

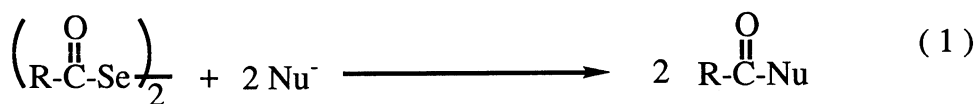
Bis(acyl) Diselenides as Convenient Acylating Reagents

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Bis(acyl) diselenides serve as useful acylating reagents for amines, alcohols, thiols, and organocopper compounds such as cuprate.

Although bis(acyl) diselenides are expected to be synthetically promising acylating agents because of the good leaving character of the selenium moiety, little is known regarding the utilization of these diselenides in organic synthesis.¹⁾ We have investigated the reaction of bis(acyl) diselenides with a variety of nucleophiles and have found that both acyl groups of diselenides can be efficiently transferred into several nucleophiles under mild conditions (Eq. 1).

R : Ph, C₁₇H₃₅Nucleophiles : RR'NH, C₂H₅ONa, PhSNa, (C₄H₉)₂CuLi

For instance, to a solution of diethylamine (2 mmol) in benzene (5 mL) was added slowly the solution of bis(benzoyl) diselenide (1 mmol)²⁾ in benzene (5 mL) and the mixture was stirred at 25 °C for 10 min under air. After the reaction was complete, elemental selenium deposited was removed by filtration and the solvent was evaporated. The residue was purified by column chromatography on silica gel to afford 0.34 g (1.92 mmol, 96% based on diethylamine) of N,N-diethylbenzamide.

Results obtained by the reaction of bis(acyl) diselenide with some nucleophiles were summarized in Table 1.³⁾ In the cases of primary and secondary amines, the corresponding amide derivatives were obtained in excellent yields (runs 1-8). Sodium ethoxide (NaOEt), sodium benzenethiolate (NaSPh),⁴⁾ and lithium dibutylcuprate were found to react with bis(acyl) diselenide to give the corresponding ester, thiolester, and ketone in good yields, respectively (runs 9-14).

Characteristic features of this reaction are as follows: (i) Both acyl groups of diselenides are effectively utilized. (ii) The reaction conditions are mild. (iii) The yields are generally high. (iv) The reactions are clean and the workup for isolation of the products is very simple.

Although the details of the reaction mechanism are not clear yet, the

present reaction may involve the attack of nucleophiles at the carbonyl carbon of diselenide.^{5,6)}

Table 1. Reaction of Bis(acyl) Diselenide with Nucleophiles^{a)}

Run	Diselenide	Nucleophile	Product	Yield, % ^{b),c)}
1	$\left(\text{Ph}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{Se} \right)_2$ (1)	PhCH ₂ NH ₂	PhCONHCH ₂ Ph	88
2	(1)	n-C ₄ H ₉ NH ₂	PhCONHC ₄ H ₉ -n	94
3	(1)	s-C ₄ H ₉ NH ₂	PhCONHC ₄ H ₉ -s	90
4	(1)	t-C ₄ H ₉ NH ₂	PhCONHC ₄ H ₉ -t	94
5	(1)	c-C ₆ H ₁₁ NH ₂	PhCONHC ₆ H ₁₁ -c	92
6	(1)	(C ₂ H ₅) ₂ NH	PhCON(C ₂ H ₅) ₂	96
7 ^{d)}	(1)	PhNH ₂	PhCONHPh	94
8	$\left(\text{C}_{17}\text{H}_{35}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{Se} \right)_2$ (2)	PhCH ₂ NH ₂	C ₁₇ H ₃₅ CONHCH ₂ Ph	88
9 ^{e)}	(1)	C ₂ H ₅ ONa	PhCOOC ₂ H ₅	87
10 ^{e)}	(2)	C ₂ H ₅ ONa	C ₁₇ H ₃₅ COOC ₂ H ₅	85
11 ^{f)}	(1)	PhSNa	PhCOSPh	86
12 ^{f)}	(2)	PhSNa	C ₁₇ H ₃₅ COSPh	90
13	(1)	(C ₄ H ₉) ₂ CuLi	PhCOC ₄ H ₉	79
14	(2)	(C ₄ H ₉) ₂ CuLi	C ₁₇ H ₃₅ COC ₄ H ₉	82

a) Reaction conditions: Bis(acyl) diselenide (1 mmol), nucleophile (2 mmol), benzene (10 mL) at 25 °C for 10 min. b) Isolated yield. c) Based on nucleophile. d) 80 °C, 3 h. e) C₂H₅OH was used as a cosolvent. f) THF was used as a cosolvent.

References

- 1) H. Ishihara, S. Sato, and Y. Hirabayashi, Bull. Chem. Soc. Jpn., 50, 3007 (1977); H. Ishihara, S. Muto, and S. Kato, Synthesis, 1986, 128.
- 2) Some synthetic methods have been developed. See: S. Kato, T. Murai, and M. Ishida, Org. Prep. Proc. Int., 18, 369 (1986) and references cited therein.
- 3) Spectroscopic data were in good accord with those of authentic sample.
- 4) Sodium benzenethiolate was prepared from diphenyl disulfide and sodium in THF.
- 5) Alternative path involving Se-attack of nucleophiles is considered. See: S. Fujiwara, N. Miyoshi, A. Ogawa, N. Kambe, and N. Sonoda, J. Phys. Org. Chem., 2, 359 (1989).
- 6) It has already been reported that the reaction of bis(benzoyl) diselenide with piperidine gave the mixture of piperidinium selenobenzoate and amide. See Ref. 1b.

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