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THE INFLUENCE OF IODIDE ION ON CARBENOID ADDITIONS TO OLEFINS (1)

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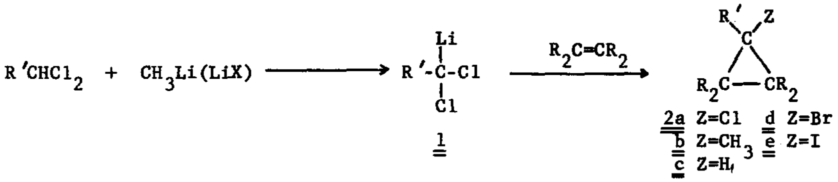
Since the initial observations by Katz and Garratt (3a), the influence of halide ions in determining the course of carbenoid reactions has been well documented. Thus, reaction of an olefin with carbenoid 1 produces not only chlorocyclopropane 2a, but also hydrocarbons 2b, 2c (3a-d,g,h) and halocyclopropanes 2d, 2e (3c,e-h) when lithium iodide or bromide is present in the organolithium reagent.

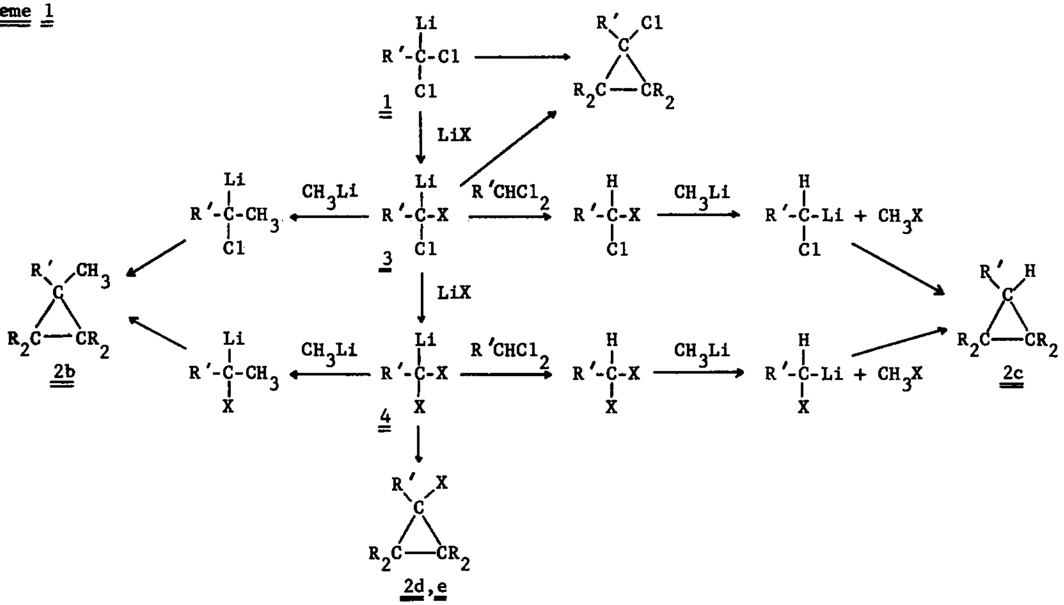
(1) 

The origin of the "abnormal" products, 2b-2e, can be explained in terms of *Scheme 1* where LiX (bromide or iodide) converts 1 into new carbenoids 3 and/or 4; subsequent reaction with methyllithium (3b) or R'$CHCl_2$ (3c), as shown, leads to hydrocarbons 2b and 2c. Although halocyclopropanes 2d and 2e had not yet been found among the reaction products at the time *Scheme 1* was first advanced, their formation can easily be accommodated.

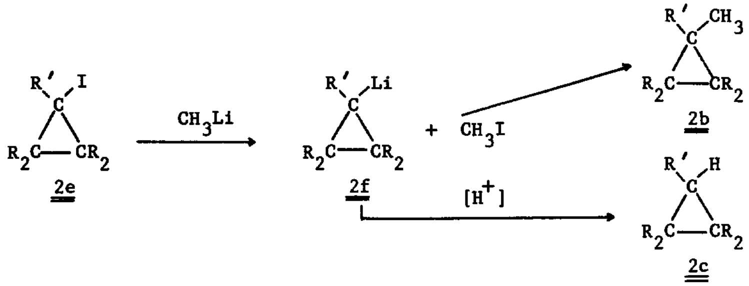
When we first isolated iodocyclopropanes 2e from the reaction of either styrene or cyclohexene with methylene chloride/methyllithium(lithium iodide) (3g,h), we suggested that an alternate route to hydrocarbons 2b, 2c was available, *Scheme 2*. In support of this, we found that iodocyclopropanes do react with methyllithium in ether, presumably *via* 2f, yielding 2b (with complete retention of configuration) and 2c. Hatch and Gardner (4), however, demonstrated that iodocyclopropane 2e from cyclohexene does *not* yield 2b when treated with methyllithium in the presence of methylene chloride (*i.e.*, under the conditions of reaction (1)). We now report the results of our studies on the mechanism of formation of the "abnormal" products, 2b-2e, from styrene; in the following communication, we describe the detailed mechanism of 2e giving 2b and 2c.

Treatment of 0.0045 mole of a mixture of *cis*- and *trans*-1-iodo-2-phenylcyclopropane (5) with 0.01 mole of methyllithium(lithium iodide) under conditions which closely approximate those of reaction (1) [0.04 mole of methylene chloride, 9.1 ml of hexane (equal in volume to 0.08 mole of styrene), 15 ml of ether, 2 hr] yields *none* of the corresponding methyl compound 6. Methane is evolved during the reaction and the sole product is phenylcyclopropane (7), formed in *ca.* 80% yield (100% base on recovered 5); the identical reaction, but in the presence of 0.01 mole of

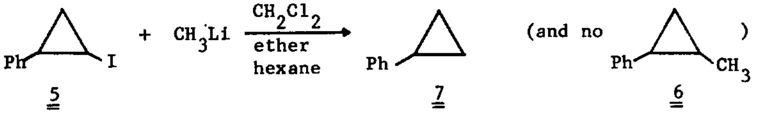
Scheme 1



Scheme 2



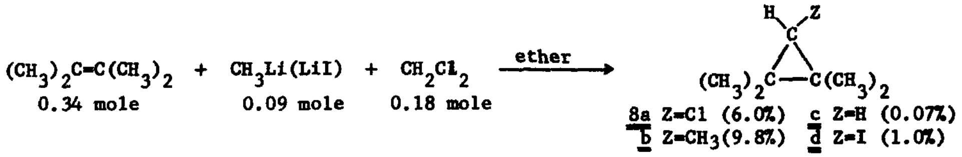
methyl iodide, leads to the same results. Thus, iodocyclopropane 2e is not the precursor of the corresponding methyl compound 2b, but may be responsible for cyclopropane 2c in reaction (1).



We believe that Scheme 2, in fact, represents the major, if not exclusive, route to 2c, and base our conclusions on the following observations. In Scheme 1, either (or both) methylene iodide or chloroiodomethane leads to 2c after halogen-metal exchange. Although both methylene iodide and chloroiodomethane (0.02 mole) do react with 0.02 mole of methyllithium(lithium chloride) to convert 0.08 mole of styrene into phenylcyclopropane, the yield is very low (*ca.* 7%); presumably $LiCH_2I$ and $LiCH_2Cl$, respectively, are formed, but are not trapped very efficiently by olefin. Furthermore, when the same reaction is run in the presence of 0.04 mole of methylene chloride, the only cyclopropyl product formed is phenylcyclopropane, again in very low yield (6.3%). Thus, despite a statistical disadvantage relative to methylene chloride, both methylene iodide and chloroiodomethane apparently scavenge all of the methyllithium, but produce very little phenylcyclopropane in return (5).

Additional evidence for Scheme 2 as the route to 2c comes from an experiment in which aliquots were removed from the reaction mixture during the addition of 0.03 mole of methyllithium (lithium iodide) to 0.15 mole of methylene chloride and 0.61 mole of styrene in ether. Analysis of the aliquots shows that the ratio of phenylcyclopropane (7) to methyl compound 6 early during the addition is very low (1:5 at 2% addition), but that this ratio increases smoothly, reaching 2.3:1 at 40% addition and remaining constant thereafter. 1-Chloro-2-phenylcyclopropane increases smoothly during the addition, but iodo compound 5 increases to a maximum at ca. 30% addition, then falls off, and is completely gone by the time 60% of the methyllithium (corresponding to 0.18 mole) has been added. Thus, Scheme 1, alone, cannot account for phenylcyclopropane formation since protonation of carbenoids 3 and 4 should be very efficient compared to their reaction with methyllithium, especially early in the addition, and yet phenylcyclopropane begins to accumulate only later when iodocyclopropane reaches its maximum and disappears.

Finally, circumstantial evidence in support of Scheme 2 for cyclopropane 2c comes from experiments involving 2,3-dimethyl-2-butene. Whereas phenylcyclopropane (7) is a major product from styrene, methylene chloride, and methyllithium(lithium iodide), tetramethylcyclopropane 8c is produced in only trace amounts from tetramethylethylene. Moreover, iodo compound 8d reacts completely with methyllithium(lithium iodide) in ether only after 2 days at reflux (cf., less than 5 minutes at room temperature for 5) and yields mostly pentamethylcyclopropane (8b).



From the above experiments, it is clear that cyclopropane 2c results from a carbenoid reaction only if iodocyclopropane 2e is also formed and only if 2e is very reactive towards methyllithium. The only question now remaining is which species neutralizes lithium reagent 2f to produce 2c, or if 2f is still present at the time of work-up. Since 1-iodo-2-phenylcyclopropane (5) yields phenylcyclopropane (7) but no methyl compound 6 when treated with methyllithium in the presence of methylene chloride (see above), this suggests that 2f is formed, but is protonated rapidly by methylene chloride. Ether, the only other likely proton source, does not neutralize 2f to any degree since reaction of 5 with methyllithium in ether yields 7 and 6 in a ratio of 1.3:1 when worked-up with water, but when worked-up with iodine produces 7 and 6 in a ratio of 0.16:1, the major product being 5 itself. Thus, 2f can survive until work-up in the absence of methylene chloride, but in its presence is protonated before it can react with methyl iodide.

We have found that even in very low concentration, lithium iodide has an enormous directing effect on reaction (1). Addition of halide-free methyllithium (0.02 mole), prepared from dimethylmercury and lithium (6), to 0.04 mole of methylene chloride and 0.08 mole of styrene in ether yields only the epimeric 1-chloro-2-phenylcyclopropanes; the same product distribution is achieved with commercial methyllithium prepared from methyl chloride (7). Table I shows the product distribution when varying amounts of lithium iodide are present in the methyllithium solution; the same results are obtained when halide-free methyllithium is added to the reaction flask containing the prescribed amount of lithium iodide. It will be noted that even at the lowest LiI/CH_3Li ratio investigated, the "abnormal" products account for 68% of the total. Thus, lithium iodide is extremely efficient in diverting carbenoid **1** from reaction with styrene, a result consistent with the very high reaction rate measured for iodide ion displacement on phenylbromomethyllithium (8).

TABLE I

Relative Yield % (9)

Mole Ratio LiI/CH_3Li	Phenyl-cyclopropane (**7**)	1-Methyl-2-phenyl-cyclopropane (**6**)	1-Chloro-2-phenyl-cyclopropane	1-Iodo-2-phenyl-cyclopropane (**5**)	Total Yield %
1.95	30.4	42.6	9.8	17.2	29
1.11	24.2	54.6	11.3	9.9	21
0.66	26.7	51.9	13.0	8.4	19
0.40	24.6	50.8	18.4	6.2	19
0.10	20.3	48.1	31.6	trace	18
0	--	--	100	--	23

REFERENCES

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4. R.L. Hatch and P.D. Gardner, *ibid.*, 1019 (1967).
5. The yield of methyl iodide in the reaction with methylene iodide is 76%; when methylene iodide is omitted, the yield is only 12%; when styrene is also omitted (*i.e.*, the reaction of methyllithium(lithium iodide) with methylene chloride in ether), it is only 6%. *Scheme* **2** suggests that the yield of methyl iodide should increase in the presence of an olefin, as it does. The very high yield in the presence of methylene iodide supports our assertion that methylene iodide is very efficient in scavenging methyllithium.
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9. All yields are based on the limiting reagent, methyllithium. Formation of all of the products requires one equivalent of methyllithium, except for compound **6** which consumes two equivalents (see text).