

ADDITION OF CHLOROCARBENE TO BENZENE

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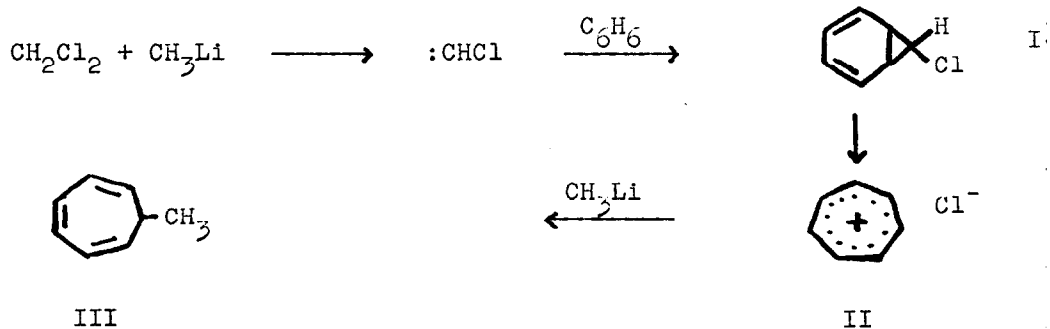
Recently, we reported the formation of chlorocarbene from methylene chloride and alkyllithium compounds and its addition to olefins to yield chlorocyclopropanes.<sup>1</sup> The reactivity of the carbene was established, as expected, to be intermediate between methylene and dichlorocarbene through competitive experiments involving olefins.<sup>2</sup> In this connection it was of interest to examine the addition of chlorocarbene to benzene, a reaction which dichlorocarbene fails to undergo.<sup>3</sup>

When methyllithium was slowly added to a refluxing solution of benzene in methylene chloride, 7-methylcyclohepta-1,3,5-triene (III) (b.p. 132.5;  $n_D^{20}$  1.5030;  $UV_{EtOH}$   $\lambda_{max}$  257  $\mu$ ,  $\epsilon$  3600; anal. calc.  $C_8H_{10}$  C 90.50, H 9.50, found C 90.27, H 9.81) was isolated in 20% yield.<sup>4</sup> Assignment of structure III to

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- (1) G.L. Closs and L.E. Closs, J. Am. Chem. Soc. 81, 4996 (1959).
  - (2) G.L. Closs and G.M. Schwartz, ibid., in press.
  - (3) W.v.E. Doering and Wm. A. Henderson, ibid. 80, 5274 (1958).
  - (4) The three other isomers of methylcycloheptatriene have been reported recently by N.A. Nelson, J.H. Fassnacht and J.U. Piper, ibid. 81, 5009 (1959).

the reaction product is based on catalytic hydrogenation to methylcycloheptane and the nuclear magnetic resonance spectrum which shows a doublet at 210 and 216 c.p.s. (relative to external benzene at 40 mc) indicating the attachment of the methyl group at a saturated carbon atom.

The mechanism for the formation of III is formulated in reaction sequence 1: Chlorocarbene, generated from methylene chloride and methyllithium, adds to benzene to form the hypothetical intermediate I. This adduct undergoes a valence tautomerization to tropylium chloride (II) which adds methyllithium to give 7-methylcyclohepta-1,3,5-triene (III).<sup>5</sup>

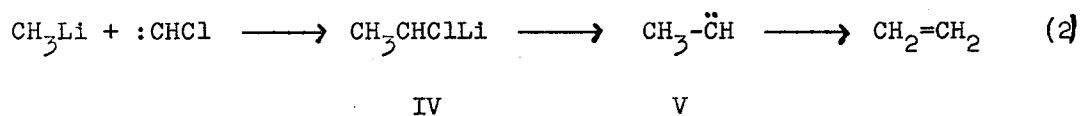


Tropylium chloride (<1%), identified by its characteristic ultraviolet spectrum was detected in the acidified, aqueous washings

- (5) The addition of phenyllithium to tropylium bromide proceeds smoothly to yield 7-phenylcyclohepta-1,3,5-triene, W.v. Doering and L.H. Knox, *J. Am. Chem. Soc.* 75, 297 (1953).

of the reaction mixture. Apparently, only a small quantity of the chloride escapes further reaction with methyllithium. In contrast to the reaction of methylene with benzene<sup>6</sup> no products resulting from insertion of the carbene into carbon-hydrogen bonds are observed and the product is obtained free of isomers.

The main fraction of the generated chlorocarbene is lost in the competing reaction with methyllithium leading to the formation of ethylene, summarized in sequence 2.<sup>7</sup>



It can be argued that III is formed by the addition of methylcarbene (V) to benzene. However, this possibility is rendered unlikely in view of the observation that adducts of methylcarbene are not formed when olefins are employed as the substrate. Presumably the intramolecular hydride shift in methylcarbene is too fast to allow an intermolecular process to compete successfully.

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(6) W.v.E. Doering and L.H. Knox, *J. Am. Chem. Soc.* 75 (1953).

(7) For the equivalent reaction of chlorocarbene with n-butyl-lithium, see ref. 1.