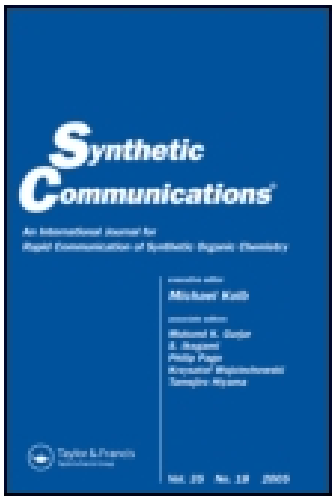

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Hua-Rong Zhao [a] , Xin-Jian Zhao [b] & Xian Huang [a]

[a] Department of Chemistry , Zhejiang University , Hangzhou, 310027, P.R. China

[b] Zhejiang Institute of Calibaration and Testing for Technical Superision , Hangzhou, 310013, P.R. China

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SELENIUM TRANSFER REACTION OF PRIMARY SELENOAMIDES: A NOVEL METHOD FOR THE SYNTHESIS OF DIACYLSELENIDES FROM ACYL CHLORIDES

Hua-Rong Zhao,[1,*] Xin-Jian Zhao,[2] and Xian Huang[1]

[1]Department of Chemistry, Zhejiang University, Hangzhou, 310027, P.R. China
[2]Zhejiang Institute of Calibaration and Testing for Technical Superision, Hangzhou, 310013, P.R. China

ABSTRACT

Diacyl selenides were afford in excent yields by reaction of primary selenoamides with acyl chlorides in chloroform. A possible mechanism is discussed.

Primary selenoamides are rather important intermediates in organic synthesis.[1] They have been utilized in the preparation of nitrogen- and selenium-containing heterocyles, such as selenazoles,[2,3] 1,2,4-diselenazolines,[4] 1,2,4-selenadiazoles[5,6] and 1,3,5-oxaselenazines.[7] Besides, selenoamides are also useful for preparation of other selenium-containing compounds such as selenoesters.[8] However synthetic application of

*Corresponding author.

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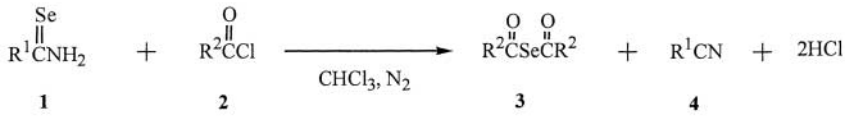
selenoamides has been greatly restricted due to its instability and difficulty in preparation. We have reported a convenient synthesis of primary selenoamides by the reaction of aryl nitriles with sodium hydroselenide in ethanol[9] and have also reported that selenobenzamides could react with reactive halides to afford alkyl diselenides as selenium transfer reagents.[10–11] We continued investigating the reactivity of primary selenoamides toward acyl chloride expecting the reaction would produce acyl diselenides. When aryl selenoamides were treated with 1 or 2 equimolar amount of alkyl halides in chloroform at 60°C, in surprise diacyl diselenides could not be found and diacyl selenides (**3a–f**) was formed (Table 1) in good yields instead (Sch. 1). Byproducts aryl nitriles were isolated.

A possible mechanism of above reaction is shown in Sch. 2 that the selenium of selenoamides attacked acyl chlorides twice and formed the intermediate **6**, which then decomposed into diacyl selenides **3** and nitriles **4**.

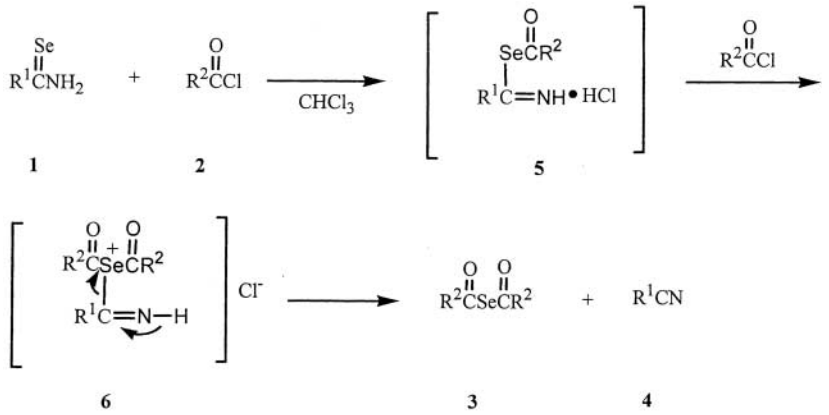
Diacyl selenides are good acylating agents in organic synthesis.[12] A variety of synthetic methods for diacyl selenides have been reported in literature such as the pyrolysis of selenobenzoic acid,[13] the deselenylation of diacyl diselenides using triphenylphosphine,[14] the reaction of aliphatic acyl chlorides with hydrogen selenide,[15] reduction of selenium by carbon monoxide and following reaction with acyl halides.[16] However, those

Table 1. Preparation of Diacyl Selenides from Selenoamides and Acyl Chlorides

Entry	R^1	R^2	Product	Time (min)	Isolated Yield (%)
1	C_6H_5	C_6H_5	**3a**	60	80
2	3-MeC_6H_4	C_6H_5	**3a**	60	82
3	C_6H_5	4-$MeOC_6H_4$	**3b**	45	85
4	3-MeC_6H_4	4-$MeOC_6H_5$	**3b**	40	87
5	C_6H_5	4-$CH_3C_6H_4$	**3c**	60	81
6	C_6H_5	4-ClC_6H_4	**3d**	90	75
7	C_6H_5	3-ClC_6H_4	**3e**	120	69
8	C_6H_5	2-Furanyl	**3f**	40	80



Scheme 1.



Scheme 2.

methods have the disadvantages of using harmful gases, being in strict conditions, multiple steps or long reaction time. The present method for preparation of diacyl selenides has the advantage of easily available starting materials, simple operation and mild condition compared with them.

EXPERIMENTAL

Melting points were recorded on an electrothermal micro melting apparatus and are not corrected. IR spectra were recorded on a PE-683 spectrometer, and ^{1}H-NMR spectra were obtained on a JEOL-60S_1 spectrometer with TMS as an internal standard. Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer.

General Procedure for the Reaction

To a solution of selenobenzoamide (1.0 mmol) in chloroform (30 mL) under N_2 atmosphere was added benzoyl chloride (2.5 mmol) slowly at room temperature. After the completion of addition, the mixture was stirred at 60°C for 1 h to give a light yellow colour solution. Then the reaction mixture was washed with water (15 mL), 10% Na_2CO_3 (15 mL × 2) and water (20 mL), dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was purified by preparative thin layer chromatography on

silica gel (cyclohexane–acetic acid as an eluent), affording pure solid **3a** in 80% yield.

3a:[14] M.p. 61–62°C (lit: 61.5–62.3°C). IR: ν_{max} (cm^{-1}) 1736, 1683 (C=O), 1603, 1495. ^{1}H-NMR: δ 7.30–8.00 (m, 10H).

3b:[14] M.p. 77–78°C (lit: 77.8–80.2°C). IR: ν_{max} (cm^{-1}) 1737, 1688 (C=O), 1608, 1512. ^{1}H-NMR: δ 3.83 (s, 6H), 6.78–8.04 (m, 8H).

3c:[14] M.p. 89–90.5°C (lit: 90–91°C). IR: ν_{max} (cm^{-1}) 1741, 1692 (C=O), 1610, 1510. ^{1}H-NMR: δ 2.4 (s, 6H), 7.10–8.00 (m, 8H).

3d:[14] M.p. 117–118°C (lit: 118.5–120°C). IR: ν_{max} (cm^{-1}) 1735, 1687 (C=O), 1599, 1492. ^{1}H-NMR: δ 7.33–8.03 (m, 8H).

3e:[12] M.p. 91–92°C (lit: 92–93°C). IR: ν_{max} (cm^{-1}) 1735, 1723 (C=O), 1578, 1481. ^{1}H-NMR: δ 7.40–7.93 (m, 8H).

3f: M.p. 46–47°C. IR: ν_{max} (cm^{-1}) 1737, 1690 (C=O), 1570, 1465. ^{1}H-NMR: δ 6.55–7.03 (m, 2H), 7.27–7.43 (d, 2H), 7.63–7.77 (d, 2H).

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