Nitroallyl-halogenide und -ester als effiziente Verknüpfungsreagenzien

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Nitroallyl-halogenide und -ester als effiziente Verknüpfungsreagenzien

Abhandlung

zur Erlangung des Titels

eines

Doktors der Naturwissenschaften

der

EIDGENÖSSISCHEN TECHNISCHEN HOCHSCHULE

ZUERICH

vorgelegt von

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Angenommen auf Antrag von

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D. SUMMARY

In this work we have shown that NPP (9b) can add stepwise two different nucleophiles \( \text{Nu}^1 \) and \( \text{Nu}^2 \). The great variety of nucleophiles used demonstrates the broad applicability of the method. Since the nitro-function can be easily transformed into a carbonyl-function, reduced to an amine, or replaced by a hydrogen atom, we can consider the NPP as a multi-coupling reagent which corresponds to the synthons \( a_1 - a_5 \). Diels-Alder reactions as well as the new HNO\(_2\)-elimination from some cycloadducts enhanced the synthetic utility of NPP.

\[
\begin{align*}
\text{NH}_2 & \quad \text{NO}_2 \\
\text{O} & \quad \text{Ph}
\end{align*}
\]

The phenyl-substituted NPP \( 14 \) shows a similar reactivity but up to now the chemistry has not been completely explored.
The nitro olefines \( \underline{5} \) undergoes a smooth Michael-addition and furnishes highly functionalised nitroalkanes. The cyclic derivates \( \underline{19} \) show a far higher reactivity than the sluggish nitrocyclohexene.

\[
\text{NO}_2
\]

19b: \( X = \text{OCOtert-Bu} \)

19c: \( X = \text{Cl} \)

In addition we found a novel mild method for the synthesis of nitroolefines as well as a new class of compounds, the stannylnitronates.