Tetrahedron Letters No. 19, pp 1675 - 1678.
0040-4039/79/0501-1675$02.00/0

# REACTION OF VINYLCYCLOPROPANES WITH BUTYLLITHIUM

W. A. Beavers*[1a] and S. E. Wilson[1b]

Department of Chemistry, Oregon State University, Corvallis, Oregon

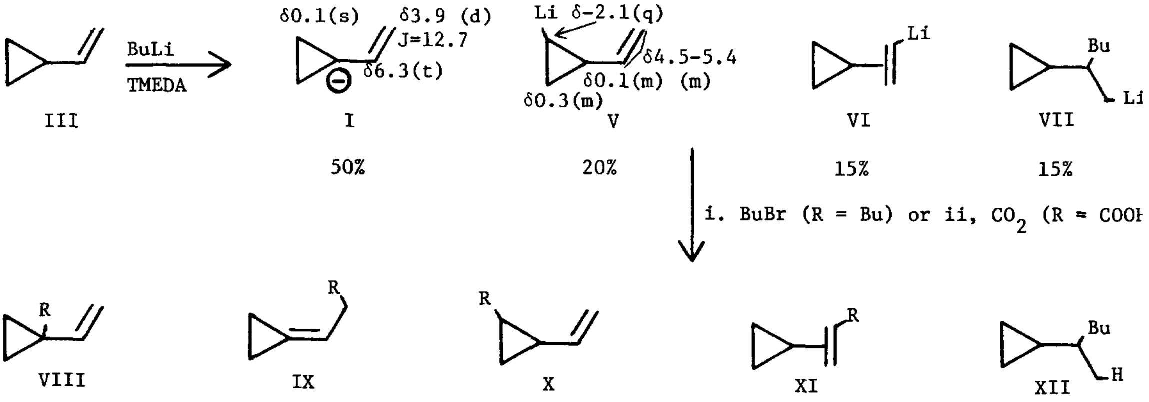
Bernard Gordon III, R. B. Bates, and A. R. Romano

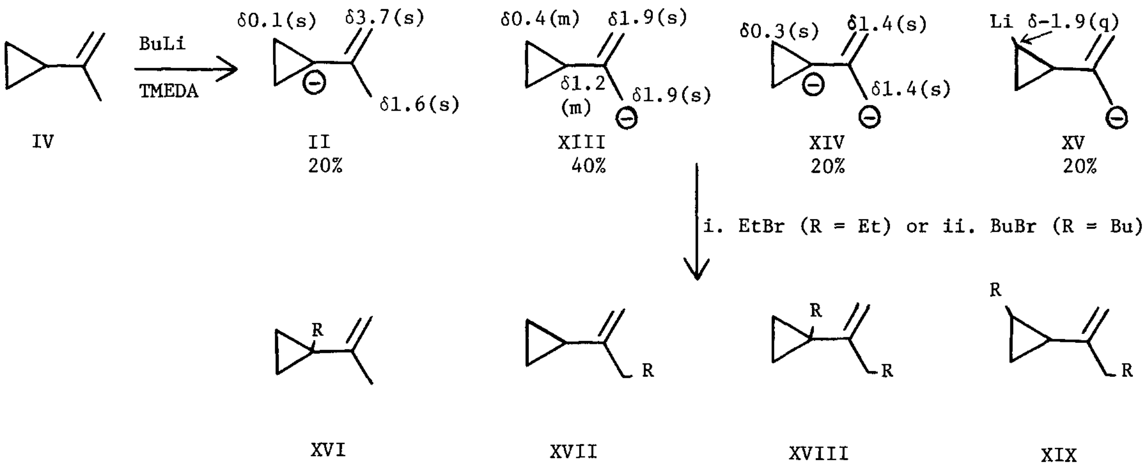
Department of Chemistry, University of Arizona, Tucson, Arizona

Abstract: Vinylcyclopropanes III and IV gave mainly allyl anions I, II, and XIII respectively under strong metalating conditions. Cyclopropyllithiums V and XV were also formed unexpectedly in significant quantities and were further explored.

Delocalized carbanions may be prepared from the corresponding olefins by hydrogen abstraction using the powerful metalating medium n-butyllithium/tetramethylethylenediamine (TMEDA).[2] In order to investigate carbanions I and II as potential sources of further delocalized anions, we used this method to metalate their alkene precursors, III and IV.

Compounds III and IV were prepared by standard procedures and were purified by preparative gc prior to use. Metalation was accomplished by mixing III with one equivalent and IV with two equivalents of a 1:1 complex of butyllithium/TMEDA[3,4] at 0°. NMR analysis showed that several anions were produced by each precursor, that most anions developed maximum concentrations 3 to 5 hours after warming to room temperature, and that these anions were stable for 1 to 5 days before eventually abstracting hydrogens from TMEDA to revert to starting hydrocarbons. Anion XIII took





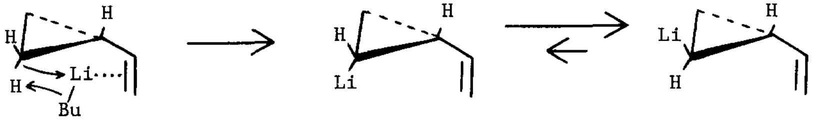
only 30 minutes to reach peak concentrations indicating a greater kinetic acidity of the methyl group than the cyclopropyl group and consistent with results from methyl cyclopropyl acetylene.[5]

Support for these schemes came from quenching each anion with water giving >83% recoveries of $C_5$ and $C_6$ materials (plus 12% of XII from III). That these compounds were mostly mono and dianions was shown by quenching with deuterium oxide. Low ionizing voltage mass spectral analysis of the $C_5$ fraction from the III reaction revealed 17.3%-$d_0$, 81.2%-$d_1$, and 1.5%-$d_2$ and on the $C_6$ fraction from the IV reaction revealed 5.9%-$d_0$, 52.0%-$d_1$, and 42.1%-$d_2$. Further support came from isolating an average of 37% VIII, 15% IX, 19% X, 12% XI, 14% XII, and 3% unidentified products[6] on reacting the III reaction with butyl bromide or carbon dioxide. A similar quench of the IV metalation mixture with ethyl bromide or butyl bromide led to an average of 18% XVI, 35% XVII, 14% XVIII, 17% XIX, and 16% of various vinyllithium and unidentified quench products.[6]

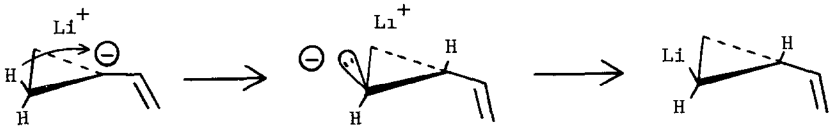
The complete assignment of the nmr spectra of several anions (and partial assignment of others) as shown on their figures (chemical shift, peak appearances in parentheses, and coupling constants where discernable) was the result of careful inspection of the slowly changing spectra. Comparison of the chemical shifts of the vinyl methylene hydrogens in I (at δ3.9) and in II (at δ3.7) with those of allyllithium[7] (at δ2.2) and crotyllithium[8] (at δ1.2) suggests that the chemical shift of methylene groups in allyl anions is a sensitive probe of the charge delocalization. Since the chemical shifts of corresponding hydrogens correlate with the charge on the adjacent carbon,[9] the low field absorptions of the vinyl methylenes come from their being part of a largely localized system in which most of the anionic charge exists on the cyclopropyl carbon. The data is consistent with either an ionic or a covalent major form as long as the anionic electrons remain associated largely with the cyclopropyl carbon. In either case a small equilibrium concentration of a species with lithium covalently bonded to the terminal methylene and spinning rapidly on the nmr time scale is needed to produce magnetic equivalence in these hydrogens.

The sizable concentrations of V and XV were unexpected and, therefore, were further explored. Evidence for these anions came from the upfield location of their highest field chemical shifts ($\delta$-2.1 and $\delta$-1.9, respectively)[10] (quartet, spacings 10.5, 10.5, and 7.6 hz for V) and the isolati of their quench products X and XIX.[8] The necessity of the vinyl group for the formation of these compounds was shown by the failure to metalate bicyclopropane using 3 equivalents of the butyllithium/TMEDA complex.[11] Carbonation of the III metalation mixture followed by work-up of the acidic components and esterification with diazomethane led to the isolation of Xii methyl ester by preparative gc. Xii was shown to be the *E* isomer (less than 3% as much of the *Z* isomer was detected) by oxidation of the vinyl group to carboxy[12] followed by mild hydrolysis to the known *E*-1,2-dicarboxycyclopropane.[13]

Scheme A



Scheme B



I V

Two schemes, A and B, can account for this data. Scheme A involves complexation of the vinyl group with butyllithium bringing the reactive centers into close proximity so that hydrogen abstraction leads initially to the *Z* isomer. Even though such cyclopropyllithiums are usually stable,[14] over long periods of time (10 hours, 25°, electron donating solvent) the anion might isomerize to the observed *E* compound (if this stereoisomer is the more stable). Scheme B, similar to the one proposed by Wittig,[15] involves initial formation of I which undergoes a 1,2 hydrogen shift giving the *E* isomer directly. Since the 5:2 ratio of I:V is maintained whether the anion is formed at -10° or at room temperature (although the relative rate of formation changes by 100-200 fold) and upon heating to 70°, either the two species must be in equilibrium or their stabilities and reactivities toward proton abstraction are coincidentally identical.

Acknowledgement. The authors wish to thank Professor P. K. Freeman for helpful discussions and Dr. P. W. Chum for improved methods of preparing vinylcyclopropane.

## REFERENCES AND FOOTNOTES

1a. Address correspondences to this author, present address Texas Eastman Company, Longview, Texas.
1b. Present address Shell Research and Development, Houston, Texas.

2. R. B. Bates, W. A. Beavers, M. G. Greene, and J. H. Klein, J. Amer. Chem. Soc., 96, 5640 (1974); J. Klein and A. Medlik, J. Chem. Soc., Chem. Commun., 275 (1973); J. M. Mallan and R. L. Bebb, Chem. Rev., 69, 693 (1969); B. J. Wakefield, "The Chemistry of Organolithium Compounds", Pergamon Press, New York (1974).

3. D. J. Peterson, J. Org. Chem., 32, 1717 (1967).

4. Unless hexane was removed (by a stream of dry nitrogen), III failed to metalate giving only limited amounts of the addition product VII.

5. D. Bauer and G. Kobrich, Chem. Ber., 109, 2185 (1976).

6. All analyses were consistent with these structures.

7. P. West, J. I. Purport, and S. V. McKinley, J. Amer. Chem. Soc., 90, 797 (1968).

8. For comparison see R. B. Bates and W. A. Beavers, J. Amer. Chem. Soc., 96, 5001 (1974).

9. H. Kloosterziel, Recl. Trav. Chim. Pays-Bas, 93, 215 (1974); H. Kloosterziel and G. J. Heizwolf, *ibid.*, 89, 413 (1970); K. Takahashi, M. Takaki, and R. Asami, J. Phys. Chem., 75, 1062 (1971).

10. D. Seyferth and H. M. Cohen, J. Organomet. Chem., 1, 15 (1963) list $\delta$-2.5 for cyclopropyllithium.

11. A small amount (<1%) of a compound with $\delta$-2.51[10] was detected.

12. M. Arai and R. J. Crawford, Can. J. Chem., 50, 2158 (1972).

13. The melting point of the diacid was 171-174° ["Handbook of Chemistry and Physics", 54th ed., R. G. West, edit., Chemical Rubber Company, Cleveland (1973) reports *cis*-1,2-dicarboxycyclopropane m.p. 139°; *trans*-1,2-dicarboxycyclopropane m.p. 175°] and the nmr spectrum was identical with spectrum 8105M in "Sadtler Standard NMR Spectra", Sadtler Research Laboratories, Inc. (1976) for *trans*-1,2-dicarboxycyclopropane, but different from spectrum 8106M for *cis*-1,2-dicarboxycyclopropane.

14. M. P. Periasamy and H. M. Walborsky, J. Amer. Chem. Soc., 99, 2631 (1977); H. M. Walborsky, F. J. Impastato, and A. E. Young, *ibid.*, 86, 3283 (1964); H. M. Walborsky and F. J. Impastato, *ibid.*, 81, 5835 (1959); K. Kitatani, T. Hiyama, and H. Nozaki, *ibid.*, 97, 949 (1975); D. E. Applequist and A. H. Peterson, *ibid.*, 83, 862 (1960); J. G. Welch and R. M. Magid, *ibid.*, 89, 5300 (1967); J. B. Pierce and H. M. Walborsky, J. Org. Chem., 33, 1962 (1968); P. K. Freeman, L. L. Hutchinson, and J. N. Blazevich, *ibid.*, 39, 3606 (1974); R. M. Magid and S. E. Wilson, Tetrahedron Letters, 4925 (1969).

15. G. Wittig, V. Rautenstrauch and F. Wingler, Tetrahedron Suppl., 7, 189 (1966).

**(Received in** USA 16 October 1978)