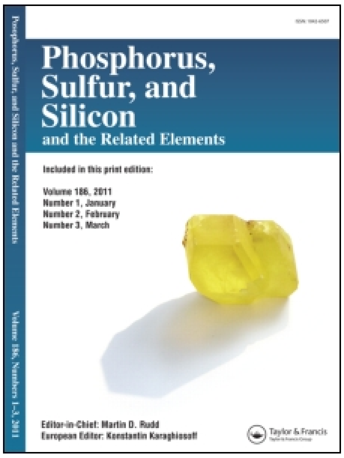

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# NEW REDUCTION OF SOME SULFINYL CARBOXYLIC ESTERS WITH SODIUM BOROHYDRIDE

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# NEW REDUCTION OF SOME SULFINYL CARBOXYLIC ESTERS WITH SODIUM BOROHYDRIDE

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The reactivity of sodium borohydride with respect to the reduction of the carbethoxy group in unsubstituted esters is increased by the introduction of a sulfinyl group in the $\alpha$ or $\beta$ positions. This effect is decreased only slightly by steric hindrance due to the presence of bulky groups in the $\alpha$ or $\beta$ positions. This behaviour is compared to that of the corresponding $\alpha$ and $\beta$ sulfenyl carboxylic esters.

*Key words:* Esters; sulfinyl group; sodium borohydride.

## INTRODUCTION

Sodium borohydride[1] has established itself as a reducing agent of great value for aldehydes and ketones, due to its low sensitivity toward moisture and the mild conditions required for its use. These properties give it a great advantage over lithium aluminum hydride, which does not possess such advantages. Sodium borohydride has been shown to be also more selective than lithium aluminum hydride, being inert toward cyano or nitro groups and of low reactivity toward carbethoxy group.[2] However, although the reduction of alkyl esters of unsubstituted carboxylic acids does not appear to proceed to any significant extent, it has been reported that the reducing properties of sodium borohydride can be increased when the carboxyl group is located in close proximity to a functional group, such as hydroxyl, carbonyl or amino[3–7] and, as more recently reported, to oxa and thia groups.[8] The rate of reduction of carboxylic esters can be also increased using large excess of sodium borohydride[9] or by the use of hydroxylic solvents.[10]

The success in the selective reduction of $\beta$-keto sulfoxides by sodium borohydride, leading to the formation of $\beta$-hydroxy sulfoxides in 98% yield,[11] has prompted us to investigate the reactivity of the $\alpha$-sulfinyl carboxylic esters.

## RESULTS AND DISCUSSION

The studies of the reaction of $\alpha$-sulfinyl carboxylic esters (**1a–c**) and $\beta$-sulfinyl carboxylic ester (**1d**) with sodium borohydride, leading to the corresponding al-

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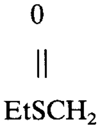
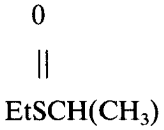
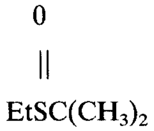
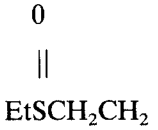
cohols (**2a–d**) were undertaken in comparison to the unsubstituted esters (**1e–g**), α-sulfenyl carboxylic esters (**1h–j**), β-sulfenyl carboxylic ester (**1k**), and α,α′-disulfenyl (**1l**) and β,β′-disulfenyl carboxylic esters (**1m**).

$$\underset{(1)}{RCO_2Et} \xrightarrow[\text{r.t. (2 hr)}]{\text{NaBH}_4\text{/ethanol}} \underset{(2)}{RCH_2OH}$$

**a**, R =

$Et\overset{\overset{0}{\|}}{S}CH_2$

**b**, R =

$Et\overset{\overset{0}{\|}}{S}CH(CH_3)$

**c**, R =

$Et\overset{\overset{0}{\|}}{S}C(CH_3)_2$

**d**, R =

$Et\overset{\overset{0}{\|}}{S}CH_2CH_2$

**e**, R = $CH_3(CH_2)_5$
**f**, R = $(CH_3)_2CH$
**g**, R = $(CH_3)_3C$
**h**, R = $EtSCH_2$
**i**, R = $EtSCH(CH_3)$
**j**, R = $EtSC(CH_3)_2$
**k**, R = $EtSCH_2CH_2$
**l**, R = $(EtS)_2C(CH_3)$
**m**, R = $(EtS)_2C(CH_3)CH_2$

All reactions were performed in very mild conditions using equimolar proportions of the reagents in ethanolic solution, at room temperature, for 2 hr (Table I).

It may be seen that ethyl heptanoate (**1e**), ethyl isobutyrate (**1f**) and ethyl pivalate (**1g**) were recovered in 88%, 84% and 100%, respectively. However, dramatic change occurred when the sulfinyl group was introduced α to the carbethoxy group, being the α-sulfinyl carboxylic ester (**1a**) absent in the final product and (**1b**) and

TABLE I

Reaction of ethyl carboxylates with $NaBH_4$ in ethanol

| Starting esters (1) | Recovered esters (%) |
|---|---|
| **a** | $0^a$ |
| **b** | $15^a$ |
| **c** | $20^a$ |
| **d** | $19^a$ |
| **e** | $88^b$ |
| **f** | $84^b$ |
| **g** | $100^b$ |
| **h** | $26^b$ |
| **i** | $75^b$ |
| **j** | $100^b$ |
| **k** | $100^b$ |
| **l** | $90^b$ |
| **m** | $100^b$ |

[a] Based on the intensity of the I.R. carbonyl band.

[b] Evaluated by g.l.c.

(**1c**) recovered in 15% and 20%, respectively. Surprisely, the $\beta$-substituted sulfinyl carboxylic ester (**1d**) also underwent reduction, as the ester was recovered in 19%. However, it should be mentioned that the attempts to purify the sulfinyl alcohols (**2a–d**), obtained from the sulfinyl esters (**1a–d**) by distillation or column chromatography failed, due to decomposition. However, they were identified by $^1H$ NMR and IR spectroscopies.

It is noteworthy that, although the $\alpha$-sulfenyl group in (**1h**) also promotes reduction of the carbethoxy group, being the ester recovered in 26%, the methyl and dimethyl substituted $\alpha$-sulfenyl carboxylic esters (**1i**) and (**1j**) and the $\beta$-sulfenyl carboxylic ester (**1k**) were recovered in 75% and 100%, respectively. It may be observed that the presence of two sulfenyl groups in the $\alpha$ (**1l**) and $\beta$ positions (**1m**) does not increase the reactivity of reduction, since the starting products were recovered in 90% and 100%, respectively.

Two aspects may be noticed: the positive influence of the sulfinyl group and the negative influence of the steric effect of the bulky groups on the effectiveness of reductions by sodium borohydride. The latter is observed in three series, strongly in the unsubstituted, as well as in the sulfenyl substituted carboxylic esters, but only slightly in the sulfinyl carboxylic esters. The fact that not only the $\alpha$-sulfinyl carboxylic esters, but also the $\beta$-sulfinyl carboxylic ester undergo reduction eliminates the possibility of the electron withdrawing effect of the sulfinyl group and suggests the coordination of the sodium borohydride at the sulfinyl oxygen facilitating the delivery of a hydride, as responsible for such reactivity.[18-20] This is in accord with the capability of the sulfoxides to form complexes with metallic salts.[21]

## EXPERIMENTAL

The IR spectra were run on a Perkin Elmer 283, in ethanolic solution, using a pair of 1.0 mm NaCl matched sealed cells. For compounds (**1a–d**) an analytical working curve (A × conc.) was obtained

TABLE II

$^1$H NMR and IR of sulfinyl carboxylic esters[a]

| Compound no. | $^1$H NMR ($\delta$ in $CDCl_3$) | IR(cm$^{-1}$) film $\nu_{C=O}$; $\nu_{S=O}$ |
|---|---|---|
| **1a** | 1.36 (t, 6H); 2.86 (q, 2H); 3.65 (d, 2H); 4.22 (q, 2H) | 1732; 1024 |
| **1b** | 1.06–1.75 (m, 9H); 2.58–3.00 (m, 2H); 3.34–3.88 (m, 1H); 4.22 (q, 2H) | 1731; 1059 |
| **1c** | 1.08–1.54 (m, 12H); 2.29–2.58 (m, 2H); 3.96–4.25 (m, 2H) | 1727; 1061 |
| **1d** | 1.10–1.46 (m, 6H); 2.49–2.69 (m, 6H); 4.15 (q, 2H) | 1720; 1049 |

[a] Decompose on distillation.

TABLE III

$^1$H NMR and IR data of sulfinyl alcohols[a]

| Compound no. | $^1$H NMR ($\delta$ in $CDCl_3$) | IR(cm$^{-1}$) film $\nu_{C—O}$ or $\nu_{S=O}$ |
|---|---|---|
| **2a** | 0.90–1.75 (t, 3H); 2.15–3.20 (m, 4H); 3.65–4.20 (m, 2H); 4.80 (bs, 1H) | 1016; 1047 |
| **2b** | 1.06–1.49 (m, 6H); 2.49–3.02 (m, 2H); 3.10–3.59 (m, 3H); 4.65 (bs, 1H) | 1004; 1042 |
| **2c** | 1.02–1.60 (m, 9H); 2.38–2.82 (q, 2H); 3.60 (bs, 2H); 4.18 (bs, 1H) | 1007; 1044 |
| **2d** | 1.32 (t, 3H); 1.85–2.10 (m, 2H); 2.58–2.90 (m, 4H); 3.65 (bs, 2H); 4.64 (bs, 1H) | 1009; 1057 |

[a] Decompose on distillation.

for concentrations ranging from $2.5 \times 10^{-4}$ g/ml to $4.1 \times 10^{-2}$ g/ml, in the region of 1800 cm$^{-1}$ to 1500 cm$^{-1}$. The absorbance of the carbonyl stretching band for a sample of known volume of each reaction mixture was measured and the ester recovered content was determined from the working curve. $^1$H NMR spectra were recorded on a Varian T-60 or on a Bruker AC-80 spectrometers. For g.l.c. analysis a Hewlett-Packard 5890A gas chromatograph was used. Compounds (**1e–g**) were of commercial grade. Compounds (**1h–m**) were prepared according to literature procedures,[12–16] and (1h–k) were oxidized to the corresponding sulfinyl derivatives (**1a–d**), using hydrogen peroxide in acetic acid.[17] Spectral data of sulfinyl carboxylic esters (**1a–d**) are reported in Table II.

*Reduction of ethyl carboxylates with sodium borohydride. General Procedure.* The ester (5 mmol) was dissolved in dry ethanol to produce a 10% w/w solution. To this solution, sodium borohydride (5 mmol) was added, the reaction mixture was stirred at r.t. for 2 hours, and then neutralized with 50% aqueous sulfuric acid. After filtration of solid material, the recovered ester content (%) in the reaction mixture was determined by g.l.c. for unsubstituted esters (**1e–g**) and sulfides (**1l–m**) or by IR spectroscopy for sulfoxides (**1a–d**). For the latter compounds $^1$H NMR spectra of crude products were recorded and showed to be mixtures of unreacted esters and the corresponding alcohols.

*α-Ethylsulfinyl alcohols* (**2a–d**). *General Procedure.* To a 10% w/w solution of sulfinyl carboxylic ester (**1a–d**) in dry ethanol, 3 equivalents of sodium borohydride were added, the resulting suspension was stirred for 5 hours, and neutralized with 50% aqueous sulfuric acid. After filtration, the solution was dried with anhydrous magnesium sulfate, and the solvent removed under reduced pressure. Spectral data of sulfinyl alcohols (**2a–d**) are reported in Table III.

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## REFERENCES

1. H. I. Schlesinger, H. C. Brown, H. R. Hoekstra and L. R. J. Rapp, *J. Amer. Chem. Soc.*, **75**, 199 (1953).
2. H. C. Brown and S. Krishnamurthy, *Tetrahedron*, **35**, 567 (1979).
3. E. Schenker, *Angew. Chem.*, **73**, 81 (1961).
4. N. W. Atwater, *J. Amer. Chem. Soc.*, **83**, 3071 (1961).
5. J. E. G. Barnet and P. W. Kent, *J. Chem. Soc.*, **1963**, 2743.
6. J. A. Meschino and H. C. Brown, *J. Org. Chem.*, **28**, 3129 (1963).
7. E. C. Pesterfield and D. M. S. Wheeler, *J. Org. Chem.*, **30**, 1513 (1965).
8. K. Hanaya, Y. Koga, A. Yamagughi, H. Kudo and Y. L. Chow, *Nouv. J. Chim.*, **6**, 149 (1982).
9. M. S. Brown and H. Rapoport, *J. Org. Chem.*, **28**, 3261 (1963).
10. H. C. Brown, E. J. Mead and B. C. Subba Rao, *J. Amer. Chem. Soc.*, **77**, 6209 (1955).
11. G. A. Russel, E. Sabourin and G. J. Mikol, *J. Org. Chem.*, **31**, 2854 (1966).
12. I. Minamida, Y. Ikeda, K. Uneyama, W. Kagaki and S. Oae, *Tetrahedron*, **24**, 5293 (1968).
13. N. Mori, S. Kaido, K. Suzuki, M. Nakamura and Y. Tsuzuki, *Bull. Chem. Soc. Jpn.*, **44**, 1858 (1971).
14. J. L. Szabo and E. T. Stiller, *J. Amer. Chem. Soc.*, **70**, 3667 (1948).
15. G. W. Stacy, I. L. Klundt, G. T. Davis, N. A. Nielsen, M. S. Power, D. L. Rector and S. L. Razniak, *J. Org. Chem.*, **31**, 1753 (1966).
16. E. Baumann, *Chem. Ber.*, **19**, 2810 (1886).
17. K. Ogura and G. Tsuchihashi, *Bull. Chem. Soc. Jpn.*, **45**, 2203 (1972).
18. D. C. Wigfield and S. Feiner, *Can. J. Chem.*, **56**, 789 (1978).
19. H. C. Brown, A. Khuri and S. Krishnamurthy, *J. Amer. Chem. Soc.*, **99**, 6237 (1977).
20. H. C. Brown, A. Khuri and S. C. Kim, *Inorg. Chem.*, **16**, 2229 (1971).
21. N. Furukawa and H. Fujihara in "The Chemistry of Sulphones and Sulphoxides" (Eds. S. Patai, Z. Rappoport and C. J. M. Stirling) Chap. 11, John Wiley & Sons Ltd, U.K., 1988.