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PHENYLCARBENE FROM BENZYLCHLORIDE AND N-BUTYLLITHIUM

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Several earlier investigators have shown that the action of strong bases on benzylic halides normally does not lead to the formation of carbenes.[1] We wish now to present evidence demonstrating that under certain conditions phenylcarbene can be produced *via* α-elimination from benzylchloride.

N-Butyllithium in ether was slowly added to a solution of benzylchloride in excess cyclohexene at 10°. Separation of the reaction mixture by distillation and subsequent chromatography gave 14°/∘ of 7-phenylbicyclo(4.1.0)heptane (I) (anal. found: C 90.66; H 9.48), 19°/∘ of 3-benzylcyclohexene (II) (anal. found: C 90.70; H 9.43), 14°/∘ of 1,2-diphenylethane (III) and 30°/∘ of amylbenzene (IV). Structures of I and II have been confirmed by chemical and spectral evidence. Thus both compounds are reduced

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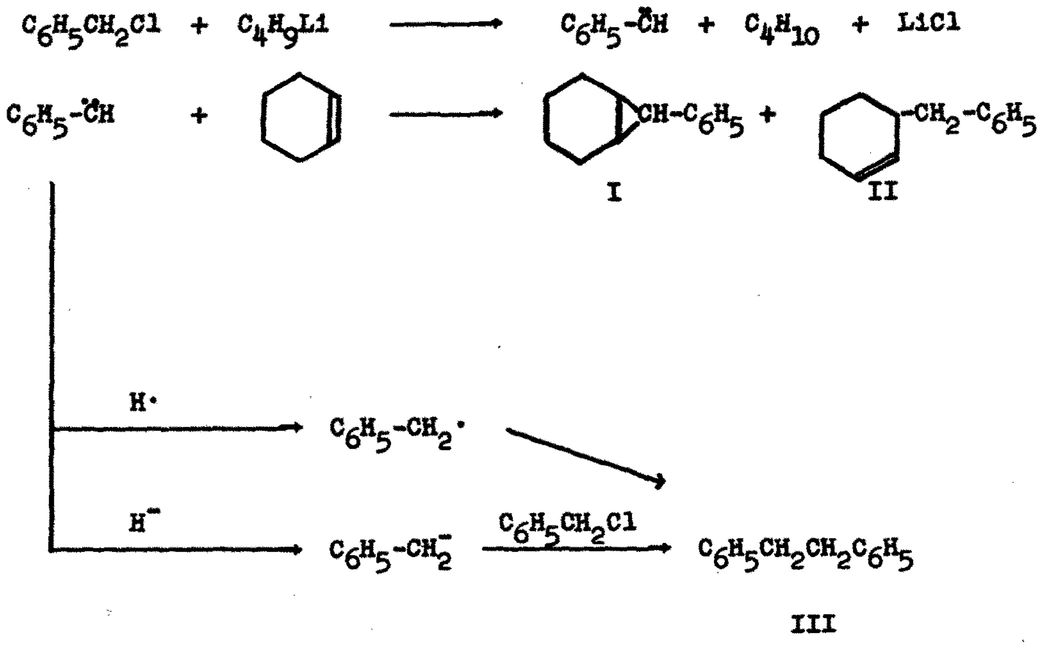
[1] M. S. Kharasch, W. Nudenberg and E. K. Fields, *J. Am. Chem. Soc.* **66**, 1276 (1944); L. A. Pinck and G. E. Hibert, *ibid.* **68**, 377 (1946); C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor and A. E. Brodhag, *ibid.* **78**, 1653 (1956).

catalytically to benzylcyclohexane. The infrared spectrum of II exhibits double bond stretching vibration at 1655 cm^{-1} and the nuclear magnetic resonance (n.m.r.) spectrum reveals the presence of two olefinic protons (broad peak at 47 c.p.s. relative to external benzene at 40 m.c.). Likewise, the attachment of the benzyl group at the 3 position of the cyclohexane ring is evident from the n.m.r. spectrum which shows resonance of 3 allylic protons. Both infrared and n.m.r. spectra of I provide no evidence for double bonds and are consistent with the cyclopropane structure. The two possible stereoisomers of I, epimeric at carbon atom 7, are both formed and the n.m.r. spectrum of the mixture shows two bands with a ratio of integrated intensities of 1:2 attributed to the phenyl protons of the isomers. Repeated chromatography resulted in partial separation of the epimers as evidenced by different intensity ratios of these bands in the spectra of the various chromatography fractions.

The presence of I among the reaction products is interpreted as evidence for the formation of phenylcarbene. The mechanism of the formation of II needs some further study, although it is strongly suspected that phenylcarbene serves as precursor to this product as well. However, at this point it cannot be decided whether II originates from an apparently selective insertion of the carbene into the allylic carbon-hydrogen bonds or is a product of a consecutive rearrangement of I.



1,2-Diphenylethane (III) had previously been isolated as major product from the reaction of benzylchloride with butyllithium.[2] It had been suggested that this compound was formed via halogen-metal interchange leading to butylchloride and benzyllithium. The latter was assumed to couple with excess benzylchloride to give III. This reaction scheme cannot be upheld in view of our finding that only traces of butylchloride are produced in this reaction as shown by vapor phase chromatography of the reaction mixture. It appears more likely that III also originates from phenylcarbene

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[2] H. Gilman and A.H. Haubein, J. Am. Chem. Soc. 66, 1515 (1944).

which by hydride or hydrogen abstraction from the solvent may produce phenylmethide ion or benzyl radical respectively. Both these hypothetical intermediates can be expected to lead to the observed product. This hypothesis is supported by the observation that photochemically generated diphenylcarbene gives rise to the formation of the equivalent product, 1,1,2,2-tetraphenylethane.[3]

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[3] W. Kirmse, L. Horner and H. Hoffmann, Ann. 614, 19 (1958).