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A METHOD FOR THE REGIOSPECIFIC SYNTHESIS OF ENOL TRIFLATES BY ENOLATE TRAPPING

by
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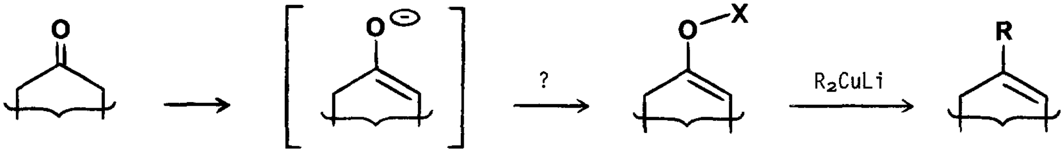
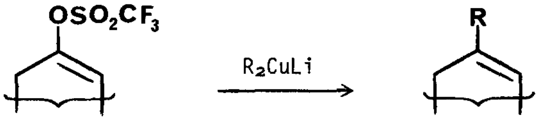
Abstract. Enol triflates can be prepared in high yield from regiospecifically generated enolates by trapping with *N*-phenyltrifluoromethanesulfonimide.

The regiospecific transformation of a ketone into a substituted olefin is a reaction of great potential value in organic synthesis. Such a process allows the conversion of a ketone into a *single* olefin, rather than into the isomeric mixture of olefins that normally results from addition of a Grignard reagent followed by dehydration. Since a large number of methods exist for the regiospecific generation of enolate ions, the ideal olefin synthesis is a two-part one in which an enolate ion is first converted into a stable enol derivative, followed by coupling with a suitable organometallic reagent.

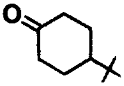
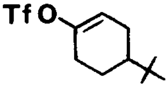
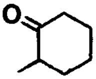
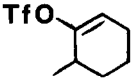
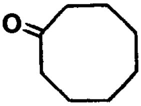
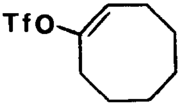
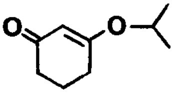
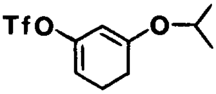
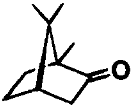
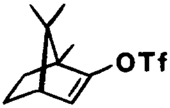
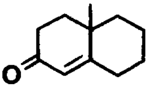
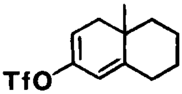
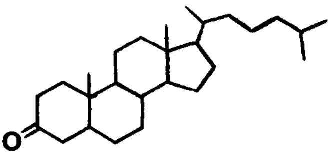
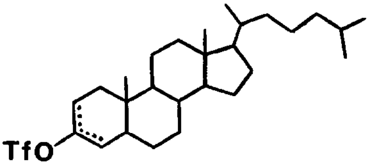


We reported recently[1] a method by which the second of these two steps, the conversion of an enol derivative into an olefin, can be accomplished: enol trifluoromethanesulfonates[2] (enol triflates) undergo regiospecific coupling reaction with lithium diorganocuprates to afford the olefinic products in high yield. A wide variety of diorganocuprate reagents, including alkyl, vinyl, aryl, and cyclopropyl, undergo the coupling reaction.

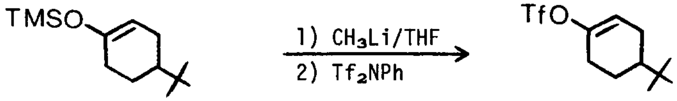


R = alkyl, aryl, vinyl

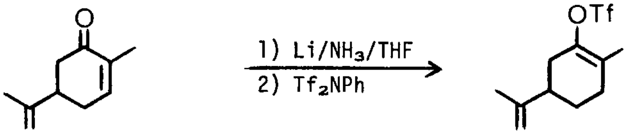
Unfortunately, the *first* step in the process, formation of the enol triflate from a regiospecifically generated enolate ion, cannot be accomplished in good yield by known methods[3]. Triflic anhydride, the most often-used triflating reagent, gives only poor to moderate yields of products on reaction with enolates in tetrahydrofuran[4]. We wish to report, however, that treatment of enolate ions with *N*-phenyltrifluoromethanesulfonimide[5] in either tetrahydrofuran or dimethoxyethane solution at room temperature leads in high yield to the desired enol triflates. Some of our results are shown in the Table.

Entry No.	Ketone	Enol Triflate	Isolated Yield (%)
A. Enolates Generated by LDA Treatment of Ketones:			
1	 $\xrightarrow[\text{2) Tf}_2\text{NPh}]{\text{1) LDA/DME}}$		82
2			78
3			80
4			65
5			72
6			65
7			75 (Δ^2:Δ^3 = 4:1)

B. Enolates Generated from Trimethylsilyl Enol Ethers:

8		95
9		97

C. Enolates Generated by Li/NH₃ Reduction of Enones:

10		80
11		65

D. Enolates Generated by Addition of Diorganocuprates to Enones:

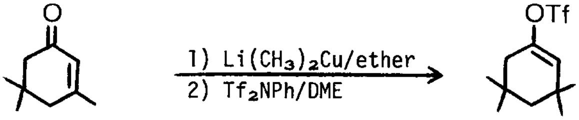
12		65
13		65

Table: Trapping of Enolates with *N*-Phenyltrifluoromethanesulfonimide

As the Table indicates, enolate ions generated by all common methods of synthesis can be trapped in good to high yields without rearrangement of the enolate double bond. Entries 5 and 9 are particularly instructive since this camphor-derived enol triflate has resisted previous attempts at preparation[6], yielding rearrangement products instead. Also instructive are entries 4 and 6, which demonstrate that specific *dienol* triflates can be easily prepared.

In a representative procedure, a solution of 4-*tert*-butylcyclohexanone (0.154 g; 1.0 mmol) in 2 ml dimethoxyethane (DME) was added to a solution of LDA (1.1 mmol) in 3 ml DME at -78°, and the resultant solution was allowed to stir for 2 hr. A solution of *N*-phenyltrifluoromethanesulfonimide (0.38 g; 1.07 mmol) in 2 ml DME was then added, and the reaction was stirred at 0° for 9 hr. After solvent removal at the rotary evaporator, the resultant yellow oil was purified by chromatography on silica gel (hexane elution) to yield the enol triflate product (0.225 g; 82%).

With this new method of synthesis now available, we believe that enol triflates will become a useful new tool in synthetic organic chemistry.

Acknowledgment We thank the National Institutes of Health for their support of this work through Grants GM-28569 and CP-05716.

Notes and References

1. J. E. Mc Murry and W. J. Scott, Tetrahedron Letters, 21, 4313 (1980).
2. For general reviews of triflate chemistry, see: a) P. J. Stang, M. Hanack, and L. R. Subramanian, Synthesis, 85 (1982). b) P. J. Stang, Accounts Chem. Res., 11, 107 (1978).
3. Enol triflates are most often prepared by treatment of the ketone with triflic anhydride in the presence of a hindered amine base: P. J. Stang and W. Treptow, Synthesis, 283 (1980). This method is not regiospecific, however.
4. For a summary of methods for preparing enol triflates, see ref 2, pp 106-115.
5. Commercially available from PCR Research Chemicals, Gainesville, Florida.
6. H. Bentz, L. R. Subramanian, M. Hanack, A. G. Martinez, M. G. Marin, and R. Perez, Tetrahedron Letters, 9 (1977).

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