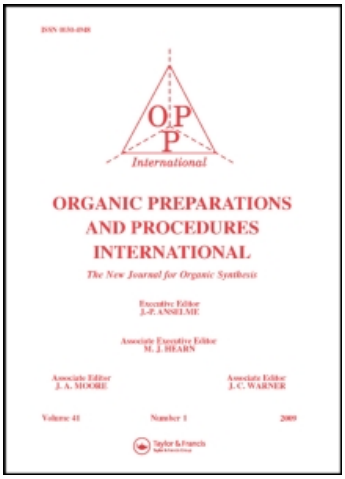

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A NEW METHOD FOR THE SYNTHESIS OF DIACYL SELENIDES

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OPPI BRIEFS

A NEW METHOD FOR THE SYNTHESIS OF DIACYL SELENIDES

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Organic selenides have attracted considerable attention in the last few years.[1-3] In contrast, only few studies of diacyl selenides have been reported. Diacyl selenides have been obtained by the pyrolysis of selenobenzoic acid,[4] the deselenylation of diacyl diselenides using triphenylphosphine[5] and the reaction of aliphatic acyl chlorides with hydrogen selenide.[4,6] We now describe a new approach for the synthesis of diacyl selenides.

Thompson *et al.* have utilized alkali metal to reduce selenium powder to Se^{2-} species and investigated the reaction of Se^{2-} species with alkyl bromides.[7] Samarium diiodide (SmI_2) is a strong one-electron transfer reducing reagent and has been widely used in organic synthesis.[8a-d] It reduces elemental selenium to Se^{2-} in THF with excellent selectivity.[8e] We found that addition of hexamethylphosphoramide (HMPA) and amorphous selenium to the deep blue solution of SmI_2 in THF resulted in a rapid color change of the solution to dark brown, showing that amorphous selenium had been reduced by SmI_2. But metallic selenium could be reduced only with difficulty under the same conditions. The acylation of the Se^{2-} species with acyl chlorides at room temperature provided diacyl selenides (**1a-f**) in high yields.

$$Se + SmI_2 \xrightarrow[THF]{HMPA} Se^{2-} \xrightarrow{RCOCl} RCO-Se-COR$$

a) C_6H_4 b) R = 4-$MeOC_6H_4$ c) R = 4-ClC_6H_4 d) R = 3-ClC_6H_4
e) R = $C_6H_5CH{=}CH$ f) $CH_3(CH_2)_{10}$

The advantages of the method are excellent selectivity, mild and neutral conditions and simple operation.

EXPERIMENTAL SECTION

Mps are uncorrected. Elemental analyses were carried out using a Carlo Erba 1106 instrument. IR spectra were recorded on a PE-683 Spectrometer using KBr discs. ^1H NMR spectra were obtained with a PMX-60 spectrometer in $CDCl_3$ solution using TMS as internal standard. Chemical shifts are expressed in ppm.

General Procedure for the Synthesis of Diacyl Selenides (1a-f).- HMPA (1 mL) and amorphous selenium (79 mg, 1 mmol) were added successively to a solution of SmI_2 (2.2 mmol) in THF (22 mL) at room temperature under nitrogen. The deep blue color of the solution disappeared immediately and the solution turned to dark brown. The mixture was stirred for 2h under reflux. After the reaction mixture was cooled to room temperature, the acyl chloride (3 mmol) in THF (2 mL) was added with a syringe. The mixture was stirred at room temperature under nitrogen for 2 hrs. The reaction mixture was then diluted with ether (60 mL) and filtered. The ethereal filtrate was washed with water (3 x 40 mL) and dried over $MgSO_4$, and solvent was removed by evaporation under reduced pressure. The product was isolated by preparative TLC on silica gel (cyclohexane-ethyl acetate as eluent). The spectral and analytical data of the product are as follows.

Compound 1a: Yield 90%; mp. 62-63°, lit.[5] mp. 61.5-62.3°. IR: 1752, 1697 (C=O), 1603, 1495 cm^{-1}. ^1H NMR: δ 7.38-8.00 (10H, m, ArH).

Compound 1b: Yield 89%; mp. 77-78°, lit.[5] mp. 77.8-80.2°. IR: 1705, 1665 (C=O), 1608, 1512 cm^{-1}. 1H NMR: δ 3.80 (6H, 8, OCH_3), 6-75-7.93 (8H, m, ArH).

Compound 1c: Yield 92%; mp. 118-119°, lit.[5] mp. 118.5-120°. IR: 1735, 1706 (O=O), 1602, 1495 cm^{-1}. ^1H NMR: δ 7.37-8.07 (8H, m, ArH).

Compound 1d: Yield 81%; mp. 92-93°. IR: 1735, 1721 (C=O), 1578, 1480 cm^{-1}. ^1H NMR: δ 7.47-7.95 (8H, m, ArH).

Anal. Calcd for $C_{14}H_8Cl_2O_2Se$: C, 46.96; H, 2.25. Found: C, 46-.70; H, 2.36

Compound 1e: Yield 94%; mp. 103-104°. IR: 1710-1700 (C=O), 1620 (C=C), 1636, 1502 cm^{-1}. ^1H NMR: δ 6.73-7.80 (14H, m, CH=CH and ArH).

Anal. Calcd for $C_{18}H_{14}O_2Se$: C, 63.35; H, 4.14. Found: C, 63.51; H, 4.03

Compound 1f: Yield 93%; mp. 68-69°. IR: 2970, 2930, 2860, 1744 (C=O) cm^{-1}. ^1H NMR: δ 0.87 (6H, t, J = 4.2 Hz, CH_3), 1.10-1.90 (36H, m, CH_2), 2.80 (4H, t, J = 7.8 Hz, CH_2).

Anal. Calcd for $C_{24}H_{46}O_2Se$: C, 64.69; H, 10.41. Found: C, 64.58; H, 10.37

Preparative Scale Synthesis of 1c and 1e. General Procedure.- HMPA (1 mL) and amorphous selenium (316 mg, 4 mmol) were added successively to the solution of SmI_2 (8.2 mmol) in THF (50 mL) at room temperature under nitrogen. After the solution was stirred for 4 min, the deep blue color of the solution disappeared and became dark brown. Stirring was continued for 2 hrs under reflux. Then the reaction mixture was cooled to room temperature and 4-chlorobenzoyl chloride or cinnamoyl chloride (9 mmol) in THF (2 mL) was added with a syringe. The mixture was stirred at room temperature under nitrogen for 2 hrs and diluted with ether (100 mL) and filtered. The ethereal filtrate was washed with water (4 x 50 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave a solid which was purified by recrystallization from hexane-ether to give **1c** (1.29g, 90%), mp. 118-120° or **1e** (1.18g, 87%), mp. 103-104° respectively.

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SYNTHESIS OF N-METHYLATED QUINOLONES

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Quinolones have received considerable attention as useful antibacterial agents.[1] Over the last few years, we have endeavored to develop new compounds of potential antimalarial activity. Although recent emphasis has been placed on vaccine development, this approach has not yet contributed to the control of this endemia.[2] The need for new drugs which are effective against drug-resistant parasites is obvious. We now report a methodology for the rapid synthesis of new N-methylated quinolones.

The starting 2-methylthio-3-cyanoquinolones **1**, easily prepared in high yields from the corresponding anilines with ketene dithioacetal,[3] were treated with methyl iodide and potassium carbonate in refluxing DMF to give the N-methylquinolones **2**; their structure was established from the spectral