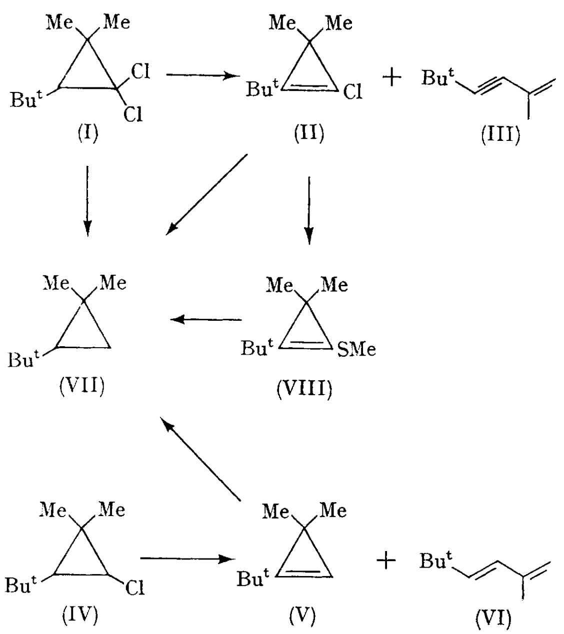
Direct Observation of Cyclopropenes from Dehydrochlorination of Chlorocyclopropanes

By T. C. SHIELDS
(*Union Carbide Corporation, South Charleston, West Virginia*)
and B. A. LOVING and P. D. GARDNER*
(*Department of Chemistry, University of Utah, Salt Lake City, Utah* 84112)

THE ready availability of halogeno-[1] and dihalogeno-cyclopropanes[2] makes them potentially attractive as cyclopropene precursors. Although many products attributable to cyclopropene intermediates have been obtained on dehydrohalogenation, only one cyclopropene has been isolated using this method.[3] More typically, isomerization products[4] or adducts with nucleophiles[5] have been obtained from such experiments. We report here two examples illustrating the practicality of the method for cyclopropenes which are structurally incapable of double-bond isomerization.

The reaction of 1,1-dichloro-2,2-dimethyl-3-t-butylcyclopropane (I) with potassium t-butoxide in dimethyl sulphoxide (inverse addition, 30°) afforded a mixture of 1-chloro-3,3-dimethyl-2-t-butylcyclopropene (II, 35%) and 2,5,5-trimethylhex-1-en-3-yne (III, 24%). All spectral properties



of (II) are consistent with its structure assignment (ν_{max} 1805 cm.$^{-1}$, parent mass 158). Similarly, the reaction of (IV) as a mixture of *cis-* and *trans-*isomers† gave 3,3-dimethyl-1-t-butylcyclopropene (V, 33%) and 2,5,5-trimethylhexa-1,3-diene (VI, 66%). The vinyl proton in (V) gives rise to a singlet in the n.m.r. spectrum, τ 3·45. Confirmation of the presence of a three-membered ring in both (II) and (V) was obtained by sodium–ammonia reductions to 1,1-dimethyl-2-t-butylcyclopropane (VII). An authentic specimen of (VII) was obtained by similar reduction of (I).

From a preliminary study of the behaviour of 1-chlorocyclopropenes, it was found that (II) reacts readily with MeS$^-$ to give 3,3-dimethyl 2-methylthio-1-t-butylcyclopropene (VIII, ν_{max} 1770 cm.$^{-1}$, λ_{max} 224 mμ, ϵ 1690). The n.m.r. spectrum possesses sharp singlets at τ 7·80 (MeS), τ 8·79 (two Me) and τ 8·86 (Bu^t). Sodium–ammonia reduction of (VIII), like that of (II), removed the functional group as well as saturating the double bond to give (VII), which was identical in all respects with samples obtained from (I), (II), and (V).

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† Prepared by the general procedure of Closs and Closs (ref. 1). This compound, as well as all others described, gave correct analytical data and consistent n.m.r. and i.r. spectra.

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