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A Novel Efficient Synthesis of α -Keto Triflates

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A Novel Efficient Synthesis of α -Keto Triflates

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ABSTRACT

The direct and efficient synthesis of α -keto triflates by the reaction of aromatic ketones with thallium(III) triflate is decribed.

Key Words: Ketones; Sulfonates; Thallium(III); Triflates.

The α -keto triflates have attracted considerable attention in both physical and synthetic organic chemistry mainly based on the intrinsically super leaving ability of trifluoromethanesulfonate ester (triflate) group.^[1–3] Preparation of α -keto triflates have been generally achieved by the reaction of α -diazo ketones with trifluoromethanesulfonic acid^[4] or treatment of α -hydroxy ketones with trifluorosulfonic anhydride.^[1,5] In addition, the reaction of trimethylsilyl enol ethers with iodosobenzene in the presence

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of trimethylsilyl trifluoromethane sulfonate had been reported as a convenient alternative for the synthesis of α -keto triflates.^[6] However, the preparation of required α -diazo ketones, α -hyrdoxy ketone, and trimethylsilyl enol ether precursors limits the utility of these reactions. Therefore, development of facile and direct method for the preparation of α -keto triflates will be quite useful for their further synthetic applications. Although there are few reports that deal with the Ritter type reactions of intermediary α -keto triflates with nitrile solvents to give substituted oxazoles,^[7,8] there has been no report on the synthesis and isolation of α -keto triflates formed from ketones. Recognizing the lack of direct method leading to a-keto triflates, we thought that thallium(III) triflate could be appropriate for the introduction of triflate group to alpha position of carbonyl groups. This prediction was based on the successful results obtained from thallium(III) sulfonate mediated α -sulfonyloxylation reaction of ketones.^[9,10] Now we wish to report here, thallium(III) triflate mediated direct synthetic method for the α -keto triflates starting from ketones. Thallium(III) nitrate trihydrate was reacted with trifluoromethanesulfonic acid (3.0 equiv.) in aectonitrile to give thallium(III) triflate. After evaporation of solvent, the residue was dissolved in dichloromethane and a ketone (1.0 equv.) was added to the reaction solution. The reaction of various ketones with thallium(III) triflate at reflux for 2-4h cleanly provided the corresponding α -keto triflates (Sch. 1). Representative examples are shown in Table 1. All of the reactions proceeded smoothly in satisfactory yields. It is important to note that most of the reactions, except for cyclohexanone, are almost quantitative in view of no starting ketones remained after the reactions. The somewhat lower isolated yields are results of the loss of the reactive products during the work-up procedures. All α -keto triflates products exhibited spectral data consistent with assigned structures in the literature.

In conclusion, the present report is the first to deal with the direct conversion of ketones to the corresponding α -keto triflates. We believe this new and facile protocol should find wide utilities particularly for the reaction of α -keto triflates with various nucleophiles.



Scheme 1.

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α-Keto Triflates

Table 1. Synthesis of α -keto triflates from ketones.

Entry	R^1	R^2	Yield (%) ^a
1	Ph	Н	83
2	p-MeC ₆ H ₄	Н	78
3	p-ClC ₆ H ₄	Н	72
4	Ph	CH_3	82
5	p-MeC ₆ H ₄	CH ₃	78
6	p-ClC ₆ H ₄	CH ₃	75
7	-(CH ₂) ₄ -		57

^aIsolated yield.

EXPERIMENTAL

¹H NMR spectra were recorded on a Varian 2000 (300 MHz) spectrometer. IR spectra were recorded with a Jasco FT/IR 5300 spectro-photometer.

General Procedure

Thallium nitrate trihydrate (1.0 mmol) and trifluoromethanesulfonic acid (3.0 mmol) were dissolved in acetonitrile (20 mL) and reaction mixture was stirred for 10 min at room temperature to give thallium(III) triflate. The acetonitrile was evaporated and the resulting residue was dissolved in 20 mL of dichloromethane. To the solution of thallium(III) triflate, a ketone (1.0 mmol) was added and the mixture was stirred for 2–4 h with reflux. The solvent was evaporated and the residue was washed with hexane (2 × 20 mL), cold water (2 × 20 mL), and dried over MgSO₄. After evaporation of the solvent, the residue was purified with column chromatography (silica gel, ethyl acetate:hexane = 1:2) to give pure α -keto triflate.

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