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Generation of a Carbenoid by Cyclization of 6-Chloro-5-hexen-1-yllithium

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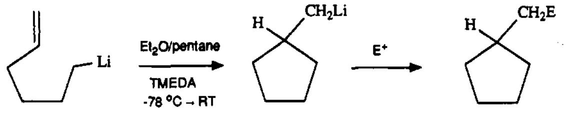
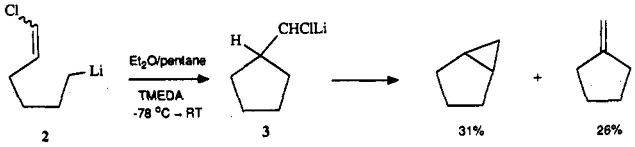
Summary: Bicyclo[3.1.0]hexane and methylenecyclopentane, products deriving from an apparent carbenoid intermediate, have been observed in the intramolecular cyclization reaction of 6-chloro-5-hexen-1-yllithium.

In recent years the facile regiospecific 5-*exo-trig* cyclization of 5-hexen-1-yllithium species has been demonstrated to be a convenient method for preparing a variety of cyclopentylmethyl-containing products.[1-6] Bailey's fundamental study in 1985 has been followed by a number of papers which have elaborated the scope and utility of this very useful process which, by its nature, is complementary to the more highly studied analogous radical cyclization reaction. Although most of the work in this area has involved hydrocarbon substrates, Broka has used such cyclizations to generate β-alkoxylithium species which were observed to undergo β-elimination to form alkenes.[6]



Although carbenes are unique as to the nature of their reactivity, and thus are of considerable potential synthetic interest, the methods available for their generation are quite limited, most of them involving the intermediacy of either diazo compounds or more commonly α–halo-organometallics. Thus, there is always interest in the discovery of new carbene-generating methodology. α-Haloalkyllithiums have always comprised an important source of carbenes. Moreover, it was apparent to us that the intramolecular cyclization of 6-halo-5-hexen-1-yllithiums had the potential to generate α-halocyclopentyllithiums, which in turn should lead to the observation of chemistry deriving from cyclopentylcarbene. In this paper we wish to report our study of the cyclization of 6-chloro-5-hexen-1-yllithium, the results of which indeed demonstrate the intermediacy of cyclopentylcarbene.

An approximate 50:50 mixture of (*E*)- and (*Z*)-1-chloro-6-iodo-1-hexene, 1, was prepared from 5-chloropentanal[7] via Wittig chloroolefination of the aldehyde[8] to form (*E*)- and (*Z*)-1,6-dichloro-1-hexene (83.5%) followed by Finkelstein displacement of the 6-chloro substituent by iodide (76%). This mixture of diastereomeric iodides underwent halogen-lithium exchange to form 6-chloro-5-hexenyllithium, 2, upon treatment with *tert*-butyllithium in ether/pentane at -78 °C following the method of Bailey.[3] TMEDA and internal standard heptane were then added and the mixture allowed to warm to room temperature and stir for 24 h. As shown in the scheme below, bicyclo[3.1.0]hexane (31.4%) and methylenecyclopentane (26.4%), which derive logically from carbenoid intermediate **3**, were observed as the only products of cyclization of **2**, along with the expected trace of cyclohexene.[9,10]



These results are consistent with those from earlier reports of more conventional methods of generation of cyclopentylcarbenes and carbenoids wherein ratios of methylenecyclopentane to bicyclo[3.1.0]hexane products varied from 0.30 to 0.90, depending upon the method of generation, the solvent, and the metal ion involved.[11-13] In general, overall yields of carbene-derived products in these earlier studies were lower than the 57% observed by us.

The above results demonstrate unambiguously that the facile carbanion cyclization reactions of 5-hexenyllithium reagents can be used efficiently, in the case of 6-*chloro-substituted* analogues, to generate cyclopentylcarbenoids which undergo the expected insertion reactions of such species. There should be no reason why analogous carbenoids from tandem 5-hexenyl cyclization processes, for example, or from allylcarbinyl to cyclopropylcarbinyl cyclizations should not also lead to useful synthetic pathways to unique carbene-derived products.

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Supplementary Material Available: Experimental procedures (3 pages). Ordering information is given on any current masthead page.

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[9] Bicyclo[3.1.0]hexane and methylenecyclopentane were unambiguously identified by comparison of their mass spectra and capillary gas chromatographic retention times with those of authentic samples. Authentic samples were available of all reasonable alternative isomeric species.

[10] A 14% yield of a ~50:50 mixture of (*E*)- and (*Z*)-1-chloro-1-hexene, products deriving from protonation of **2** (and independently synthesized for comparison), was also obtained.

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