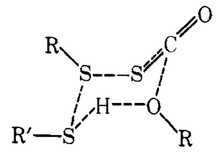
event. In our mechanistic proposal, we envision the *synchronous* fragmentation of III to be rapid with the loss of carbonyl sulfide acting as a potent driving force.



III

Complete details of the synthetic and mechanistic aspects of this work will be elaborated in the full paper.

Acknowledgment. We acknowledge support of this work by the U. S. Army Medical Research and Development Command.

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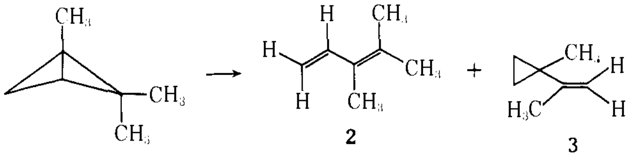
A Formal Retrocarbene Addition. The Reaction of 1,2,2-Trimethylbicyclo[1.1.0]butane with Transition Metal Catalysts[1]

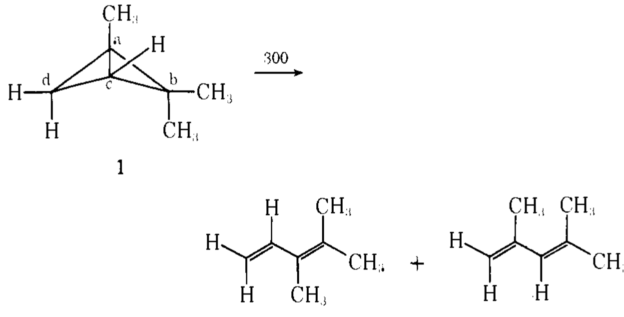
Sir:

The thermal isomerization of derivatives of bicyclo[1.1.0]butane to derivatives of 1,3-butadiene has been investigated by numerous workers[2] and the mechanism of this interesting thermal rearrangement has been discussed in detail.[2m,2o,3,4] Although the bicyclo[1.1.0]butane nucleus has a strain energy of *ca.* 66 kcal/mol,[5] temperatures of 150–300° and activation energies in excess of 40 kcal/mol[2d,2g] appear necessary for a reasonable rate of isomerization. We now wish to report that 1,2,2-trimethylbicyclo[1.1.0]butane[6] (**1**) is rapidly isomerized to a mixture of 3,4-dimethyl-1,3-pentadiene (**2**) and the vinylcyclopropane **3** at room temperature by specific transition metal catalysts. We also wish to record that these facile exothermic reactions differ dramatically from the well-established thermal rearrangements in that different carbon–carbon bonds are cleaved in the two processes.



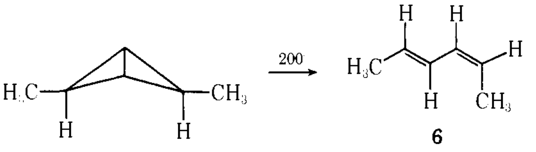
1 2 3

Skattebøl and Moore and coworkers have shown[6] that **1** was readily isomerized to a 53:47 mixture of **2** and **4**

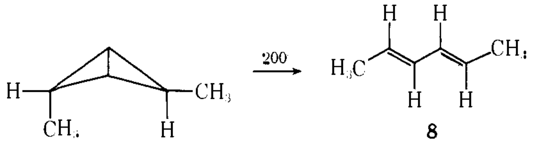


1 2 4

in the vicinity of 300°. These thermolysis products are readily rationalized in terms of a molecular orbital allowed concerted process[4] as discussed for the 2,4-dimethylbicyclo[1.1.0]butanes by Closs and Pfeffer,[3c] who found that **5** gave 93% of **6** while **7** yielded 95% of **8**. The rearrangements of **5** and **7** required that one cyclopropyl ring be cleaved in a disrotatory manner while the other be opened predominantly in a conrotatory manner. Although the same stereochemical aspects are not present, it can be seen that similar pyrolysis of **1** would give **2** *via* cleavage of the a–d and b–c bonds and **4** *via* cleavage of the a–b and c–d bonds. The results of Closs and Pfeffer[3c] leave no doubt concerning the lack of cleavage of the a–c bond in such thermal reactions.



5 6



7 8

When **1** was treated with 3 mol % of rhodium dicarbonyl chloride dimer in chloroform at room temperature an immediate exothermic reaction occurred to yield, after 5 min, 58% **2** and 30% **3**.[7] In contrast to the pyrolysis of **1**, no trace of **4** could be detected. In principle the formation of **2** in the transition metal catalyzed reaction could occur either *via* cleavage of the

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[1] Paper XIV of a series on The Chemistry of Bent σ Bonds. For the preceding paper in this series see P. G. Gassman and G. D. Richmond, *J. Amer. Chem. Soc.*, **92**, 2090 (1970).

[2] (a) W. Mahler, *J. Amer. Chem. Soc.*, **84**, 4600 (1962); (b) D. M. Lemal, F. Menger, and G. W. Clark, *ibid.*, **85**, 2529 (1963); (c) K. B. Wiberg and G. M. Lampman, *Tetrahedron Lett.*, 2173 (1963); (d) J. P. Chesick, *J. Phys. Chem.*, **68**, 2033 (1964); (e) R. Srinivasan, A. A. Levi, and I. Haller, *ibid.*, **69**, 1775 (1965); (f) H. M. Frey and I. D. R. Stevens, *Proc. Chem. Soc.*, 144 (1964); (g) H. M. Frey and I. D. R. Stevens, *Trans. Faraday Soc.*, **61**, 90 (1965); (h) A. Small, *J. Amer. Chem. Soc.*, **86**, 2091 (1964); *J. Org. Chem.*, **33**, 1441 (1968); (i) W. von E. Doering and J. F. Coburn, Jr., *Tetrahedron Lett.*, 991 (1965); (j) S. Masamune, *ibid.*, 945 (1965); (k) E. P. Blanchard, Jr., and A. Cairncross, *J. Amer. Chem. Soc.*, **88**, 487, 496 (1966); (l) J. Pusset and R. Beugelmans, *Tetrahedron Lett.*, 3249 (1967); (m) K. B. Wiberg and R. A. Fenoglio, *J. Amer. Chem. Soc.*, **90**, 3395 (1968); (n) D. P. G. Hamon, *ibid.*, **90**, 4513 (1968); (o) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968); K. B. Wiberg, *Advan. Alicyclic Chem.*, **2**, 185 (1968); (p) R. B. Woodward and D. L. Dalrymple, *J. Amer. Chem. Soc.*, **91**, 4612 (1969); I. A. D'yakonov, V. V. Razen, and M. I. Komendantov, *Tetrahedron Lett.*, 1127, 1135 (1966).

[3] (a) K. B. Wiberg and J. M. Lavanish, *J. Amer. Chem. Soc.*, **88**, 5272 (1966); (b) K. B. Wiberg and G. Szeimies, *Tetrahedron Lett.*, 1235 (1968); (c) G. L. Closs and P. E. Pfeffer, *J. Amer. Chem. Soc.*, **90**, 2452 (1968).

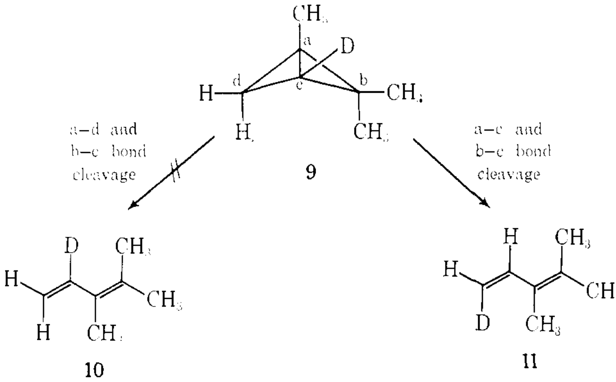
[4] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969). In particular see pp 810–814.

[5] For recent discussions of strain in polycyclic molecules see R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Amer. Chem. Soc.*, **90**, 4315 (1968); N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262 (1969); P. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Amer. Chem. Soc.*, **92**, 2377 (1970); S. Chang, D. McNally, S. Shary-Tehrany, M. J. Hickey, and R. H. Boyd, *ibid.*, **92**, 3109 (1970); N. C. Baird, *Tetrahedron*, **26**, 2185 (1970).

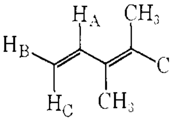
[6] L. Skattebøl, *Tetrahedron Lett.*, 2361 (1970); W. R. Moore, K. G. Taylor, P. Müller, S. S. Hall, and Z. L. F. Gaibel, *ibid.*, 2365 (1970).

[7] The structures of the products were established by a combination of infrared, ultraviolet, and nmr spectroscopy. In addition **2** was reduced to 2,3-dimethylpentane which was identical in all respects with an authentic sample and **3** was compared with an authentic sample[6] of **3**.

a–d and b–c bonds of **1**, in a manner similar to the thermal reaction, or *via* cleavage of the a–c and b–c bonds of **1**. In order to distinguish between these two possibilities we subjected **9**[6,8] to our catalytic conditions. If the catalytic reaction involved cleavage of the a–d and b–c bonds of **9** in a manner similar to the thermal reaction, the deuterium at position c of **9** would end up at C-2 as represented by the formation of **10**. However, if bonds a–c and b–c were opened, 1-deuterio-3,4-dimethyl-1,3-pentadiene would be expected. In fact, the transition metal catalyzed rearrangement was found to be amazingly stereospecific in that the only diene formed was **11** which had the deuterium at C-1 in a cis configuration.



The structure of **11** was readily established by nmr spectroscopy through comparison of the nmr spectra of **2** and **11**. The nmr spectrum of **2** consisted of two overlapping singlets at τ 8.26 and 8.22 (9 H) for the three methyl groups, a one-proton doublet (H_B) at τ 5.10



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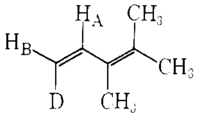
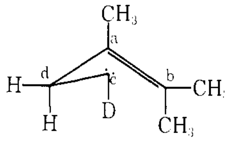


11

(J_{AB} = 11 cps), a one-proton doublet (H_C) at τ 4.95 (J_{AC} = 17 cps),[9] and a one-proton doublet of doublets (H_A) at τ 3.20. The nmr of **11** showed no change in the pattern for the methyl groups. However, H_A now appeared as a well-defined doublet of triplets at τ 3.20 (J_{AB} = 11 cps, J_{H-D} = 2.8 cps[10]), H_B appeared as a one-proton doublet at τ 5.10 (J_{AB} = 11 cps), and H_C, which had been replaced to the extent of *ca.* 80% with deuterium, appeared as a doublet at τ 4.95 with only 18% of its former intensity. Thus, the structure of our diene was firmly established as being that shown by **11**.

The presence of deuterium on only the terminal carbon indicated that the transition metal catalyzed opening of **1** resulted in cleavage of the a–c and b–c bonds in contrast to the thermal cleavage which cleaves the a–d and c–b bonds. In addition the presence of the deuterium cis to the rest of the carbon chain indicated an amazing degree of stereospecificity in the reaction. Formally, cleavage of the a–c and b–c bonds of **9** would result in the formation of **12** (neglecting the presence of the transition metal catalysis). Stereospecific transfer of a hydrogen from C_d to C_c would then give **11**. Overall, this reaction can be formally envisaged as a transition metal catalyzed[11] retrocarbene addition.



12

We are continuing to investigate the mechanism and scope of the metal-catalyzed isomerizations of strained ring systems.

Acknowledgment. We are indebted to the National Science Foundation and to the Alfred P. Sloan Foundation for funds which supported this investigation.

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[8] Nmr analysis indicated that **9** was *ca.* 80% monodeuterated.

[9] Normal ranges for J_{AB}, J_{AC}, and J_{BC} are 6–14 cps, 11–18 cps, and 0–3.5 cps, respectively (L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1959, p 85).

[10] H. J. Bernstein and N. Sheppard (*J. Chem. Phys.*, 37, 3012 (1962)) have shown that $J_{HH} \cong 6.55 J_{HD}$. On the basis of the J_{H-H} of 17 cps, a value of 2.6 cps would have been predicted for J_{HD} in our system.

[11] This reaction is not limited to the rhodium dicarbonyl chloride dimer catalyst. Dichlorotricarbonylruthenium dimer decomposed **1** to give 46% **2** and 22% **3**.

[12] Alfred P. Sloan Research Fellow, 1967–1969.

[13] Goodyear Fellow, 1968–1969; Dow Chemical Fellow, 1969–1970.

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Book Reviews

Chemical Energetics and the Curriculum. Edited by Professor D. J. Millen, Ph.D., D.Sc., F.R.I.C. American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York, N. Y. 1970. 192 pp. 14 × 22 cm. $6.50.

Collect eleven lectures by as many distinguished English chemists and chemical educators who participated in a course at University College London on Modern Trends in Chemistry and the Sixth Form dedicated to the proposition that in chemical education energetic considerations constitute a desirable, integrating theme—because "the trend today in science education is towards programmes which try to develop in the student the desire to investigate, to ask why and to seek understanding in place of the former emphasis on rote memory of a large number of facts. . .[and this approach] demands that students be provided, as early as possible, with guiding general principles"—add an editor and a willing publisher, and one sends forth to an unspecified audience (presumably chiefly teachers of high-level general chemistry courses) eleven workmanlike yet readable, introductory and nonmathematical, snapshot-like, nonhistorical, expository, ten- to twenty-page essays on energetics, and the atom and education (Nyholm), bond energies (Ross), endothermic reactions (Heslop), equilibrium (Ashmore), ionic crystals and solutions (Tobe), kinetics (Sykes), radiation (Walmsley), statistics (Millen), volatility (Maccoll), structure (Raitt), and, again, equilibria (E. H. Coulson), together with five separate elementary discussions of the NO_2–N_2O_4 equilibrium; four sketchy plausibility arguments for the relation $\Delta G = \Delta H - T\Delta S$ (everyone wants to get to this equation); several endorsements of the view that ΔH represents the "total energy push," $T\Delta S$ the "probability