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Rapid synthesis of 3-organosulfonyloxy-2-alkanones under microwave irradiation

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Abstract

Remarkably fast microwave assisted direct regiospecific sulfonyloxylation reactions of 2-alkanones in solvent free condition is described.

Keywords: microwave; ketones; regiospecificity; copper.

The microwave assisted organic transformations,[1,2] coupled with under solvent-free conditions,[3] has attracted much attention due to their enhanced reaction rates, cleaner reactions, and ease of manipulation. We have previously reported an efficient method for the regiospecific preparation of various 3-organosulfonyloxy-2-alkanones from the reaction of 2-alkanones with copper(II) organosulfonates in acetonitrile at reflux for 14 h.[4]

It appeared to us of interest to apply the above method to a microwave irradiation system in the absence of the solvent. Accordingly, we have conducted the reaction of copper(II) organosulfonate and 2-alkanones under microwave irradiation for 3 min without solvent. As shown in Table 1, the microwave assisted sulfonyloxylation reactions proceeded very well to give 3-organosulfonyloxy-2-alkanones as a sole product with remarkable rate enhancement. The origin of regioselectivity can be attributed to the formation of thermodynamic enols in the reaction conditions. The yields were comparable to those obtained in conventional heating[4] as indicated in Table 1. It is important to note that sterically hindered α-methine ketone (i.e. 3-methyl-2-butanone), a system known to be difficult to be sulfonyloxylated selectively, afforded the corresponding 3-organosulfonyloxy substituted compounds in good yields. When the same reactions were conducted under conventional heating in acetonitrile at reflux, product formation were not detected in all cases of sulfonyloxylation reactions either by TLC or GC after the reaction period of 16 h. Although sulfonyloxylation of α-methine ketones utilizing enol acetate[5] or silyl enol ether[6] substrates were reported under conventional heating conditions, there is no direct regiospecific sulfonyloxylation method reported to date. This result coupled with drastic reduction of reaction times

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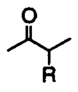
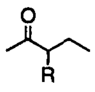
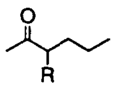
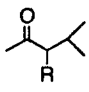
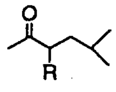
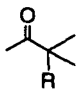
Table 1
Microwave assisted preparations of 3-organosulfonyloxy-2-alkanones

R	Yields of products obtained (%)[a]					
						
-OMs	72(71)	65(66)	67(65)	64(66)	65(70)	60
-OTs	59(63)	63(62)	62(65)	68(67)	62(67)	55
-ONs	80(84)	78(78)	75(81)	75(80)	79(84)	60

[a] Isolated yields of pure product. Yields in parenthesis are obtained in ref. 4 by conventional heating in acetonitrile for 14 h.

under environmentally benign solventless conditions demonstrated a salient advantage of the microwave assisted reaction over the conventional heating conditions.

In conclusion, this microwave assisted process provides a facile and highly efficient method for the regiospecific synthesis of various 3-organosulfonyloxy-2-alkanones.

General procedure: A mixture of 2-alkanone (1.0 mmol) and a copper(II) organosulfonate (3.0 mmol) was irradiated in an open glass scintillation vial (10 mL) in a domestic microwave oven for 3 min. After reaction mixture was allowed to cool, the residue was extracted with dichloromethane (2×50 mL). The extract was washed with water (2×25 mL), dried over $MgSO_4$, and the solvent was evaporated to dryness. The residue was purified by silica gel flash column chromatography using ethyl acetate:hexane (1:3) as eluent to give an analytically pure product.

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