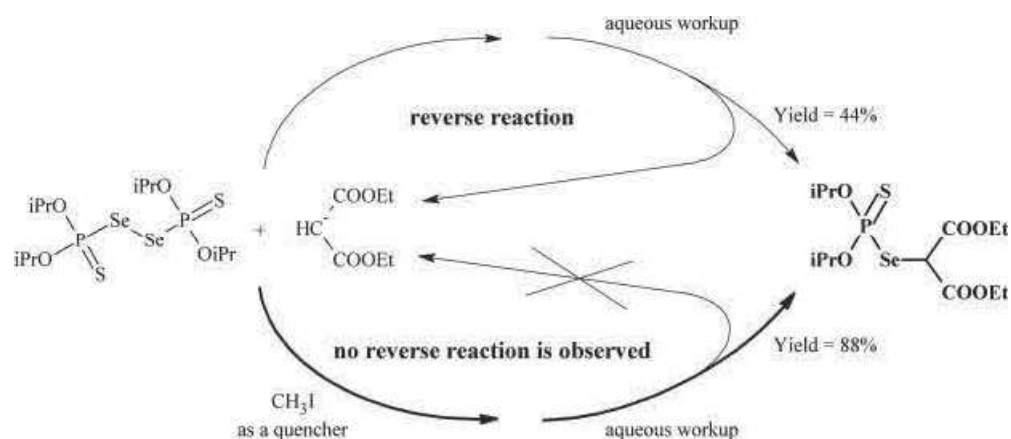


EFFICIENT SELENENYLATION OF MALONATES USING BIS(PHOSPHOROTHIOYL) DISELENIDE

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GRAPHICAL ABSTRACT



Abstract Bis(*O,O*-diisopropoxyphosphinothioyl) diselenide reacts readily and quickly with the sodium salt of malonates to give quantitatively stable sodium 2-(*O,O*-diisopropyl phosphorothioselenenyl)propanedioates. No traces of the corresponding *C,C*-diselenenylation products were detected. A standard aqueous workup procedure affords the products, albeit in poor yield (about 45%). It was proved that the reaction is reversible due to the presence of nucleophilic sodium *O,O*-diisopropylphosphoroselenothioate in the reaction mixture. The reaction conducted with methyl iodide as a coreactant significantly improved the yield of the selenenylated product up to 88%. In contrast to the respective *C*-(phenylselenenyl)malonate that undergoes thermal disproportionation, the diethyl 2-(*O,O*-diisopropyl phosphorothioselenenyl)propanedioate is stable and remains unchanged even after prolonged heating in boiling toluene. The mechanism of phosphorothioselenenylation of malonates is described.

Keywords *C*-nucleophiles; electrophilic diselenides; phosphorothioselenoic acid *Se*-esters; selenenylation

INTRODUCTION

Electrophilic selenenylation, as the *C*-*Se* bond formation reaction, is usually carried out with the use of phenylselenenyl bromide, which is generated from diphenyl diselenide in situ. As was shown by Byers and Lane,^{1b} the phenylselenenylation of

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