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ADDITION OF AN ALKYL LITHIUM COMPOUND TO A SIMPLE DOUBLE BOND

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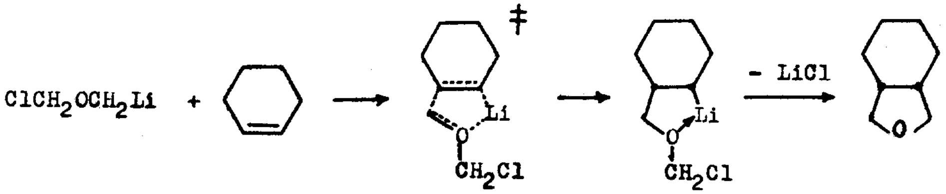
Whereas alkyl lithium reagents add to conjugated unsaturated systems and to strained unconjugated double bonds[1] they generally do not add to simple double bonds. Examples of additions to alkenyl ethers, - sulphides and - amines[2] and to allyl alcohols[3] have been reported, however. Formation of a complex with a favourable geometry was believed to be the driving force of the reaction in these cases[2].

In our investigation of the synthesis of furans it was found, however, that chloromethoxymethyl lithium (1) does add to simple double bonds. Thus when 1 was allowed to react with cyclohexene in ether a good yield of *cis*-8-oxabicyclo [4,3,0] nonane (2) was obtained. The reaction presumably takes place *via* a cis-addition of the lithium compound, followed by cyclization:



1 3 4 2

The reagent 1 was prepared *in situ* from 1,1'-dichlorodimethyl ether by treatment with lithium iodide and methyl lithium (i.e. the mixture obtained by the reaction of lithium and methyl iodide in ether)[4]:

$$ClCH_2OCH_2Cl + LiI \longrightarrow ClCH_2OCH_2I$$

$$ClCH_2OCH_2I + CH_3Li \longrightarrow \underset{1}{ClCH_2OCH_2Li} + CH_3I$$

The reaction was carried out as follows: to equimolar amounts of cyclohexene and 1,1'-dichlorodimethyl ether in diethyl ether was added 1.5 to 2 times the calculated amount of CH_3Li/LiI in diethyl ether at 0 under a dry nitrogen atmosphere. After being stirred for 1 hr at 0 the reaction mixture was poured in water. The ether layer was separated and dried over anhyd. $MgSO_4$ and over sodium hydride[5]. Distillation *in vacuo* afforded 2 in 70% yield, n_D^{20} 1.4702, bp. 64-65 /15 mm (lit.[6] : bp. 180, n_D^{20} 1.4700).

The structure of 2 was further confirmed by the mass spectrum (M^+ at 126, main fragments at m/e = 96, 95, 81, 68, 67, 55 and 54) and the nmr spectrum (multiplets at τ = 6.4, 7.8 and 8.5 ppm, integration ratio 2 : 1 : 4).

The reason for the unusual reactivity of 1 is not quite clear. It is, however, likely that intramolecular complexation between the lithium atom and the ether oxygen facilitates the formation of the intermediate 4. The reaction might proceed *via* a cyclic transition state (3). This is in accord with the finding that only *cis*-2 was formed and not the more stable *trans*-isomer.

References:

1. For examples cf. M.J.Jorgenson, Organic Reactions, 18, Chapter 1, references 68a -69b.
2. A.H.Veefkind, J.v.d.Schaaf, F.Bickelhaupt and G.W.Klumpp, Chem. Commun., 722 (1971). A.H.Veefkind, F.Bickelhaupt and G.W.Klumpp, Rec.Trav.Chim., 88, 1058 (1969).
3. J.K.Crandall and A.C.Clark, Tetrahedron Letters, 325 (1969). H.Felkin, G.Swierczewski and A.Tambute, ibid., 707 (1969).
4. Cf.: U.Schöllkopf and J.Paust, Chem.Ber., 98, 2221 (1965).
5. In this manner an impurity - an alcohol probably formed by cleavage of 2 by the excess of methyl lithium - was removed.
6. S.F.Birch, R.A.Dean and E.V.Whitehead, J.Org.Chem., 19, 1449 (1954).