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LETTERS TO THE EDITOR

Catalysis of Electrophilic Addition of Alcohols to Alkoxyalkenes by Lithium Salts

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The examples of bytoxyethene and 1-butanol were used to show for the first time that neutral lithium salts $[CF_3SO_3Li, LiBr, LiN(SO_2CF_3)_2]$ can be used to success as catalysts in electrophilic addition reactions of proton-donor reagents to electronically saturated alkenes. Such reactions are usually catalyzed by acids.

The addition takes place on heating $(60-90^{\circ}\text{C})$ of equimolar amounts of the reagents in the presence of 1–10 wt % of a lithium salt (dissolved in 1,2-dimethoxyethane) and gives 1,1-dibutoxyethane in an yield of up to 90%. Lithium trifluoromethanesulfonate is a more effective catalyst than lithium bromide or lithium bis(trifluoromethanesulfonyl)amide.

$$CH_2 = CHOBu-n + n-BuOH \xrightarrow{Li^+} Me-CH \begin{pmatrix} OBu-n \\ OBu-n \end{pmatrix}$$

Under the same conditions in the absence of

lithium salts no adduct is formed, implying that the lithium cation catalyzes alcohol addition to a nucleophilic double bond. Hence, this fact principally complements the scarce data on the use of lithium complexes (for example, LiClO₄–diethyl ether) in organic synthesis, in particular in the Diels–Alder [3, 4] and Michael [5] reactions, aldol condensation [6], acetalization of aldehydes [7], and polymerization of vinyl ethers [8].

Mechanistically, the catalysis of electrophilic addition to alkoxyalkenes by neutral lithium salts is evidently similar to the catalysis by protons and Lewis acids. It is based on polarization of alkoxyalkene by complex formation with the electronically saturated double bond, as well as with the neighboring oxygen atom. The catalytic activity of lithium salts is increased in such solvents as 1,2-dimethoxyethane, acetals, oligoethyleneglycol ethers, etc., capable of complex formation with the lithium cation.



The role of the complex-forming solvent for lithium salt (for example, 1,2-dimethoxyethane) is to separate the ion pair and to weaken the bond between the lithium cation and the anion, thus increasing the electrophilicity of the latter. In terms of this concept, lithium salts with bulky complex anions and delocalized negative charge must have increased catalytic activity, which is indeed the case. Hence, it is safe to state that complexes of lithium salts will find wide use in organic synthesis as a special group of soft metal-complex catalysts.

Addition of 1-butanol to butoxyethene in the presence of lithium trifluoromethanesulfonate. To a

mixture of 4.4 g of butoxyethene and 3.3 g of 1-butanol, a 10% solution of CF_3SO_3Li (0.1 g, 1.4 wt %) in 1,2-dimethoxyethane was added. The resulting mixture was stirred at 90°C for 4 h until complete conversion of bytoxyethene (control by GLC). Dibutylamine, 0.2 g, was then added, and the mixture was distilled in a vacuum to obtain 6.9 g (90%) of 1,1dibutoxyethane. The reaction product was identified by comparison with an authentic sample [9].

Reaction in the presence of lithium bromide and bis(trifluoromethanesulfonyl)amide. Heating of the same reagents (60°C, 5 h) in the presence of 3 wt % of LiBr and 1 wt % of LiN(SO₂CF₃)₂ (10% solutions in 1,2-dimethoxyethane) gives 1,1-dibutoxyethane in 95% yield (per reacted butoxyethene; the conversions of butoxyethene were 19% and 37%, respectively).

Commercial lithium salts were dried in a vacuum. Butoxyethene and 1,2-dimethoxyethane were distilled over sodium. 1-Butanol was refluxed with CaO and distilled. The reaction progress was followed by GLC on an LHM-80 chromatograph, detector katharometer, column 3000×3 mm, packing 1% of PEG 20000 on NaCl, carrier gas helium.

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