

Functionalization of Sulfoxonium Ylides with molecular iodine: Synthesis of α - (Xanthates, Dithiocarbamates, Thiocyanato)- α -Carbonyl Sulfoxonium Ylides

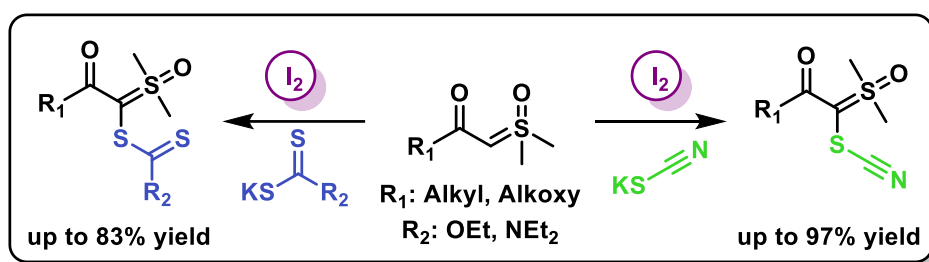
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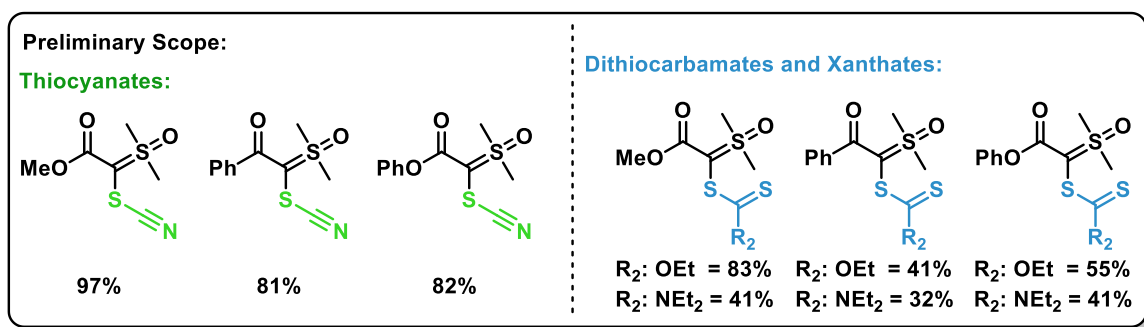
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ABSTRACT



Sulfoxonium ylides have captivated the attention of chemists since their emergence in the 1960s¹, gaining even greater interest in recent years². This attention has brought forth significant advancements in ylide chemistry, including known reactions with molecular iodine³. Here, we present a novel and distinctive method for functionalizing both ester and keto sulfoxonium ylides using molecular iodine and sulfur-based nucleophiles such as xanthates, dithiocarbamates, and thiocyanates. This approach yields α - (xanthates, dithiocarbamates, thiocyanato)- α -carbonyl sulfoxonium ylides. The functionalization is a topic of interest as these reactions are uncommon, and new methods to synthesize more complex ylides are still necessary⁴. Furthermore, both dithiocarbamates and thiocyanates are reported to be present in different molecules with biological activity⁵. Nine examples were prepared in a preliminary study, achieving yields of up to 97%⁶. Additionally, experiments using TEMPO suggests a radical mechanism, which provides insight into the formation of functionalized sulfoxonium ylides rather than functionalized ketones.



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REFERENCES

- ¹ Eur. J. Org. Chem., 2013: 5005-5016
- ² Chem. Sci., 2022,13, 1192-1209
- ³ A) Eur. J. Org. Chem. 2022, e202200441, B) J. Org. Chem. 2024, 89, 8, 5536–5545
- ⁴ A) Adv. Synth. Cat., 366, 3, 396-401, 2023 B) Green Chem., 2023,25, 7068-7072, C) Tetrahedron Letters 114, 2023, 154244
- ⁵ A) J. Med. Chem. 2000, 43, 1826-1840, B) Pharmaceuticals 2021, 14(11), 1153
- ⁶ Results not yet published. Manuscript in preparation.