

THE EFFECT OF HALIDE IONS ON AN  $\alpha$ -ELIMINATION REACTION

Ronald M. Magid and J. Gary Welch (1)

Department of Chemistry, William Marsh Rice University,

Houston, Texas 77001

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In the course of our mechanistic study of the formation of phenylcyclopropane from allyl chloride and phenyllithium (2), we found it necessary to prepare the cis and trans isomers of 1-chloro-2-phenylcyclopropane. The simplest route to these compounds is the addition of the carbenoid (3) from methylene chloride and an alkylolithium (4) to styrene. In the synthesis of the chlorocyclopropanes, we have observed that the relative yields and the cis/trans ratios of the desired compounds and side products depend upon the particular halide ion present in the methylolithium solution. This indicates that a "salt effect" similar to that noted by others (5) is operative. We wish to report some observations which led us to the conclusion that a mechanism quite different from that suggested (5b) can explain the "salt effect."

We first realized that a "salt effect" might be present when we observed that the chlorocyclopropanes are produced in good yield using methylolithium prepared from methyl bromide, while Dilling (6) has reported that the only products from the reaction of styrene with methylolithium from methyl iodide are phenylcyclopropane and 1-methyl-2-phenylcyclopropane. We have repeated the Dilling experiment and have also run the reaction with methylolithium from methyl chloride(7); the results are summarized in Table I.

It is possible to explain these data with the mechanistic scheme in Fig. 1 (8), similar to that proposed by Closs and Coyle (5b). 1-Methyl-2-phenylcyclopropane is presumed to arise via the addition of carbenoids IV and/or V to styrene; formation of IV and V by displacement of halide ion from I, II, or III should be progressively easier in going from chloride to bromide to iodide (9). The bromo- and iodocyclopropanes (VI) (10) could arise from II (11), but since we feel that II should be primarily a source of chlorocarbene (12), we have

TABLE I  
Yields<sup>a,b</sup> of Products and cis/trans Ratios<sup>b</sup>

Inorganic halide in methylithium	1-Chloro-2- phenylcyclopropane		Phenylcyclopropane		1-Methyl-2- phenylcyclopropane		1-Bromo-2- phenylcyclopropane		1-Iodo-2- phenylcyclopropane	
	Yield	<u>cis/trans</u>	Yield	<u>cis/trans</u>	Yield	<u>cis/trans</u>	Yield	<u>cis/trans</u>	Yield	<u>cis/trans</u>
Lithium bromide <sup>c</sup>	42%	1.7	---	---	f	---	3%	1.2	---	---
Lithium chloride <sup>d</sup>	18%	2.3	---	---	f	---	---	---	---	---
Lithium iodide <sup>e</sup>	4%	1.6	44%	---	16%	1.0	---	---	8%	1.0

<sup>a</sup> Yields based upon methylithium as the limiting reagent and using the mechanism outlined in the text; glpc analysis indicated no more than trace amounts of unidentified materials.

<sup>b</sup> Yields and cis/trans ratios were calculated from glpc data; the nmr and mass spectra of all products are consistent with the assigned structures.

<sup>c</sup> Alfa Inorganics, Inc.

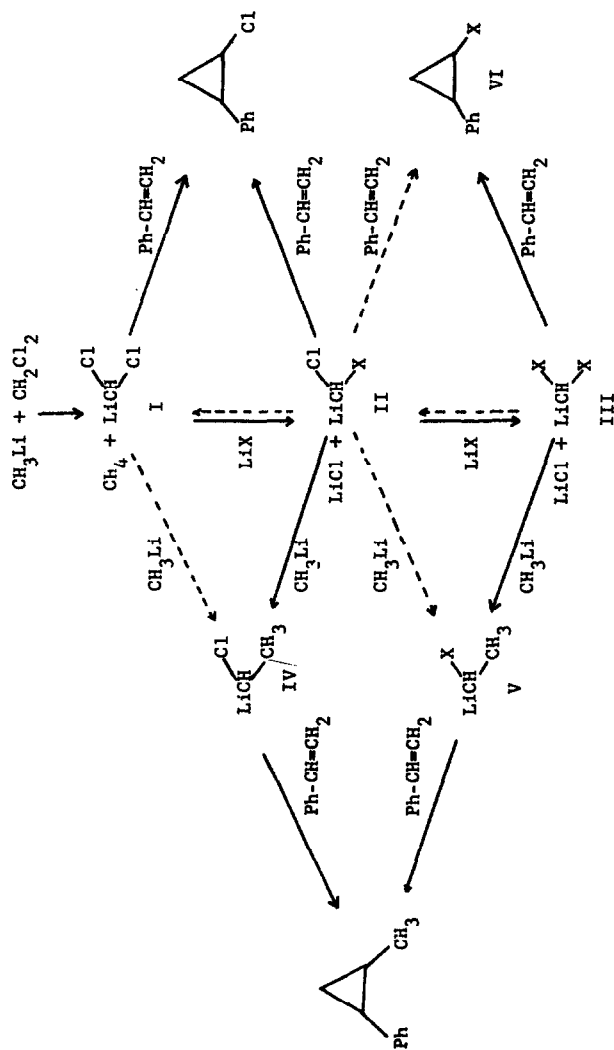
<sup>d</sup> Foote Mineral Company.

<sup>e</sup> Filtered solution from the reaction of methyl iodide with lithium.

<sup>f</sup> Possibly present in trace amounts by glpc analysis.

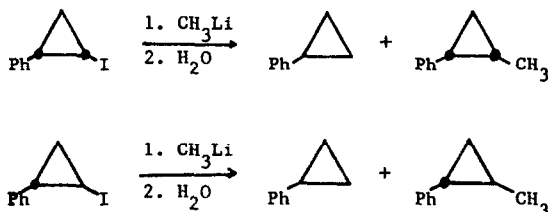
FIG. 1

Mechanistic Scheme (Closs and Coyle (5b)) for Formation of Products



introduced carbenoid III into the scheme as the most likely precursor of VI.

While the reaction scheme outlined in Fig. 1 could account for the formation of all of the products, another mechanism for the production of the methylcyclopropanes may be operating concurrent with or, perhaps, to the exclusion of the Closs and Coyle mechanism. It is conceivable that 1-iodo-2-phenylcyclopropane, a product of the reaction in the presence of lithium iodide, can react with methyllithium to product 1-methyl-2-phenylcyclopropane and phenylcyclopropane. We have, in fact, found that cis-1-iodo-2-phenylcyclopropane reacts quantitatively and within 5 min. with excess methyllithium (from methyl iodide) to produce phenylcyclopropane (49%) and cis-1-methyl-2-phenylcyclopropane (51%). Similarly, trans-1-iodo-2-phenylcyclopropane yields phenylcyclopropane (59%) and trans-1-methyl-2-phenylcyclopropane (41%). Neither the chloro- nor the bromocyclopropanes undergo this reaction.

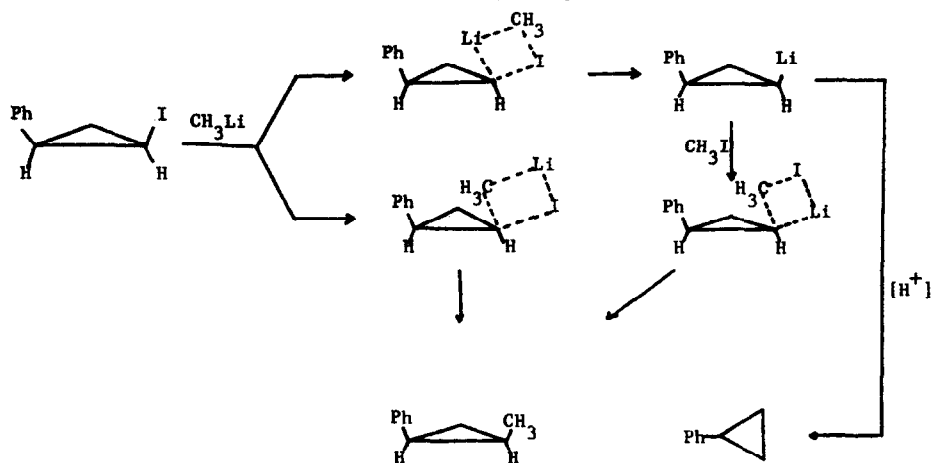


Phenylcyclopropane undoubtedly arises from halogen-metal exchange followed by protonation; this exchange is expected to occur more readily with 1-iodo-2-phenylcyclopropane than with either of the other halo compounds (13). Since each of the iodo compounds is converted specifically into the methyl compound of retained configuration, we suggest that the mechanism involves either a one-step or a two-step Wurtz reaction (as illustrated for the cis-iodo compound, Fig. 2)(5c,14).

We have, therefore, demonstrated that intermediates IV and/or V may not be necessary for the formation of the methylcyclopropanes. We are, however, reasonably confident that III and possibly II are required for the formation of the bromo- and iodocyclopropanes since 1-iodo-2-phenylcyclopropane is not produced by the action of anhydrous lithium iodide on a mixture of cis- and trans-1-chloro-2-phenylcyclopropane.

FIG. 2

## Proposed Scheme for Methyl Compound Formation



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## REFERENCES

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- (6) W.L. Dilling, *J. Org. Chem.*, **29**, 960 (1964).
- (7) All experiments were performed by adding a 1.2-1.7 M solution of methyllithium in ether over 1 hr. to a mixture of methylene chloride and styrene at room temperature, the three reagents being present in the mole ratio 1:2:4, respectively.
- (8) The dashed arrows represent reactions which we feel probably do not occur.
- (9) J. Hine, "Physical Organic Chemistry," second edition, McGraw-Hill Book Company, Inc., New York, N.Y., 1962, p. 184.

- (10) Isolation of these products from the reaction of methylene chloride with an alkyl-lithium represents only the third example (5d, 5e) of the formation of a bromocyclopropane and the first of an iodocyclopropane in addition to the expected chlorocyclopropane.
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- (14) 7-Iodonorcarane produced similarly from the reaction of cyclohexene with methylene chloride/methylolithium (lithium iodide) reacts with methylolithium (lithium iodide) to produce norcarane and 7-methylnorcarane. The separated cis- and trans-iodo isomers react stereospecifically with retention of configuration yielding the cis and trans methyl compounds, respectively. Once again, the Wurtz mechanism accounts for the stereochemical result (15).
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