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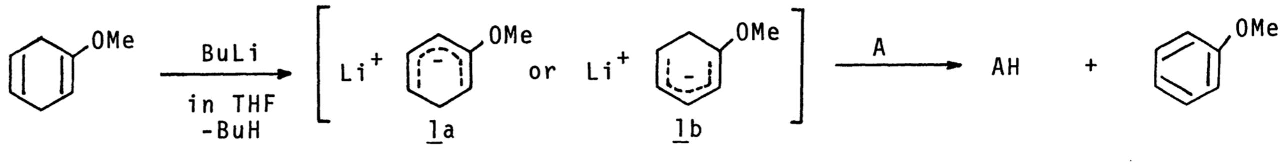
HYDROGEN TRANSFER OF 2,5-DIHYDROANISOLE TO HYDROGEN ACCEPTORS PROMOTED BY BUTYLLITHIUM

Mitsuo HIRAMATSU,[†] Tatsuo FUJINAMI,[††] and Shizuyoshi SAKAI[†,††]
† Department of Electronic Material Science, Graduate School of Electronic Science and Technology, Shizuoka University, Hamamatsu 432
†† Department of Industrial Chemistry, Faculty of Engineering, Shizuoka University, Hamamatsu 432

2,5-Dihydroanisole treated with butyllithium reacts with hydrogen acceptors as hydrogen donor more predominantly than carbanion to give the corresponding hydrogenated products in good yields.

The reactions for hydrogen transfer involving various 1,4-dihydropyridine derivatives as models for the reduced nicotinamide adenine dinucleotides have been widely investigated because of their biochemical significances.1) The studies on hydrogen donors including 1,4-dihydrobenzene derivatives have been also reported.2) In both cases, however, hydrogen acceptors need to be activated so that the applications of these hydrogen transfer reactions are limited. On the other hand, it has been reported that the treatment with butyllithium3) or amylsodium4) quantitatively converts 1,4-dihydrobenzene into benzene. However, hydrogen transfer of metallated 1,4-dihydrobenzenes to hydrogen acceptors as carbonyl compounds has not been established.

In this communication, we wish to describe the reaction of lithiodihydroanisole (1a or 1b),5) prepared *in situ* from 2,5-dihydroanisole and butyllithium, with hydrogen acceptors (A). That is, we found that the hydrogen donating ability of 2,5-dihydroanisole was increased by treatment with stoichiometric amount of butyllithium.



Firstly, 1 was prepared *in situ* from 2,5-dihydroanisole in THF and butyllithium, accompanying with slow evolution of butane. The red color of the solution, which was developed at a temperature above -30°C, would indicate the formation of 1. It was also supported by the reported fact that the stable dimethylcyclohexadienyl anion was obtained from 3,3-dimethyl-1,4-cyclohexadiene and butyllithium, and its structure was confirmed by the NMR spectrum.6) To confirm the formation of 1, D_2O was added to the solution of 1 prepared from 2,5-dihydroanisole and butyllithium at room temperature. Deuterated unconjugated diene (42%), deuterated conjugated diene (17%), and dehydrogenated product, anisole (41%), were obtained. This fact shows that 1 reacted with D_2O as not only carbanion but also hydrogen donor. Next, the results of reactions with the other hydrogen acceptors are summarized in Table 1. The reactions proceeded under the mild conditions to give the corresponding hydrogenated products in good yields. Interestingly, 1 did not attack carbonyl carbon of hydrogen acceptors as a usual carbanion in spite of its carbanion structure, but acted as hydrogen donor at room temperature or above.5) A driving force of the reaction would be the recovery of aromaticity.

In oder to confirm that the hydrogen donor is not LiH which may be produced by decomposition of 1, the reactions of hydrogen acceptors with LiH were carried out under similar reaction conditions to give the corresponding hydrogenated products in very poor yields (less than 5%). In the reaction of benzaldehyde with LiH, not benzyl alcohol (14%) but benzyl benzoate (86%) was obtained predominantly under severer conditions (in THF for 8 h at reflux).7) From these facts, the probability that the reaction proceeded by way of LiH would be fairly small.

The simplicity of the present procedure is demonstrated by the following example. A mixture of 2,5-dihydroanisole (1.10 g, 10 mmol) in tetrahydrofuran (4 ml) and butyllithium (10 mmol) in petroleum ether (about 8 ml) was prepared at -78°C, and allowed to warm to room temperature. At about -30°C, an exothermic reaction occurred, and red color was developed. To the red solution, benzaldehyde (1.06 g, 10 mmol) in tetrahydrofuran (4 ml) was added at 0°C, and the color of the solution was changed from red to pale yellow. The mixture was stirred for 5 h at room temperature. After removal of the solvent, the mixture was treated with dil. HCl, and extracted with diethyl ether. From the extract, benzyl alcohol was isolated by column chromatography.

Table 1. Reaction of 1 with hydrogen acceptor (A)

Hydrogen acceptor	Reaction conditions Temp.(°C)	Time(h)	Molar ratio(1/A)	Product	Yield$^{a)}$ (%)
PhCHO	r.t.	5	1	$PhCH_2OH$	100
PhCOCl	r.t.	5	1	$PhCOOCH_2Ph$	80
PhCOOMe	reflux	24	2	$PhCH_2OH$	90
PhCOPh	reflux	24	1	PhCH(OH)Ph	77
PhCOMe	reflux	24	1	b)	-

a) Yields are determined by NMR.

b) Attack of 1 to α-acidic hydrogen atom occurred to evolve hydrogen gas as detected by GC.

References

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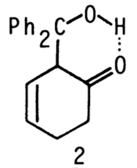
5) Treatment of 1 with Ph_2CO at -78°C gave 2, which would be formed by the addition of 1a to Ph_2CO followed by hydrolysis, in 18% yield.



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7) It has been reported that benzyl benzoate (87%) and benzyl alcohol (2%) were obtained by the reaction of benzaldehyde with NaH. See F. W. Swamer and C. R. Hauser, *J. Am. Chem. Soc.*, 68, 2647(1946).

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