Transition Metal Complex Promoted Rearrangements. Bicyclo[2.1.0]pentane and 1-Carbomethoxybicyclo[2.1.0]pentane[1]

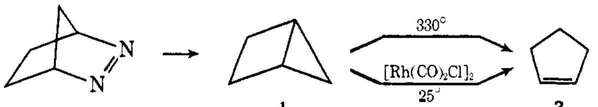
Paul G. Gassman, Thomas J. Atkins,[2] and J. Trevor Lumb

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received February 18, 1972*

Abstract: Bicyclo[2.1.0]pentane was found to rearrange to cyclopentene in the presence of rhodium dicarbonyl chloride dimer. Deuterium labeling of the bicyclo[2.1.0]pentane at the 2, 3, and 5 positions indicated that extensive deuterium scrambling was occurring at some stage of the reaction. Although specifically labeled cyclopentene was not scrambled by rhodium dicarbonyl chloride dimer in chloroform or acetonitrile, it was found that the addition of small amounts of bicyclo[2.1.0]pentane to the solution of 1-deuteriocyclopentene and rhodium dicarbonyl chloride dimer led to isomerization of the 1-deuteriocyclopentene. These results are interpreted as an indication that the bicyclo[2.1.0]pentane reacted with the rhodium dicarbonyl chloride dimer to provide an intermediate which was capable of scrambling labeled cyclopentene. It is suggested that this intermediate is a metal hydride.

The preceding papers in this series[1,3] indicate the ease with which various transition metal complexes promote the rearrangement of derivatives of bicyclo[1.1.0]butane. The facility with which these highly strained ring systems isomerize has been attributed in part to the 64 kcal/mol of strain energy incorporated into this fused ring system.[4] In addition, the transition metal complex promoted isomerizations of quadricyclanes,[5] and of other cage type molecules,[6] have been associated with the strained nature of these molecules. This paper presents the details of our studies of the transition metal complex promoted isomerization of bicyclo[2.1.0]pentane,[7,8] a molecule whose strain energy (54 kcal/mol) is considerably less than most other saturated molecules which have been found to rearrange in the presence of transition metal complexes.

Cleavage of the central bond of bicyclo[2.1.0]pentane results in the release of *ca.* 47 kcal/mol of strain energy.[4,9] Despite the large amount of energy which can be released through cleavage of this bond, bicyclo[2.1.0]pentane (1) possesses remarkable thermal stability. In the pyrolytic preparation of 1 from 2,3-diazabicyclo[2.2.1]hept-2-ene (2) at 200°[10] there was no detectable isomerization of 1. Criegee and Rimmelin have reported[11] that a temperature of 330° was needed in order to observe a reasonable rate of thermal isomerization of 1 to cyclopentene (3). We have found that treatment of either a chloroform or acetonitrile solution of 1 with 5 mol % of rhodium dicarbonyl chloride dimer, at 25°, resulted in the smooth isomerization of 1 into 3. The half-life for the reaction at 25° was *ca.* 8 hr. At 65°, no trace of 1 could be detected after 48 hr, when 2 mol % of rhodium dicarbonyl chloride dimer was used to promote the isomerization. Vpc analysis indicated that the conversion of 1 into 3 was essentially quantitative.



2 1 3

The transformation of 1 into 3 represents an interesting example of a transition metal complex promoted isomerization.[12] It is distinctly different from the isomerization of bicyclo[1.1.0]butanes, in which two carbon–carbon bonds were cleaved.[1] Furthermore, in the transition metal complex promoted isomerization of bicyclo[1.1.0]butanes, it has been suggested that

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[1] Paper XXXV of a series on The Chemistry of Bent Bonds. For the preceding paper in this series see P. G. Gassman and T. J. Atkins, *J. Amer. Chem. Soc.*, 94, 7748 (1972).

[2] National Science Foundation Trainee, 1968–1972.

[3] P. G. Gassman and F. J. Williams, *J. Amer. Chem. Soc.*, **94**, 7733 (1972); P. G. Gassman, G. R. Meyer, and F. J. Williams, *ibid.*, **94**, 7741 (1972).

[4] R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *ibid.*, **90**, 4315 (1968); S. Chang, D. McNally, S. Shary-Tehrany, M. J. Hickey, and R. H. Boyd, *ibid.*, **92**, 3109 (1970).

[5] P. G. Gassman, D. H. Aue, and D. S. Patton, *ibid.*, **90**, 7271 (1968); P. G. Gassman and D. S. Patton, *ibid.*, **90**, 7276 (1968); H. Hogeveen and H. C. Volger, *ibid.*, **89**, 2486 (1967).

[6] L. Cassar, P. E. Eaton, and J. Halpern, *ibid.*, **92**, 3515, 6366 (1970); H. C. Volger and H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, 86, 830 (1967); B. L. Booth, R. N. Hazeldine, and M. Hill, *Chem. Commun.*, 1118 (1967); P. V. Balakrishnan and P. M. Maitlis, *ibid.*, 1303 (1968); J. W. Kang, K. Mosley, and P. M. Maitlis, *ibid.*, 1304 (1968); J. W. Kang and P. M. Maitlis, *J. Amer. Chem. Soc.*, **90**, 3259 (1968); K. L. Kaiser, R. F. Childs, and P. M. Maitlis, *ibid.*, **93**, 1270 (1971); W. Merk and R. Pettit, *ibid.*, **89**, 4788 (1967); R. Pettit, H. Sugahara, J. Wristers, and W. Merk, *Discuss. Faraday Soc.*, **47**, 71 (1969); J. Wristers, L. Brener, and R. Pettit, *J. Amer. Chem. Soc.*, **92**, 7499 (1970); W. G. Dauben, M. G. Buzzolini, C. H. Schallhorn, and D. L. Whalen, *Tetrahedron Lett.*, 787 (1970); L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 2584 (1970); L. A. Paquette, *ibid.*, **92**, 5765 (1970); R. Askani, *Tetrahedron Lett.*, 3349 (1970).

[7] For a preliminary report of part of this work see P. G. Gassman, T. J. Atkins, and J. T. Lumb, *ibid.*, 3349 (1970). Presented in part before the 13th Conference on Reaction Mechanisms, Santa Cruz, Calif., June 23–26, 1970.

[8] The transition metal complex promoted rearrangement of a 1,4-bridged bicyclo[2.1.0]pentane has also been studied. This bridged derivative appears to differ significantly from simple derivatives of bicyclo[2.1.0]pentane. For details see P. G. Gassman and E. A. Armour, *Tetrahedron Lett.*, 1431 (1971).

[9] R. B. Turner, *Theor. Org. Chem., Pap. Kekulé Symp., 1958*, 67 (1959).

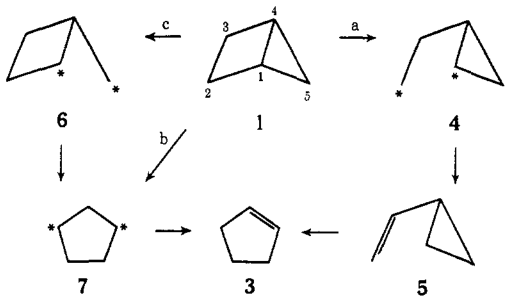
[10] P. G. Gassman and K. T. Mansfield, *Org. Syn.*, **49**, 1 (1969).

[11] R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 414 (1957).

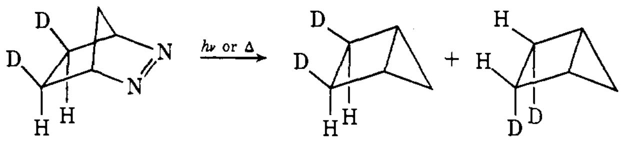
[12] From one point of view this rearrangement can be classified as a cyclopropyl to allyl type isomerization. Although such transition metal complex promoted rearrangements are known, they generally do not occur readily at room temperature. For typical examples see K. G. Powell and F. J. McQuillin, *Chem. Commun.*, 931 (1971); D. M. Roundhill, D. N. Lawson, and G. Wilkinson, *J. Chem. Soc. A*, 845 (1968); R. J. Ouellette and C. Levin, *J. Amer. Chem. Soc.*, **90**, 6889 (1968); T. J. Katz and S. A. Cerefice, *ibid.*, **91**, 2405 (1969); T. J. Katz and S. A. Cerefice, *ibid.*, **93**, 1049 (1971); R. G. Miller and P. A. Pinke, *ibid.*, **90**, 4500 (1968); H. C. Volger, H. Hogeveen, and M. M. P. Gaasbeek, *ibid.*, **91**, 2137 (1969).

cleavage of a side bond preceded cleavage of the center bond. Formally, with bicyclo[2.1.0]pentane, only the center bond was broken. In view of the obvious differences between the transition metal complex promoted isomerizations of bicyclo[1.1.0]butane and bicyclo-[2.1.0]pentane, we attempted to obtain a more detailed mechanistic insight into the mode of rearrangement of the latter. In principle, numerous mechanisms could be invoked to rationalize the observed isomerization of **1** in the presence of rhodium dicarbonyl chloride dimer. Three of the more likely possibilities are outlined in Scheme I, which shows the reaction routes possible *via* initial cleavage of the C_1–C_2 bond (path a), the C_1–C_4 bond (path b), or the C_1–C_5 bond (path c). Initial cleavage of the C_1–C_2 bond would yield an intermediate **4**,[13] which, on 1,3-hydrogen shift, could produce vinylcyclopropane (**5**). If the rhodium dicarbonyl chloride dimer could catalyze a vinylcyclopropane to cyclopentene rearrangement, this route would be feasible. This mechanistic possibility was readily tested by exposing vinylcyclopropane to rhodium dicarbonyl chloride dimer. The lack of any rearrangement of **5** under these conditions[14] indicated the unlikelihood of path a as a route from **1** to **3**. Paths b and c are quite different in that different bonds are initially broken to convert **1** into **6** and **7**. Since **6** would have to undergo a ring expansion to yield the observed product, paths b and c become indistinguishable experimentally.

Scheme I

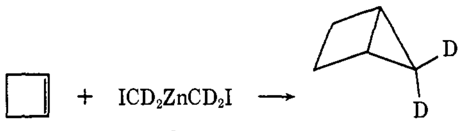


In view of the intriguing nature of the rearrangement of **1** by transition metal complexes, we attempted to obtain more information about this reaction *via* a study of deuterium-labeled **1**. In order to determine which of the hydrogens were migrating during the rearrangement, we prepared *exo*-2,3-dideuteriobicyclo-[2.1.0]pentane (**8**), *endo*-2,3-dideuteriobicyclo[2.1.0]pentane (**9**), and 5,5-dideuteriobicyclo[2.1.0]pentane (**10**). A 2.9:1 mixture of **8** and **9**, respectively, was prepared in 65% yield *via* pyrolysis of *exo*-5,6-dideuterio-2,3-diazabicyclo[2.2.1]hept-2-ene (**11**) at 200°.[15] The relative ratios of **8** and **9** were determined by nmr spectroscopy which showed peaks at τ 7.92 (0.51 H, exo protons at C_2 and C_3) and 8.67 (1.49 H, endo protons at C_2 and C_3). Photolysis of **11** in an *n*-butyl alcohol glass at $-70°$ with a high-pressure mercury lamp afforded a 37% yield of a 1.3:1 mixture of **8** and **9**, respectively.



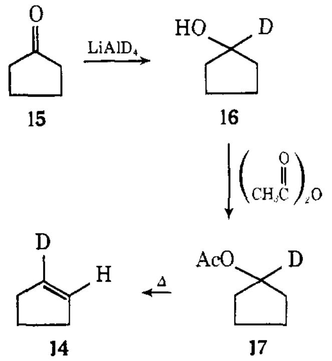
11 **8** **9**

The synthesis of 5,5-dideuteriobicyclo[2.1.0]pentane (**10**) was accomplished in 23% yield through the reaction of cyclobutene (**12**)[16] with bis(dideuterioiodomethyl)zinc (**13**) utilizing a modification of the procedure of Wittig and Wingler to prepare **13**.[17] The sample of **10** prepared by this procedure was 84% deuterated at the 5 position as shown by the nmr spectrum of **10** which had peaks at τ 9.35 (exo H) and 9.52 (endo H).[18]



12 **13** **10**

Treatment of the 2.9:1 mixture of **8** and **9**, the 1.3:1 mixture of **8** and **9**, or the sample of **10** with 2 mol % of rhodium dicarbonyl chloride dimer in chloroform at 65° gave identical mixtures of deuterated cyclopentenes. The nmr and ir spectra of these product mixtures were identical. The nmr spectra of the mixtures of deuterated cyclopentenes showed a ratio of low-field vinylic protons to upfield protons (both allylic and nonallylic) of 1:3.21 ± 0.10, respectively. Totally random distribution of the deuteriums should give a ratio of 1:3, assuming no deuterium isotope effects on the product distribution.[19] It became clear at this point that essentially complete scrambling of the deuterium label was occurring during the course of this reaction. In order to determine the stage of the reaction at which scrambling of the deuterium occurred, we carried out several control experiments. The rearrangement of the 2.9:1 mixture of **8** and **9** was run to 50% completion. The remaining labeled bicyclo[2.1.0]pentane was recovered and shown by nmr spectroscopy to be unscrambled. We next prepared 1-deuteriocyclopentene (**14**) by reduction of cyclopentanone (**15**) with lithium aluminum deuteride to yield **16**, followed by acetylation of **16** with acetic anhydride in pyridine to give **17** in 65% overall



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(13) The nature of the intermediate formed in the first step of the cleavage has not been determined. It is our opinion that the transition metal must be strongly associated with the intermediate (whether **4**, **6**, or **7** is the intermediate of importance). Hence, the structures shown for **4**, **6**, and **7** are only meant to show which bonds were broken, not how they were broken nor the role of the transition metal complex.

(14) We wish to thank Mr. William Greenlee for carrying out this control experiment.

(15) This is essentially the procedure of W. Roth and M. Martin, *Justus Liebigs Ann. Chem.*, 702, 1 (1967).

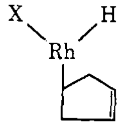
(16) A. C. Cope, A. C. Haven, Jr., F. L. Ramp, and E. R. Trumbull, Jr., *J. Amer. Chem. Soc.*, 74, 4867 (1952).

(17) G. Wittig and F. Wingler, *Chem. Ber.*, 97, 2146 (1964).

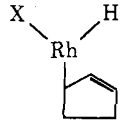
(18) The nmr assignments are those of Roth and Martin.[15]

(19) Measurements of cyclopentene, cyclohexene, and cycloheptene gave ratios of 1:3.31, 1:4.49, and 1:5.72 (average of three determinations), respectively, on the nmr spectrometer used for these analyses. These values indicate that the ratio of 1:3.21 represents complete scrambling of the label.

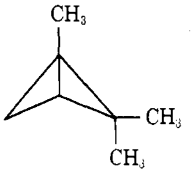
yield. Pyrolysis of **17** in the vapor phase at 450° gave an 80% yield of **14**. The nmr spectrum of **14** showed a ratio of olefinic to saturated aliphatic hydrogens of 1:6.22, respectively. Treatment of **14** with rhodium dicarbonyl chloride dimer at 65° in chloroform, for a time equivalent to 4 half-lives for the bicyclo[2.1.0]pentane isomerization, gave no detectable isomerization of the 1-deuteriocyclopentene. This control indicated that the deuterium scrambling in the isomerization of **1** was either occurring during the interaction of **1** with the transition metal complex and before the isomerized product from **1** had dissociated from the transition metal complex, or that an intermediate was being generated in the reaction of **1** with the transition metal complex which was capable of promoting the rearrangement of the labeled cyclopentene product in an ***intermolecular*** reaction. In order to distinguish between these two possibilities, we carried out a series of experiments in which we added small amounts of highly strained bicyclic molecules to a chloroform solution of 1-deuteriocyclopentene and rhodium dicarbonyl chloride dimer. Addition of 10 mol % of **1** to a deuteriochloroform solution of **14** and rhodium dicarbonyl chloride dimer gave, after 3.5 hr at 10°, a solution of cyclopentene which showed an olefinic hydrogen to saturated aliphatic hydrogen ratio of 1:3.6, respectively. This indicated that the 1-deuteriocyclopentene was almost completely equilibrated during the course of the reaction of **1** with the rhodium dicarbonyl chloride dimer. Once the added bicyclo[2.1.0]pentane was completely isomerized, no further scrambling of the labeled cyclopentene was observed. This indicated that it was a transitory intermediate, involved in the rearrangement of **1**, which was the active catalyst for the isomerization of the labeled cyclopentene and *not* some new derivative of the transition metal (which would have remained after **1** had completely disappeared). In view of the extensive evidence for the role of metal hydrides in the isomerization of olefins, we feel that the active intermediate which promotes the rearrangement of the 1-deuteriocyclopentene may be the same intermediate which accounts for the hydrogen transfer step in the isomerization of **1**. It is probable that this intermediate is a metal hydride such as is shown by structure **18**, in which the transition metal is "bonded" to both the residue from the bicyclo[2.1.0]pentene and to the hydrogen which is being transferred. This would formally involve a rhodium(III) hydride.[20] Intermolecular hydrogen transfer would then lead to isomerization of the 1-deuteriocyclopentene (**14**), whereas collapse of **18** would produce cyclopentene from **1**. The unusual nature of the isomerization of **1** in comparison to the transition metal complex promoted isomerization of derivatives of bicyclo[1.1.0]butane was demonstrated by the failure of added 1,2,2-trimethylbicyclo[1.1.0]butane (**19**) or added tricyclo[4.1.0.0^{2,7}]heptane (**20**) to facilitate rearrangement of **14** in a chloroform solution of **14** containing rhodium dicarbonyl chloride dimer.[21]



18a



18b



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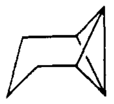

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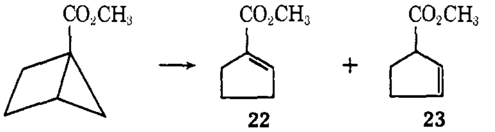
In the hope of trapping an electrophilic species (intermediate), we ran the isomerization of **1** with rhodium dicarbonyl chloride dimer in the more nucleophilic solvent, methanol. Whereas bicyclo[1.1.0]butane derivatives gave high yields of methyl ethers under these conditions,[1] **1** gave only cyclopentene.[22,23]

In order to evaluate the effect of an electron-withdrawing substituent at C-1 on the rearrangement of **1** we studied the rearrangement of 1-carbomethoxybicyclo[2.1.0]pentane[24] (**21**) in the presence of 5 mol % of rhodium dicarbonyl chloride dimer in chloroform.[25] After 22 hr at 65°, **21** was converted into 1-carbomethoxycyclopentene (**22**) and 3-carbomethoxycyclopentene (**23**) in 36 and 33% yields, respectively. In addition, less than 1% each of two unidentified products were produced. The structures of **22** and **23** were established by spectral and vpc comparisons with independently synthesized authentic samples. Reduction of methyl cyclopentanone-2-carboxylate with sodium borohydride, dehydration with phosphorus pentoxide, and equilibration of the product mixture with sodium methoxide gave **22** as the major product. The synthesis of **23** involved addition of 1 mol of hydrogen chloride to cyclopentadiene, Grignard formation, and carboxylation, followed by esterification with diazomethane.



21 **22** **23**

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(20) It could be shown that preformed rhodium(I) hydrides were not satisfactory for the isomerization of **14** under our reaction conditions. After 24 hr at 10° with 1 mol % of tris(triphenylphosphine)-carbonylrhodium(I) hydride, no detectable isomerization of **14** was noted. For leading references to the mechanism(s) of rhodium complex promoted olefin isomerizations see: M. Orchin, *Advan. Catal.*, **16**, 1 (1966); R. Cramer and R. V. Lindsay, Jr., *J. Amer. Chem. Soc.*, **88**, 3534 (1966), and references contained therein. See also, C. W. Bird in "Transition Metal Intermediates in Organic Synthesis," Academic Press, New York, N. Y., 1967.

(21) This observation was based on the nmr spectrum of the 1-deuteriocyclopentene in solution. Needless to say, both **19** and **20** were rapidly isomerized in this solution. If an intermediate metal hydride is generated in the isomerization of **19** and **20**, it must be either too short-lived or too unreactive to promote the isomerization of **14**. It was suggested by a referee that our hypothetical intermediate **18** might convert vinylcyclopropane [if formed in a separate or related reaction (*vide supra*)] into cyclopentene which could have a scrambled deuterium label. This possibility was eliminated by control experiments which showed that added vinylcyclopropane could be recovered from the reaction of **1** with rhodium dicarbonyl chloride dimer.

(22) Within the limits of analysis by nmr spectroscopy no methyl ether could be detected from the reaction of **1** with rhodium dicarbonyl chloride dimer in methanol.

(23) The postulate of the formation of a hydride intermediate in the isomerization of **1** was supported by recent observations from the laboratory of Professor K. B. Wiberg. These workers observed that the use of methanol-*O-d* as solvent for this isomerization of **1** led to the incorporation of deuterium into the cyclopentene. We wish to thank Professor Wiberg for informing us of his results prior to publication.

(24) P. G. Gassman and K. T. Mansfield, *J. Org. Chem.*, **32**, 915 (1967).

(25) For a recent σ–ρ study of silver ion promoted isomerizations of highly strained polycyclics, see G. F. Koser, *Chem. Commun.*, 388 (1971).

In summary, we have found that bicyclo[2.1.0]pentane and its derivatives rearrange readily in the presence of rhodium dicarbonyl chloride dimer.[26] The mechanism of the rearrangement of **1** appears to be significantly different from that suggested for the rearrangement of derivatives of bicyclo[1.1.0]butane in the presence of the same transition metal complex. Unfortunately, insufficient data are available for the presentation of a detailed mechanism at this time. We are continuing to explore the mechanistic intricacies of this transition metal complex promoted isomerization.

Experimental Section

Infrared spectra were taken on a Perkin-Elmer Model 137 Infracord as neat liquids or in solution. Nuclear magnetic resonance spectra were obtained on a Varian Associates A-60-A spectrometer and are reported in τ units relative to tetramethylsilane (τ = 10.00). Boiling points are uncorrected.

Bicyclo[2.1.0]pentane (1). This compound was prepared according to the method of Gassman and Mansfield.[10]

Reaction of 1 with Rhodium Dicarbonyl Chloride Dimer. A solution of 260 mg (3.82 mmol) of **1**, 1 ml of deuteriochloroform, and 29 mg (0.075 mmol, 2 mol %) of rhodium dicarbonyl chloride dimer was sealed in a tube and heated at 65° for 48 hr. After cooling to 25°, the contents were distilled to give 93%[27] of cyclopentene (**3**) in deuteriochloroform, bp 40–56°, which was identified by spectral comparison to an authentic sample.

Preparation of a 2.9:1 Mixture of *exo*-2,3-Dideuteriobicyclo[2.1.0]pentane (8) and *endo*-2,3-Dideuteriobicyclo[2.1.0]pentane (9). *exo*-5,6-Dideuterio-2,3-diazabicyclo[2.1.1]hept-2-ene (**11**)[15] (7.6 g) was pyrolyzed as in the preparation of **1**.[10] Distillation of the pyrolysate afforded 3.5 g (65%) of clear colorless liquid: bp 44–45°; nmr (CCl$_4$)[15] τ 7.92 (0.51 exo H at C$_2$ and C$_3$), 8.49 (2 bridgehead H), 8.67 (1.49 endo H at C$_2$ and C$_3$), 9.35 (1 exo H at C$_5$), 9.52 (1 endo H at C$_5$).

Preparation of a 1.3:1 Mixture of 8 and 9. A solution of 3.00 g (30.6 mmol) of **11** in 150 ml of *n*-butyl alcohol was placed in a 200-ml photolysis cell which was immersed in a Dry Ice–isopropyl alcohol bath, and isopropyl alcohol at −70° was circulated through the quartz immersion well. Irradiation of the *n*-butyl alcohol glass was carried out at 5-min intervals due to excessive heating by the high-pressure mercury lamp and the actual irradiation time was 2 hr. Distillation of the photolysis solution through a 10-cm Vigreux column gave 0.70 g (33%) of clear colorless liquid, bp 44–46°, which, by nmr analysis, was found to be a 1.3:1 mixture of **8** and **9**: nmr (CCl$_4$) τ 7.92 (0.87 H), 8.49 (2 H), 8.67 (1.13 H), 9.35 (1 H), 9.52 (1 H).

5,5-Dideuteriobicyclo[2.1.0]pentane (10). To an ice-cooled solution of 17.0 g (53 mmol) of anhydrous zinc iodide in 150 ml of anhydrous ether in a 500-ml three-necked flask equipped with a polished stopcock for nitrogen introduction, Nalgene addition funnel, mercury bubbler, and magnetic stirrer was added 230 ml of 0.30 *M* ethereal dideuteriodiazomethane[28] under nitrogen over a 0.5-hr period with stirring. After 15 min, the volume of ether was reduced to *ca.* 30 ml by evacuation of the apparatus and stirring at 0°.[29] The solution of **13** was then cooled to *ca.* −30° and 3.0 g (55.5 mmol) of cyclobutene (**12**)[16] was added. The tightly stoppered flask was warmed slowly (3 hr) to 14° and stirred for 12 hr. The volatile products were vacuum transferred to a cooled (−78°) receiver and the solution was carefully concentrated by distillation of the ether through a 30-cm glass helices packed column at a reflux ratio of 60:1. Preparative vpc of the residue on a 10 ft × $^1/_4$ in. 20% D.C. Silicone Fluid No. 200, 1000 cs on 60–80 Columpak column at 25°, gave 442 mg (23%) of **10**. Nmr analysis indicated 84% of dideuteration at the 5 position. The nmr spectrum of **10** in CCl$_4$ showed peaks at τ 7.94 (2 H), 8.4–8.9 (4 H), and 9.2–9.6 (0.32 H).

Reaction of a 2.9:1 Mixture of 8 and 9 with Rhodium Dicarbonyl Chloride Dimer. A solution of 108 mg (1.55 mmol) of a 2.9:1 mixture of **8** and **9**, respectively, 0.5 ml of deuteriochloroform, and 11 mg (0.028 mmol, 2 mol %) of rhodium dicarbonyl chloride dimer was heated at 65° in a sealed tube for 70 hr. The products and solvent were distilled and analyzed by nmr spectroscopy (CDCl$_3$ solution) to show peaks at τ 4.22 (1 H, s) and 7.4–8.5 (3.21 H, m). This was consistent with the presence of only deuterated cyclopentenes.

Reaction of a 1.3:1 Mixture of 8 and 9 with Rhodium Dicarbonyl Chloride Dimer. Using the above procedure, the product from the reaction of a 1.3:1 mixture of **8** and **9** with rhodium dicarbonyl chloride dimer was analyzed by nmr spectroscopy (CDCl$_3$) to show peaks at τ 4.22 (1 H, s) and 7.4–8.5 (3.21 H, m).

Reaction of 10 with Rhodium Dicarbonyl Chloride Dimer. Using the above procedure the product from the reaction of **10** with rhodium dicarbonyl chloride dimer was analyzed by nmr spectroscopy (CDCl$_3$) to show peaks at τ 4.22 (1 H, s) and 7.4–8.5 (3.22 H, m).

1-Deuterio-1-acetoxycyclopentane (17). In a 500-ml round-bottomed flask equipped with a magnetic stirrer, addition funnel, reflux condenser, and drying tube was placed 2.0 g (47.7 mmol) of lithium aluminum deuteride and 125 ml of anhydrous ether. To the stirred solution was added 15.0 g (179 mmol) of cyclopentanone (**15**) in 75 ml of anhydrous ether at a rate sufficient to reflux the solution. After 3 hr at reflux, the solution was cooled to 25°, decomposed *via* dropwise addition of 8 g of 10% sodium hydroxide solution, and stirred at 25° for 4 hr. After drying over anhydrous magnesium sulfate, the solution was filtered, and the ether was removed by distillation. The residue was dissolved in 100 ml of pyridine, 40 g of acetic anhydride was added, and the solution was stirred overnight, poured onto ice, and extracted with two 100-ml portions of ether. The extracts were washed with dilute hydrochloric acid, water, and saturated sodium bicarbonate solution, and dried over anhydrous magnesium sulfate. After filtering the solution, the ether was removed by distillation, and distillation of the residue afforded 16.11 g (65%) of clear, colorless **17**: bp 85–87° (80 mm); ir spectrum (neat) 4.57 (w), 5.85, 7.28, 7.90, 8.42, and 9.73 μ.

1-Deuteriocyclopentene (14). Pyrolysis of **17** (16.0 g) in the vapor phase under nitrogen at 450° in a Lindberg Hevi-duty pyrolysis oven afforded 6.32 g of **14**, bp 41–43°, upon distillation of the pyrolysate. The ir spectrum of **14** (CCl$_4$) showed absorptions at 4.42 and 9.96 μ. The nmr spectrum (CCl$_4$) consisted of peaks at τ 4.22 (1 H, s) and 7.4–8.5 (6.22 H, m).

Using the correction factor required by the data in ref 19, we determined 93% deuterium incorporation at the 1 position by nmr analysis.

Scrambling of 14. In an nmr tube was placed 100 mg (1.45 mmol) of **14**, 0.5 ml of deuteriochloroform, 5.6 mg (1 mol %) of rhodium dicarbonyl chloride dimer, and 10 mg (10 mol %) of **1**. The solution was allowed to stand at 10° for 3.5 hr and then the nmr was recorded to show peaks at τ 4.22 (1 H, s) and 7.4–8.5 (3.59 H, m).

The control experiments utilizing derivatives of bicyclo[1.1.0]butane and bis(triphenylphosphine)carbonylrhodium(I) hydride were run using the procedure described above.

1-Carbomethoxybicyclo[2.1.0]pentane (21). This compound was prepared according to the method of Gassman and Mansfield.[24]

Reaction of 21 with Rhodium Dicarbonyl Chloride Dimer. A solution of 400 mg (3.18 mmol) of **21**, 1 ml of chloroform, and 62 mg (0.159 mmol, 5 mol %) of rhodium dicarbonyl chloride dimer was heated in a sealed tube at 65° for 22 hr. After cooling to 25°, the volatile contents of the tube were vacuum transferred and the two major products were collected by preparative vpc at 120° on a 10 ft × $^1/_4$ in. 15% DEGS on 60–80 Chromosorb P column. These were shown to be 1-carbomethoxycyclopentene (**22**) and 3-carbomethoxycyclopentene (**23**) by spectral comparison with authentic samples. Vpc analysis of the product mixture in duplicate runs *vs.* an internal standard at 130° on a 10 ft × $^1/_8$ in. 5% DEGS on 60–80 Chromosorb P column showed 36% of 1-carbomethoxycyclopentene (**22**), 33% of 3-carbomethoxycyclopentene (**23**), and ≤1% each of two minor products. The spectral properties of **22** were: ir (CCl$_4$) 5.81, 6.13, 6.98, 7.40, 7.72, 7.92, 8.39, and 9.20 μ; nmr (CDCl$_3$) τ 3.21 (1 H, br t, J = ~2 Hz), 6.29 (3 H, s), 7.1–8.4 (6 H, m). The spectral properties of **23** were: ir (CCl$_4$) 5.75,

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[26] For a reaction of **1** in the presence of bis(acrylonitrile)nickel(0), see R. Noyori, T. Suzuki, and H. Takaya, *J. Amer. Chem. Soc.*, **93**, 5896 (1971).

[27] The yield reported is an average of duplicate runs as determined by vpc at 25° on a 10 ft × $^1/_8$ in. 20% D.C. Silicone Fluid No. 200, 1000 cs on 60–80 Columpak column *vs.* an internal standard.

[28] A diazomethane solution, which was prepared from 20 g of nitrosomethylurea, 300 ml of ether, and 60 ml of 45% potassium hydroxide solution and dried over potassium hydroxide pellets overnight, was stirred over 8 ml of 1 *N* sodium deuterioxide in deuterium oxide and 6 ml of tetrahydrofuran for 3 hr at 0°. The solution was decanted and the process was repeated. The ethereal solution was then dried over anhydrous potassium carbonate and found to be 0.30 *M* in dideuteriodiazomethane by standard titration.

[29] An 80% yield based on dideuteriodiazomethane gives 27.6 mmol of reagent **13**.[17]

6.20 (w), 6.96, 7.51, 8.33, 8.50, and 9.61 μ; nmr ($CDCl_3$) τ 4.19 (1 H, d of d, $J = 6.5$, 2 Hz), 4.38 (1 H, m), 6.33 (3 H, s), 6.2–6.6 (1 H, s), 7.2–8.2 (4 H, m).

1-Carbomethoxycyclopentene (22). The procedure used was a modification[30] of the literature procedures.[31,32] 2-Carbomethoxycyclopentanone was reduced with sodium borohydride to 2-carbomethoxycyclopentanol, bp 83–91° (1.3 mm). Dehydration of the alcohol with phosphorus pentoxide in benzene afforded a mixture of carbomethoxycyclopentenes which was equilibrated by treatment with methanolic sodium methoxide. Distillation afforded impure **22**, bp 71–75° (33 mm) [lit. bp 63–65° (10 mm),[31] 52° (12 mm)[33]]. Purification by preparative vpc at 120° on a 10 ft × 1/4 in. 25% DEGS on 60–80 Chromosorb P column gave pure **22**.

3-Carbomethoxycyclopentene (23). 3-Chlorocyclopentene was prepared by the method of Moffett[34] and was converted to the Grignard reagent and subsequently to cyclopentene-3-carboxylic acid by the method of Jørgensen and Berg.[35] Esterification with diazomethane afforded 3-carbomethoxycyclopentene (**23**), bp 66–67° (26 mm) [lit. bp 60–65° (15 mm),[31] 46° (10 mm)[35]].

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The Effect of Methyl Substitution on the Competitive Rearrangements of Tricyclo[4.1.0.0^{2,7}]heptanes by Silver(I) Ion. Product and Kinetic Considerations[1,2]

Leo A. Paquette,* Stanley E. Wilson,[3a] Richard P. Henzel,[3b] and George R. Allen, Jr.[3c]

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received April 4, 1972*

Abstract: The Ag(I)-catalyzed rearrangements of tricycloheptane (**1a**), the 1- and 2-methyl homologs, and the 1,2-, 1,7-, and 2,6-dimethyl derivatives have been investigated. Kinetic studies relating to the relative rates of formation of 1,3-cycloheptadienes have revealed an interesting dependence on the position and number of methyl substituents. These same features control the product distribution; whereas the placement of methyl groups at C-2 and C-6 does not alter the propensity of the strained hydrocarbon for C-1,2 and C-3,4 bond cleavage, substitution at the bridgehead sites introduces considerable complexity. The formation of Ag^+–tricycloheptane complexes has been demonstrated by kinetic methods. The implications of these results as they relate to mechanism are briefly discussed.

Bicyclo[1.1.0]butanes, the most highly strained of the two-ring carbocyclic compounds,[4] have enjoyed a preeminent position in alicyclic chemistry since the successful synthesis of the first authentic derivative in 1959.[5] Of the various known transformations of these molecules, those resulting from metal ion catalyzed isomerization are certainly among the most intriguing.[6] The complex ground-state molecular changes of bicyclobutanes have now been meaningfully placed on a reasonable theoretical foundation;[7] at the outset of our study of the metal-catalyzed rearrangements of this class of hydrocarbons, even the basic theory allowing one to consider possible mechanisms was replete with confusing predictions. As a result, the present investigation began with two goals—first, elucidation of the types of skeletal isomerizations which tricyclo[4.1.0.0^{2,7}]heptanes would undergo under conditions of Ag^+ catalysis, and second, determination of the extent to which suitable placement of alkyl groups on this system would affect the rate of rearrangement and the product distribution.

Tricyclo[4.1.0.0^{2,7}]heptane (1).[8] Addition of **1a**, the archetype of *endo,endo*-2,4-disubstituted-bicyclobutanes, to anhydrous silver fluoroborate in deuteriochloroform at 40° resulted within minutes in quantitative conversion to *cis,cis*-1,3-cycloheptadiene (**2a**). When the hydrogen atoms positioned at C_1 and C_3 were replaced by deuterium as in **1b**,[9] *cis,cis*-1,3-cycloheptadiene-*2,3-d*$_2$ (**2b**)

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[1] Part XII of the series dealing with Ag^+-catalyzed rearrangements. For the previous paper, see L. A. Paquette and G. Zon, *J. Amer. Chem. Soc.*, **94**, 5096 (1972).

[2] Various aspects of this work have been presented at the Meeting of the Chemical Institute of Canada, Halifax, Nova Scotia, May, 1971, the 22nd National Organic Chemistry Symposium, Ann Arbor, Mich., June, 1971, and the Second Belgian Chemical Society Symposium on Small Rings and Activated Multiple Bonds, Louvain, Belgium, Sept 1971.

[3] (a) National Institutes of Health Postdoctoral Fellow, 1970–1971; National Science Foundation Postdoctoral Fellow, 1971–1972; (b) National Science Foundation Graduate Trainee, 1970–1972; (c) Senior Education Awardee, American Cyanamid Co., 1969–1970.

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