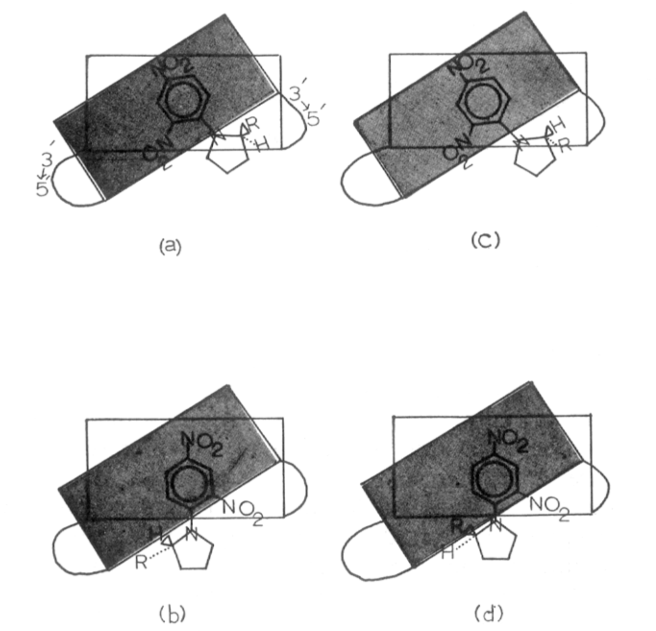

Figure 1. Schematic illustration (top view) of the possible intercalated complexes of the D-prolyl derivative **2** (a and b) and L-prolyl derivative **1** (c and d) between base pairs of a right-handed DNA helix. The direction of the 3' → 5' sugar phosphate chain with respect to the base pairs at the top (shaded) and bottom is indicated.

For example, the pmr signal of the H_a proton of **2** is upfield shifted by 64 Hz on binding to DNA at 39° and also at 50°. In contrast, the pmr signal of the H_a proton of **1** is upfield shifted by 52 Hz at 39° and 50 Hz at 50° on binding to DNA. Moreover, the entire pmr spectrum of the DNA–**2** complex shows that the pmr signals of **2** are more broadened than the corresponding pmr signals observed for the DNA–**1** complex. The results are indicative that the dinitroaniline ring of **2** experiences greater shielding (*i.e.*, *via* ring current anisotropy) and restricted tumbling than **1**. (4) It is noted from the viscometric titration studies shown in Figure 2 that the specific viscosity, η_{sp}, of the DNA solution increases with increasing concentrations of the D enantiomer and levels off at a base pair to reporter concentration of 4.0. The results are consistent with an intercalation model. In contrast, the L enantiomer causes a lowering of the specific viscosity of the DNA solution which indicates a decrease in the effective length of the helix in the DNA–**1** complex. The results are consistent with a model whereby intercalation of the dinitroaniline ring of **1** between base pairs of DNA results in a distortion of the helical rod, *i.e.*, bending at the point of intercalation. This effect might be expected from examination of molecular framework models of the DNA–L-prolyl derivative complex (Figure 1).

Binding studies were also carried out on the DNA–**1** and **2** complexes. The D enantiomer gave a binding constant of 1.18 × 10^5 and a maximum number of strong binding sites of one molecule per 4.55 base pairs. A lower binding constant is observed for the DNA–**1** complex, $K = 6.5 \pm 0.3 \times 10^4$, and a maximum number of strong binding sites of one molecule per 5.42 base pairs.[3]

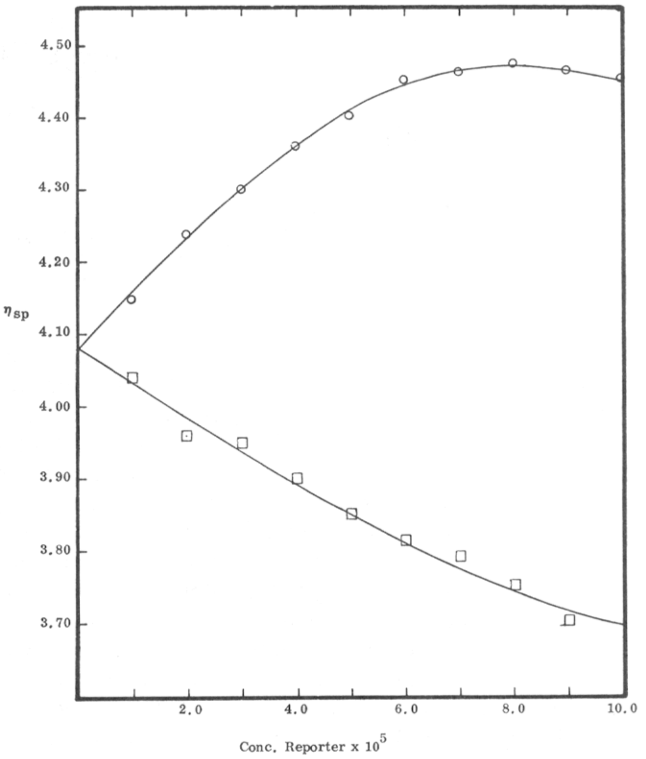

Figure 2. The effect of L- and D-prolyl derivatives **1** and **2** on the specific viscosity of DNA (□—□, L-prolyl; ○—○, D-prolyl derivative). Viscosity measurements were carried out using 6.3 × 10^{-4} mol of phosphorus/l. in 0.01 *M* 2-(*N*-morpholino)ethanesulfonic acid buffer at 37.5° using the low-shear Zimm viscometer.

In summary, the dissymmetric recognition of the helical sense of native DNA *in solution* has been accomplished *via* the interaction specificities of the DNP derivatives of L- and D-prolines **1** and **2**. The results of the absorption, circular dichroism, viscosity, pmr, and binding studies are consistent with a right-handed helical structure for native DNA in solution, in agreement with the Watson–Crick–Wilkins model.

Acknowledgment. This work was supported by Grants GM 17503 and GM 18653 from the U. S. Public Health Service and Grant No. GB 16044 from the National Science Foundation.

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Received December 6, 1971

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[3] Scatchard type plots were carried according to the modified spectrophotometric procedure of R. W. Hyman and N. Davidson, *Biochim. Biophys. Acta*, **228,** 38 (1971).

[4] Recipient of a U. S. Public Health Career Development Award (1970).

Transition Metal Complex Specificity and Substituent Effects in the Transition Metal Complex Promoted Rearrangement of Phenyl-Substituted Bicyclo[1.1.0]butanes[1]

Sir:

Of the various mechanistic proposals which have been presented for the transition metal complex promoted rearrangements of derivatives of bicyclo[1.1.0]butane,

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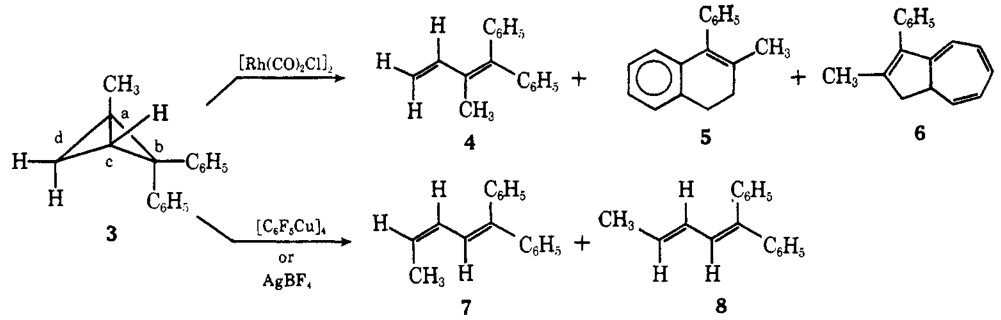
[1] Paper XXVIII on The Chemistry of Bent Bonds. For the previous papers in this series, see P. G. Gassman and F. J. Williams, *J. Chem. Soc., Chem. Commun.*, 80 (1972); P. G. Gassman and T. Nakai, *J. Amer. Chem. Soc.*, **93,** 5897 (1971).



the suggested intermediacy of a transition metal complexed carbene–transition metal bonded carbonium ion resonance hybrid[2] and the recently proposed formation of an "argento carbonium ion"[3,4] have substantial experimental support. Both intramolecular[5] and intermolecular[6] trapping experiments lend credence to the carbenoid character of the reaction intermediates generated in the transition metal complex promoted isomerizations of simple bicyclo[1.1.0]butanes. One of the more perplexing problems which remains to be answered, relative to these reactions, is concerned with the effect of both the metal and the substituents on the bicyclo[1.1.0]butane. For instance, 1,2,2-trimethylbicyclo[1.1.0]butane (**1**) gave a mixture of 3,4-dimethyl-1,3-pentadiene and 1-methyl-1-(2-propenyl)cyclopropane (**2**) with rhodium dicarbonyl chloride dimer,[7] while a mixture of the isomeric 2-methyl-2,4-hexadienes and **2** was obtained with either pentafluorophenylcopper tetramer[8] or silver fluoroborate.[3] In order to obtain a better understanding of the diverse behavior discussed above, we have explored in detail the role of rhodium dicarbonyl chloride dimer and pentafluorophenylcopper tetramer in the rearrangement of methylated derivatives of 2,2-diphenylbicyclo[1.1.0]butane. We now wish to report on the results of these studies and on their mechanistic implications.

The reaction of 1-methyl-2,2-diphenylbicyclo[1.1.0]butane (**3**) with rhodium dicarbonyl chloride dimer has been shown to give **4**, **5**, and **6** as primary products, in at least 19, 7, and 35% yields,[9] respectively.[5] When **3**[10] was treated with 4 mol % of pentafluorophenylcopper tetramer in chloroform for 2 hr at 25°, we obtained 20% of **7** and 61% of **8** as a mixture, which was only separable with great difficulty.[11] Similar treatment of **3** with silver fluoroborate gave 22% of **7** and 53% of **8**. Significantly, both pentafluorophenylcopper tetramer and silver fluoroborate failed to produce any dihydronaphthalenes or dihydroazulenes from **3**. The structures of **7** and **8** were established by a comparison of their ir and nmr spectra[12] and vpc retention times with those of authentic *cis*- and *trans*-1,1-diphenyl-1,3-pentadiene prepared according to the literature procedure.[13]

In close analogy to the mode of isomerization of **1** in the presence of rhodium dicarbonyl chloride dimer *vs.* pentafluorophenylcopper tetramer or silver fluoroborate, **3** suffered cleavage of the a–c and b–c bonds in the rhodium dicarbonyl chloride dimer promoted reaction and cleavage of the a–b and a–c bonds with pentafluorophenylcopper tetramer or silver fluoroborate. In contrast to the behavior of **1**, which gave similar types of products with all three of the transition metal derivatives discussed in this communication, **3** gave major amounts of a dihydronaphthalene and of a dihydroazulene with rhodium dicarbonyl chloride dimer, but no trace of analogous dihydro aromatics in the presence of either pentafluorophenylcopper tetramer or silver fluoroborate. Evidence supporting the hypothesis that the rhodium(I) complex converted **3** into a resonance hybrid represented by the resonance contributors **9** and **10** has already been presented and discussed.[5] The eventual formation of **6** was readily interpreted in terms of a carbenoid type insertion of **9** into the benzene ring to give a norcaradiene derivative, followed by valence tautomerism to produce **6**. The formation of **5** could result from either a direct C–H insertion reaction (resonance hybrid showing carbenoid character) or a Friedel–Crafts type alkylation of a benzene ring (resonance hybrid showing cationic character). By analogy, the copper(I) and silver(I) derivatives would be expected to convert **3** to a resonance hybrid represented by **11** and **12**. Simple hydrogen shift in the **11** ↔ **12** hybrid and loss of the metal would readily explain the formation of **7** and **8**. The failure of the **11** ↔ **12** hybrid to convert to any dihydro aromatic derivatives raised the question of whether the attached metal or the added methyl substituent at the reactive site was the determining factor. In order to answer this question we synthesized 1,3-dimethyl-2,2-diphenylbicylo[1.1.0]butane (**13**),[14] which, being symmetrical, should yield an intermediate represented by the resonance contributors **14** and **15** with all three transition metal derivatives. When **13** was treated with 4 mol % of rhodium dicarbonyl chloride dimer in chloroform for 3 hr at 25°, we obtained 11% of **16**, 38% of **17**, 11% of **18**, and 23% of **19**.[15] Compounds **16**, **17**, and **18** were primary

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[2] P. G. Gassman, T. J. Atkins, and F. J. Williams, *ibid.*, **93**, 1812 (1971).

[3] L. A. Paquette, R. P. Henzel, and S. E. Wilson, *ibid.*, **93**, 2335 (1971).

[4] The "argento carbonium ion" can be viewed as an extreme resonance contributor of our proposed hybrid intermediate.

[5] P. G. Gassman and T. Nakai, *J. Amer. Chem. Soc.*, **93**, 5897 (1971).

[6] R. Noyori, T. Suzuki, Y. Kumagai, and H. Takaya, *ibid.*, **93**, 5894 (1971).

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

[8] P. G. Gassman and F. J. Williams, *Tetrahedron Lett.*, 1409 (1971).

[9] The yields of **5** and **6** were based on the overall yields of the corresponding dehydrogenated aromatic compounds. Since the yields given are for the two-step sequence (rearrangement and dehydrogenation), the yields for the rearrangement step should be significantly higher than those quoted.

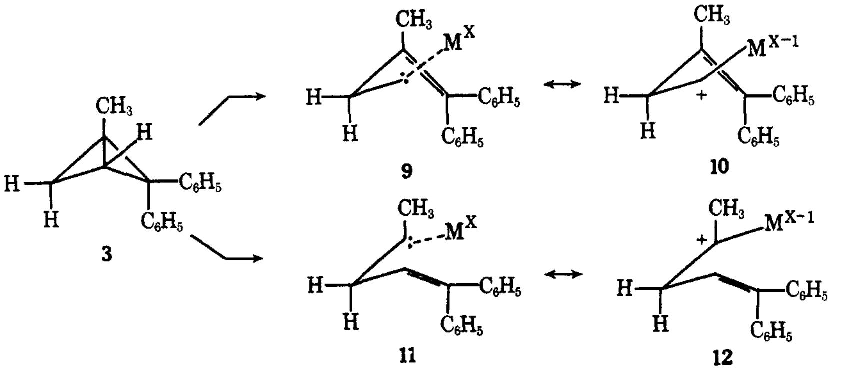
[10] For the preparation of **3**, see W. R. Moore and J. B. Hill, *Tetrahedron Lett.*, 4553 (1970).

[11] It was demonstrated that **7** and **8** were interconvertible in the presence of pentafluorophenylcopper tetramer.

[12] A detailed description of the spectral basis for the stereochemical assignments will be presented in a full paper on this subject.

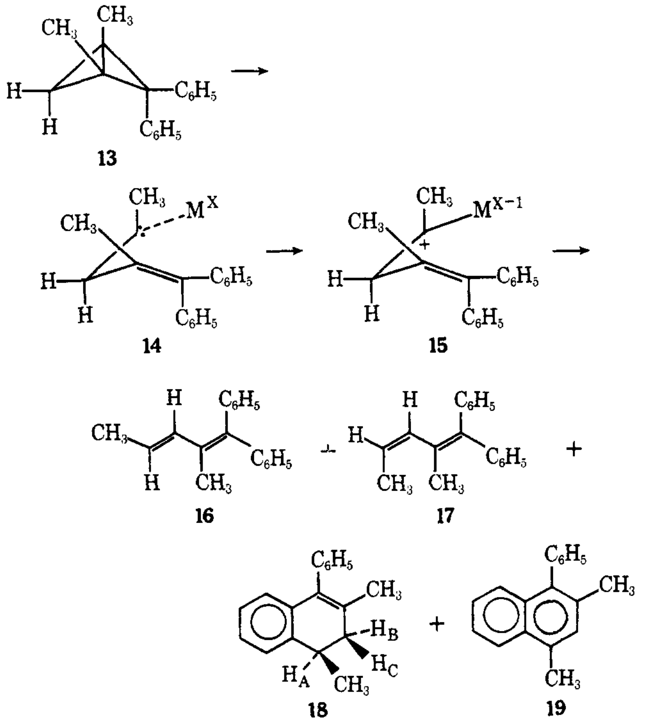
[13] B. Cheminat and R. Rambaud, *C. R. Acad. Sci., Ser. C.*, **264**, 897 (1967).

[14] Treatment of **3** with *n*-butyllithium and tetramethylethylenediamine, followed by methyl iodide, gave a 76% yield of **13**: mp 56–57°; *m/e* 234.1412 (calcd 234.1409).



3, 9, 10, 11, 12

products, while **19** was a secondary product derived from the dehydrogenation of **18**. When the rearrangement of **13** was promoted by 4 mol % of pentafluorophenylcopper tetramer for 3 hr at 25°, we obtained a 60% yield of a mixture of **16** and **17** in the ratio of 7:3, respectively. No indication could be found for the formation of either **18** or **19** in the pentafluorophenylcopper tetramer promoted reaction. The formation of **18** and **19** when M$^+$ was rhodium(I) and the absence of **18** and **19** when M$^+$ was copper(I) indicated that *the formation of dihydroaromatic products from phenyl-substituted bicyclo[1.1.0]butanes was a function of the transition metal complex used to promote the isomerization,* and did not depend on the presence of the methyl group at the reactive site.



13, 14, 15, 16, 17, 18, 19

The conclusion reached above is not meant to imply that the methyl group was completely without influence. In relation to the rhodium(I) complex promoted rearrangement, the added methyl group was very important. Relative to the products formed in the rhodium(I) complex promoted rearrangement of **3**, the reaction of **13** with the same complex resulted in a significant increase in the amount of the dihydronaphthalene derivative and the complete absence of a dihydroazulene. Consideration of the intermediate resonance hybrid represented by **14** and **15** offered an insight into the origin of these changes. Addition of the bridgehead methyl group converts the "primary" reactive site of the **9** ↔ **10** resonance hybrid into the "secondary" reactive site of the **14** ↔ **15** resonance hybrid. The change from a "primary" to a "secondary" center would be expected to result in a greater contribution to the resonance hybrid by **15** than by **10**. Thus, the added methyl group makes the intermediate take on more cationic character at the expense of its carbenoid character. As a result, the formation of dihydroazulene derivatives stopped due to the lack of "carbenoid" addition to the aromatic ring, while the amount of the dihydronaphthalene derivative increased, presumably due to the increased Friedel-Crafts type alkylation of the phenyl group.[16]

In summary, we have shown that product formation depends on both the nature of the transition metal complex and on the substitution of the bicyclo[1.1.0]butane. In addition, we have shown that the change from a "primary" reactive site to a "secondary" reactive site dramatically changes the character of the reactive intermediate as demonstrated by a significant change in product ratios. We are continuing these studies in the hope of elucidating why different transition metal complexes promote the initial cleavage of different bonds of the substituted bicyclo[1.1.0]butanes.

Acknowledgment. We are indebted to the National Science Foundation for a grant which supported this investigation.

(15) The structures of **16**, **17**, **18**, and **19** were established on the basis of ir, uv, nmr, and mass spectral analysis. In addition, treatment of **18** with sulfur at 250° gave **19**. The extensive spectral data on **16**, **17**, **18**, and **19** will be presented in a full paper.

(16) If more cationic "carbenoids" are better at C–H insertion and poorer at adding to aromatic rings, the formation of dihydronaphthalene derivatives could also be interpreted in terms of a C–H insertion reaction of a very "cationic" carbene.

(17) The Ohio State University, Postdoctoral Fellow, 1970–1971.

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Received January 22, 1972

On the Formation of C_2O_4 in Chemiluminescent Reactions

Sir:

In a recent communication[1] to this journal, mass spectrometric evidence for the carbon dioxide dimer, C_2O_4, as a chemiluminescent intermediate was presented. Because of the interest of this laboratory in

(1) H. F. Cordes, H. P. Richter, and C. A. Heller, *J. Amer. Chem. Soc.*, **91**, 7209 (1969).