Tetrahedron Letters,Vol.23,No.37,pp 3769-3772,1982 0040-4039/82/373769-04\$03.00/0 Printed in Great Britain ©1982 Pergamon Press Ltd.

HOMOALLENYL RADICALS¹⁸

J.K. Crandall, " G.L. Tindell^{1b} and A. Manmade

Department of Chemistry, Indiana University, Bloomington, IN 47405

<u>Summary</u>: Several homoallenyl radicals have been generated by the reaction of the corresponding iodides with Bu₃SnH and found to produce small amounts of vinylcyclopropanes in addition to allene hydrocarbons establishing that homoallenyl radicals cyclize to isomeric 1-cyclopropylvinyl radicals.

The interconversion of isomeric homoallyl (1) and cyclopropylcarbinyl (2) radicals has been the subject of considerable scrutiny.² Although this is not the situation in all molecular environments, it is generally true that 1 is favored over 2 by a considerable margin at equilibrium. Nonetheless, isomerization is kinetically rapid under most experimental conditions,³ resulting in interesting radical rearrangements in suitable instances.² An intriguing variant of this system consists of the homoallenyl radical 3 and its cyclic isomer 4. Other possible modes of cyclization of 3 would lead to radicals 5 and 6. In this study we examine the behavior of simple derivatives of 3.



The subject radicals were generated from the corresponding iodides by reaction with tri-<u>n</u> butyltin hydride in the usual manner.⁴ The iodides 7 were obtained from the readily available esters 8^5 by LiAlH₄ reduction to the alcohols 9 follwed by formation of the <u>p</u>-toluenesulfonate esters and subsequent displacement with the NaI in acetone.

The slow addition (3 hr) of a 0.1 <u>M</u> solution of Bu_3SnH in benzene to a dilute (0.07 <u>M</u>) solution of 7a in refluxing benzene produced a 96:4 mixture of allene lOa and vinylcyclopropane

lla.^{6,7} When the reaction was performed by adding pure 7a to neat Bu_3SnH at room temperature, only allene 10a was observed.

The slow addition of 0.6 <u>M</u> Bu₃SnH in mineral oil to a 0.08 <u>M</u> solution of 7b in mineral oil at 80° gave a 96:4 ratio of allene 10b and vinylcyclopropane 11b. A similar reaction in hexane at room temperature gave a 66% yield of the same products in a 98:2 ratio. On the other hand, the addition of iodide 7b to Bu₃SnH at room temperature showed only allene 10b under GC analysis conditions where as little as 0.2% of 11b would have been detected.

$$\xrightarrow{\text{7a,b}} \longrightarrow \mathbb{R}_1 \mathbb{R}_2 \mathbb{C} = \mathbb{C} = \mathbb{C} + \mathbb{C} + \mathbb{H}_2 \mathbb{C} + \mathbb{R}_1 \mathbb{R}_2 \mathbb{C} = \mathbb{C} + \mathbb{C} +$$

Thus, the generation of radicals of type 3 gives rise to vinylcyclopropane products derived from cyclic radicals of type 4 in addition to the predominant unrearranged allene. Although the percentage of cyclic product 11 is small, this material is favored significantly relative to the situation with simple examples of the $1 \neq 2$ system.⁸ The cyclication of homoallenyl radicals of type 3 proceeds highly regioselectively to give the cyclopropyl species 4. In particular, products derived from type 5 radicals were not observed. Four-ring formation by radical attack on the central carbon of the allene moiety would have generated a thermodynamically more stable allylic radical.⁹ Nonetheless, kinetic control dictates preferential three-ring cyclization as with the olefinic system 1.² The lack of products corresponding to radicals of type 6 is not surprising in view of the inability of the radical center of 3 to approach within bonding distance of the remote carbon of the allene unit. Interestingly, increasing the temperature of the reaction of 7b appears to enhance cyclization, whereas running the reaction in neat Bu₃SnH, where radical lifetimes are greatly shortened, supresses this process effectively.

The reaction of 12, the dideutero analog of 7b, provides information concerning the reversibility of the cyclization. Reaction of a 0.09 \underline{M} solution of 12 in mineral oil at room temperature by the very slow addition (8 hr) of 0.17 \underline{M} Bu₃SnH gave a 97:3 ratio of 10b:11b. The volatile product was vacuum transferred from the reaction mixture and analyzed by both proton and deuterium NMR demonstrating that at least 95% of the deuterium label remained at the terminal carbon of the allene product. Consequently, the equilibration of the intermediate radicals must be slow under these conditions, since reversible cyclization would have scrambled the label between the two positions of the ethyl side-chain.

$$(CH_3)_2C=C=CHCH_2CD_2I$$
 (12) \longrightarrow (CH₃)₂C=C=CHCH₂CD₂H

The interconversion was also approached from a cyclic precursor. Thus, reaction of a 0.1 \underline{M} solution of cyclic iodide 13¹⁰ in mineral oil at 80° by the slow addition of 0.1 \underline{M} Bu₃SnH gave a 61:39 mixture of allene 10b and vinylcyclopropane 11b. A similar experiment on 0.05 \underline{M} 13 in hexane at room temperature resulted in a 47:53 ratio, whereas adding 13 to neat Bu₃SnH produced 10b and 11b in a 1:99 ratio. Clearly, cyclic radicals of type 4 open to their acyclic isomers. However, this process is relatively slow as shown by the supression of ring-opened product in neat hydride. The temperature dependence of the products of 13 also indicates a significant

activation barrier to isomerization. By way of contrast, cyclopropylcarbinyl radicals ring-open so rapidly that they cannot be trapped by Bu₃SnH under these conditions.¹¹ A stereoelectronic feature may retard the opening of vinyl radicals of type 4 relative to those of 2.¹²

$$(CH_3)_2C=CI \longrightarrow 10b + 11b$$

Finally, the behavior of iodide 7c, with a methyl substituent on the side-chain, was examined. Reaction of 0.07 <u>M</u> 7c in refluxing benzene with 0.15 <u>M</u> Bu₃SnH resulted in a 26:73:3 mixture of the corresponding allene 14, rearranged allene 15 and vinylcyclopropane 16. A comparable experiment in hexane at room temperature gave an 81:15:2:2 mixture of 14, 15, 16 and an unidentified compound. The addition of 7c to neat Bu₃SnH at room temperature yielded a 95:2.5:1.5:1 mixture of the same products.

$$\begin{array}{c} \overbrace{\text{CH}_3}_2\text{C}=\text{C}=\text{CHCHCH}_3\text{CH}_2\text{C} \text{ (17)} \longrightarrow (\text{CH}_3)_2\text{C}=\text{C}=\text{CHCH}(\text{CH}_3)_2 \text{ (14)} \\ & & & & & \\ (\text{CH}_3)_2\text{C}=\stackrel{\circ}{\text{C}} \longrightarrow (\text{CH}_3)_2\text{C}=\text{C} \text{H}\stackrel{\circ}{\text{C}} \text{H}_2 \text{C} \text{H}_3 \text{ (18)} \longrightarrow (\text{CH}_3)_2\text{C}=\text{C} \text{H}\stackrel{\circ}{\text{C}} \text{H}_2 \text{C} \text{H}_3 \text{ (16)} \\ & & & & \\ (\text{CH}_3)_2\text{C}=\text{C}=\text{C}\text{H}\text{C}\text{H}_2 \stackrel{\circ}{\text{C}} \text{H}\text{C} \text{H}_3 \text{ (19)} \longrightarrow (\text{C}\text{H}_3)_2\text{C}=\text{C}=\text{C}\text{H}\text{C}\text{H}_2\text{C}\text{H}_2 \text{C} \text{H}_3 \text{ (15)} \end{array}$$

Evidently the cyclization process in this instance is reversible. Thus, the rearranged allene 15 almost certainly arises by cyclization of the initial radical 17 to give cyclic radical 18 which isomerizes to the more stable secondary radical 19 by cleavage of the alternate cyclopropyl bond. The formation of rearranged allene 15 is retarded by lowering the temperature or increasing the Bu₃SnH concentration as expected. However, cyclization of 7c is apparently more facile than its analogs without the side-chain methyl group. Other radical cyclizations show similar rate accelerations promoted by substitution in the side-chain.¹³

Thus, the homoallenyl radical $\frac{3}{2}$ behaves qualitatively much like the analogous homoallyl radical 1 in that regioselective cyclization to generate a cyclopropyl ring occurs in a reasonably facile manner and this process can result in skeletal rearrangements in appropriately substituted cases. These isomerizations appear to be somewhat slower in the allene system but equilibrium seems to favor the cyclic form relative to the olefinic case. The available data is insufficient to determine K for $3 \neq 4$ since the experimental conditions did not permit rapid equilibration and the steady state product ratios can only be bracketed. Furthermore structural differences should result in significant variations in the rates of reaction of $\frac{3}{2}$ and $\frac{1}{4}$ with Bu₃SnH. Nonetheless, the observation of vinylcyclopropane products strongly suggests that K is appreciably larger than the very small value for $1 \neq 2$.^{8,14} The inability of $\frac{3}{2}$ to partake of the thermochemical advantages of cyclization to allylic radical $\frac{5}{2}$ is consistent with bimolecular radical additions to allenes, where there is little allylic stabilization of the transition state for addition to the sp carbon owing to the severe molecular distortions required to achieve the appropriate geometry.¹⁵

REFERENCES AND NOTES

- 1. (a) Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. (b) NIH Predoctoral Fellow 1969-1971.
- For recent reviews, see: A.L.J. Beckwith and K.U. Ingold in "Rearrangements in Ground and Excited States," P. de Mayo, Editor, Vol. I, p. 161, Academic Press, New York, 1980; A.L.J. Beckwith, <u>Tetrahedron</u>, 37, 3073 (1981).
- A.Effio, D. Griller, K.U. Ingold, A.L.J. Beckwith and A.K. Serelis, <u>J. Am. Chem. Soc.</u>, 102, 1734 (1980); B. Maillard, D. Forrest and K.U. Ingold, <u>J. Am. Chem. Soc.</u>, <u>98</u>, 7024 (1976); L.K. Montgomery and J.W. Matt, <u>J. Am. Chem. Soc.</u>, <u>89</u>, 3050, 6556 (1967).
- 4. H.G. Kuivila, Adv. In Organomet. Chem., 1, 47 (1964).
- 5. J.K. Crandall and G.L. Tindell, J. Chem. Soc. Chem. Commun., 1411 (1970).
- 6. The minor vinylcyclopropane products were identified by GC-MS comparison with samples obtained from Cr(II) reduction of the iodides 7a-c. In the latter experiments it was possible to isolate and fully characterize these products.
- 7. The <u>cis:trans</u> ratio of <u>lla</u> was not determined since these isomers were not separated under the GC conditions employed.
- 8. The $l \neq 2$ system has been estimated to have K = 3.8 x 10⁻⁵ at 25°C.³
- The formation of a radical of type 5 should result in the corresponding hydrocarbon products, since this radical would be stable to ring-opening: K.U. Ingold, B. Maillard and J.C. Walton, <u>J. Chem. Soc.</u>, Perkin Trans. 2, 970 (1981).
- Iodide 13 was prepared from cyclopropyl isopropyl ketone by the method of D.R. Kelsey and R.G. Bergman, <u>J. Am. Chem. Soc.</u>, <u>93</u>, 1941 (1971).
- M. Castaing, M. Pereyre, M. Ratier, P.M. Blum and A.G. Davies, <u>J. Chem. Soc.</u>, Perkin Trans. 2, 287 (1979).
- Stereoelectronic requirements control the direction of ring-opening of unsymmetrical cyclopropylcarbinyl radicals: A.L.J. Beckwith and G. Moad, <u>J. Chem. Soc.</u>, Perkin Trans. 2, 1473 (1980).
- 13. D. Griller and K.U. Ingold, Acc. Chem. Res., 13, 317 (1980).
- 14. Thermochemical estimates suggest similar K's for the two systems. Thus, the "strain energy" of the allene unit should destabilize 3 relative to 1 by about 11 kcal/mole [J.L. Jensen, Prog. Phy. Org. Chem., 12, 189 (1976)], whereas a vinyl radical is about 10 kcal/mole less stable than a primary one [S.W. Benson, "Thermochemical Kinetics," 2nd Ed., Wiley, New York, 1976, p. 309].
- 15. M.C. Caserio in "Selective Organic Transformations," B.S. Thyagarajan, Editor, Wiley-Interscience, New York, 1970, p. 239.

(Received in USA 25 May 1982)