Tetrahedron Letters No. 28, pp 2437 - 2438, 1974. Pergamon Press. Printed in Great Britain.

LOCALIZED TRANSITION STATES FOR REACTIONS OF DELOCALIZED MOLECULES. IONIC AND RADICAL REDUCTIONS OF CHLOROCYCLOPROPENES WITH TRI-n-BUTYLTIN HYDRIDE.

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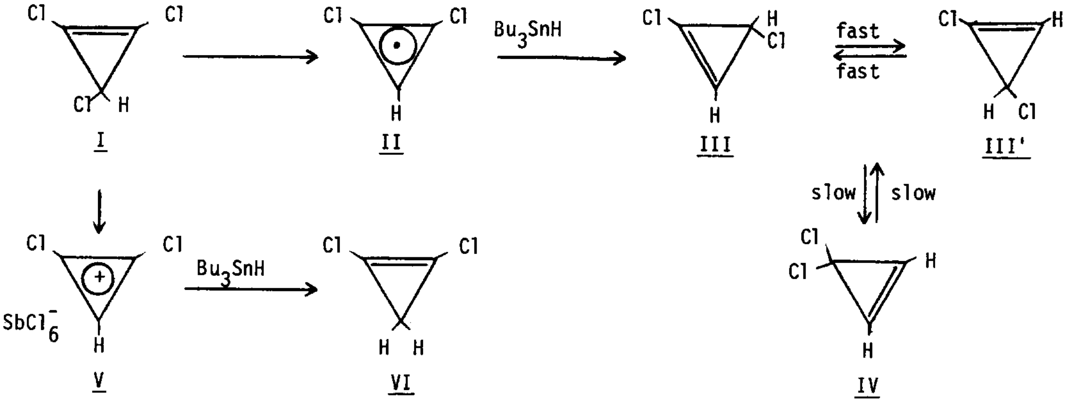
(**Received in USA 18 March 1974; received in UK for publication 31 May 1974**)

In our syntheses of unsubstituted cyclopropenone[1,2] and of unsubstituted cyclopropenyl cation[3] a key process involved the sequential reductive dechlorination of tetrachlorocyclopropene by the use of tri-n-butyltin hydride. We found[1] a remarkable effect of very subtle changes in reaction conditions on this process. Thus, treatment of tetrachlorocyclopropene with Bu_3SnH afforded 1,2,3-trichlorocyclopropene (I) which equilibrated with the 1,3,3-trichlorocyclopropene isomer. With carefully purified reagents in a rigorously nonpolar medium this mixture was converted to 1,3-dichlorocyclopropene (III), which then equilibrated with the 3,3-isomer (IV). These were hydrolyzed to cyclopropenone, and they also could be reduced further to generate 3-chlorocyclopropene. By contrast, if the reduction of I was performed in a polar medium, or even a nonpolar medium contaminated by small amounts of ether solvents or of tin oxide impurities, then the principal reduction product was 1,2-dichlorocyclopropene (VI), and only traces of III were formed.

We indicated that the reduction of I in nonpolar media went by a free radical process involving dichlorocyclopropenyl radical (II) as an intermediate. It seemed clear that the polar impurities were instead promoting an ionic pathway which afforded VI, but the precise nature of this ionic mechanism was not clear. The most interesting possibility was that it involved the intermediacy of dichlorocyclopropenyl cation (V), and that this had a different positional selectivity for reaction with Bu_3SnH. We now wish to report that this is indeed the case.

A solution of dichlorocyclopropenyl hexachloroantimonate[1] (V) was prepared in tetramethylene sulfone solution, and to this was added a small excess of Bu_3SnH. The volatile cyclopropenes were vacuum transferred, and the pmr spectrum showed only the singlet at $\delta 2.10$ for the methylene group of VI. No signals due to III, IV, or other cyclopropenes could be detected. Furthermore, product VI was converted to its known adduct with 1,3-diphenylisobenzofuran. By contrast, no detectible amount of isomer VI is formed under the careful free radical conditions.



The contrasting substituent effects on the reactions of II and V are best understood in terms of transition states involving localization of charges and bonds, with appropriate substituent effects. Thus, a chlorine atom will stabilize[1] a radical localized on the adjacent carbon atom. The transition state for reaction of II with Bu$_3$SnH will thus involve the transfer of a hydrogen atom in such a localized transition state to one of the carbons bearing chlorine, to afford III. By contrast, in the corresponding cation V a localized transition state for hydride transfer will preferentially[1,3] put positive charge on the carbon bearing hydrogen, not chlorine. This preference for transition states in which positive charge is localized next to hydrogen was also invoked to account for our previous observation[1] that III and III' equilibrate rapidly through the ultimately delocalized chlorocyclopropenyl cation, although the equilibration of III with IV is slow in both directions since the localized positive charge in this equilibration is on the chlorine-substituted carbon. The general situation is of course also analogous to substituent effects on allylic and other delocalized systems.

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