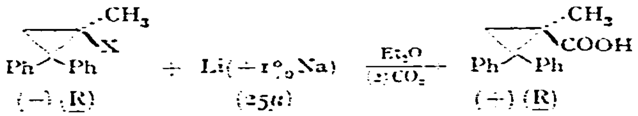
Cyclopropanes
XIX. Reaction of lithium metal with optically active halides

It was recently reported[1] that the halogen–lithium interchange reaction between butyllithium and (+)-(S)-1-bromo-1-methyl-2,2-diphenylcyclopropane proceeded with complete retention of configuration as well as optical activity. Vinyllithium derivatives have also been shown to retain their configuration as demonstrated by the observation that halogen–lithium interchange between butyllithium and *cis* or *trans* derivatives of vinylic bromides leads to the retention of geometric configuration[2–4]. Of special significance was the further observation that direct metallation of the geometric isomers with metallic lithium also gave complete retention of configuration[2–4]. We wish to report that in contrast to the trigonally hybridized vinylic systems the direct metallation of (+)-(S)-1-bromo-1-methyl-2,2-diphenylcyclopropane leads to the formation of the corresponding lithium derivative which is *partially racemized*. Furthermore, the amount of racemization obtained is dependent not only on the nature of the halogen (Cl, Br, I) but also on the percentage of sodium in the lithium, and the particle size of the lithium.



(1)

Table 1 describes the results obtained on changing the halogen from chlorine to bromine to iodine.

TABLE 1

EFFECT OF HALOGEN ON PERCENTAGE OF RACEMIZATION[a]

X	*Time (min)*	*% Yield*	*% Optical purity*	*% Racem.*
Cl	40	73	71	29
Cl	60	76	66	34
Br	32	60	46	54
Br	42	70	42	58
I	33	42	36	64
I	41	60	36	64

[a] All reactions were run in a vacuum line under an atmosphere of argon. All reagents and solvents were carefully dried and degassed.

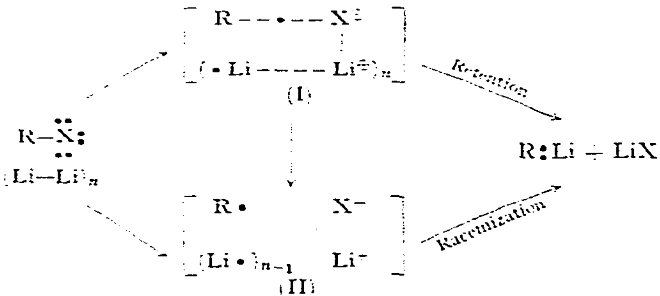
Both the sodium content of the lithium and the particle size of the dispersion were held constant in this series of reactions. The overall stereochemistry of the reaction is that of retention of configuration. The amount of racemization is highest for the iodide (64 %) and lowest for the chloride (29–34 %) with the bromide falling roughly in between (54–58 %) the other two halogens.

The sodium content of the lithium dispersion used also has a marked effect on the stereochemical results. The optically active iodide was treated with lithium dispersions of 25 μ average particle size with the sodium content varying from 0.002 %, 0.02 % and 1 %. Carbonation of the reaction mixtures yielded 1-methyl-2,2-diphenylcyclopropanecarboxylic acid with optical purity of 13 %, 16 % and 36 %

respectively. Although the optical purity varies only slightly using the low sodium content (0.002 and 0.02 %) lithium, there is a large effect on the stereochemical results when the high sodium content (1 %) lithium is used. The results indicate that the higher the sodium content the higher the retention of optical activity and configuration.

Again, using the optically active iodide and a 1 % sodium in lithium dispersion but varying the average particle size from 25 μ to 150 μ produced an interesting result. The optical purity of the carbonation product was reduced from 36 % to 20 % respectively. These results serve to emphasize the complexity of this heterogeneous surface reaction. At this time it is difficult to assess the significance of the effect of increased sodium content but the effect of particle size is in keeping with the surface character of the reaction. The smaller the particles the greater the surface area and the higher the retention of activity.

The racemization observed in forming the lithium reagent finds a parallel in the formation of the analogous Grignard reagent[6]. In both cases the amount of racemization increases as one goes from chloride to bromide to iodide. The increase in the amount of retention of optical activity and configuration in the reaction of the halides with lithium metal over that with magnesium is possibly due to the greater availability of electrons due to the lower ionization potential of lithium. We hold the view that these reactions involve one-electron transfers from the metal surface to the carbon–halogen bond. In the case of the lithium reaction one electron is transferred from the lithium surface to the alkyl halide to produce either an ion-radical (I) which can collapse to produce a lithium reagent with retained configuration or a loose radical pair (II) which leads to racemic lithium reagent. Whether (I) or (II) or both are formed will depend on the nature of R, X and the type of metal involved*.



It should be recalled at this point that once the lithium reagent is formed it is configurationally stable. This was demonstrated by preparing the lithium reagent by an exchange reaction between butyllithium and the cyclopropyl bromide[1]. However, when metallic lithium is used the question arises as to whether the observed racemization could not be due to metal–metal exchange occurring on the surface of the lithium. This possibility was excluded by demonstrating that the optically active

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[*] It should be appreciated that (I) is comparable to a four-centered transition state if the transfer of the second electron is very rapid. It has recently been reported[5] that the cleavage of an optically active disilane by lithium resulted in the formation of an optically active R_3SiLi of 77 % minimum optical purity. Although a concerted cyclic mechanism is postulated, we feel that this result can also be accommodated by our views.

lithium reagent, prepared by butyllithium exchange with the bromide, did not racemize when treated with a large excess of lithium metal (25 μ) for 15 minutes.

There is another possibility to be considered, at least in the case of the bromide and iodide, and that is that one is initially observing the formation of racemic or partially racemic lithium reagent by direct metallation but that the optical activity observed is due to the interchange of the racemic lithium reagent with the optically active halide. Such an interchange would be expected to lead to retention of optical activity. Experiments in our laboratory have shown that such an exchange can occur but that under the conditions of our reaction it is of minor importance. Moreover, such an exchange mechanism would not account for the observed order of retention of optical activity being $Cl > Br > I$.

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1 H. M. WALBORSKY, F. I. IMPASTATO AND A. E. YOUNG, *J. Am. Chem. Soc.*, 86 (1964) 3283.
2 D. Y. CURTIN AND J. W. CRUMP, *J. Am. Chem. Soc.*, 80 (1958) 1922.
3 F. G. BORDWELL AND P. S. LANDIS, *J. Am. Chem. Soc.*, 79 (1957) 1593.
4 D. SEYFERTH AND L. G. VAUGHAN, *J. Organometal. Chem.*, 1 (1963) 201.
5 L. H. SOMMER AND R. MASON, *J. Am. Chem. Soc.*, 87 (1965) 1619.
6 H. M. WALBORSKY AND A. E. YOUNG, *J. Am. Chem. Soc.*, 86 (1964) 3288.

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