Base-catalyzed Rearrangement of Bromomethylenecyclobutane

By K. L. ERICKSON* and B. E. VANDERWAART
(*Department of Chemistry, Clark University, Worcester, Massachusetts* 01610)
and J. WOLINSKY
(*Department of Chemistry, Purdue University, Lafayette, Indiana* 47907)

ACID-CATALYZED REARRANGEMENTS of cyclobutylmethyl systems are well-known.[1] We report such a rearrangement with bromomethylenecyclobutane under strongly basic conditions. This rearrangement, effecting the transformation of (I) into (II), finds no analogy in the behaviour of related vinyl bromides.

When bromomethylenecyclobutane (I) was treated with sublimed potassium t-butoxide at 245° an instantaneous reaction occurred, and 1-bromocyclopentene (II)[2] (ν_{max} 6·22, 9·67, 10·63, 12·06, and 12·60 μ; n.m.r. signals (δ from Me_4Si) at 1·70—2·80 and 5·74 p.p.m.) was isolated in 53% yield. Produced in small amounts were 1-t-butoxycyclopentene, (III)† (3%) (ν_{max} 5·98, 7·22, 7·36, and 8·66 μ) and an extremely volatile compound which could not be obtained in sufficient quantity for characterization. The balance of the

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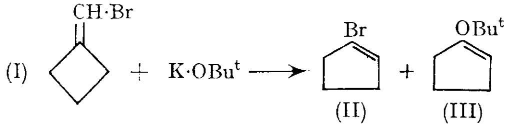
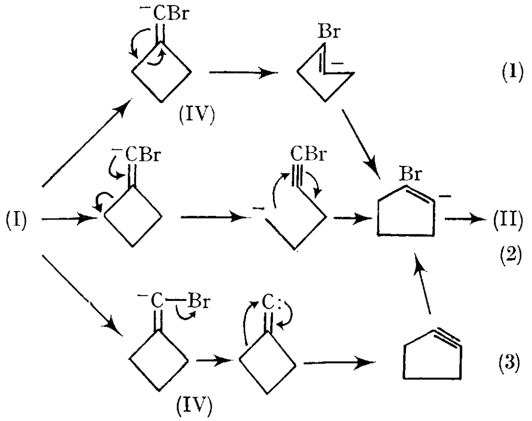
† Identified by conversion to the 2,4-dinitrophenylhydrazone of cyclopentanone.

bromine was found as ionic bromide (47%) in the aqueous phase produced during the reaction work-up.





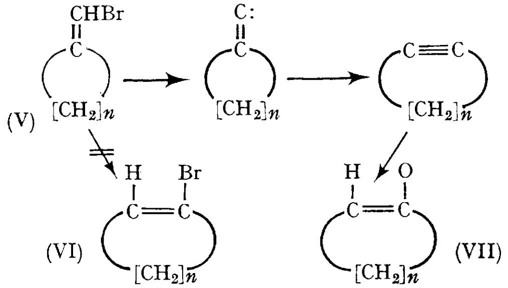
Although initially observed at high temperatures, rearrangement of (I) occurs even at 25°, albeit at a slower rate. Polar solvents appear to have a deleterious effect. In neat potassium t-butoxide, or with toluene as solvent at 100°, the rearrangement is complete in five minutes. In refluxing tetrahydrofuran only 45% of (I) is converted into (II) in one hour. Similarly, in dimethyl sulphoxide at 100° for one hour 27% conversion results. Alcoholic solvents markedly inhibit rearrangement. Thus, after one hour in refluxing t-butanol less than 5% of (II) is produced.

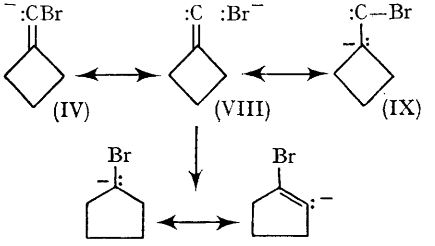
Evidence for the production of 1-t-butoxycyclopentene (III) in this reaction *via* a cyclopentyne intermediate has previously been presented.[3] 1-Bromocyclopentene (II) is not a significant precursor of the enol ether. When subjected to the reaction conditions, (II) gives only 0·3—0·5% yields of (III), and 45—55% of (II) is recovered. Clearly the yield of 1-bromocyclopentene (II) obtained in the rearrangement reaction of (I) is minimal since (II) is not stable under the reaction conditions.

The rearrangement of (I) to the ring-enlarged bromide (II) is formally analogous to the Wittig rearrangement of ethers[4] and amines.[5] Comments regarding the mechanism of the vinyl bromide rearrangement are speculative at this time. Several pathways may be written, none of which is wholly satisfactory: (1) a carbanion rearrangement involving migration of a ring carbon atom without its electrons (equation 1); (2) a cleavage–recombination mechanism (equation 2); and (3) a carbene rearrangement to cyclopentyne followed by readdition of bromide (equation 3).

Carbanion rearrangements (equation 1) have been observed in highly arylated systems[6] but are unknown in completely aliphatic systems where molecular-orbital calculations indicate that they are energetically unfavourable. Moreover, the reaction as written would give rise initially to the highly-strained *trans*-cyclopentene system.

The cleavage–recombination mechanism (equation 2) involves cyclobutyl ring-opening to an unstabilized anion, an unlikely process.[7] In addition, the direction of reclosure of the acetylenic anion is contrary to what one would predict on electronic grounds. It is perhaps significant that no acyclic products derived from the ring-opened species are observed.





The carbenoid mechanism (equation 3) is also unattractive. This mechanism is operative in the formation of ring-enlarged t-butyl enol ethers (VII) from larger ring homologues of bromomethylenecyclobutane (V).[3] However, in the six cases studied (n = 4—7,9, or 11) no trace of ring-enlarged bromides (VI) was observed. It is not clear why cyclopentyne should be the only cycloalkyne to undergo re-addition of bromide ion in this reaction. However, the extreme instability of cyclopentyne[8] may invalidate any attempt to relate its chemical behaviour to that of its larger ring homologues. It is possible that the bromide does not completely dissociate in this case, but that a carbenoid bromide complex is actually involved. Such a complex may be written as resonance forms of anion (IV) [(VIII) and (IX)], rearrangement of which avoids a discrete cyclopentyne intermediate. Such a scheme blends the carbanion mechanism (equation 1) with the carbenoid mechanism (equation 3), but in so doing some of the difficulties of both mechanisms are overcome. Preliminary deuterium-exchange experiments support the existence of anion (IV) in the reaction mixture. The strange solvent effects observed in this reaction suggest that stabilization of anion (IV) is an important factor in inhibiting its rearrangement.

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