380]. Our best experimental pH values of *ca.* 0.2 *M* aqueous solutions of $AgClO_4$ and NH_4ClO_4 were 5.5 and 5.4, respectively, and the addition of a trace of base to these solutions changed the pH's to more than 8.5. **1** was perfectly stable in acid-free methanol, at least, for a few days.

(5) The change of solvent causes a significant change in the ligand coordination of the metal and the present argument assumes that this change does not affect the main features of the initial stage of the Ag(I)–bicyclobutane reaction in benzene. Conversion of **1** to **2** appears quite general and we have observed that the reaction can be effected by various transition metals. Professor P. G. Gassman kindly informed us of his extensive studies on this subject (June 2, 1971). Since most of the metal complex, *e.g.*, $[Rh(CO)_2Cl]_2$, could be recovered from methanol (Gassman), the above assumption appears justified. However, in a rigorous sense, a change of mechanism in methanol is not ruled out.

(6) Mesylates **10a**, **10b**, and **12** and their precursor, hydroxy compounds, are new. The latter compounds were prepared from the corresponding alkenes by the Simmons–Smith reaction and the stereochemistry of the products was assigned based on the established course of this reaction. Spectral and glpc data showed that the new compounds were pure and supported the structures assigned herein.

(7) See Table I of ref 1 for the product distribution of the Ag(I)–bicyclobutane reaction.

(8) Alternatively, it is not impossible to interpret the results invoking a carbene (derived from a species of structure II) insertion mechanism.

bicyclobutanes into **13** and **14** appears not to require any further elaboration.

This and the preceding communication have demonstrated that there are not sufficient data that compel one to invoke the intermediacy of carbenoid–Ag(I) or argentocarbonium ions[2a] in nearly all the Ag(I)-catalyzed reactions. All the experimental evidence presently available to us tends to suggest that the initial one-bond cleavage intermediate I is *the dividing point leading to various types of products for the bicyclobutanes examined thus far.*[9] Evidence is (i) trapping of I, (ii) the stereoselectivity observed in the reactions of **10a**, **10b**, and the corresponding dimethylbicyclobutanes, (iii) formation of **5** from **1** and **9**, and (iv) reasonable explanation for the formation of uncommon products, **13** and **14**. However, several assumptions have been made and, in the absence of detailed knowledge of C-Ag and C:-Ag(I), additional work is demanded before one can define the precise mechanism of the Ag(I)-catalyzed reaction. An issue central to the whole subject is concerned with the origin of different behavior exhibited by Ag(I) and Pd(II) and certainly it remains to be answered.

Acknowledgment. We are grateful to the National Research Council for financial support.

---

[9] Since we have not studied extensively the trapping experiment, we are at present unable to state that the C-1,2 bond is *invariably* the one initially cleaved by Ag(I). Therefore, the possibility exists that the C-1,3 bond may be in some cases attacked to provide cyclobutyl cations which collapse into products, following pathways reasonably expected for this type of species.

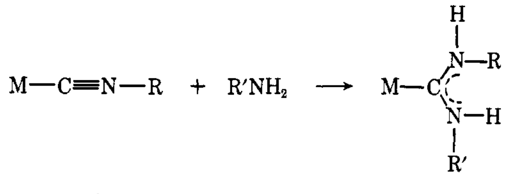
M. Sakai, H. H. Westberg, H. Yamaguchi, S. Masamune*
Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada

Received June 7, 1971

Addition of Methylamine to Hexakis(methyl isocyanide)iron (II). The Formation of an Unusual Chelating Ligand

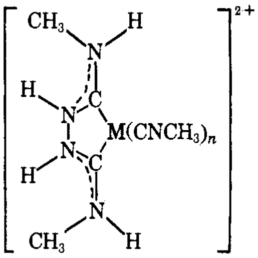
Sir:

Several cases of addition of amines to coordinated isocyanides (eq 1) have been described.[1–6] In all of



$$\mathrm{M{-}C{\equiv}N{-}R} + \mathrm{R'NH_2} \longrightarrow \mathrm{M{-}C(NHR)(NHR')} \qquad (1)$$

these cases, the addition has been limited to a single isocyanide. However, hydrazine has been shown to react with the complexes $Pd(CNCH_3)_4{}^{2+}$,[7,8] $Pt(CNCH_3)_4{}^{2+}$,[7,8] and $Fe(CNCH_3)_6{}^{2+}$ [9] to yield products **1**, **2**, and **3**, respectively, in which addition to two adjacent isocyanide ligands has occurred to form a chelate ring. We now report the first example of addition of a monofunctional amine to two isocyanide ligands.



1, M = Pd; *n* = 2
2, M = Pt; *n* = 2
3, M = Fe; *n* = 4

Refluxing a methanolic solution of $Fe(CNCH_3)_6(HSO_4)_2$ with an excess of methylamine for 12 hr yields, after precipitation with ammonium hexafluorophosphate and recrystallization from methanol–2-butanol, the very pale yellow complex **4** having the empirical formula $[Fe(CNCH_3)_6 \cdot CH_3NH_2][PF_6]_2$. In nitromethane, **4** is a 2:1 electrolyte (Λ = 182 ohms^{-1} cm^2 M^{-1} at 10^{-3} M). The infrared spectrum (fluorocarbon mull, 4000–1500 cm^{-1}) exhibits absorptions at 3330, ν(N—H); 2960, ν(C—H); 2244, 2205, ν(C≡N); 1613, 1589, ν(N$\cdots$C$\cdots$N) and δ(N—H).

Crystals of **4** belong to the monoclinic space group $P2_1/c$. Unit cell data are: a = 8.17 (1), b = 20.08 (2), c = 16.32 (2) Å, cos β = −0.0997 (14); Z = 4; d_{calcd} = 1.526, d_{obsd} = 1.53 (1) g cm^{-3}. A crystal of dimensions 0.06 × 0.05 × 0.36 mm was mounted about a, the needle axis, and 797 data having $F_o{}^2 > \sigma(F_o{}^2)$ and $2\theta \leqslant 30°$ were collected using Mo Kα radiation and a four-circle diffractometer. The positions of the Fe and P atoms were located from a Patterson function, and the C, N, and F atoms appeared in successive electron-density maps. These maps also revealed a twofold disorder of one of the $PF_6{}^-$ ions. An occupancy factor was included as a variable in the least-squares refinement, and the $PF_6{}^-$ ions were treated as rigid groups.[10] Isotropic refinement converged to a conventional R factor of 0.147. A difference electron-density map shows that there is still complex thermal motion and/or disorder of the $PF_6{}^-$ ions which is not adequately described by the present isotropic model. The geometry of the cation is that shown for **4**; distances and angles in the novel chelate system appear in Figure 1. The limited number of nonzero data obtained from the small crystal and the overly simple model for the $PF_6{}^-$ ions have resulted in rather large uncertainties for interatomic distances and angles. These large errors preclude any detailed comparisons of the distances found here to those observed in other related complexes. However, the average Fe-C(chelate) distance of 2.02 (4) Å is similar to the Fe-C(sp^2) distance of 1.987 (5) Å reported[11] for $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2C_2H_4$.

The pmr spectrum of **4** in trifluoroacetic acid is consistent with the X-ray structure and provides unambiguous evidence for the locations of the protons.

---

[1] E. M. Badley, J. Chatt, R. L. Richards, and G. A. Sim, *Chem. Commun.*, 1322 (1969); E. M. Badley, J. Chatt, and R. L. Richards, *J. Chem. Soc. A*, 21 (1971).

[2] R. J. Angelici and L. M. Charley, *J. Organometal. Chem.*, **24**, 205 (1970).

[3] F. Bonati and G. Minghetti, *ibid.*, 24, 251 (1970).

[4] F. Bonati, G. Minghetti, T. Boschi, and B. Crociani, *ibid.*, **25**, 255 (1970).

[5] B. Crociani, T. Boschi, and U. Belluco, *Inorg. Chem.*, **9**, 2021 (1970).

[6] E. M. Badley, B. J. L. Kilby, and R. L. Richards, *J. Organometal. Chem.*, 27, C37 (1971).

[7] A. Burke, A. L. Balch, and J. H. Enemark, *J. Amer. Chem. Soc.*, **92**, 2555 (1970).

[8] W. M. Butler and J. H. Enemark, *Inorg. Chem.*, in press.

[9] A. L. Balch and J. Miller, submitted for publication.

[10] J. A. McGinnety, N. C. Payne, and J. A. Ibers, *J. Amer. Chem. Soc.*, **91**, 6301 (1969)

[11] M. R. Churchill and J. Wormald, *Inorg. Chem.*, **8**, 1936 (1969).