demonstrated by employing a σ–π separation, modifying the VSEPR treatment.[3]

To compare quantitative predictions, the following VSEPR model was examined: bonded and lone electron pairs were placed on a sphere and were assumed to repel one another according to a potential of the form $1/r^n$. Appropriate values of n have been considered elsewhere.[9] Calculations using $n = 2$ and 4 appear in Table I. Mutual bond-pair repulsions were weighted by a factor of 0.5, lone-pair repulsions by 1.0, and bond-pair–lone-pair repulsions by the geometric mean, 0.7. A single unpaired electron was given half the weight of a pair. These factors represent the lessened presence of bonding electrons in the valence shell, as assumed in VSEPR discussions.[4] For $^2A_1$ NH_2 and $^3B_1$ CH_2 a pπ orbital was used as in the TSP calculations. For O_3, two C_s symmetry models gave predicted bond angles differing by less than a degree. In one model, the double bond was represented by two coincident pairs. Alternatively, the two pairs of a bent-bond double bond were placed above and below the molecular plane.

Table I. Bond Angle Predictions from Various Models

Symmetry[a]	Calcd angle[a] $n = 2$	$n = 4$	Exptl[b] angle	Calcd TSP	Molecule
$^2A_1$	128	126	131	118	BH_2
			119	117	AlH_2
$^1A_1$	112	114	101	99	SiF_2
			102	100	CH_2
$^3B_1$	128	126	136[c]	120	CH_2
$^2A_1$	128	126	144	120	NH_2
			123	118	PH_2
$^1A_1$	103	104	105	102	H_2O
			92	99	H_2S
			104	107	OF_2
$^1A_1$, $^1A'$	120	118	117	128	O_3
			120	120	SO_2
			118	122	SSO
$^1A_1$	106	107	108		NH_3
			93		PH_3
$^1A_1$	85	86	87[d]		ClF_3
			86[d]		BrF_3

[a] Given for each new configuration. [b] Same sources as ref 1 unless otherwise indicated. [c] G. Herzberg and J. W. C. Johns, *J. Chem. Phys.*, **54**, 2277 (1971). [d] L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. **11**, M87 (1958); No. **18**, M49s (1965).

This is to our knowledge the first attempt to apply a quantitative VSEPR-type model to a variety of molecules.[10] No claim is made that the form is optimal—for example, ligand electronegativity was ignored. However, the model gives encouraging results, comparable to those from the TSP. Neither model handles well the frequent sharp difference between second-shell and third-shell valence angles; the TSP angle change is in the right direction, but in each case is much too small. The small dependence of the VSEPR predictions on n is encouraging, since the best function is probably not a single reciprocal power.

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(9) H. B. Thompson and L. S. Bartell, *Inorg. Chem.*, **7**, 488 (1968); W. J. Adams, H. B. Thompson, and L. S. Bartell, *J. Chem. Phys.*, **53**, 4040 (1970).

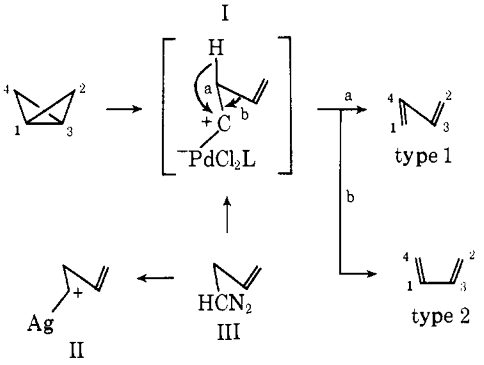
(10) See, however, A. W. Searcy, *ibid.*, **28**, 1237 (1958), for an electrostatic model using different weighting for differing electron pairs. Recent electron-domain models (see ref 3–6) have assumed that localized pairs are separated primarily by exclusion-principle considerations. Searcy determined empirically a different weighting for each type of ligand, and for a second-period central atom as opposed to a third- or higher period atom. With this flexibility, Searcy duplicated well a variety of bond angles.

Silver(I)-Catalyzed Rearrangement of Bicyclobutanes. Some Aspects of the Mechanism. I

Sir:

Numerous reports have appeared recently concerning the rearrangement of the bicyclobutane system promoted by metals of the second and third transition series, in particular, Rh(I), Pd(II), and Ag(I).[1] Three aspects of this rearrangement soon became apparent: (i) various alkyl-substituted bicyclobutanes are isomerized to butadienes in almost all cases investigated; (ii) products can be classified into two groups, those (type 1) resulting from a formal C-1,2 and C-1,3 cleavage of bicyclobutanes and those (type 2) from a C-1,2 and C-3,4 bond cleavage; and (iii) the distribution between the two types of products is very sensitive to the positions of alkyl substituents on the starting material and the kind of metal catalyst employed in the reaction. In the case of Pd(II) we proposed the intermediacy of a metal complex of structure I[1b,2] which led to the type 1 and presumably also to the type 2 product. However, we avoided proposing a similar Ag(I) complex II[3] as an intermediate common to all reactions. In this communication we present experimental results which are consistent with our earlier proposals for the Pd(II)–bicyclobutane reaction but suggest that intermediate II may not necessarily be involved in several Ag(I)-catalyzed reactions, in particular, those producing the type 2 product.

Scheme I



Recent studies[4] have indicated that reactions of diazoalkanes with transition metals [including Ag(I)] lead to the formation of complexes consisting of the

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(1) For Rh(I): (a) P. G. Gassman, T. J. Atkins, and F. J. Williams, *J. Amer. Chem. Soc.*, **93**, 1812 (1971), and references quoted therein. For Pd(II): (b) M. Sakai, H. Yamaguchi, and S. Masamune, *Chem. Commun.*, 486 (1971), and references quoted therein. For Ag(I): (c) L. A. Paquette, R. P. Henzel, and S. E. Wilson, *J. Amer. Chem. Soc.*, **93**, 2335 (1971), and (d) M. Sakai, H. Yamaguchi, H. H. Westberg, and S. Masamune, *ibid.*, **93**, 1043 (1971), and references therein.

(2) In ref 1a, a Rh complex similar to I is described, using two resonance structures.

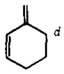
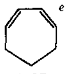
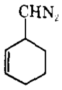
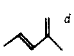
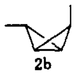
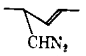
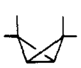
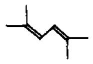
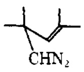
(3) The argentocarbonium ion proposed by Paquette, *et al.*,[1c] is essentially the representation of an extreme resonance form of the formal Ag(I)–carbene complex.

(4) W. Kirmse and K. Horn, *Chem. Ber.*, 100, 2698 (1967); W. R. Moser, *J. Amer. Chem. Soc.*, **91**, 1135 (1969).

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**	[d] **4** (90)			[e] **5** (97)		
 CHN$_2$ **1**-III	**4** (95)			**4** (95)		
 **2a**	 **6** (37)	 **7** (16)	[d] **8** (47)	**6** (78)	**7** (22)	**8** (0)[e]
 **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.

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[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).

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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

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[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.