Tetrahedron Letters No. 48, pp 4909 - 4912, 1972. Pergamon Press. Printed in Great Britain.

REVERSIBLE COMPLEX FORMATION AND KINETIC SUBSTITUENT EFFECTS IN THE SILVER(I) ION INDUCED BOND REORGANIZATION OF HOMOCUBANES[1]

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(Received in USA 1 September 1972; received in UK for publication 28 October 1972)

1,8-Bishomocubanes, homocubanes, and cubanes are recognized to undergo remarkably facile valence isomerization to less strained dicyclopropane isomers when treated with catalytic quantities of soluble Ag^+ salts.[3] The precise manner in which such rearrangements occur has been the subject of considerable controversy, with suggestions running the gamut from a concerted $[\sigma 2_a + \sigma 2_a]$ electrocyclic process[4] to the involvement of carbonium ions[5] or radical cations.[6] Presently, we describe experiments utilizing homocubane and several 4-substituted derivatives of this hydrocarbon which attest to the operation of initial reversible metal ion-carbon σ bond complexation and to the absence of mechanistic crossover with substantial modification of the electronic nature of the substituent.

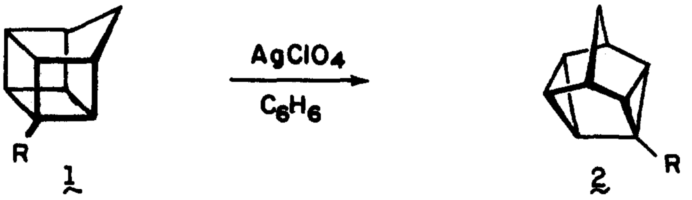
Kinetically, the rates of conversion of **1** to **2**[7,8] (Table I) follow the second-order catalytic rate law $-d[\mathbf{1}]/dt = k_{Ag}[\mathbf{1}][AgClO_4]$. All rates were measured at 40.3° in anhydrous benzene except those for **1g** which were determined at 122.8°, 130.7°, and 142.8° and

Table I. Isomerization Rate Data for **1** ($AgClO_4$, C_6H_6, 40.3°)[a]

Compd. No.	R	k_{Ag}, M^{-1} sec^{-1}	Rel Rate
1a	H	7.36×10^{-4}	1.0
1b	CH_3	7.15×10^{-3}	9.7
1c	CD_3	7.37×10^{-3}	(k_H/k_D = 0.970)
1d	CH_2OAc	7.39×10^{-5}	0.1
1e	CH_2OCH_3	1.10×10^{-3}	1.5
1f	CH_2OH	8.49×10^{-3}	11.5
1g	$COOCH_3$	1.83×10^{-7}[b]	2.5×10^{-4}

[a] Rates of conversion of **1a**-**1g** to **2a**-**2g** were determined by vpc methods.

[b] Extrapolated from data obtained at higher temperatures.



extrapolated to this lower temperature ($\Delta H^{\ddagger}$ = 23.9 kcal/mole; $\Delta S^{\ddagger}$ =-13.1 eu). A study of the initial rates of conversion of 1b to 2b as a function of the concentration of 1b revealed the nonlinear variation in rate shown in Figure 1. This adherence to equation 1 demonstrates unambiguously that rapid and reversible Ag^+- homocubane complex formation obtains.[9] The preequilibrium constant for 1b at 40.3° is 0.19.

$$\frac{-d[\text{homocubane}]}{dt} = \frac{k_2K[\text{homocubane}][\text{AgClO}_4]}{K[\text{homocubane}] + 1} \qquad (1)$$

A plot of log k_{Ag} against the appropriate Taft σ^* constants[10] (Figure 2) defines a straight line of excellent precision (r = 0.995).[11] The slope of this line (ρ^*) as defined by the method of least squares is -2.33. These results suggest that certain limitations of mechanism are warranted in that segment of reaction leading to the rate-determining transition state. Firstly, since the kinetic behavior conforms to a linear free energy relationship and because σ^* is defined as characteristic of chemical change occurring at a single reaction site, multicenter reactivity in progressing from 1a to 1g can be excluded.[13] Specifically, this means that the same bond or bonds of the strained carbon framework necessarily comprise the reaction center, despite substantial electronic modification of the substituent.

Secondly, although the observed ρ^* value is appreciably negative, it does not appear compatible with the development of positive charge on the corner carbon atom adjacent to the substituent in the rate-determining step. In such a case, ρ^* would be expected to be significantly more negative.[10] This conclusion is substantiated on a quantitative basis by the kinetic behavior of 1c for which an inverse isotope effect (k_H/k_D) of 0.970 ± 0.005 was measured. Hyperconjugative electron release from the CD_3 group is clearly not operative; were this so, a positive fractionation factor in the vicinity of 1.068-1.092[14] would be in evidence and it is not. Rather, the magnitude and sign of ρ^* are consistent with the

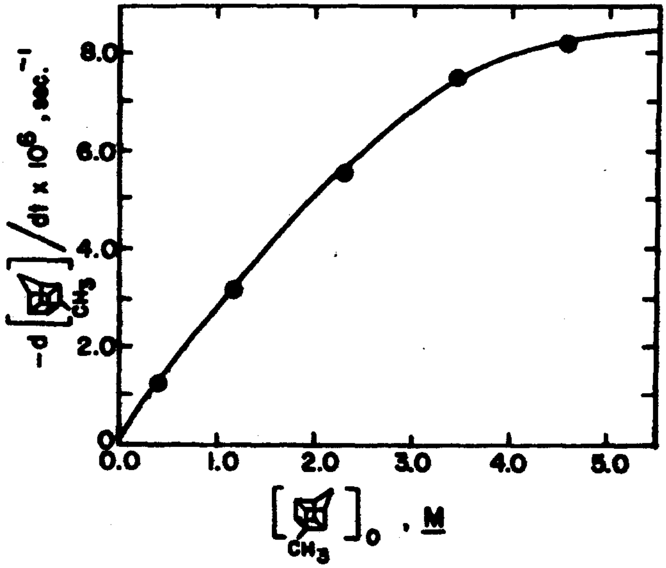


Figure 1. Initial rates of conversion of 4-methylhomocubane (1b) to 2b as a function of the concentration of 1b. All runs were performed at 40°C in 3.03×10^{-4} *M* silver perchlorate solutions consisting of 30% benzene and 70% cyclohexane -- 1b (v : v).

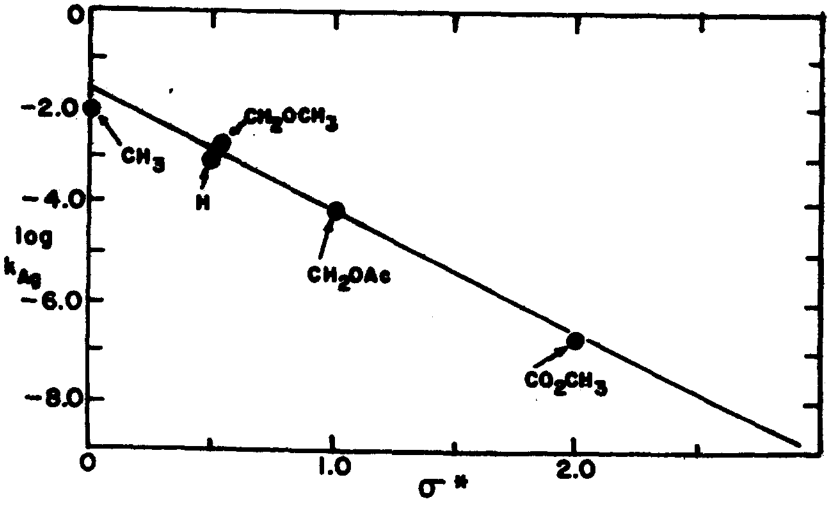
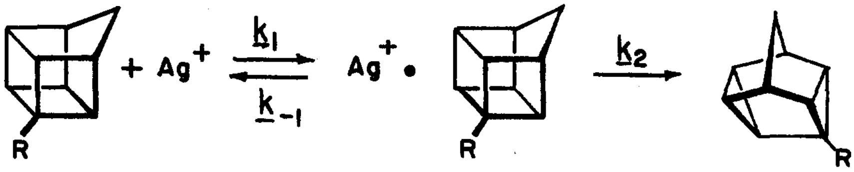


Figure 2. Plot of log $\underline{k}_{Ag}$ *vs* σ^*.

prequilibrium nature of the isomerization.[15]



FOOTNOTES AND REFERENCES

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5) (a) J.E. Byrd, L. Cassar, P.E. Eaton, and J. Halpern, *Chem. Commun.*, 40 (1971); (b) W.G. Dauben and A.J. Kielbania, Jr., *J. Amer. Chem. Soc.*, **93**, 7345 (1971).
6) K.L. Kaiser, R.F. Childs, and P.M. Maitlis, *ibid.*, **93**, 1270 (1971).
7) The various homocubanes were prepared by well precedented chemical manipulation of homocubane-4-carboxylic acid: G.L. Dunn, V.J. DiPasquo, and J.R.E. Hoover, *J. Org. Chem.*, **33**, 1454 (1968); L.A. Paquette and J.S. Ward, *J. Org. Chem.*, in press.
8) The various rearrangements afforded only **2** for which supportive spectral and analytical data were obtained, except **1g** which yielded along with **2g** approximately 10% of a minor, as yet unidentified, component. The sums of the quantities of these compounds *vs.* time were used in the kinetic computations.
9) K.J. Laidler, ''Chemical Kinetics,'' McGraw-Hill, New York, N.Y., 1950, pp 276-281.
10) The values of σ^* were those of Taft [R.W. Taft, Jr., in ''Steric Effects in Organic Chemistry,'' M.S. Newman, ed., John Wiley and Sons, Inc., New York, N.Y., Chap. 13]. In the case of R = CH_2OAc, the value of 1.01 was employed [G.F. Koser, *Chem. Commun.*, 388 (1971)].
11) It is to be noted that the point for **1b** is not included in this graph. Incorporation of the data for this alcohol leads to an r value of 0.957. Such a deviation in the case of R = CH_2OH, which has been noted also in the addition of oxymercuric salts to olefins,[12] presumably arises because of efficient coordination of the hydroxyl oxygen to the metal ion of mechanistic consequence (note requisite kinetic dependence on k_2K).
12) J. Halpern and H.B. Tinker, *J. Amer. Chem. Soc.*, **89**, 6427 (1967).
13) For a recent example of competitive attack throughout a wide range of substituents resulting in a non-linear reactivity correlation, see M.-F. Ruasse and J.E. Dubois, *Tetrahedron Lett.*, 1163 (1970).
14) M. Nikoletic, S. Borcic, and D.W. Sunko, *Tetrahedron*, **23**, 649 (1967).
15) See, for example, T. Fueno, O. Kajimoto, T. Okuyama, and J. Furukawa, *Bull. Chem. Soc. Japan*, **41**, 785 (1968); M. Charton, *J. Org. Chem.*, **31**, 2991 (1966).