ON THE REACTION OF

CYCLOPENTADIENYLSODIUM AND EPICHLOROHYDRIN. 1

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Recently, Schaltegger reported on the reaction of cyclopentadienylsodium with epichlorohydrin and proposed structure I for the product. This assignment was based on the fact that hydrogenation of the product gave II whose structure was established by its interrelationship with known compounds.

Prior to Schaltegger's publication we had also carried out the reaction of cyclopentadienylsodium with epichloro-hydrin and our product agrees completely in its physical properties as well as its ultraviolet and infrared spectra with that described by Schaltegger. However, a reasonable

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²H. Schaltegger, <u>Helv</u>. <u>Chim</u>. <u>Acta</u> <u>45</u>, 1368 (1962).

mechanistic interpretation (see below) would predict III, rather than I, as the structure of the product.

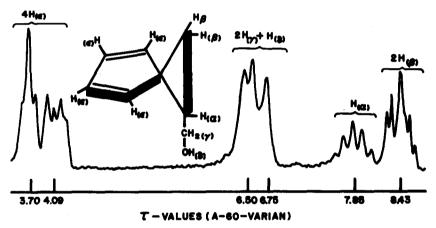
$$\begin{array}{c} O^{-} \text{ No}^{+} \\ CH_{2} - CH - CH_{2}CI \rightarrow H \\ CH_{2} - CH - CH_{2$$

The reaction of cyclopentadienylsodium with 1,2-dibromoethane yields the corresponding parent compound, spiro(2,4)hepta-4,6-diene, as has been shown by Chiurdoglu and Tursch.³ There is a close correspondence between the infrared spectrum of our product and spiro(2,4)-hepta-4,6-diene and complete agreement in the ultraviolet. Further, the Belgian workers have shown that the usual catalytic hydrogenation may lead to rupture of the cyclopropane ring and, thus, the formation of II on hydrogenation of III is not unusual.

However, the most convincing evidence that III is the correct structure is that derived from n.m.r. spectral comparisons. As shown below, the n.m.r. spectrum can be fully interpreted in terms of structure III, both with regard to the chemical shifts of the designated protons and the integrated areas. The signals at 7.85 and 8.43 as well as the ratio of vinyl to saturated protons (4:6) can not be explained

³G. Chiurdoglu and B. Tursch, <u>Bull</u>. <u>Soc. Chim. Belg.</u> <u>66</u>, 600 (1957).

by I. Although the signals at 7.85 and 8.43 (are somewhat low for the usual cyclopropane ring, it could be shown that this is an effect due to the associated spiro diene system. Treatment of III with N-phenylmaleimide in methanol readily gave the corresponding Diels-Alder adduct, m.p. 162.5-163.5° (Anal. Calcd. for C₁₈H₁₇NO₃: C, 73.20; H, 5.80; N, 4.74. Found: C, 73.19; H, 5.68; N, 4.88). In the n.m.r. spectrum of the adduct, these signals are shifted to 8.70 and 9.35 (corresponding to the more usual region for protons of a cyclopropane ring.



Our interest in structure III related to the unusual possibilities inherent in the molecule for carbonium ion rearrangements and its possible utility as a precursor for pentalene. Publication regarding structure III is being made at this time because pursuit of these longer range goals has had to be deferred.