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THE CLEAVAGE OF A STRAINED PROPELLANE BY TRANSITION METAL CARBONYLS

Paul G. Gassman and Eugene A. Armour

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

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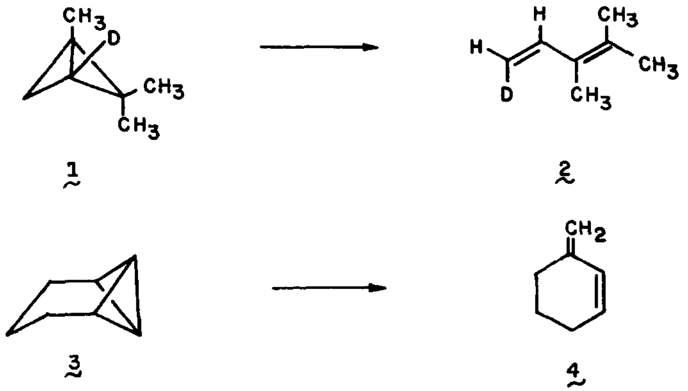
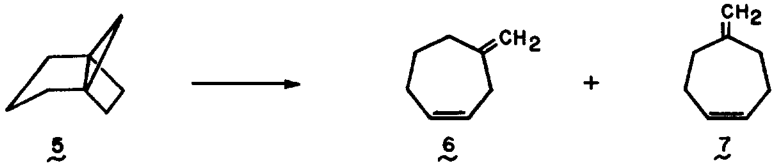
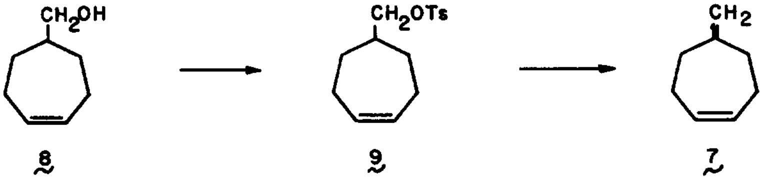
Recently, we have demonstrated that various derivatives of bicyclo[1.1.0]butane are extremely susceptible to rearrangement in the presence of certain transition metal complexes. This principle is illustrated by the facile conversion of 1 to 2[1] and of 3 to 4[2]

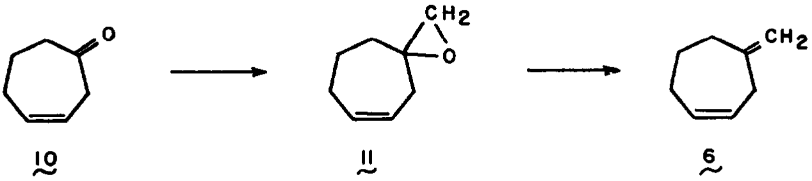


promoted by certain transition metal carbonyls such as rhodium dicarbonyl chloride dimer. Both of these rearrangements are complete in a few minutes at 25° in the presence of 2 mole % of rhodium dicarbonyl chloride dimer. In a *formal* sense both of these rearrangements can be viewed as retro-carbene additions accompanied by a hydrogen shift. We now wish to report that the cleavage of polycyclic molecules in a formal retro-carbene sense is not limited to derivatives of bicyclo[1.1.0]butane and that derivatives of bicyclo[2.1.0]pentane, such as the propellane, 5, are prone to isomerization in the presence of trace amounts of transition metal complexes.

When tricyclo[3.2.1.0^{1,5}]octane[3] (5) was exposed to 5 mole % of chlorotricarbonyliridium(I) dimer in chloroform solution for 24 hr. at 50°, it was completely isomerized to a 36:64 mixture of 4-methylenecycloheptene (6) and 5-methylenecycloheptene (7) in 52% yield.[4] Catalytic reduction of the mixture of products over 5% palladium on carbon produced only methylcycloheptane which was identical in all respects to an authentic sample.[5] In order to establish the nature of the initially formed dienes, both were independently synthesized. The preparation of 7 was relatively straightforward. The alcohol, 8, was converted to the tosylate 9 utilizing p-toluenesulfonyl chloride in pyridine.[6] Reaction of 9 with potassium t-butoxide in dimethyl sulfoxide gave 7. The synthesis of the isomeric diene, 6, proved considerably more difficult. Cyclohepten-4-one (10) was prepared according to literature directions.[7] When conversion of 10 into 6 *via* the classical Wittig procedure proved unsuccessful in our hands, we synthesized 11 *via* reaction of 10 with trimethylsulfonium ylid. When 11 was reacted with sodium iodide and zinc powder in acetic acid buffered with sodium acetate,[8] 4-methylenecycloheptene (6) was formed, which was identical in all respects to that obtained from the isomerization of 5. The nmr spectrum of 6 showed absorptions at

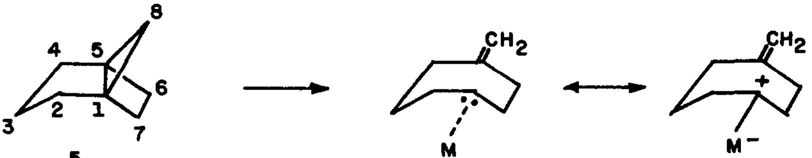






τ 4.35 (2H, multiplet), 5.38 (2H, singlet), 7.18 (2H, broad doublet), 7.43-8.01 (4H, broad multiplet), and 8.10-8.58 (2H, broad multiplet). The nmr spectrum of 7 showed absorptions at τ 4.14 (2H, multiplet), 4.28 (2H, singlet), and 7.76 (8H, broad singlet). The synthesis of authentic samples of 6 and 7 firmly established the structural assignments. The isomerization of 5 was not limited to chlorotricarbonyliridium(I) dimer. Similar results were obtained when the isomerization was promoted by either rhodium dicarbonyl chloride dimer or dichlorotricarbonylruthenium(II).

Formally, the isomerization of 5 in the presence of the various transition metal complexes involves the cleavage of the C_1-C_8 and C_1-C_5 bonds of 5, accompanied by either migration of a hydrogen from C_2 to yield 7, or from C_7 to produce 6. From a mechanistic point of view it is helpful to view this isomerization in terms of the intermediate formation of a metal-carbene complex which can be envisioned as a resonance hybrid of 12 and 13. Hydrogen shift with concomitant loss of the metal would produce the observed products. The overall process would then be one of oxidative addition of the metal in the early stages of the reaction followed by reductive loss of the metal at the terminating step of the reaction.[9,10]



5 12 13

We are continuing to investigate the mechanistic details of the fascinating isomerization of highly strained polycyclics by transition metal complexes. The support of this investigation by the National Science Foundation is gratefully acknowledged.

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2. P. G. Gassman and T. J. Atkins, ibid., in press.

3. P. G. Gassman, A. Topp, and J. W. Keller, Tetrahedron Letters, 1093 (1969); K. B. Wiberg and G. J. Burgmaier, ibid., 317 (1969).

4. In addition to **6** and **7** a high molecular weight residue was formed.

5. An authentic sample of methylcycloheptane was purchased from Chemical Samples Co., Columbus, Ohio.

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9. For a recent discussion of oxidative addition see J. E. Byrd, L. Cassar, P. E. Eaton, and J. Halpern, *Chem. Commun.*, 40 (1971).

10. It is tempting to think of these reactions as simple Lewis acid-base reactions, in which the transition metal complex plays the role of the Lewis acid. In all cases studied by us thus far, this approach will adequately explain the observed products. However, in most cases the products observed from the reaction of the highly strained polycyclics with transition metal complexes are different from those observed when conventional Lewis acids are used. Intriguingly, both sets of products can be rationalized in terms of psuedo carbonium ion processes.