Nickelocene–Lithium Aluminium Hydride, A New Effective Desulphurization Reagent

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The carbon–sulphur bonds in thiols, sulphides, and thioacetals are reductively cleaved by nickelocene–lithium aluminium hydride.

Raney nickel is one of the most commonly used reagents for reductive cleavage of carbon–sulphur bonds in organic synthesis.[1] The mechanism for this reaction is, however, not well understood. Only a handful of reports are known using homogeneous organonickel compounds to desulphurize dibenzothiophene[2] or sulphides.[3] $LiAlH_4$ has been employed to reduce titanium or copper halides yielding the active species for the reduction of carbon–sulphur bonds.[4] We report here the application of this reducing agent for the reduction of nickelocene to generate a very effective desulphurization reagent.

In a typical run, organosulphur compounds were treated with the active reagent prepared *in situ* by mixing 1 equiv. nickelocene and 1 equiv. lithium aluminum hydride in tetrahydrofuran (THF). In general, 1 equivalent of the nickel reagent is required for each carbon–sulphur bond reduced. Thus, 2 equiv. nickelocene–$LiAlH_4$ were employed for the desulphurization of sulphides. The results are summarized in Table 1. It is noteworthy that most sulphur-containing compounds such as thiols, sulphides, and thioacetals were reductively desulphurized in moderate to good yields. Benzylic, α-acyl substituted, or aryl carbon–sulphur bonds were found to be very reactive under the conditions used. In contrast, more drastic conditions were required for simple alkyl analogues. Thus, decane-1-thiol was reduced to n-decane in 41% yield under refluxing conditions. Although the high reactivity for the benzylic or α-acyl substrates is not unexpected, the fact that the aryl carbon–sulphur bond is more reactive than the simple aliphatic carbon–sulphur bond is interesting. It is noted that the aryl carbon–sulphur bond of alkyl aryl sulphides is selectively cleaved with $Os_3(CO)_{12}$.[5]

As can be seen from Table 1, various functional groups are stable under the reaction conditions. Thus, carbonyl, ester groups, as well as olefinic double bonds remain intact during the course of the reaction. As observed with Raney nickel,[1] the nitro group can be reduced to the corresponding amino group. To illustrate this, the ethylene dithioacetal of 2-nitrofluorenone was transformed into 2-aminofluorene upon treatment with the nickel reagent.

It is noteworthy that a mixture of $NiBr_2$ and $LiAlH_4$ was inactive under similar conditions and $LiAlH_4$ alone does not undergo reductive desulphurization. Water, in general, was employed to quench the reaction mixture simply for convenience; however, non-aqueous work-up also afforded the

Table 1.

Substrate[a]	Molar ratio Substrate : Ni : $LiAlH_4$	Product (% Yield)	
2-Naphthylmethanethiol	1 : 1 : 1	2-Methylnaphthalene	(80)
1-Naphthylmethanethiol	1 : 1 : 1	1-Methylnaphthalene	(83)
Bis(2-naphthylmethyl) sulphide	1 : 2 : 2	2-Methylnaphthalene	(67)
Dibenzothiophene	1 : 2 : 2	Biphenyl	(70)
2-Naphthalenethiol	1 : 1 : 1	Naphthalene	(74)
α-Methylthioacetophenone	1 : 2 : 2	Acetophenone	(74)
α-Methylthio-α-allylacetophenone	1 : 2.5 : 2.5	5-Phenyl-5-oxopent-1-ene	(78)
4-Methoxycarbonylphenylmethanethiol	1 : 1 : 1	4-Methoxycarbonyltoluene	(40)
9,9-Ethylenedithiofluorene	1 : 8 : 8[b]	Fluorene	(55)
9,9-Ethylenedithio-2-nitrofluorene	1 : 8 : 8[b]	2-Aminofluorene	(40)
Decane-1-thiol	1 : 2 : 2[c]	Decane	(41)

[a] The reaction mixture was stirred at room temperature for approx. 14—16 h. [b] An excess of reagent is required, otherwise the yield is poor. [c] The mixture was heated under reflux for 16 h.

desired product without reducing the yield of the reaction. Thus, 2-methylnaphthalene was obtained in 82% yield from the reduction of 2-naphthylmethanethiol by such procedure. In addition, no deuterium was incorporated in the product, 2-methylnaphthalene (85% yield), during a similar reaction using D_2O to scavenge the reaction mixture. When 2-naphthylmethanethiol was treated with the reagent prepared from nickelocene–lithium aluminium deuteride followed by normal work-up procedure, more than 80% of deuterium incorporation was found in the product, 2-methylnaphthalene.

Preliminary examination of the nature of the active species by spectroscopic methods was carried out. The i.r. spectrum shows no absorption in the region 1600—2200 cm^{-1} other than the signals due to the absorption of the solvent, THF. The ^{13}C n.m.r. spectrum of the active species shows only *one* signal at δ 104.0 in the range δ -100 to 240 and the ^{1}H n.m.r. spectrum exhibits a sharp singlet at δ 5.85 (20H) in addition to two broad singlets at δ 2.40 (2H) and δ 1.90 (1H). The two latter signals disappeared when $LiAlD_4$ was used as the reducing agent. Both ^{13}C and ^{1}H n.m.r. spectra remain unchanged from -100 °C to ambient temperature. The i.r. and n.m.r. data suggest that $LiAlH_4$ has been consumed and some kind of metal hydride may be present.† Based on our results, the possible hydrogen source for the reductive cleavage of the carbon–sulphur bond could arise from the active species. Further characterization of this active reagent is under way.

In summary, we have depicted a new homogeneous organonickel reagent for the reductive cleavage of carbon–sulphur bonds. The composition of the reagent is similar to that of Raney nickel and, therefore, the reaction may serve as a homogeneous model for the study of the mechanism of the reaction promoted by the latter reagent.

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† The hydride, if any, should not be terminal based on i.r. data. It is, however, difficult to assign the absorption in the i.r. region attributed to other kinds of hydride (ref. 6).