## AN UNUSUAL C-C BOND CLEAVAGE IN A FIVE MEMBERED RING

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Abstract: 1,2-Dichlorocyclopentene undergoes dehalogenation-ring opening with sodium and chlorotrimethylsilane to form silylated pentynes.

1,2-Dihalocycloalkenes have long been known to dehydrogenate with alkali metals to cycloalkynes. which. if unstable (5 - 8)membered rings). would undergo oligomerization or other cycloaddition reactions with trapping reagents<sup>1</sup>. We have now noticed that the same reaction leads to ring cleavage in five membered ring system, and the results are presented here.

When 1.2-dichlorocyclopentene<sup>2</sup> (1) was heated with sodium and chlorotrimethylsilane at 50-55° in dry ether<sup>3</sup> for 45-50 h (15 h in dry THF), a product was obtained in 90% yield<sup>4</sup>, which contained mainly the pentynes 2 and 3 along with 4 (in 15:65:12 ratio respectively) and traces of a few unidentified products<sup>5</sup> (Scheme I).



Five membered heterocycles are known to yield ring opened products when The driving force for these reactions is believed to be treated with strong bases. electronegative heteroatom in the finally on the the stabilization of the anion The formation of 4 indicates that the anion  $5^7$  is likely to be cyclic isomer<sup>b</sup>. formed initially which then leads to the ring cleavage products<sup>8</sup>. When this reaction was extended to 1,2-dichlorocyclohexene (6), it was found to react at room temperature giving a complex mixture of products, which did not, however, include any silylated Thus the ring strain appears to be responsible for the homocyclic ring hexvne. Considering the very poor yields of the identifiable opening in the case of 1.

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products reported previously in the dehalogenation of 1,2-dihalocyclopentenes<sup>1</sup>, the excellent yields of 2 and 3 from 1 imply that the ring cleavage is perhaps the major path of the reaction and that the intermediates would lead to intractable material if not trapped by suitable reagents such as chlorotrimethylsilane used here.

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## Notes and References

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- For such Wurtz-type coupling reactions see, G. Nagendrappa, <u>Synthesis</u>, (1980)
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- 4. Typical procedure: To 1.09 g (47.4 mmol) of tiny pieces of sodium in 30 mL dry ether were added 2.98 g (27.4 mmol) of ClSiMe<sub>3</sub> and 1.22 g (8.9 mmol) of
  1. The mixture was stirred and refluxed at 50-55° (oil bath) until 1 disappeared (GC) and worked up<sup>3</sup>.
- 5. The compounds 2, 3 and 4 were isolated by preparative GC and identified by their IR, NMR ( $^{1}$ H and  $^{13}$ C), MS and C-H analysis data. Further structural evidence for 2 and 3 was derived by hydrogenating them to their saturated analogues and by an independent synthesis from 5-chloro-1-pentyne.
- 6. For relevant examples see, R.B. Bates and C.A. Ogle. 'Carbanion Chemistry', Springer Verlag, 1983, pp 69.
- Similar anions have been characterised. See for example, ref.1, and F. Wudl and E. Aharon-Shalom, <u>J.Amer.Chem.Soc.</u>, 104 (1982) 1154, and references cited therein.
- 8. The anion S or its radical precursor or cyclopentyne could be an intermediate that undergoes ring-opening. There is some circumstantial evidence for the last route but we have not yet been able to prove it. (Received in UK 9 November 1988)

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