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# REDUCTION OF β-SULFENYLATED α,β-UNSATURATED KETONES WITH $NaBH_4$-METAL HALIDE

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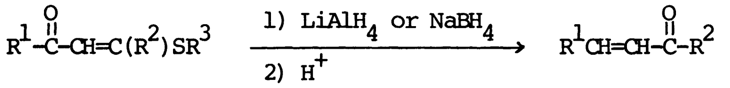
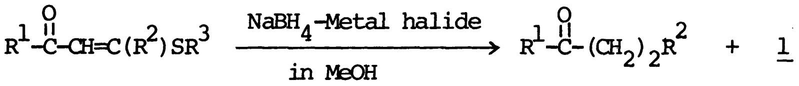
Reduction of β-sulfenylated α,β-unsaturated ketones (1) with sodium borohydride ($NaBH_4$) in the presence of a catalytic amount of metal halide ($CoCl_2$ or $NiCl_2$) gave the saturated ketones (3). However, $FeCl_2$, $FeCl_3$, CuI, and $CuCl_2$ showed no effect in the reduction of 1.

We previously reported the smooth conversion of β-sulfenylated α,β-unsaturated ketones (1) to α,β-unsaturated ketones (2) via selective 1,2-reduction, followed by hydrolysis (eq. 1).[1)]



$$\underset{\underline{1}}{R^1\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH{=}C(R^2)SR^3} \xrightarrow[2)\ H^+]{1)\ LiAlH_4\ \text{or}\ NaBH_4} \underset{\underline{2}}{R^1CH{=}CH\text{-}\overset{\overset{O}{\|}}{C}\text{-}R^2} \qquad (1)$$

It is well known that the regiospecific reduction of the conjugated enones is difficult to perform. It has been shown recently that the addition of metal halides to the conjugated enone and $NaBH_4$ affords selective reduction compounds.[2,3)] A number of metal halides and the hydride reducing reagents, which are claimed to give selective addition products, have been investigated in recent years.[4)] We report here its application to the reduction of β-sulfenylated α,β-unsaturated ketones (1). When 3-ethylthio-1-phenylbut-2-en-1-one (1a) was reduced with $NaBH_4$ in the presence of cobalt(II) chloride in MeOH and then the reaction products were decomposed under acidic conditions, 1-phenylbutan-1-one (3a), which was 1,4-reduction and desulfenylation product, was obtained.[5)] Reduction of 1a with $NaBH_4$ in the presence of nickel chloride also gave 3a. However, $NaBH_4$-$FeCl_2$, $NaBH_4$-$FeCl_3$, $NaBH_4$-CuI, $NaBH_4$-$CuCl_2$, and $LiAlH_4$-$CoCl_2$ showed no activity at all toward the reduction of 1a. Similarly, other β-sulfenylated α,β-unsaturated ketones (1b-f) were reduced with $NaBH_4$-$CoCl_2$ to give the saturated ketones (3b, e, f). The results are summarized in Table 1.



$$\underset{\underline{1}}{R^1\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH{=}C(R^2)SR^3} \xrightarrow[\text{in MeOH}]{NaBH_4\text{-Metal halide}} \underset{\underline{3}}{R^1\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_2R^2} + \underline{1}$$

In order to know catalysis of the metal halides, 1.0:2.0:0.1 ratio of 1a-$NaBH_4$-metal halide was used in experiment (runs 2, 4, 12, 14, 16, 18 and 20). The results show clearly that β-sulfenylated α,β-unsaturated ketones (1a-f) can be reduced to the saturated ketones (3a-b, e-f) by the combination of $NaBH_4$ with a catalytic amount of $CoCl_2$ or $NiCl_2$. The mechanism for the formation

Table 1. The Yields of the Saturated Ketones (3)

| Run | Compound | | | | Metal | Molar Ratio | Yields (%)[a] | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $R^1$ | $R^2$ | $R^3$ | halide | 1 : $NaBH_4$ : Metal halide | 3 | Other products | 1 (recovered) |
| 1 | 1a | Ph | Me | Et | $CoCl_2$ | 1 : 0.5 : 0.1 | 8.0 | | 86.5 |
| 2 | 1a | Ph | Me | Et | $CoCl_2$ | 1 : 2 : 0.1 | 71.0 | $PhCH(OH)CH_2CH(Me)SEt$ (4) 15.5 | 8.0 |
| 3 | 1a | Ph | Me | Et | $CoCl_2$ | 1 : 2 : 2 | 47.0 | 4 trace | 44.0 |
| 4 | 1a | Ph | Me | Et | $NiCl_2$ | 1 : 2 : 0.1 | 68.5 | 4 4.0 | 23.5 |
| 5 | 1a | Ph | Me | Et | $NiCl_2$ | 1 : 2 : 2 | 50.0 | 4 4.5 | 44.0 |
| 6 | 1a | Ph | Me | Et | $FeCl_2$ | 1 : 2 : 2 | trace | | quant. |
| 7 | 1a | Ph | Me | Et | $FeCl_3$ | 1 : 2 : 0.4 | trace | PhCH=CHCOMe (5) 6.5 | 91.5 |
| 8 | 1a | Ph | Me | Et | $FeCl_3$ | 1 : 2 : 2 | trace | 5 trace | 79.5 |
| 9 | 1a | Ph | Me | Et | CuI | 1 : 2 : 0.1 | trace | 5 trace | quant. |
| 10 | 1a | Ph | Me | Et | CuI | 1 : 2 : 2 | trace | 5 trace | quant. |
| 11 | 1a | Ph | Me | Et | $CuCl_2$ | 1 : 2 : 0.1 | trace | 5 trace | quant. |
| 12 | 1b | Ph | H | Et | $CoCl_2$ | 1 : 2 : 0.1 | 70.5 | $PhCH(OH)CH_2CH_2SEt$ (6) 15.0 | 13.0 |
| 13 | 1b | Ph | H | Et | $CoCl_2$ | 1 : 2 : 2 | 63.0 | 6 32.0 | 1.0 |
| 14 | 1b | Ph | H | Et | $NiCl_2$ | 1 : 2 : 0.1 | 61.5 | 6 24.0 | trace |
| 15 | 1c | Ph | Me | $Pr^n$ | $CoCl_2$ | 1 : 2 : 2 | 57.0 | | 30.0 |
| 16 | 1d | Ph | Me | Ph | $CoCl_2$ | 1 : 2 : 0.1 | 44.0 | PhSSPh (7) 34.5 | 56.0 |
| 17 | 1d | Ph | Me | Ph | $CoCl_2$ | 1 : 2 : 2 | 78.5 | 7 59.5 | 21.0 |
| 18 | 1e | Ph | Ph | Et | $CoCl_2$ | 1 : 2 : 0.1 | 84.5 | | 10.0 |
| 19 | 1e | Ph | Ph | Et | $CoCl_2$ | 1 : 2 : 2 | 75.0 | | 15.5 |
| 20 | 1f | Me | Ph | Et | $CoCl_2$ | 1 : 2 : 0.1 | 73.0 | MeCH=CHCOPh (8) 2.5 | 15.5 |
| 21 | 1f | Me | Ph | Et | $CoCl_2$ | 1 : 2 : 2 | 19.5 | 8 21.0 | 47.5 |

a) The yields were determined by G.L.C..

of the saturated ketones (3) is not clear at present but the formation of 3 is presumed to proceed via selective 1,4-reduction and desulfenylation of 1 on reduction by $NaBH_4$-metal halide.

References and notes

1) T. Nishio and Y. Omote, Chem. Lett., 1979, 365.

2) J.L.Luche, J. Am. Chem. Soc., 100, 2226 (1978).

3) J.L.Luche, L.Rodriguez-Hahn, and P.Crabbé, J. Chem. Soc. Chem. Commun., 1978, 601.

4) E.g., E.C.Ashby and J.J.Lin, J. Org. Chem., 43, 2567 (1978) and references therein.

5) In a typical experiment, a solution of $NaBH_4$ (76 mg, 2 mmol) in MeOH (5 ml) was added drop by drop into a stirred solution of 3-ethylthio-1-phenylbut-2-en-1-one (1a, 206 mg, 1 mmol) and $CoCl_2$ (258 mg, 2 mmol) in MeOH (10 ml) at room temperature and the reaction mixture was stirred for an additional 3 h. Then the reaction mixture was decomposed with 10% aqueous HCl solution (5 ml) and extracted with dichloromethane. The product (3a) was purified through a silica gel column chromatography eluted with benzene.

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