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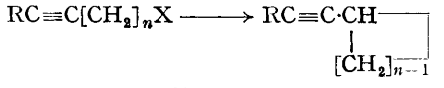
An Intramolecular Alkylation Route to Cycloalkylacetylenes

By J. K. CRANDALL* and D. J. KEYTON

(*Department of Chemistry, Indiana University, Bloomington, Indiana*, 47401)

INTRAMOLECULAR alkylation is a versatile and well studied method for the construction of cyclic compounds from precursors possessing appropriately situated leaving groups and carbon nucleophiles. The latter moiety is usually generated by base removal of a proton from a carbon centre adjacent to a polar substituent capable of stabilizing the intermediate carbanionic species. We now record several instances of intramolecular cyclization in which the carbon nucleophile is formed adjacent to an acetylenic bond.† These conversions were performed by treating the acetylenic halide with one equivalent of lithium diethylamide in tetrahydrofuran at −10° for 1—3 hr. The results are summarized in the Table.



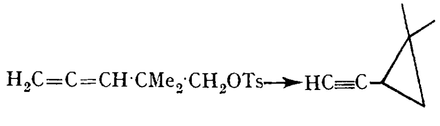
$$RC{\equiv}C[CH_2]_nX \longrightarrow RC{\equiv}C{\cdot}CH{-}[CH_2]_{n-1}$$

TABLE

n	R	X	Yield
3	Ph	Br	68%
3	$C_3H_7^n$	Cl	68%
4	Ph	Br	Polymer
4	$C_5H_{11}^n$	Br	Olefin
5	Ph	Br	74%
5	$C_5H_{11}^n$	Br	Olefin

The usual ring-size dependence for cyclization was noted.[1] Thus, cyclopropylacetylenes were produced cleanly with both alkyl and phenyl substituted substrates. Phenylcyclopentylacetylene was also obtained in good yield although this material was contaminated with several percent of its allene isomer.‡ However, cyclization of the alkyl substituted analogue of this compound is not competitive with simple dehydrohalogenation to form the terminal olefin, a result which demonstrates the importance of the phenyl substituent in promoting formation of the intermediate carbanionic species.[2] Not unexpectedly, cyclobutane formation was not competitive with dehydrohalogenation. The possibility of forming cyclohexyl or larger rings was not investigated.

Interestingly, intramolecular cyclization to cyclopropane derivatives could also be performed starting with the allene isomer of favourable acetylenes. Thus, 2,2-dimethylpenta-3,4-dienyl toluene-*p*-sulphonate was converted cleanly in 63% yield into 1-ethynyl-2,2-dimethylcyclopropane.



Attempts to effect intermolecular alkylation of acetylenes under these conditions were less successful. Both oct-2-yne and oct-4-yne returned

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† For a discussion of the role of carbanionic intermediates in allene–acetylene interconversions, see: W. Smadja, *Ann. Chim* (*France*), **1965**, **10**, 105.

‡ More complete isomerization to the unstable allene isomer could be effected by treatment of the halide with three equivalents of base.

mainly starting material upon sequential treatment with base and methyl iodide. However, 1-phenylprop-1-yne did give a 71% yield of 3-phenylbut-1-yne, apparently by alkylation of the mesomeric carbanion to give 1-methyl-1-phenylallene which was subsequently isomerized to the observed product.

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[1] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, 1962, pp. 198—202.

[2] Recent data supporting a delocalized carbanionic description for related allylic lithium species in tetrahydrofuran solvent is found in the following: P. West, J. I. Purmort, and S. V. McKinley, *J. Amer. Chem. Soc.*, 1968, **90**, 797; V. R. Sandel, S. V. McKinley, and H. H. Friedman, *ibid.*, 495; H. H. Friedman, V. R. Sandel, and B. P. Thill, *ibid.*, 1967, **89**, 1762.