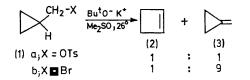
Base-catalysed Ring Expansions in Cyclopropylmethyl Systems

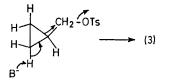
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Summary A novel base-catalysed ring expansion of cyclo- NON-CATIONIC ring expansions of cyclopropylmethyl syspropylmethyl derivatives to cyclobutenes is reported; tems are not common. One probable example is the conthe scope of the reaction and its mechanism are discussed. version of 1,1-bisbromomethylcyclopropane into methylenecyclobutane by reductive elimination with zinc.1,2

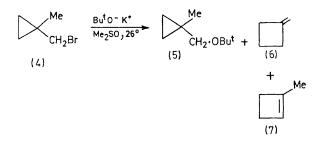
We report here a base-catalysed ring-expansion reaction of cyclopropylmethyl systems. When cyclopropyl methyl tosylate is treated with potassium t-butoxide in dimethyl sulphoxide for 1 h at room temperature, an essentially quantitative yield of C_4H_6 compounds is produced, with cyclobutene (2) and methylenecyclopropane (3) being



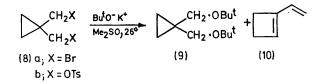
formed in approximately equal amounts.† These products could arise from (a) an α -elimination mechanism proceeding via a cyclopropylcarbene intermediate; (b) β -elimination from an equilibrating cyclopropylmethyl cation system; or (c) competing one-step γ - and β -eliminations. The α elimination alternative was eliminated by demonstrating that identical treatment of cyclopropyldideuteriomethyl tosylate yielded only 3,3-dideuteriocyclobutene and dideuteriomethylenecyclopropane. In fact utilization of the bromide analogue in this reaction is perhaps the most convenient way of preparing dideuteriomethylenecyclopropane in quantity.



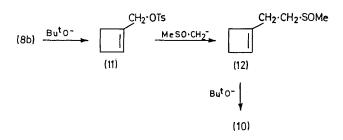
The carbonium ion alternative was ruled out by subjecting each of the cyclopropyl derivatives to the reaction conditions in the absence of base for 12 h; no rearrangement to a cyclobutyl derivative was detected by n.m.r., thus indicating that the reaction proceeded purely by a bimolecular eliminative mechanism with cyclobutene being formed as illustrated.



The generality of this reaction has not been fully tested, but there seem to be limitations when the 1-position is disubstituted. 1-Methylcyclopropylmethyl bromide (4) under the same conditions produced largely the ether (5), but also about a 20% yield of a 2:1 ratio of elimination products (6) and (7). Thus methyl proton abstraction seems to be competing with cyclopropyl proton abstraction in this case. We believe that in all cases the main driving forces for the ring-expansion process are the relief of angle strain of the cyclopropyl system and the reluctance (for strain reasons) of the system to generate an sp^2 site on the cyclopropyl ring by simple β -elimination.



In each of the reactions of (8) the diether (9) was the major product. However, while the reaction of (8a) produced no additional products, the ditosylate (8b) was converted in about 15% yield into 1-vinylcyclobutene (10), identified from its spectral properties and from its ready thermal conversion into 2-vinylbutadiene.



The formation of (10) can be rationalized as a sequential process involving bimolecular ring expansion to the cyclobutene species (11) followed by nucleophilic attack by the methylsulphonylmethanide ion to produce the sulphoxide (12); this could then undergo an apparently ready β elimination. Displacement of tosylates and bromides by methylsulphonylmethanide ion^{3,4} and β -eliminations of sulphoxides⁵ have been reported in isolated cases. We have found that in general this anion will displace primary tosylates at room temperature; this reaction, combined with subsequent thermal or base-catalysed β -elimination, should comprise a general process for preparing terminal alkenes with one extra carbon atom.

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† All products were identified by comparison of their i.r., n.m.r., and mass spectra with those of authentic samples.

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