to be as in eq 3. This reaction represents the most

$$P + I_2 + 2AgNO_2 \longrightarrow P\text{-}NO_2 + 2AgI + HNO_2 \qquad (3)$$

convenient way of mononitrating perylene at the present time.

In principle, nitration *via* the cation radical should be applicable to other aromatic hydrocarbons. We have prepared 1-nitropyrene in 80% yield as follows.

A solution of 100 mg of pyrene (0.5 mmol) in 50 ml of dry acetonitrile was cooled to 0° and to it were added 200 mg (2.9 mmol) of dry sodium nitrite, 500 mg (2 mmol) of iodine, and 825 mg (4 mmol) of silver perchlorate. Tlc showed that no pyrene remained after stirring the mixture at 0° for 30 min. Work-up as with the perylene reactions gave 98 mg of 1-nitropyrene (80% of theory), mp (crude) 147–149°, mp (glacial acetic acid) 151–151.5° (lit. mp 153–154°,[8] 155°[9]).

It is apparent that the position of "nitration" in each case is that at which positive charge density is highest, as calculated by simple HMO.[10]

Adaptation of this method to some other hydrocarbons (phenanthrene, chrysene, triphenylene, and anthracene) has not as yet proved successful. The causes are probably related to the oxidation potentials of the hydrocarbons and electrophilicity of the cation radicals, and are being investigated further.

[8] H. V. Vollman, H. Becker, and H. Streeck, *Justus Liebigs Ann. Chem.*, 531, 1 (1957).

[9] M. J. S. Dewar and P. M. G. Bavin, *J. Chem. Soc.*, 4486 (1955).

[10] C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π-Electron Calculations," Pergamon Press, Elmsford, N. Y., 1965.

[11] Postdoctoral Fellow.

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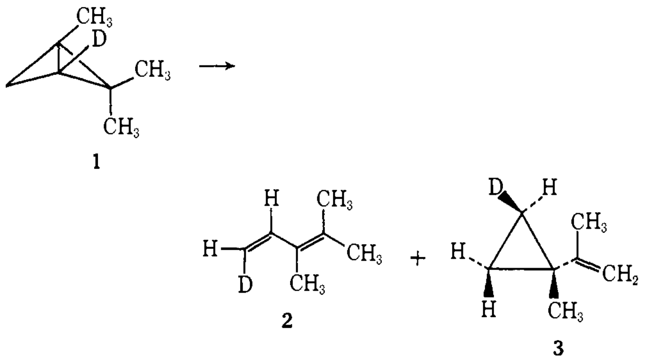
The Effect of Alkyl Substitution on the Course of the Rearrangements of Derivatives of Bicyclo[1.1.0]butane Promoted by Metal Carbonyls[1]

Sir:

Recently, we reported[2,3] on the metal-promoted conversion of **1** to **2** and **3**, and of **4** to **5**. Within the limits of analysis by nmr methods the isomerization of **1** to give **2** and **3** was completely stereospecific.[4] We now wish to report that the course and stereospecificity of these transition metal carbonyl-promoted rearrangements are extremely sensitive to the presence of alkyl substituents on the bicyclo[1.1.0]butane ring systems.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2
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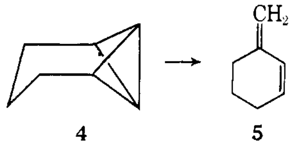
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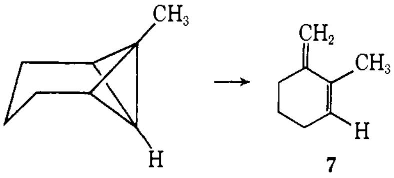
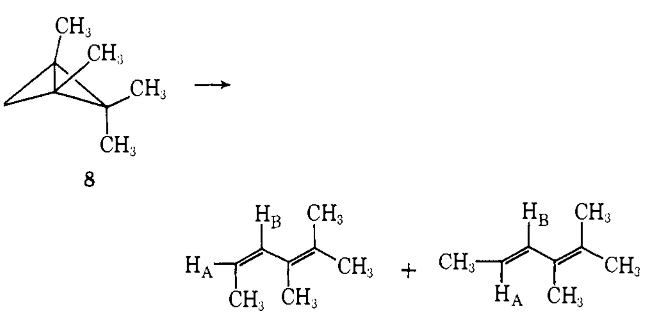

6
7

Treatment of **6**[5] with rhodium dicarbonyl chloride dimer for 15 min at 25° (room temperature), followed by vacuum transfer of the volatile materials, gave a 96% yield of **7**. Similarly, the use of iridium tricarbonyl chloride dimer allowed **6** to be converted into **7** in 93% yield. The structure of **7** was established on the basis of its characteristic spectral data: nmr τ 4.37 (one-proton multiplet), 5.17 (broad one-proton singlet), and 5.30 (broad one-proton singlet); ir 6.09, 6.22, and 11.28 μ; uv $\lambda_{\max}^{\text{hexane}}$ 234 nm (ε 16,200).[6] In addition, **7** was catalytically hydrogenated to give a mixture of *cis*- and *trans*-1,2-dimethylcyclohexane and dehydrogenated to give *o*-xylene. The transition metal carbonyl-promoted opening of **6** was extremely specific. No trace of any isomeric hydrocarbon could be detected by vpc.

Whereas the rearrangement of the methylated version of **4** occurred with unusual stereospecificity, the addition of another methyl group to **1** resulted in a loss of stereospecificity. When **8**[7] was treated with 5 mol % of rhodium dicarbonyl chloride dimer in chloroform at room temperature, no trace of **8** remained after 5 min. We found that during this time **8** had rearranged to give a 46% yield of **9** and a 50% yield of **10**.[8] Both **9** and **10** were readily hydrogenated to 2,3-dimethylhexane which was identical in all respects with an authentic sample. The stereochemistry of the two isomers was established on the basis of both nmr and ultraviolet


8
9
10

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[1] Paper XVII on "The Chemistry of Bent Bonds." For the previous paper in this series see P. G. Gassman, J. Seter, and F. J. Williams, *J. Amer. Chem. Soc.*, 93, 1673 (1971).

[2] P. G. Gassman and F. J. Williams, *ibid.*, 92, 7631 (1970).

[3] P. G. Gassman and T. J. Atkins, *ibid.*, 93, 1042 (1971).

[4] The stereochemistry of 3 was established by analysis of the nmr spectrum of 3 with that of its epimer. We wish to thank Professor William Moore for providing the nmr spectrum of the epimer of 3.

[5] For the preparation of 6 see G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, 85, 2022 (1963).

[6] Exact mass mol wt calcd for C_8H_{12}: 108.09389. Found: 108.09379.

[7] For the preparation of 8 see W. R. Moore, K. G. Taylor, P. Müller, S. S. Hall, and Z. L. F. Gaibel, *Tetrahedron Lett.*, 2365 (1970).

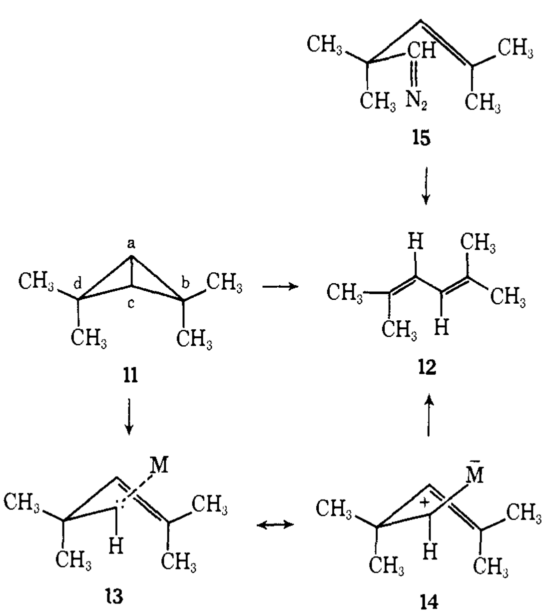
[8] Both 9 and 10 are known compounds: D. F. Schneider and C. F. Garbers, *J. Chem. Soc.*, 2465 (1964).

spectroscopy. Diene **10** was quite normal, showing a uv maximum in isooctane at 240 nm (ϵ 17,750). In contrast, **9** gave an abnormal uv spectrum with $\lambda_{\max}^{\text{isooctane}}$ 220 nm (ϵ 3850). The unusually short wavelength, weak absorption for **9** was consistent with expectations, since the strong methyl–methyl interactions in **9** would be expected to twist the double bonds out of coplanarity.[9] The nmr spectrum of **9** showed H_A at τ 4.63 and H_B at 4.12 with J_{AB} = 11 cps. In comparison, **10** had H_A at τ 4.54 and H_B at 3.56 with J_{AB} = 15 cps. Both the positions of the protons and the larger coupling constant between the vinylic protons of **10** are consistent with the assigned structures.

It is obvious that the presence of the additional bridgehead methyl group dramatically changes the course and stereospecificity of the isomerization of **1**. Whereas diene formation from **1** was stereospecific, diene formation from **8** was almost statistical. In addition, **8** failed to yield any vinylcyclopropane derivative with rhodium dicarbonyl chloride dimer.

In view of the strong influence of the additional methyl group on the rearrangement of **1** we decided to study the transition metal carbonyl-promoted rearrangement of 2,2,4,4-tetramethylbicyclo[1.1.0]butane (**11**),[10] which is isomeric with **8**. This bicyclo[1.1.0]butane derivative was of particular interest because it could not follow the same type of reaction paths followed by **1**, **4**, **6**, and **8**. In the transition metal carbonyl-promoted isomerizations observed for **1**, **4**, **6**, and **8**, the central bond and one peripheral bond of the bicyclo[1.1.0]butane moiety were cleaved in each case. We have noted[2] that this *formally* corresponds to a transition metal carbonyl-promoted retrocarbene addition or to an elimination of a carbenoid–metal complex. In each of the examples presented above, the cleavage reaction must be followed by hydrogen shift in order to produce the observed dienes. 2,2,4,4-Tetramethylbicyclo[1.1.0]butane lacks such a suitably situated hydrogen.

When **11** was treated with 5 mol % of rhodium dicarbonyl chloride dimer at 25° in chloroform for 5 min, an 83% yield of **12** was obtained. Similar treatment of **11** with 5 mol % of iridium tricarbonyl chloride dimer at 25° for 12 hr gave an 87% yield of **12**. On the surface it would appear that the presence of the two methyl groups at C-4 of **11** had completely changed the course of the rearrangement, even to the extent of changing which bonds were cleaved. The simplest explanation for these observations would be that the transition metal carbonyl complexes were promoting the cleavage of either bonds a–b and c–d, or a–d and b–c, while leaving a–c intact in a manner similar to the cleavage noted for the thermal rearrangement of bicyclo[1.1.0]butanes.[11] However, this would be quite inconsistent with the precedent set by the transition metal carbonyl-promoted isomerizations of **1**, **4**, **6**, and **8**. We feel that an alternate explanation can be provided which is consistent with our other findings. Cleavage of **11** could occur to give a metal complex of a carbenoid intermediate such as **13**. It is known that migratory aptitudes to a carbenoid center are hydrogen > vinyl > methyl.[12] Since there is no adjacent hydrogen available for migration in **13**, migration of the vinylic portion might be expected to occur, producing **12**. Such a vinyl migration should be especially favored in the case of a metal complexed carbene such as **13** which would have considerable positive charge on carbon as illustrated by its resonance contributor **14**. Thus, the metal-bonded cation, **14**, should be able to readily sustain a vinyl migration. Evidence for the feasibility of this concept was amply provided by the rhodium dicarbonyl chloride dimer promoted decomposition of **15** which occurred violently at low temperatures to yield **12** as the only volatile product.



We are continuing to investigate the mechanistic details of these fascinating metal complex promoted rearrangements.

Acknowledgment. We are indebted to the National Science Foundation for support of this work.

[9] For a twisted diene system such as 1,3-cyclooctadiene we have found $\lambda_{\max}$ 228 nm (ϵ 4300).

[10] For the preparation of 11 see H. K. Hall, Jr., C. D. Smith, E. P. Blanchard, Jr., S. C. Cherkofsky, and J. B. Siega, *J. Amer. Chem. Soc.*, **93**, 121 (1971). We wish to thank Dr. Cherkofsky for providing us with the experimental procedure for the preparation of **11** prior to publication.

[11] K. B. Wiberg and J. M. Lavanish, *J. Amer. Chem. Soc.*, **88**, 5272 (1966); G. L. Closs and P. E. Pfeffer, *ibid.*, **90**, 2452 (1968); and R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

[12] Professor H. Shechter, private communication. We wish to thank Professor Shechter for an enlightening and helpful discussion of this problem.

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

[14] National Science Foundation Trainee, 1968–1971.

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

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Structures and Relative Stabilities of $C_3H_7^+$ Cations

Sir:

There has been considerable recent interest in the $C_3H_7^+$ series of cations both from an experimental and theoretical viewpoint. A great deal of the attention has been focused on the possibility of protonated cyclopropanes and other nonclassical cations as reaction intermediates.[1] Although both semiempirical[2–6] and

[1] For recent reviews see C. J. Collins, *Chem. Rev.*, **69**, 541 (1969); C. C. Lee, *Progr. Phys. Org. Chem.*, 7, 129 (1970); J. L. Fry and G. J.