Nitroallyl-halogenide und -ester als effiziente Verknüpfungsreagenzien

Abhandlung

zur Erlangung des Titels

eines

Doktors der Naturwissenschaften

der

EIDGENOESSISCHEN TECHNISCHEN HOCHSCHULE

ZUERICH

vorgelegt von

PAUL KNOCHEL

Dipl. Ing.-Chem. ENSCS

geboren am 15. November 1955

von Strassburg (Frankreich)

Angenommen auf Antrag von

Prof. Dr. D. Seebach, Referent

Prof. Dr. A. Eschenmoser, Korreferent

1982
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 121 - 125. Diels-Alder reactions as well as the new $\text{HNO}_2$-elimination from some cycloadducts enhanced the synthetic utility of NPP.

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

\[
\begin{align*}
5 & \quad \text{Hal} - \text{NO}_2 \\
19b & \quad X = \text{OCO}_{\text{tert-Bu}} \\
19c & \quad X = \text{Cl}
\end{align*}
\]

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