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PENTAFLUOROPHENYLCOPPER TETRAMER - AN INTRIGUING CATALYST FOR THE REARRANGEMENT OF HIGHLY STRAINED POLYCYCLIC MOLECULES

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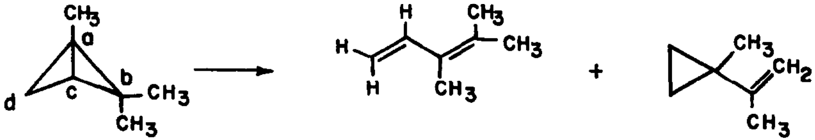
Recently we reported that transition metal complexes such as rhodium dicarbonyl chloride dimer and dichlorotricarbonylruthenium dimer promote the facile isomerization of derivatives of bicyclo[1.1.0]butane and bicyclo[2.1.0]pentane.[1] As a specific example, it was demonstrated that 1,2,2-trimethylbicyclo[1.1.0]butane (1) was rapidly isomerized by these transition metal complexes to a mixture of 2 and 3 at 25°. Isotopic labelling showed that this isomerization involved the cleavage of the a-c and b-c bonds of 1. We now wish to report that pentafluorophenylcopper[2] is also an efficient catalyst for the isomerization of 1 and related bicyclo[1.1.0]butanes. However, in the case of 1, pentafluorophenylcopper promotes the cleavage of different bonds and results in the formation of different products.



1 2 3

When 2 mol % of pentafluorophenylcopper tetramer was added to a chloroform solution of 1 at 0° under a nitrogen atmosphere, an immediate exothermic reaction occurred. Vacuum transfer of the solvent and volatile products away from the non-volatile residue, followed by removal of the solvent gave 39% of 4, 33% of 5, and 11% of ring methylated vinylcyclo-

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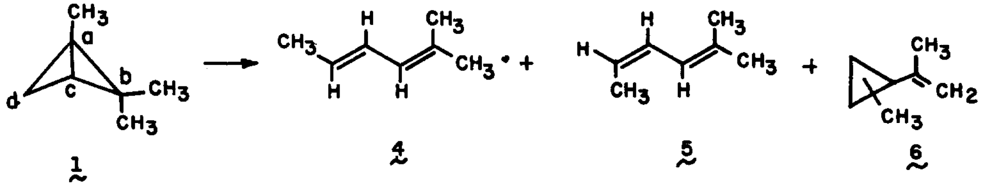
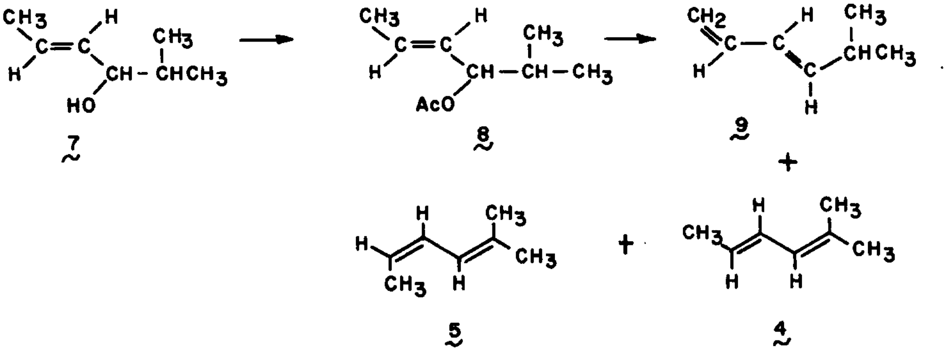
propane derivatives, 6.



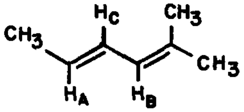
The dienes, 4 and 5, appeared as a single peak on most vapor phase chromatography columns. They were finally separated by preparative vpc on a 25' x $^{1}/_{4}$'' 20% D.C. silicone fluid 200 on $^{60}/_{80}$ chromosorb P column at 75°. Since this separation was only accomplished with great difficulty, 4 and 5 were catalytically hydrogenated as the mixture. Reduction over 5% palladium on carbon gave only 2-methylhexane, which was identical to an authentic sample[3] in all respects.

An independent synthesis of 4 and 5 was accomplished starting with commercially available[3] 7, which was converted into the corresponding acetate, 8, with acetic anhydride in pyridine. Pyrolysis of 8 in the vapor phase at 450° gave a mixture of 4, 5, and 9 in the ratio of 28:22:50.[4] Separation of 9 from the mixture of 4 and 5 was readily accomplished by preparative vpc. The mixture of 4 and 5 obtained from 8 was spectroscopically almost



identical to the mixture of 4 and 5 obtained from 1. In addition pure 4 was synthesized from *trans*-2-butenal *via* a Wittig reaction.[5]

The stereochemistry of samples of 4 and 5 isolated from the reaction mixture obtained from 1 was established spectroscopically. The infrared spectrum of 4 showed a strong absorption at 10.44 μ (*trans* olefin) while the spectrum of 5 had a strong absorption at 14.02 μ (cis olefin). The nmr spectrum of 4 had absorptions at τ 8.28 (9H, singlet), 4.48 (1H, multiplet), 4.25 (1H, multiplet), and 3.77 (1H, multiplet). Spin decoupling of the methyl hydrogens permitted determination of J_{AC} = 15 cps, J_{BC} = 11 cps, and $J_{A\text{-}CH_3}$ = 7 cps. The



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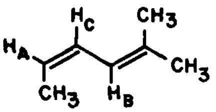

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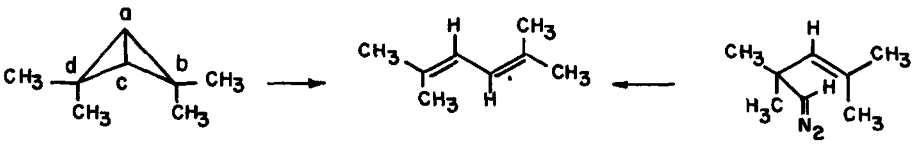
value of J_{AC} supported the structure assigned on the basis of the infrared spectrum. The nmr spectrum of 5 showed absorptions at τ 8.27 (9H, multiplet), 4.60 (1H, multiplet), and 3.85 (2H, multiplet). Irradiation of the methyl hydrogen multiplet centered at τ 8.27 simplified H_A into a doublet with J_{AC} = 9 cps. This substantiated the stereochemical assignment.

The results discussed above provide the basis for some perplexing thought. Clearly, pentafluorophenylcopper tetramer is an efficient material for promoting the rearrangement of 1. However, a dramatic difference exists between pentafluorophenylcopper tetramer and transition metal complexes such as rhodium dicarbonyl chloride dimer. Whereas the latter bring about the cleavage of the a-c and b-c bonds of 1, the use of pentafluorophenylcopper tetramer results in the cleavage of the a-b and a-c bonds of 1. This amazing specificity indicates the presence of factors which are far from being understood. It seems apparent that we will need a much larger body of empirical data before a general theory of predictive value can be established for these metal induced rearrangements.

The effect of pentafluorophenylcopper tetramer is not limited to 1. 2,2,4,4-Tetramethylbicyclo[1.1.0]butane (10) rearranges readily in the presence of this arylcopper to yield 11.



10 11 12

The symmetry of this molecule prevents us from determining whether the formation of 11 involves the cleavage of the a-b and c-d bonds or the cleavage of the a-b and a-c bonds in a *formal* retro-carbene addition[1] accompanied by vinyl group migration. The feasibility of the latter possibility was supported by the observation that **12** was violently decomposed by pentafluorophenylcopper tetramer to produce **11** in good yield.

We are continuing to design experiments for the purpose of elucidating the mode of reaction of various transition metal complexes with various highly strained polycyclic molecules. We hope that the availability of sufficient experimental data will lead to the advent of a cohesive theory concerning these facile metal promoted rearrangements. The financial assistance of the National Science Foundation is greatfully acknowledged.

References

1. P. G. Gassman and F. J. Williams, *J. Amer. Chem. Soc.*, **92**, 7631 (1970); P. G. Gassman and T. J. Atkins, *ibid.*, **93**, 1042 (1971); P. G. Gassman, T. J. Atkins, and J. T. Lumb, submitted for publication.
2. A. Cairncross, H. Omura, and W. A. Sheppard, *J. Amer. Chem. Soc.*, **93**, 248 (1971). We wish to thank Dr. Sheppard for generously supplying us with a sample of pentafluorophenylcopper tetramer.
3. Purchased from Chemical Samples Co., Columbus, Ohio.
4. For a closely related reaction see F. L. Greenwood, *J. Org. Chem.*, **27**, 2308 (1962).
5. We wish to thank Dr. G. R. Meyer for this preparation of pure **4**.