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SUBSTITUENT EFFECTS ON SULFONATE ESTER BASED OLEFINATIONS

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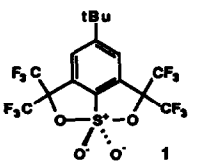
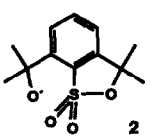
Summary: The anions of sulfonate esters derived from acidic alcohols olefinate carbonyl compounds. The dependence of the yield and stereochemistry of olefination on the sulfonate ester's alkoxy substituent are consistent with a mechanism where apicophilic alkoxy groups promote olefination via 10-S-5 intermediate 3.

Electronegative apical ligands can stabilize five-coordinate trigonal-bipyramidal main group element structures.[1] For example, 1 has a five-coordinate hypervalent 10-S-5 geometry,[2] while 2 has a four-coordinate sulfur.[3] The electron withdrawing trifluoromethyl groups are considered to stabilize the five-coordinate structure of 1 by making the apical alkoxide ligands more electronegative. We sought to determine whether electronegative alkoxides could stabilize the five-coordinate structure not of an isolable product, but of a reactive intermediate in order to promote a new reaction pathway, the olefination of carbonyl compounds with sulfonate ester anions.

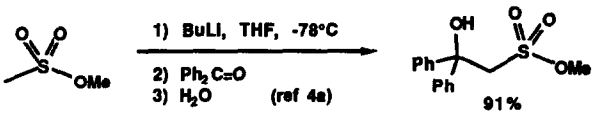


1



2

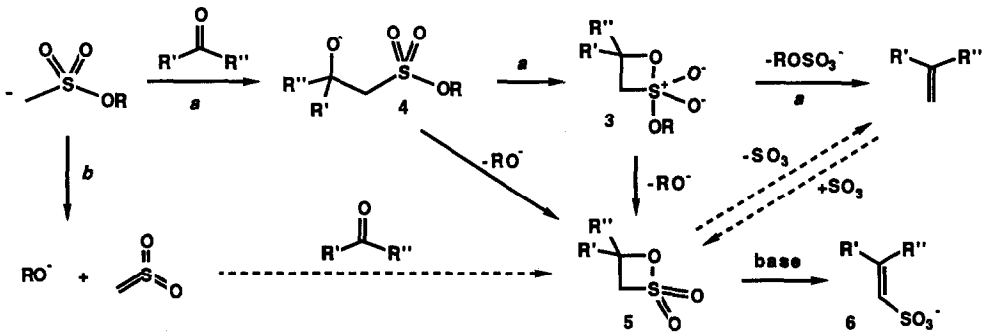
The mesylates of "ordinary" alcohols (e.g. methanol) can be deprotonated adjacent to sulfur and the corresponding carbanions add to ketones.[4] The resulting alkoxides are stable and can be protonated to yield aldol-like products in high yield (e.g. eq 1). For sulfonate esters derived from more acidic alcohols, we hypothesized that the alkoxide resulting from carbonyl addition might add to sulfur giving a hypervalent trigonal-bipyramidal 10-S-5 intermediate, 3, the more electron withdrawing alcohol-derived fragment favoring this species due to its enhanced apicophilicity. Intermediate 3 could then eliminate a stable alkylsulfate anion giving the requisite olefin (Scheme I, path *a*).[5,10] In this study, we explored the effect of sulfonate ester alkoxy groups on the olefination of carbonyl compounds with metallated sulfonate esters.



(1)

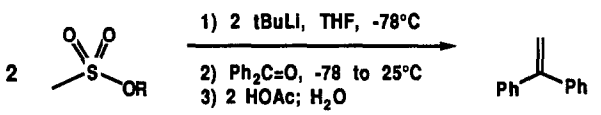
Selected methanesulfonate esters were lithiated with *tert*-butyllithium[11] in tetrahydrofuran at -78°C, treated with benzophenone, and allowed to warm to room temperature for one hour (Table I). As expected from eq 1, methyl methanesulfonate did not yield any diphenylethylene (entry 1). The 2,2,2-trifluoroethyl ester, however, gave a 56% yield of the olefination product (entry 2). Use of 1.1 as opposed to 2.0 equiv-

Scheme I



alents of the sulfonate ester anion decreased the yield to 33% (entry 3); some of the anion may be decomposing to sulfene (Scheme I, path *b*).[12] 2,2,2-Trichloroethyl methanesulfonate gave a similar yield of diphenylethylene as the trifluoro compound (entry 5). In contrast, the hexafluoroisopropyl ester did not yield any of the olefin (entry 6). Hexafluoroisopropoxide may be a sufficiently good leaving group to cause the carbanion to undergo β-elimination (path *b*) before it can add to the ketone. An increase in the size of the trifluoroalkyl group resulted in a decrease in the yield of the olefin (entries 7-9).

Table I. Methylenation of Benzophenone with Alkyl and Aryl Methanesulfonate Anions



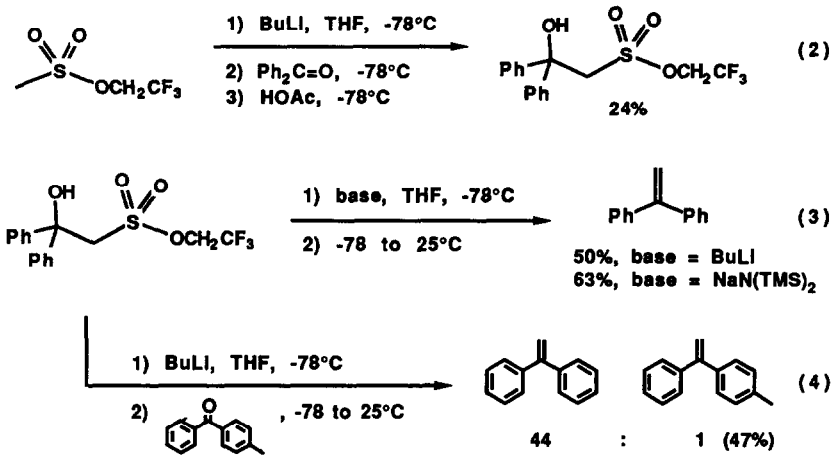
entry	R	yield %[a]
1	Me	0
2	CH_2CF_3	56
3	CH_2CF_3	33[b]
4	CH_2CF_3	53[c]
5	CH_2CCl_3	52
6	$CH(CF_3)_2$	0
7	$CH(CF_3)CH_3$	43
8	$C(CF_3)(CH_3)_2$	23
9	$C(CF_3)Bu_2$	14
10	C_6H_5	10
11	C_6H_5	73[d]
12	4-$(CF_3)C_6H_4$	3
13	4-$(OMe)C_6H_4$	22
14	2,6-$(Me)_2C_6H_3$	32
15	2,6-$(iPr)_2C_6H_3$	57
16	2,6-$(iPr)_2C_6H_3$	2[e]
17	2,6-$(iPr)_2C_6H_3$	28[f]
18	2,6-$(tBu)_2$-4-$(Me)C_6H_2$	2

[a] GC yield with respect to internal standard. [b] Reaction with 1.1 equiv of sulfonate ester anion. [c] Reaction in DME at -63 to 25°C. [d] Reaction with NaH as the base at 23°C, anion generated in the presence of benzophenone, isolated yield. [e] Reaction in toluene. [f] Reaction with $NaN(TMS)_2$ as the base.

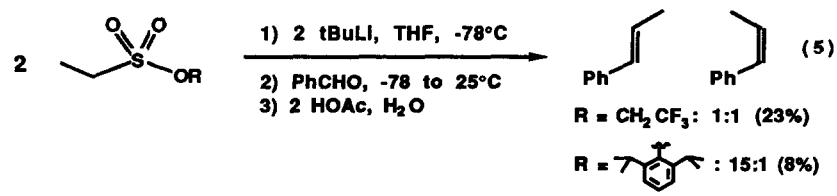
Aryl methanesulfonate anions were also tested. The parent phenyl ester gave a 10% yield of the olefin (entry 10). Electron withdrawing and donating para substituents had a small effect (entries 12 and 13). The size of the ortho substituents had a much greater effect (entries 14 and 15). In contrast to the trend observed with the fluorinated alkyl substituents, increasing the size of the ortho substituents increased the yield of diphenylethylene from 10% (H) to 32% (Me) to 57% (iPr). The extreme case, tBu, gave only 2% (entry 18), probably due to elimination of the very hindered phenoxide giving sulfene.[13]

Alternate solvents (DME and toluene) did not improve olefination yields (entries 4 and 16) and use of $NaN(TMS)_2$ as the base lowered the yield (entry 17). Generation of the sulfonate ester anion in the presence of benzophenone with NaH, however, greatly improved the yield of diphenylethylene (73%, entry 11). Generation of the anion in the presence of the ketone may circumvent sulfene formation by allowing the anion to be trapped as it is formed.

Quenching the reaction mixture from the 2,2,2-trifluoroethyl methanesulfonate anion and benzophenone with one equivalent of acetic acid at -78°C allowed the isolation of the corresponding β-hydroxysulfonate ester (eq 2). Deprotonation of this species gave diphenylethylene upon warming to room temperature (eq 3). Deprotonation and then warming in the presence of 4-methylbenzophenone again gave diphenylethylene with only a trace amount of the crossover product (eq 4). This establishes that the β-hydroxide (4, Scheme I) is an intermediate in the reaction.



The stereochemistry of olefination was examined by treating metallated ethanesulfonate esters with benzaldehyde (eq 5). Although the yields of 1-phenylpropene were low, the olefin geometry showed a dependence on the sulfonate ester's alkoxy group with a 15:1 E/Z ratio arising from the bulky aryl derivative.



The results described above are consistent with olefination according to path *a* of Scheme I. Apicophilic alkoxy substituents favor olefin formation provided that RO^- is not prone to elimination. Electronically, these are competing effects which must be carefully balanced since increased electronegativity promotes both apicophilicity and elimination. The incorporation of apicophilic ligands such as fluorinated alkoxides may alter other main group element based organic reactions.

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References and Notes

1. (a) Muetterties, E. L.; Schunn, R. A. *Q. Rev. Chem. Soc.* **1966**, *20*, 245. (b) Smith, D. J. H. In "Comprehensive Organic Chemistry"; Barton, D., Ed.; Pergamon Press: New York, 1979; Vol. II, Chapter 10.4.
2. Perkins, C. W.; Wilson, S. R.; Martin J. C. *J. Am. Chem. Soc.* **1985**, *107*, 3209.
3. Wagenaar, A.; Engberts, J. B. F. N. *J. Org. Chem.* **1988**, *53*, 768.
4. (a) Corey, E. J.; Durst, T. *J. Am. Chem. Soc.* **1968**, *90*, 5548. (b) Truce, W. E.; Vrencur, D. J. *Can. J. Chem.* **1969**, *47*, 860. (c) Truce, W. E.; du Manoir, J. *Can. J. Chem.* **1969**, *47*, 1230. (d) Truce, W. E.; Vrencur, D. J. *J. Org. Chem.* **1970**, *35*, 1226.
5. Sulfur based olefinations employing sulfides,[6] sulfoxides,[7] sulfones,[8] sulfinamides,[4a] and sulfoximides[9] have been developed. They each require two or more synthetic steps, one involving the addition of a sulfur stabilized carbanion to the carbonyl compound, and one or more for the activation and elimination of the resulting alcohols under thermal, oxidative, or reductive conditions.
6. (a) Sowerby, R. L.; Coates, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 4758. (b) Mukaiyama, T.; Watanabe, Y.; Shiono, M. *Chem. Lett.* **1974**, 1523.
7. (a) Corey, E. J.; Durst, T. *J. Am. Chem. Soc.* **1966**, *88*, 5656. (b) Jung, F.; Sharma, N. K.; Durst, T. *J. Am. Chem. Soc.* **1973**, *95*, 3420.
8. (a) Julia, M.; Paris, J. *Tetrahedron Lett.* **1973**, 4833. (b) Kocienski, P. J.; Lythgoe, B.; Ruston, S. *J. Chem. Soc., Perkin I* **1978**, 829.
9. Johnson, C. R.; Shanklin, J. R.; Kirchhoff, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 6462.
10. We cannot rule out olefination via β-sultone **5**, however, **5** would be expected to undergo elimination to **6** under the basic reaction conditions rather than expel SO_3 giving the olefin (Scheme I): Knunyants, I. L.; Sokolski, G. A. *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 583.
11. *tert* -Butyllithium was employed to limit possible displacement of RO^- by the base: Baarschers, W. H. *Can. J. Chem.* **1976**, *54*, 3056.
12. (a) Christensen, L. W. *Synthesis* **1973**, 534. (b) King, J. F. *Acc. Chem. Res.* **1975**, *8*, 10.
13. Analogous BHT ester lithium enolates readily eliminate LiO-BHT giving ketenes: Haner, R.; Laube, T.; Seebach, D. *J. Am. Chem. Soc.* **1985**, *107*, 5396.

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