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REDUCTIVE CLEAVAGE OF Se-Si BOND IN ARYLSELENOTRIMETHYLSILANE: A NOVEL METHOD FOR THE SYNTHESIS OF SELENOESTERS

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ABSTRACT: Arylselenotrimethylsilane is reduced by samarium diiodide to yield samarium arylselenolates. These new selenolate anion species reacted smoothly with acyl halides to give selenoesters.

Samarium diiodide is a powerful one electron transfer reductant¹. It has wildly been applied in organic synthesis^{2,3}. Our previous work on the reductive cleavage of C-S, S-S, Se-Se, Te-Te and S-Si bond with SmI_2^{4-7} has led us to investigate the reductive cleavage of Se-Si bond by SmI_2 .

Organoselenium compounds have attacted considerable interest as reagents and intermediates in organic synthesis recently⁸⁻¹⁰. Selencesters are useful intermediates in the synthesis of natural compounds¹¹, but, relatively few syntheses of selencesters have been described. A useful approach to the synthesis of selencesters is the reaction of acyl halide with selencl^{11,12}. Another approach is based on the alkylation of selence ion¹³. These methods have been applied successfully to the synthesis of selencesters.

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Here we wish to report that SmI_2 reduces arylselenotrimethylsilane to samarium arylselenolate under nitrogen atmosphere. The new selenolate anion species react with acyl halides mildly to give selenoesters in good yield under neutral condition (scheme).

Scheme

ArSe-SiMe₃
$$\xrightarrow{SmI_2}$$
 ArSeSmI₂ \xrightarrow{RCOCl} RCO-SeAr

Experimental

The solvent tetrahydrofuran was freshly distilled from sodum/benzophenone ketyl prior to its use. H NMR spectra were recorded on a PMX-60MHzinstrument using TMS as internal standard. IR spectra were determined on a PE-683 spectrometer. MS were determined on Maghum instrument. Element analyses were carried out using Carlo Erba 1106 instrument.

General procedure: A solution of arylselenotrimethylsilane (1mmol) in THF (1ml) was added by syringe to a deep blue solution of $SmI_2(2, 2mmol)$ in THF (10ml) at refluxing temperature under an atmosphere of nitrogen. The deep blue colour of the solution gradually became brown within 3 h, which showed that the Se—Si bond had been reductively cleaved by SmI_2 and that the samarium arylselenolate (ArSeSmI₂) had been generated. Acyl chloride(1, 5mmol) in THF (1ml) was then added by syringe to the mixture and stirred at room temperature under nitrogen atmosphere for 1 h. A dilute solution of HCl and ether were added. The organic layer was washed with water ($20ml \times 2$) and dried over anhydrous Na₂SO₄. The solvent was removed in vacuo. The crude product was purified by preparative TLC on silica gel (light pertroleum: ethyl acetate=100 : 1 as eluent).

Isolated yields and data for products

PhCO-SePh⁶, yield, 89%; mp 39-40°C (lit⁶, 39-40°C); IR (C=O), 1695 cm⁻¹; ¹H NMR, 7.77-7.93(2H,m), 7.23-7.57(8H,m), ppm.

 $CH_{3}CO - SePh^{6}$, yield, 85%; Oil; IR (C = O), 1740 cm⁻¹; ¹H NMR, 7. 40 (5H,m), 2. 39(3H,s), ppm.

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 $CH_3(CH_2)_4CO-SePh^{14}$, yield, 83%: Oil; IR(C=O), 1735 cm⁻¹; H NMR, 7. 33(5H,m), 2. 60(2H,t), 1. 10-1. 40(6H,m), 0. 87(3H,t), ppm.

PhCO—Se C₆H₄CH₃-o¹⁵, yield, 87%; Oil; IR(C=O), 1700 cm⁻¹, ⁴H NMR, 7.80–7.96(2H,m), 7.20–7.50(7H,m), 2.35(3H,s), ppm.

p-BrC₆H₄CO-SeC₆H₄CH₃-o⁹, yield, 87%; Oil; IR(C=O), 1700 cm⁻¹; ¹H NMR, 7. 60-7. 90(2H,m), 7. 20-7. 50(6H,m), 2. 33(3H,s), ppm.

 $CH_{3}CO - SeC_{6}H_{4}CH_{3}-o^{15}$, yield, 81%; Oil; IR (C = O), 1740 cm⁻¹; ¹H NMR, 7.00-7.53(4H,m), 2.35(3H,s), 2.23(3H,s), ppm.

 $CH_{3}(CH_{2})_{4}CO-SeC_{6}H_{4}CH_{3}-o^{15}$, yield, $82\frac{9}{16}$; Oil; IR(C=O), 1740 cm⁻¹; ¹H NMR, 7. 00-7. 43(4H,m), 2. 53(2H,t), 2. 23(3H,s), 1. 13-1. 43 (6H,m), 0. 85(3H,t), ppm.

p-BrC₆H₄CO—SePh, yield, 86%; mp 94—95°C; IR(C=O), 1659 cm⁻¹; ^h NMR, 7.63—7.80(2H,m), 7.30—7.53(7H,m),ppm; m/z(M⁺), 340; Anal. Calc. for C₁₃H₉BrOSe₁C 45.83, H 2.68; found C 45.69, H 2.67.

 $CH_{3}(CH_{2})_{10}CO-SePh$, yield, 80%; Oil; IR(C=O), 1753 cm⁻¹; H NMR, 7. 33(5H,m) 2. 60(2H,t), 1. 10–1. 47 (18H,m), 0. 84 (3H,t), ppm; m/z (M⁺), 339; Anal. Calc. for $C_{18}H_{28}OSe$: C 63. 70, H 8. 32; found: C 63. 56, H 8. 23.

CH₃(CH₂)₁₀CO-SeC₆H₄CH₃-o, yield, 80%; Oil; IR(C=O), 1740 cm⁻¹; ¹H NMR, 7. 03-7. 47(4H,m), 2. 57(2H,t), 2. 23(3H,s), 1. 13-1. 45 (18H,m), 0. 83(3H,t), ppm. m/z(M⁺), 353; Anal. Calc. for C₁₉H₃₀OSe; C 64. 58, H 8. 55; found: C 64. 45, H 8. 70.

In summary, a novel method for the preparation of selencester has been provided. The advantages of the present procedure are single product, simple manipulation, mild and neatral conditions. Acknowledgement: We are grateful to the National Natural Science Foundation of China and the Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, for financial support.

References

- Girard, P., Namy, J.L. and Kagan, H.B., J. Am. Chem. Soc., 1980, 102, 2693.
- 2. Molander, G. A., Chem. Rev., 1992, 92, 29.
- 3. Molander, G. A. and Harris, C. R., Chem. Rev., 1996, 96. 307.
- Guo. H. Y., Ye, S. M., Wang, J. Q. and Zhang, Y. M., J. Chem Res., 1997, 3, 114.
- 5. Jia, X. S. and Zhang, Y. M., Synth. Commun., 1994, 24, 787.
- Zhang, Y. M., Yu, Y. P. and Lin, R. H., Synth. Commun., 1993, 23, 189.
- 7. Zhang, S. L. and Zhang, Y. M., J. Chem. Res., 1998, 1, 48.
- 8. Reich, H. J., Acc. Chem. Res., 1979, 12, 22.
- 9. Kato, S., Murai, T. and Masura, M., Org. Prep. Proced. Int., 1986, 18, 369.
- 10. Perrick, L. T., Tetrahedron, 1978, 34, 1049.
- Griceo, P. A., Yokyama, Y. and Willians, J. Org. Chem., 1978, 43, 1283.
- Kato, S., Kabuta, H., Ishiara, H. and Murai, T., Synthesis, 1985, 5, 520.
- Ishihara, S. and Hirabayashi, H., Bull. Chem. Soc. Jpn., 1977, 50, 3007.
- 14. Bates, G., Diakur, T. and Masamure, S., *Tetrahedron Lett.*, 1976, 49. 4423.
- Bajwiret, M. and Gabriel, L., Spectrochim Acta, PartA, 1982, 38A, 575.

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