naphthalene although there is very strong spectral overlap the oscillator strength of the naphthalene transition is low.[14]

Acknowledgment. The assistance of Messrs. Dennis Rushforth, Charles Lombard, and Jeffrey K. McVey during various phases of this work is acknowledged. The author wishes to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, The Research Corporation, and the National Science Foundation (GP-32953) for support of this research.

(14) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, 1971, p 330.

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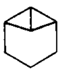
Received June 20, 1973

Transition Metal Catalyzed Rearrangements of Bicyclobutanes. Mechanism of Acid Production in Methanolysis[1]

Sir:

In our recent investigation of the transition metal catalyzed isomerization of tricyclo[4.1.0.0^{2,7}]heptane (**1**), the involvement of an organometallic carbene intermediate (**2**) was indicated.[2] It was also shown that the formation of 2-norcarane methyl ether (**3**) in the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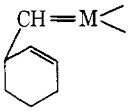

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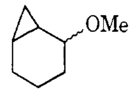

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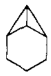
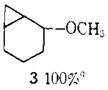
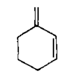
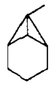
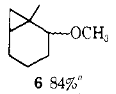
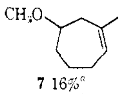
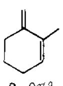
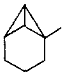
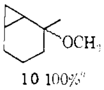
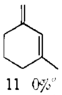
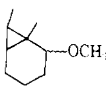
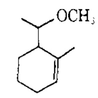
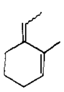
reaction of **1** with $[Rh(CO)_2Cl]_2$ in methanol resulted from a protic acid catalyzed reaction. These methanolic studies have been extended to substituted bicyclobutanes and, again, all reaction solutions became acidic. We now present evidence as to the nature of the acid-forming species.

As in our initial studies, solid $[Rh(CO)_2Cl]_2$ was added to a methanol solution of the bicyclobutane, with and without solid $NaHCO_3$. Table I lists the results of the study. When $NaHCO_3$ was absent, the pH[3] rapidly dropped from about 8.0 for the bicyclobutane–methanol solution to about 2.5 when the Rh(I) catalyst was added, and the pH slowly increased.[4] With $NaHCO_3$ present, the pH only dropped to 5.0 and then rapidly increased.[5]

Table I. Reactions of $[Rh(CO)_2Cl]_2$ and Bicyclobutanes in Methanol

Reactant	Products and reaction conditions		
 1	 3 100%[a] 10%[b]		 4 0%[a] 90%[b]
 5	 6 84%[a] 72%[b]	 7 16%[a] 13%[b]	 8 0%[a] 15%[b]
 9	 10 100%[a] 90%[b]		 11 0%[a] 10%[b]
 12	 13 75%[a] 75%[b]	 14 25%[a] 25%[b]	 15 0%[a] 0%[b]

[a] Reactions were performed using 5 ml of methanol and a mole ratio of bicyclobutane to Rh(I) catalyst of approximately 20:1; 8 mg of Rh(I) catalyst was added to a methanolic solution of the bicyclobutane. Reaction times were approximately 10 min. Product distributions were analyzed by nmr and vpc and are normalized. In general as the degree of substitution on the bicyclobutane increased, product formation was not as quantitative as in the case of **1**. [b] Same reaction conditions as in footnote *a* with 50 mg of sodium bicarbonate present.

Recently, Gassman and Reitz[6] showed that the pH value obtained when a bicyclobutane solution was added to a methanolic solution of $[Rh(CO)_2Cl]_2$ depended upon the rate of addition of the hydrocarbon. The results of a similar study with substituted bicyclobutanes are reported in Table II. As the rate of addition of the bicyclobutane solution was decreased, larger amounts of diene were formed; the presence of $NaHCO_3$ also increased the amount of dienes formed.

Table II. Reaction of Bicyclobutanes and $[Rh(CO)_2Cl]_2$ in Methanol

Reactants	Products and reaction conditions (%) I[a]	II[b]	III[c]
1	**3** (49)	**3** (35)	**3** (5)
	4 (51)	**4** (65)	**4** (95)
5	**6** (71)	**6** (70)	**6** (34)
	7 (13)	**7** (14)	**7** (13)
	8 (16)	**8** (16)	**8** (53)
9	**10** (83)	**10** (75)	**10** (18)
	11 (17)	**11** (25)	**11** (72)
12	**13** (75)	**13** (62)	**13** (2)
	14 (20)	**14** (18)	**14** (1)
	15 (0)	**15** (0)	**15** (0)
	12 (5)	**12** (20)	**12** (97)

[a] Reactions were carried out by dropwise addition (~1 drop every 12 sec) of a solution of bicyclobutane (~0.05 ml) and 2 ml of methanol to a solution of 8 mg of $[Rh(CO)_2Cl]_2$ and 3 ml of methanol. Products were analyzed by vpc. [b] Rate of addition of the bicyclobutane solution was decreased to about one drop every minute. [c] Rate of addition was the same as in footnote *b* with 20 mg of $NaHCO_3$ present.

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(1) This work was supported by National Science Foundation Grant No. GP-8700.

(2) (a) W. G. Dauben and A. J. Kielbania, Jr., *J. Amer. Chem. Soc.*, **94**, 3669 (1972); (b) see also S. Masamune, M. Sakai, and N. Darby, *J. Chem. Soc., Chem. Commun.*, 471 (1972).

(3) We monitored the pH of reaction solutions using a Sargent-Welch Model NX digital pH meter with a Sargent-Welch combination glass electrode S300 72-15. See R. G. Bates, "Determination of pH—Theory and Practices," Wiley, New York, N. Y., 1964.

(4) (a) The addition of $[Rh(CO)_2Cl]_2$ to methanol without bicyclobutanes present results in a rapid decrease in pH from about 8.0 to 4.0. This pH drop may be due to a bridge splitting reaction by methanol resulting in a rhodium complex in which methanol has been incorporated as a ligand. (b) See D. N. Lawson and G. Wilkinson, *J. Chem. Soc.*, 1900 (1965). (c) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Wiley, New York, N. Y., 1972, p 1020.

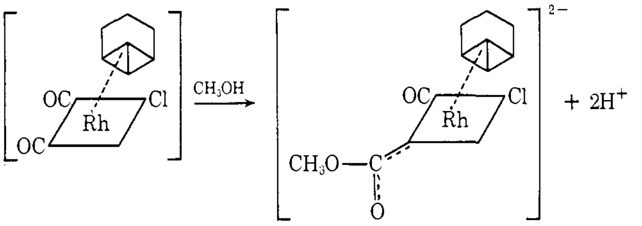
(5) It was found that when **1** was allowed to react for 2 min in methanol of pH 3.4 only **3** was detected in the reaction solution. Using methanol of pH 4.4 after 2 min both **1** (66%) and **3** (34%) were identified.

(6) P. G. Gassman and R. R. Reitz, *J. Amer. Chem. Soc.*, **95**, 3057 (1973).

The lack of diene formation from dimethylbicyclobutane **12** can be attributed to steric retardation effects of the two methyl groups on the metal-catalyzed rearrangement resulting in methyl ethers **13** and **14** arising from the protic acid catalyzed ring opening. This hindrance is also seen in the metal-catalyzed reaction in deuteriochloroform, the rate of reaction of **12** being about 2000 times slower than that of the unsubstituted **1**.[7]

The results in Tables I and II as well as previously published results[6] indicate that a short-lived acidic species is formed when [Rh(CO)$_2$Cl]$_2$ and a bicyclobutane react in methanol. Insight as to the nature of this acidic species was gained by an infrared study of the metal carbonyl absorptions during the course of the reactions. Almost instantaneously after injection of 10 μl of **1** into 0.05 ml of methanol containing 2 mg of [Rh(CO)$_2$Cl]$_2$ three weak bands appeared[8] in the ir at 1905, 1850, and 1780 cm^{-1}, in addition to the two original strong bands at 2060 and 1995 cm^{-1} for the catalyst.[9,10] The three new bands disappeared in about 10 min but reappeared upon addition of 10 μl of **1**. The ir bands also appeared when NaHCO$_3$ was present but their intensities were less when a dilute methanolic solution of **1** was added. The appearance and disappearance of these new ir bands correspond directly with the observed decrease and increase in the pH of the reaction solution.

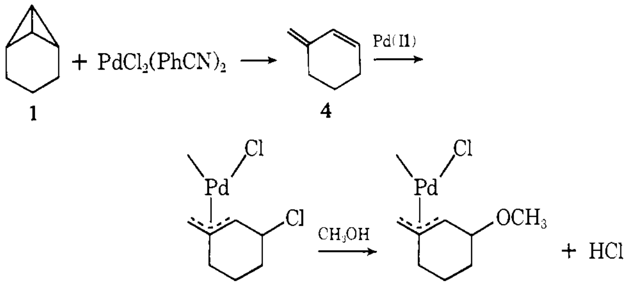
These infrared and acidic properties are suggestive of the initial formation of a dissociated methanolic anionic carbene complex, like **16**, which is unstable[11] and rapidly disproportionates to a diene, methanol, and starting Rh(I) complex.[12–14] This reaction sequence accounts for the rise and fall of the acidity. In the overall process as the highly strained bicyclobutane approaches coordination with the transition metal, or undergoes an oxidative addition,[15,16] the resulting bicyclobutane moiety can act as a strong accepting ligand. Methanol can now attack the now electrophilic carbonyl group to give complex **16**;[13,17–19] indeed, it is possible that the rhodium analog of metal carbene complex **2** may be the ligand which enhances the electrophilicity of the metal carbonyl, carbene carbons being good π acceptors.[13,20]



16

Next, PdCl$_2$(PhCN)$_2$ was studied as a catalyst and found to behave differently than [Rh(CO)$_2$Cl]$_2$. The reversible pH changes shown by the Rh(I)–bicyclobutane–methanol system were not found; the pH dropped to a value of 1 and remained. In an ir study, upon addition of the bicyclobutane to PdCl$_2$(PhCN)$_2$ in methanol two new bands appeared, briefly, at 1630 and 1590 cm^{-1}; further addition of the bicyclobutane did not reproduce the bands. When the reaction was run in methanol-d_4, these new bands were shown to be due to a small amount of diene **4** by nmr.[21]

It is well known that Pd(II) in the presence of a diene in MeOH gives rise to the π-allyl complex in which methoxide has been incorporated giving rise to an acidic solution.[22,23] We should like to suggest that in the Pd(II)–bicyclobutane–methanol system, the initial reaction is a Pd(II)-catalyzed rearrangement of a small amount of **1** to **4**. The diene then forms the π-allyl complex **17** which in the presence of MeOH gives π-allyl complex **18** and hydrogen chloride which, in turn, catalyzes the rearrangement of **1** to methyl ether **3**.[24,25] The direct formation of **18** from **2** cannot be ruled out.



17 **18**

The above results suggest that the reaction of various bicyclobutanes with [Rh(CO)$_2$Cl]$_2$ in methanol forms

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[7] Reactions were carried out in nmr tubes with a molar ratio of bicyclobutane to catalyst of about 20 : 1.

[8] These bands were not due to the bicyclobutane and were not formed when chloroform instead of methanol was used as the reaction solvent.

[9] Similar results were obtained using **5**, **9**, and **12**.

[10] There are three ir-active carbonyl bands for [Rh(CO)$_2$Cl]$_2$ but in methanol we observe only two and this may be due to masking of one band by the other two or a bridge splitting reaction may be involved. See ref 4a,b and 4c, pp 697–698.

[11] Previous attempts at isolating the protonated form of an anionic carbene complex have been unsuccessful due to the instability of the complex. For example, see E. O. Fischer and A. Maasbol, *Angew. Chem., Int. Ed. Engl.*, 3, 588 (1964).

[12] (a) E. O. Fischer, *Pure Appl. Chem.*, **24**, 407 (1970); (b) O. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, **72**, 545 (1972); *Chem. Soc. Rev.*, **2**, 99 (1973), and references therein.

[13] O. J. Darensbourg and M. Y. Darensbourg, *Inorg. Chim. Acta*, **5**, 247 (1970).

[14] The dimeric structure for **16** is based on analogy with [Rh(CO)Cl]$_2$ also; the bicyclobutane ligand may still be incorporated.

[15] (a) J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.*, 7, 53 (1968); (b) J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968); (c) R. Cramer, *ibid.*, **1**, 186 (1968); (d) L. Vaska, *ibid.*, **1**, 335 (1968); (e) G. W. Parshall, *ibid.*, **3**, 139 (1970); (f) J. Halpern, *ibid.*, **3**, 386 (1970).

[16] The oxidative addition reaction has previously been used to describe other metal-catalyzed rearrangements of compounds containing strained carbon σ bonds. For example, see (a) T. J. Katz and S. Cerefice, *J. Amer. Chem. Soc.*, **91**, 2405 (1969); (b) L. Cassar, P. E. Eaton, and J. Halpern, *ibid.*, **92**, 3515 (1970); (c) L. Cassar and J. Halpern, *Chem. Commun.*, 1082 (1970); (d) W. G. Dauben and A. J. Kielbania, *J. Amer. Chem. Soc.*, **93**, 7345 (1971); (e) R. J. Roth and T. J. Katz, *ibid.*, **94**, 4770 (1972); (f) N. Acton, R. J. Roth, T. J. Katz, J. K. Frank, C. A. Maier, and I. C. Paul, *ibid.*, **94**, 5446 (1972).

[17] F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, **93**, 1123 (1971); (b) F. D. Mango, *Intra-Sci. Chem. Rep.*, **6**, 71 (1972).

[18] O. J. Darensbourg and M. Y. Darensbourg, *Inorg. Chem.*, **9**, 1691 (1970).

[19] The reaction of metal carbonyls with alcohols is known. See J. E. Byrd and J. Halpern, *J. Amer. Chem. Soc.*, **93**, 1634 (1971), and references therein.

[20] R. Noyori, *Tetrahedron Lett.*, 1691 (1973).

[21] The region of the ir at about 875 cm^{-1} could not be used with certainty to detect **4** due to the interference of other bands.

[22] (a) S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 4807 (1963); (b) P. M. Maitlis, "The Organic Chemistry of Palladium," Academic Press, New York, N. Y., 1971, pp 175–251.

[23] The addition of **4** to a methanolic solution of PdCl$_2$(PhCN)$_2$ resulted in a rapid drop in pH. This was not observed in the case of [Rh(CO)$_2$Cl]$_2$. Also, the addition of **4** to a methanol solution of [Rh(CO)$_2$Cl]$_2$ did not result in the appearance of the ir bands assigned to complex **16**.

[24] Both complexes **17** and **18** have been independently synthesized.

[25] The presence of complex **18** in the reaction solutions has been detected by nmr.

an acidic solution and the formation of methyl ethers is a result of an acid-catalyzed ring opening of the bicyclobutane.[26] This acid in the case of $[Rh(CO)_2Cl]_2$ can be formulated as arising from an anionic carbene complex[2] and the first spectroscopic evidence of the detection of this carbene complex in the bicyclobutane reaction solution has been presented.[27] For $PdCl_2(PhCN)_2$, the formation of methyl ethers is also the result of an acid-catalyzed ring opening, this acid resulting from the reaction of palladium π-allyl complexes with methanol.

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[26] The acid-forming reaction of bicyclobutanes and other metals in alcohols has also been described. See (a) L. A. Paquette, S. E. Wilson, G. Zon, and J. A. Schwartz, *J. Amer. Chem. Soc.*, **94**, 9222 (1972); (b) E. Muller, *Tetrahedron Lett.*, 1201, 1203 (1973).

[27] The possibility that a rhodium complex containing a methanol ligand which increases in acidity upon coordination with the bicyclobutane cannot be ruled out as a competing process. See ref 4 and 10.

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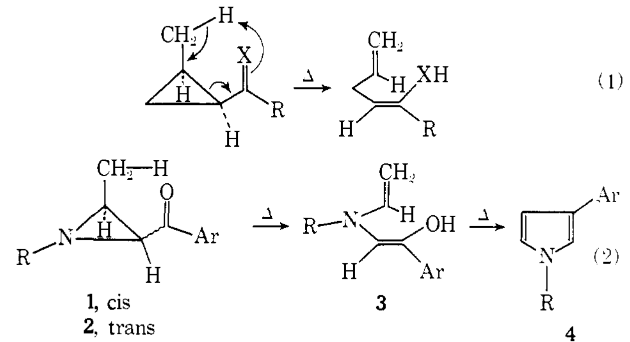
Mechanism and Stereochemical Control in the Thermal Rearrangement of Aziridinyl Ketones to Pyrroles

Sir:

The thermal "ene reaction" of three-membered rings, which takes place with a sigmatropic 1,5-hydrogen shift and concomitant ring cleavage, is a well-documented reaction (eq 1).[1–14] A cis relationship between the π system and the alkyl group on the vicinal ring carbon has been proposed as being necessary for these rearrangements to proceed.[3–7] The lack of reaction of the corresponding trans isomer under more vigorous conditions and the low energy and large negative entropy of activation for the cis isomer constitute compelling support for the concertedness of the reaction.[3–7] We now wish to report that the thermal rearrangement of a related series of aziridinyl ketones (**1** and **2**) to *N*-alkyl-3-arylpyrroles[15] (**4**) (eq 2) differs dramatically from heretofore observed three-membered ring ene reactions, in that the trans isomer reacts at a faster rate than the corresponding cis form.



1, cis
2, trans
3
4

a, R = *t*-Bu; Ar = Ph
b, R = *t*-Bu; Ar = Biph
c, R = C_6H_{11}; Ar = Biph

Thermolysis of 140 mg of *cis*-aziridine **1a** in methanol at 120° for 3 hr afforded 110 mg (80%) of *N-tert*-butyl-3-phenylpyrrole (**4a**). This compound was identified by comparison with an authentic sample.[16] Similar reactions were observed with *trans*-aziridine **2a** as well as with aziridines **1b**,**2b** and **1c**,**2c**. The disappearance of *cis*-**1a** and the appearance of pyrrole **4a** in ethylene glycol was followed simultaneously by nmr spectroscopy. The reaction followed first-order kinetics, and rate constants were determined at three different temperatures constant to ±0.5°, 100 (k = 1.18×10^{-4} sec^{-1}), 110 (k = 3.23×10^{-4} sec^{-1}), and 120° (k = 1.05×10^{-3} sec^{-1}). An Arrhenius plot gives $E_a = 28.6 \pm 0.5$ kcal/mol and $\log A = 12.8$, from which values of $\Delta H^{\ddagger} = 27.7$ kcal/mol and $\Delta S^{\ddagger} = -2.3$ eu can be calculated. The reaction kinetics encountered with *trans*-aziridine **2a** were more complicated since the thermolysis of **2a** in methanol at 80° produced *cis*-aziridine **1a** as well as pyrrole **4a**. The concentration of all three compounds was followed simultaneously by nmr spectroscopy. By using steady-state approximations and by numerical integration of the resultant differential equations with the program KINET,[17] an analytical function was obtained for the concentration of the trans isomer.[18] The results indicate that *trans*-**2a** also proceeds on to pyrrole by a first-order rate process (*i.e.*, $k_{2a} = 1.52 \times 10^{-4}$ sec^{-1} (70°), $k_{2a} = 4.54 \times 10^{-4}$ sec^{-1} (80°), and $k_{2a} = 2.16 \times 10^{-3}$ sec^{-1} (90°), $E_a = 26.4 \pm 0.5$ kcal/mol, and $\log A = 13.0$). Extrapolation of the data for the cis isomer to 80° indicates that the *trans*-aziridine rearranges 39 times more rapidly than the corresponding cis isomer.

In order to help elucidate the mechanism for the *trans*- → *cis*-aziridine isomerization, we have studied the thermal rearrangement of both aziridines in deuteriomethanol at 77° for 15 hr. Recovered starting material (80%) from the *cis*-aziridine run was found to have incorporated one deuterium atom into the 3 position of the aziridine ring. The fact that addition of an excess of dimethyl fumarate to a solution of **1a** did not significantly affect either the rate of disappearance of starting ketone or the amount of pyrrole formed strongly argues against the involvement of azomethine

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[1] K. von Auwers and O. Ungemach, *Justus Liebigs Ann. Chem.*, 511, 152 (1934).

[2] D. S. Class, J. Zirner, and S. Winstein, *Proc. Chem. Soc.*, 276 (1963).

[3] D. E. McGreer, N. W. K. Chiu, and R. S. McDaniel, *ibid.*, 415 (1964); *Can. J. Chem.*, **46**, 2217 (1968).

[4] R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, 5578 (1968).

[5] R. M. Roberts and R. G. Landolt, *J. Amer. Chem. Soc.*, 87, 2281 (1965).

[6] R. M. Roberts, R. G. Landolt, R. N. Greene, and E. W. Heyer, *ibid.*, 89, 1404 (1967).

[7] J. M. Watson, J. L. Irvine, and R. M. Roberts, *ibid.*, **95**, 3348 (1973).

[8] G. Ohloff, *Tetrahedron Lett.*, 3795 (1965).

[9] P. Scribe, M. R. Monot, and J. Wiemann, *ibid.*, 5157 (1967).

[10] W. Ando, *ibid.*, 929 (1969).

[11] M. Jones, Jr., and W. Ando, *J. Amer. Chem. Soc.*, 90, 2200 (1968); **94**, 7469 (1972).

[12] E. J. Corey, H. Yamamoto, D. K. Herron, and K. Achiva, *ibid.*, **92**, 6635 (1970).

[13] D. V. Kashelikar and P. E. Fanta, *ibid.*, **82**, 4930 (1960).

[14] H. L. Wehrmeister, *J. Org. Chem.*, 30, 664 (1965).

[15] The thermal conversion of several 4-isoxazolines into pyrroles has been postulated to involve aroylaziridines as transient intermediates; see A. K. Harada and H. Kano, *Tetrahedron Lett.*, 4875 (1969).

[16] A. Padwa, F. Albrecht, P. Singh, and E. Vega, *J. Amer. Chem. Soc.*, **93**, 2928 (1971).

[17] Appreciation is expressed to J. L. Dye of Michigan State University for a copy of the program KINET; see J. L. Dye and V. Nicely, *J. Chem. Educ.*, **48**, 433 (1971).

[18] With the lower temperature and short reaction times used for the thermolysis of *trans*-**2a**, the cis isomer did not appreciably rearrange to pyrrole **4a**.