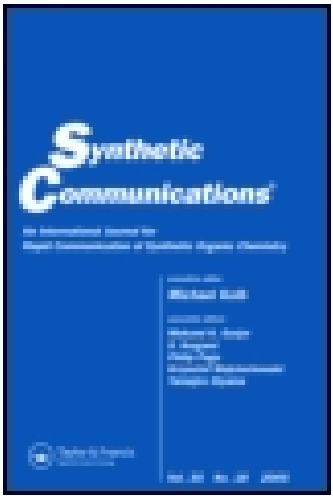

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Reductive Cleavage of S-S Bond in Diphenyl Disulfide by Samarium Diiodide: A Novel Method for the Synthesis of Thiolesters

Xueshun Jia [a] , Yongmin Zhang [a] & Xungun Zhou [a]
[a] Department of Chemistry , Hangzhou University , Hangzhou, 310028, P. R. China
Published online: 23 Sep 2006.

To cite this article: Xueshun Jia , Yongmin Zhang & Xungun Zhou (1994) Reductive Cleavage of S-S Bond in Diphenyl Disulfide by Samarium Diiodide: A Novel Method for the Synthesis of Thiolesters, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 24:3, 387-392

To link to this article: http://dx.doi.org/10.1080/00397919408011197

SYNTHETIC COMMUNICATIONS, 24(3), 387-392 (1994)

REDUCTIVE CLEAVAGE OF S-S BOND IN DIPHENYL DISULFIDE BY SAMARIUM DIIODIDE: A NOVEL METHOD FOR THE SYNTHESIS OF THIOLESTERS

Xueshun Jia, Yongmin Zhang* and Xunjun Zhou

Department of Chemistry, Hangzhou University,
Hangzhou 310028 P.R. China

ABSTRACT: Diphenyl disulfide is reduced by samarium diiodide to yield samarium phenylthiolate. This new thiolate anion species mildly reacts with acyl chlorides to give thiolesters in good yields.

As a result of the increasing interest in the utility of thiolesters in organic synthesis[1-3], many new methods have been developed for the preparation of thiolesters in recent years[4-11], for example, the

*To whom correspondence should be addressed.

reaction between sodium thiobenzoate and arenediazonium tetrafluoroborates[6], treatment of nitrosoamides or nitroamides with mercaptans in the presence of sodium hydride[8], the cobalt carbonyl catalyzed carbonylation of mercaptans[9] and the cobalt chloride catalysed coupling of thiols and anhydrides[11].

Here we wish to report that samarium diiodide (SmI_2), a powerful one electron transfer reductant[12-15], reduces diphenyl disulfide to samarium phenylthiolate at room temperature under nitrogen atmosphere. This new thiolate anion species mildly reacts with acyl chlorides to give thiolesters in good yields under neutral condition(Scheme).

Scheme

$$Ph\text{-}S\text{-}S\text{-}Ph + 2SmI_2 \xrightarrow[THF]{} 2PhSSmI_2 \xrightarrow{RCOCl} R\text{-}CO\text{-}S\text{-}Ph$$

We have discovered that when a solution of diphenyl disulfide in THF was added to a deep blue solution of SmI_2 in THF, the deep blue colour of the solution gradually turned into brown with 1h, which showed that the S-S bond had been reductively cleaved by SmI_2 and that the samarium phenylthiolate($PhSSmI_2$) had been generated, and the subsequent acylation with acyl chlorides gave thiolesters in 70-89% yield.

Table 1

Product	Yield[a] %	IR(film) $\nu_{C=O}$ cm^{-1}	^1H NMR($CDCl_3$) (δ, ppm)
Ph-CO-S-Ph	87	1692	7.24-7.63(8H, m), 7.93-8.2(2H, m)
3-ClC_6H_4-CO-S-Ph	89	1708	7.17-7.6(7H, m), 7.77-7.97(2H, m)
2-BrC_6H_4-CO-S-Ph	84	1706	7.23-7.85(9H, m)
PhCH=CH-CO-S-Ph	77	1650	6.57(1H, d), 7.27-7.6(11H, m)
$CH_3(CH_2)_4$CO-S-Ph	70	1725	0.9(3H, t), 1.17-1.83(6H, m), 2.63(2H, t), 7.4(5H, s)
$CH_3(CH_2)_{10}$CO-S-Ph	72	1726	0.87(3H, t), 1.23-1.83(18H, m) 2.62(2H, t), 7.37(5H, s)

a. Yield of isolated product.

In summary, a novel method for the preparation of thiolesters has been developed. The advantages of the present procedure are single product, simple manipulation, mild and neutral conditions.

EXPERIMENTAL

The solvent tetrahydrofuran was freshly distilled from sodium/benzophenone ketyl prior to its use. NMR spectra were recorded on a PMX-60MHz instrument using TMS as internal standard. IR spectra were determined on a PE-683 spectrometer.

General procedure for preparation of thiolesters:

A solution of diphenyl disulfide(1mmol) in THF (1ml) was added by syringe to a deep blue solution of SmI_2(3mmol) in THF(25ml) at room temperature under an inert atmosphere of nitrogen. The deep blue colour of the solution gradually became brown within 1h. Acyl chloride(3mmol) in THF(1ml) was then added by syringe to the mixture and stirred at room temperature under nitrogen atmosphere for 1h. The reaction solution was diluted with ether(50ml) and filtered. The filtrate was washed with water(30mlx3). The organic layer was dried over $MgSO_4$, and the solvent was removed in vacuo. The crude product was purified by preparative TLC on silica gel(cyclohexane as eluent). The results are summarized in Table 1.

Acknowledgement. We are grateful to the National Natural Science Foundation of China for financial support.

References

1. Yoshiyuki, O., Masanori, T., Masaaki, K. and Yoshio, I., Uakromol. Chem. Rapid Commun., 1991, 12, 465.
2. El-Zohry, M.F., El-Khawaga, A.M., Ismail, M.T. and Abdel-Wahab, A.A., Phosphorus Sulfur Silicon Relat. Elem., 1991, 61, 373.
3. Waldemar, A. and Lazaros, H., Tetrahedron Lett., 1992, 33, 469.
4. Isao, F., Naomi, T. and Shizunobu, H., Chem. Express, 1989, 4, 337.
5. Gauthier, J.Y., Bourdon, F. and Young, N., Tetrahedron Lett., 1986, 27, 15.
6. Giovanni, P., Marino, N., Giacomo, G. and Marcos, F., Tetrahedron, 1989, 45, 7411.
7. Gulevich, Y.V., Bumagin, N.A. and Beletskaya, Z.P., Zh. Org. Khim., 1988, 24, 2126.
8. Ramon, B., Jordi, G. and Jaume, V., Synthesis, 1989, 4, 305.
9. Shlomo, A. and Howard, A., Organometallics, 1986, 5, 596.
10. Cardellicchio, C., Fiandanese, V., Marchese, G. and Ronzini, L., Tetrahedron Lett., 1985, 26, 3595.
11. Saeed, A. and Javed, I., Tetrahedron Lett., 1986, 27, 3791.

12. Girard, P., Namy, J.L. and Kagan, H.B., J. Am. Chem. Soc., 1980, 102, 2693.

13. Zhang, Y., Lin, R. and Liu, T., Acta Chimica Sinica, 1990, 48, 577.

14. Kamochi, Y. and Kudo, T., Tetrahedron Lett., 1991, 32, 3511.

15. Sasaki, M., Collin, J. and Kagan, H.B., Tetrahedron Lett., 1991, 32, 2493.

(Received in The Netherlands 20 July 1993)