Novel Syntheses of Functionalized Heterocyclic and Carbocyclic Compounds using KCN or KSCN

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In view of our general interest in reactions involving zwitterionic species [1], we report on the one-pot reactions involving KSCN or KCN. The KSCN-catalyzed reaction of dialkyl acetylenedicarboxylates with pentane-2,4-dione in acetone, led to dialkyl 2-(1-acetyl-2-oxopropyl)-2-butenedioates in excellent yields. When these reactions were carried out in butane-2-one, dialkyl 4-oxo-2,3-dihydro-2,3-furandicarboxylates were obtained exclusively. This difference in reactivity is discussed in terms of the possibility of cationic exchange in butane-2-one.

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\begin{align*}
\text{RO}_2\text{C} & \quad \text{CHCO}_2\text{R} \\
\text{Acetone, r.t.} & \quad \text{CO}_2\text{R} \\
\end{align*}
\]

94-95%

The reaction of dialkyl acetylenedicarboxylates with arylidenemalononitriles in the presence of KSCN in acetonitrile leads to a mixture of (3E)-dialkyl 3-(arylideneamino)-5,5-dicyano-4-arylcyclopenta-1,3-diene-1,2-dicarboxylates and dialkyl 5-cyano-4-arylthiophene-2,3-dicarboxylates. When these reactions were performed in the presence of KCN, only the functionalized 5,5-dicyanocyclopenta-1,3-dienes are obtained.

\[
\begin{align*}
\text{Ar} & \quad \text{CN} \\
\text{CN} & \quad \text{CO}_2\text{R} \\
\text{MeCN, r.t.} & \quad \text{Ar} \\
\end{align*}
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REFERENCES