Addition of Alkyl-lithium Reagents to Alkenylamines and to an Alkenyl Sulphide

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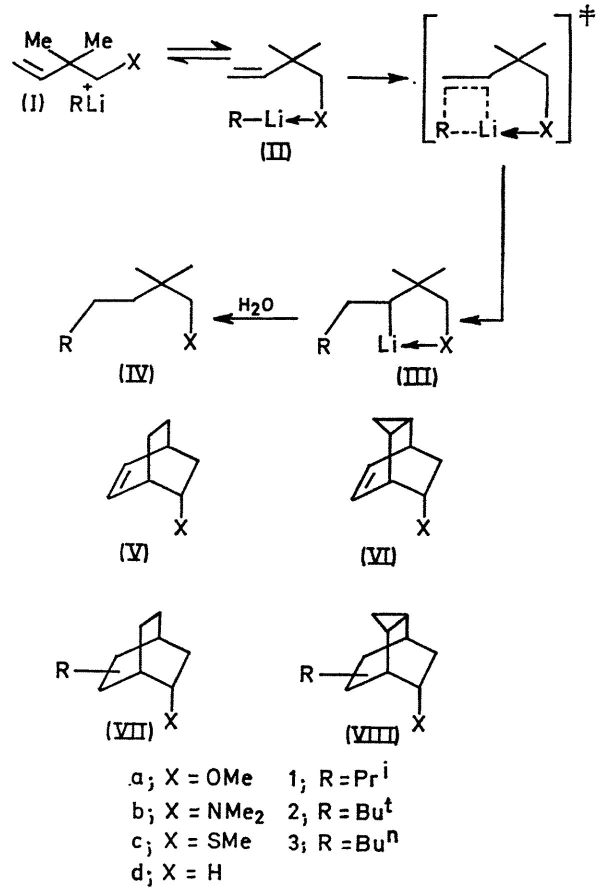
Summary Alkyl-lithium reagents add to unstrained unconjugated C=C double bonds if the alkene contains a dimethylamino-group or a thio-ether group in such a position, that intramolecular complexation of the new alkyl-lithium formed is possible.

PREVIOUSLY we reported that isopropyl-lithium adds to unstrained unconjugated carbon–carbon double bonds of alkenyl methyl ethers.[1] These experiments were based on the rationale that initial complexation of the lithium by the alkoxy-group should not only activate the isopropyl-lithium,[2] but also, more important, make the addition an intramolecular process [(IIa) → (IIIa), Scheme 1], in which stabilizing complexation is maintained throughout the passage along the reaction co-ordinate. This hypothesis is supported by the finding[1] that additions were successful only in those cases where five- or six-membered rings are possible. Apparently stabilization from intramolecular complexation in the products is an important driving force in the cases we studied, which were all of the type:[3]

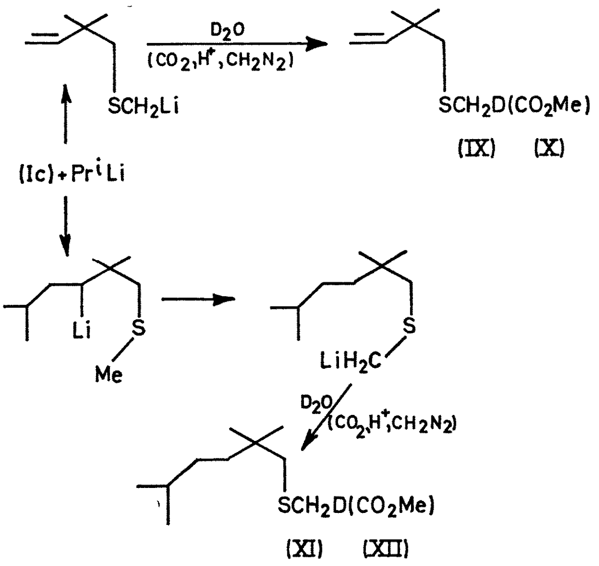
$$\text{sec-R}^1\text{Li} + \text{C=C} \rightarrow \text{sec-R}^2\text{Li} \quad (\text{Ia}) \rightarrow (\text{IIIa})$$

Since the solvating capacity of trialkylamines towards organolithium reagents is comparable to that of ethers,[2] we have extended our investigations to the corresponding



SCHEME 1

NN-dimethylalkenylamines (Ib), (Vb), and (VIb), and the reactions of alkyl-lithium reagents with 2,2-dimethylbut-3-enyl methyl sulphide (Ic) were also studied. Treatment [2 h; room temp., pentane–Et_2O (2 : 1)†] of resp., (Ib), (Vb), and (VIb) with isopropyl-, t-butyl-, or n-butyl-lithium followed by hydrolysis gave (% conversion of starting material‡): (IVb)-1 (95), (IVb)-2 (76), (VIIb)-1 (98), (VIIb)-2 (97), (VIIb)-3 (35), (VIIIb)-1 (98), and (VIIIb)-2 (98). Quenching with deuterium oxide yielded mono-deuteriated products.§ The importance of intramolecular complexation is seen from the failure of (Id), (Vd), and the *anti*-isomers of (Vb) and (VIb) to add isopropyl- or t-butyl-lithium.¶ Optimum conditions for addition are present in



SCHEME 2

bicyclo[2,2,2]oct-5-ene derivatives, since even n-butyl-lithium added to (Va) and (Vb). To the best of our knowledge this is the first example of the transformation primary-R^1Li + C=C → sec-R^2Li with an unstrained unconjugated olefin. When equimolar amounts of (Va) and (Vb) were treated with excess of n-butyl-lithium the ratios after hydrolysis were: (Va) : (VIIa)-3 = 86 : 14 and (Vb) : (VIIb)-3 = 65 : 35 indicating a slight superiority of the dimethylamino-group in promoting addition.

Isopropyl- and t-butyl-lithium also add to 2,2-dimethylbut-3-enyl methyl sulphide (Ic) leading to (IVc)-1 (50) and (IVc)-2 (8), respectively. The relatively low conversion of (Ic) is caused by competing metallation of the *S*-methyl group of (Ic); moreover, formation of (XI) and (XII) by deuteriolysis and carboxylation, respectively, shows that intramolecular translithiation may have occurred in the addition products.[4] (Scheme 2).

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† As observed earlier[1,2] additions are much faster in the presence of ether.

‡ Analysis by g.l.c. The mass balance is generally good; no other main products were found. Starting materials and products gave satisfactory spectral and analytical data. Synthetic and structural details will be given later.

§ After the mixture is set aside, the yield of D-(IVb)-1 from (IIIb)-1 is lowered by competing cleavage of diethyl ether and addition of (IIIb)-1 to the ethylene formed.

¶ Negative results with *anti*-(VIa), *anti*-(VIb), *endo*-6-methoxy-*endo*-tricyclo[3,2,2,0^{2,4}]nonane, and 1-methoxy-2-methyl-2-cyclopropylpropane shows that organolithium reagents do not add to simple cyclopropane derivatives.

[1] A. H. Veefkind, F. Bickelhaupt, and G. W. Klumpp, *Rec. Trav. chim.*, 1969, **88**, 1058; similar results have been obtained with allyl alcohols: J. K. Crandall and A. C. Clark, *Tetrahedron Letters*, 1969, 325; H. Felkin, G. Swierczewski, and A. Tambute, *ibid.*, p. 707.

[2] P. D. Bartlett, C. V. Goebel, and W. P. Weber, *J. Amer. Chem. Soc.*, 1969, **91**, 7425; E. A. Kovrizhnykh and A. I. Shatenshtein, *Russ. Chem. Rev.*, 1969, **38**, 840.

[3] *Cf.* P. T. Lansbury and F. J. Caridi, *Chem. Comm.*, 1970, 714, for a discussion of reactivity in intramolecular organolithium additions to alkenes.

[4] *Cf.* U. Schöllkopf, in Houben-Weyl, Methoden der Organischen Chemie, XIII/1, 110, 1970.