

SMALL RING COMPOUNDS XXV CYCLOPROPENYL RADICAL

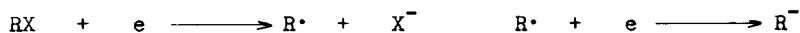
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The stability of cyclopropenium cation as a non-benzenoid 2π aromatic system has been established by many chemical and theoretical evidences¹⁾, while the corresponding anion has been proposed as an unstable anti-aromatic species²⁾. On the other hand, very few has been studied on the formation and chemical behavior of cyclopropenyl radical. The polarographic half-wave reduction potential of cyclopropenium cation has suggested that the cyclopropenyl radical is rather unstable than triphenylmethyl radical³⁾. The photochemical formation of hexaphenylbenzene from triphenylcyclopropenium cation would be only reaction explained by the generation of cyclopropenyl radical⁴⁾.

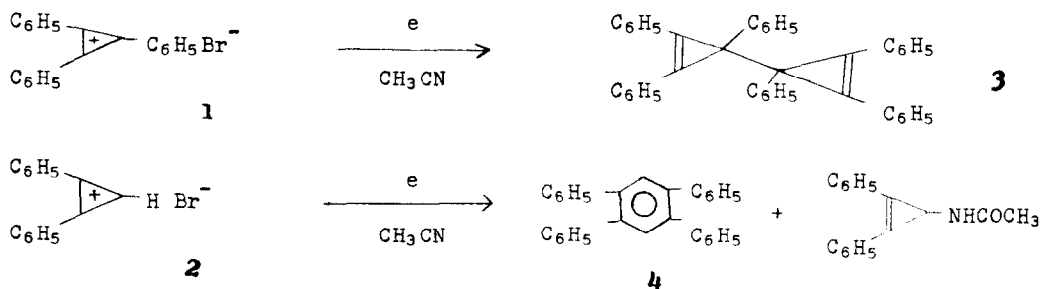
In the present study, we wish to report the electrochemical formation and chemical behavior of the cyclopropenyl radical. Generally, the electrochemical reduction of alkyl halide, RX seemed to proceed according to the following two consecutive reactions.



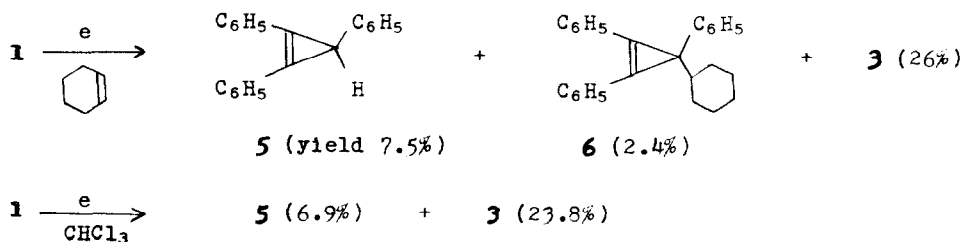
The intermediate radical, $\text{R}\cdot$, however, may not be free radical but it may be adsorbed on the electrode and have much anionic character. In the reduction of cyclopropenium halide, however, the behavior of this halide is rather resembled to salt and hence the intermediate is anticipated to have much free radical nature. Furthermore, owing to the instability of cyclopropenyl anion, two electron reduction of the cyclopropenium cation may be less probable. Thus, the formation of cyclopropenyl radical by the electrochemical reduction of the cation could be expected⁵⁾.

The electrochemical reduction (20~50v. 0.3A) was carried out at room temperature under an atmosphere of nitrogen using a cylindrical cell with a ceramic diaphragm. A carbon rod was used as the electrode and lithium perchlorate was used as a supporting electrolyte. The starting compounds were triphenylcyclopropenium bromide (**1**) and diphenylcyclopropenium bromide (**2**). The initial concentration of the starting compounds was about 0.2M in acetonitrile and the reaction was carried out until about 3F/mol of charge was passed. The products were isolated by column chromatographic technique (silica gel) and identified by the comparisons of their melting points and spectroscopic data with those of authentic samples.

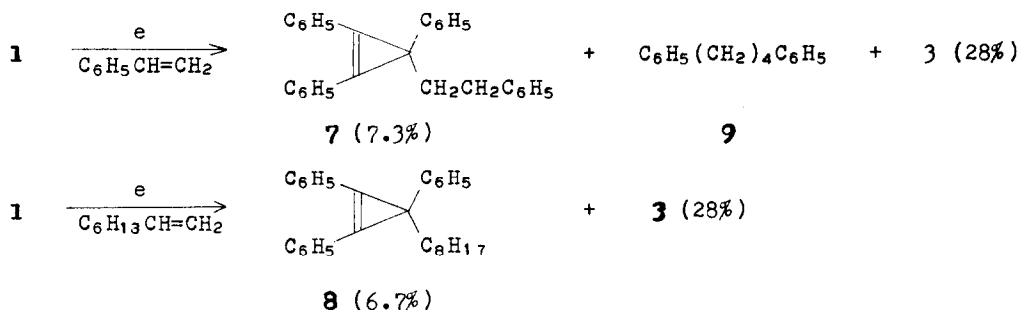
The reduction of **1** in acetonitrile gave bis-triphenylcyclopropenyl (**3**), a dimer of intermediate radical, in a 61% yield. Compound **2** gave 1,2,4,5-tetraphenylbenzene (**4**) (yield 39%) and N-acetyldiphenylcyclopropenyl amine (yield 24%) upon reduction. The latter amide might be yielded by the reaction of **2** with solvent, but the formation of the amide was not observed without passing charge.



The reduction of **1** in the presence of cyclohexene or chloroform yielded triphenylcyclopropene (**5**) and other products.



The formation of compound **5** indicated the hydrogen abstraction reaction of the intermediate cyclopropenyl radical. In the existence of an olefinic compound such as styrene or 1-octene, an alkylated product was obtained suggesting the addition of cyclopropenyl radical to the olefinic bond.



Compound **3** or **4** might be given by the reaction of the starting cyclopropenium cation **1** or **2** with corresponding anion generated by two electron reduction. However, the controlled potential reduction of **1** or **2** at the one electron reduction potential $\{-0.7\text{V vs. sce}\}$ gave **3** or **4**. Thus the formations of **3, 4** and **5** clearly indicated that cyclopropenyl radical was generated by the electrolytic reduction of cyclopropenium cation. The facts that the dimerization of the radical is the main reaction pathway and that hydrogen abstraction on reaction with radical acceptor is rather minor route are explained by the assumption that the electrolytically generated radical is adsorbed on the electrode and the diffusion of the radical into solution is slower than the dimerization of the adsorbed radical on the electrode. Although the formation of **7** or **8** is explained by radical mechanism, the electrolytic reduction of the olefin to an anion radical and subsequent reaction of the anion radical with **1** are the other possible route to yield **7** or **8**. The reduction potential of 1-octene would be sufficiently negative to exclude the anion radical mechanism, while the formation of **7** might be partly resulted from the reduction of styrene since the dimeric compound (**9**) of styrene anion radical was detected in the products. The cyclopropenyl radical is expected to show some characteristic selectivity or polarity in the hydrogen abstraction reaction. The deuterium isotope effect in the hydrogen abstraction reaction of triphenylcyclopropenyl radical from

chloroform and chloroform-d₁ was 2.3 ± 0.16 . This value is similar to that of chlorine atom and suggests the low selectivity of cyclopropenyl radical. It was observed in the previous study that the reactivity of cyclopropyl radical was resembled to that of phenyl radical⁶). The deuterium isotope effect determined for 2-phenylcyclopropyl radical was 2.8 ± 0.1 . It thus appeared that cyclopropenyl radicals do not indicate any special stability or instability originated in the interaction between radical electron and double bond. The relative reactivities of triphenylcyclopropenyl radical in the hydrogen abstraction reaction from some hydrogen donors were as follows. Chloroform (1.00); Chloroform-d₁(0.44); Cyclohexene(1.22); Cyclohexadiene-1,4(1.34). The values suggested that the reactivity of cyclopropenyl radical is similar to phenyl radical.

References

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