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INTRAMOLECULAR CYCLIZATION OF AN ALLENIC GRIGNARD REAGENT

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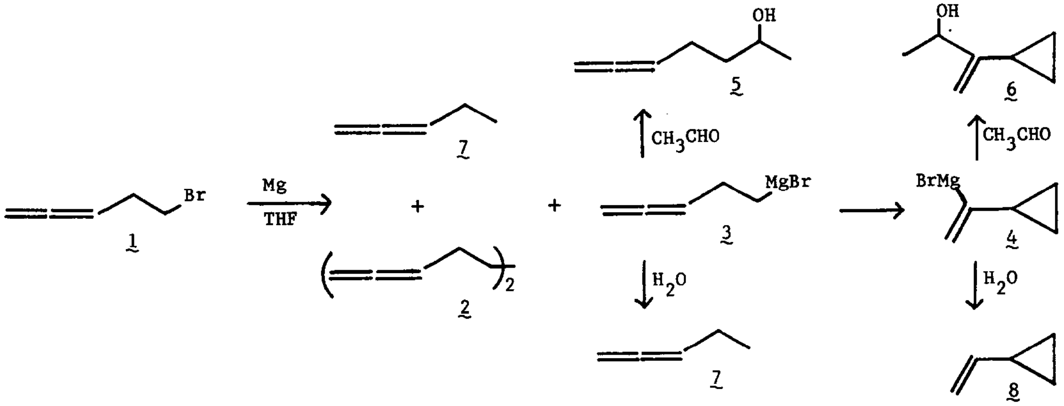
A ready intramolecular addition of the Grignard function of the 3,4-pentadien-1-yl Grignard reagent (3) to an allenic double bond furnished the 1-cyclopropylvinyl Grignard reagent (4).



This cyclization is related to previously reported intramolecular cyclizations of alkenyl (1,2) and alkynyl (3,4) Grignard reagents. However, in the reactions of those alkenyl (1,5) and alkynyl (4) Grignard systems that could furnish three-membered rings, the equilibrium concentrations of the cyclic isomers were far too low to permit the isolation of significant amounts of cyclic products; only through observations (1,4) of scrambling of isotopic labels or substituents was it known that cyclization (followed by ring opening) occurred. Therefore, syntheses of highly strained rings by intramolecular cyclizations of Grignard reagents, though not practical with alkenyl or alkynyl systems, are feasible with allenic systems.

5-Bromo-1,2-pentadiene (1) in tetrahydrofuran reacted completely with magnesium in a few hours at room temperature. After addition of acetaldehyde to freshly prepared Grignard solutions, 5,6-heptadien-2-ol[*] (5), isolated in ~25% yield, was the only significant alcoholic product. In contrast, 3-cyclopropyl-3-buten-2-ol* (**6**), isolated in ~25% yield, was the only significant alcoholic product if a solution was refluxed for 12 hours before the addition of acetaldehyde. These data indicate that Grignard reagent **3** formed in ~25% yield and then isomerized to **4**. The relative amounts of alcohols **5** and **6** obtained after addition of acetaldehyde to aliquots removed from Grignard solutions indicated that the isomerization of **3** to **4** has a half-time of ~4 days at 25°. Conversion of the remainder of bromide **1** to 1,2,8,9-decatetraene (**2**) and 1,2-pentadiene (**7**) during the preparation of the Grignard reagent was responsible for the relatively low yields of **3**. Grignard solutions hydrolyzed soon after their preparation furnished ~30% of the tetraene and ~70% of mixtures of 1,2-pentadiene and vinylcyclopropane (**8**) of which the cyclopropane ultimately constituted about one-third. The one-third of the 1,2-pentadiene that was slowly replaced by vinylcyclopropane must have arisen from Grignard reagent **3** and the remainder from attack on solvent by 3,4-pentadien-1-yl radicals formed during the reaction of the bromide with magnesium.

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REFERENCES

1. M. S. Silver, P. R. Shafer, J. E. Nordlander, C. Rüchardt, and J. D. Roberts, J. Am. Chem. Soc., **82**, 2646 (1960).
2. E. A. Hill, H. G. Richey, Jr., and T. C. Rees, J. Org. Chem., **28**, 2161 (1963); H. G. Richey, Jr., and T. C. Rees, Tetrahedron Letters, 4297 (1966); W. C. Kossa, Jr., unpublished observations.
3. H. G. Richey, Jr., and A. M. Rothman, Tetrahedron Letters, 1457 (1968).
4. A. M. Rothman, unpublished observations.
5. D. J. Patel, C. L. Hamilton, and J. D. Roberts, J. Am. Chem. Soc., **87**, 5144 (1965); M. E. H. Howden, A. Maercker, J. Burdon, and J. D. Roberts, ibid., **88**, 1732 (1966); A. Maercker and J. D. Roberts, ibid., **88**, 1742 (1966).

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* The structure of this new compound is consistent with its elemental analysis and ir and nmr spectra.

Key Words: strained ring synthesis, vinylcyclopropane, organometallic, Wurtz coupling