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PRELIMINARY COMMUNICATION

Evidence for *cyclo*hexyne as an intermediate in the coupling of phenyllithium with 1-chlorocyclohexene*

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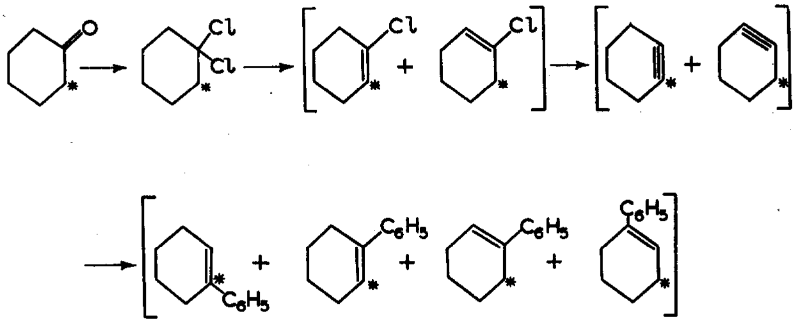
ELIMINATION-ADDITION mechanisms involving "benzyne"-type (C_6H_4) intermediates have been established for the rearrangements which occur in the amination of non-activated aryl halides,[1] high temperature alkaline hydrolysis of aryl halides[2] and the coupling of phenyllithium with aryl halides.[3] Wittig and Harboth[4] have reported small yields of 1-phenyl*cyclo*hexene from the coupling of phenyllithium with 1-chloro*cyclo*hexene and it appeared possible that this reaction might well proceed by way of *cyclo*hexyne as an intermediate. Of interest in this connection is the report by Favorsky and Boshowsky[5] that a *cyclo*hyexne trimer (dodecahydrotriphenylene) is formed in the reaction of 1,2-dibromo*cyclo*hexene with sodium.

We have studied the conversion of *cyclo*hexanone-2-^{14}C† to 1-phenyl*cyclo*hexene by way of 1,1-dichloro*cyclo*hexane and 1-chloro*cyclo*hexene. If all of the reaction were to proceed by intermediary formation of *cyclo*hexyne (and kinetic isotope effects were absent) then 25 per cent of the resulting 1-phenyl*cyclo*hexene would be expected to have the ^{14}C-label at the 1-position. This prediction is based on the following considerations. *cyclo*Hexanone-2-^{14}C with phosphorus pentachloride should yield 1,1-dichloro*cyclo*hexane-2-^{14}C without rearrangement. Dehydrohalogenation would then yield a 1 : 1 mixture of 1-chloro*cyclo*hexene labeled at the 2- and 6-positions. Coupling of this mixture with phenyllithium by any non-rearranging reaction such as formulated earlier[4] would lead to 1-phenyl*cyclo*hexene labeled at the 2- and 6-positions without formation of 1-phenyl*cyclo*hexene-1-^{14}C. On the other hand, if the phenyllithium were to effect an elimination of hydrogen



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[1] J. D. Roberts, H. E. Simmons, Jr., L. A. Carlsmith and C. W. Vaughan *J. Amer. Chem. Soc.* **75**, 3290 (1953); J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr. and L. A. Carlsmith *Ibid.* **78**, 601 (1956).

[2] J. D. Roberts, A. T. Bottini, and D. A. Semenow *Science*. **122**, 881 (1955); A. T. Bottini and J. D. Roberts *J. Amer. Chem. Soc.* **79**, 1458 (1957); A. Lüttringhaus and D. Ambros *Ber. Dtsch. Chem. Ges.* **89**, 463 (1956).

[3] G. Wittig, G. Pieper and G. Fuhrmann *Ber. Dtsch. Chem. Ges.* **73**, 1193 (1940); G. Wittig *Z. Angew. Chem.* **69**, 245 (1957); R. Huisgen and H. Rist *Naturwissenschaften* **41**, 358 (1954); *Liebigs Ann.* **594**, 137 (1955); E. Jenny and J. D. Roberts *Helv. Chim. Acta* **38**, 1248 (1955).

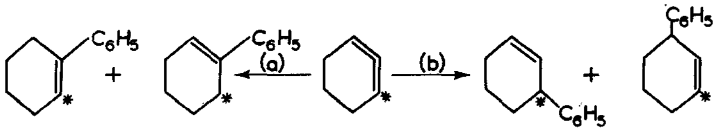
[4] G. Wittig and G. Harboth *Ber. Dtsch. Chem. Ges.* **77**, 306 (1944).

[5] A. E. Favorsky and W. Boshowsky *Ann. Dtsch. Chem.-Ges.* **390**, 122 (1912).

chloride from the labeled 1-chloro*cyclo*hexene, a 1 : 1 mixture of *cyclo*hexyne-1-^{14}C and *cyclo*hexyne-3-^{14}C would be formed. Since each differently labeled *cyclo*hexyne can add phenyllithium in two equally probable ways, one predicts formation of 25 per cent each of the labeled 1-phenyl*cyclo*hexenes with ^{14}C at the 1-, 2-, 3-, and 6-positions.

*cyclo*Hexanone-2-^{14}C with phosphorus pentachloride followed by elimination of hydrogen chloride[6] afforded 40 per cent of 1-chloro*cyclo*hexene-2-and-6-^{14}C. The reaction of the labeled 1-chloro*cyclo*hexenes with 2·5 moles of phenyllithium in ether in a steel bomb at 150° gave 28 per cent of 1-phenyl*cyclo*hexene-*x*-^{14}C. The product was characterized as 1-phenyl-2-(2,4-dinitrophenylmercapto)-*cyclo*hexene-*x*-^{14}C, m.p. 139·5-140·5°. Oxidation of the latter substance with sodium permanganate gave the 1-carbon and phenyl group as benzoic acid. This benzoic acid had a ^{14}C assay of 0·0280 ± 0·0005 μc per mole which was 23 ± 0·7 per cent of the activity (0·1217 ± 0·0015 μc per mole) of the dinitrophenylmercapto derivative. Thus 23 per cent of 1-phenyl*cyclo*hexene labeled at the 1-position was formed in the reaction as compared to 25 per cent predicted for the elimination-addition mechanism involving *cyclo*hexyne as an intermediate. The small difference between the experimental and theoretical results may be due to the incursion of some non-rearranging reactions or very reasonable inter- and intra-molecular ^{14}C-isotope effects[7] in the preparative or degradative sequences. The validity of the degradative scheme was checked by adding phenyllithium to *cyclo*hexanone-2-^{14}C and dehydrating the carbinol with sulfuric acid. The dinitrophenylmercapto derivative of the resulting 1-phenyl*cyclo*hexene-2-^{14}C gave benzoic acid with about 0·1 per cent of the total activity.

1,2-*cyclo*Hexadiene-1-^{14}C might result from elimination of hydrogen chloride from the labeled 1-chloro*cyclo*hexene with phenyllithium. Such an allenic intermediate is unlikely to be important since, if it were to add phenyllithium so that the phenyl combined with the 2-carbon, equation (a),



no 1-phenyl*cyclo*hexene-1-^{14}C would be formed. If the phenyl were to add to the 1- or 3-carbons, equation (b), then the final product would be 3-phenyl*cyclo*hexene instead of the isolated 1-phenyl*cyclo*hexene.

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[6] M. Mousseron and R. Jacquier *Bull. Soc. Chim. Fr.* 648 1950.

[7] G. A. Ropp *Nucleonics* **10**, (10), 22 (1952).