to carbon migrations.[12] The reaction gives an 80:20 mixture of cyclohexyl and thexyl group migration products in an overall 100% GC yield. Interestingly, the thexyl product was 80% enantiomerically pure while the cyclohexyl product was 44% enantiomerically pure. This increase in enantioselectivity with increasing degree of substitution at the α-carbon of the migrating alkyl group as well as the exclusive formation of the trans double bond seems to indicate that conformational effects about the sp^2–sp^3 bonds may be playing an important role in the stereochemical outcome of the reaction.

The overall transformation described here accomplishes an alkylation and a 1,3 alcohol transposition with a high degree of stereoselectivity both at the new alcohol center and about the double bond. Optically active propargyl alcohols are now readily available,[10,13] and dialkylboranes are becoming readily available. This reaction should therefore provide an effective method for preparing a variety of enantiomeric materials such as those found in many natural products. We are continuing to explore these possibilities.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Committee on Research, University of California at Riverside, for support of this Research.

Registry No. (*S*)-*trans*-1-diethylbora-3-acetoxy-1-octene, 72390-37-5; (*S*)-*trans*-1-dicyclohexylbora-3-acetoxy-1-octene, 72390-38-6; (*R*)-*trans*-4-decen-3-ol, 72441-82-8; (*S*)-*trans*-4-decen-3-ol, 72441-83-9; (*R*)-*trans*-1-cyclohexyl-2-octen-1-ol, 72390-39-7; (*S*)-*trans*-1-cyclohexyl-2-octen-1-ol, 72390-40-0; (*R*)-*trans*-2,3,3-trimethyl-5-undecen-4-ol, 72390-41-1; (*S*)-*trans*-2,3,3-trimethyl-5-undecen-4-ol, 72390-42-2; (*S*)-3-hydroxy-1-octynyl acetate, 54315-38-7; diethylborane, 5518-25-2; dicyclohexylborane, 1568-65-6; thexylcyclohexylborane, 72390-43-3.

---

(12) Negishi, E.; Brown, H. C. *Synthesis* **1974**, 77.
(13) Pirkle, W. H.; Hauske, J. R. *J. Org. Chem.* **1977**, *42*, 1839.
(14) Alfred P. Sloan Foundation Fellow, 1978–1980.

M. Mark Midland,*[14] Scott B. Preston

Department of Chemistry
University of California
Riverside, California 92521

Received September 11, 1979

Anomalous Behavior of Tosylates in Elimination Reactions

Summary: Deprotonation of the tosyl methyl group affects the behavior of tosylates in elimination reactions.

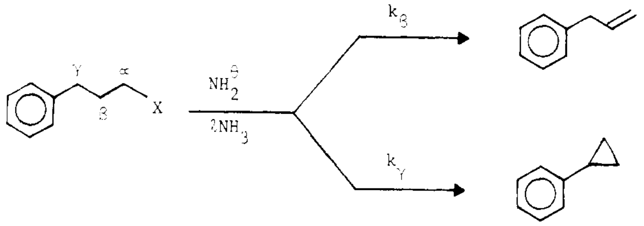
Sir: Alkyl halides or sulfonate esters serve as the substrates for the great majority of displacement and elimination reactions. Tosylate is often the leaving group of choice as its preparation from the corresponding alcohol takes place under mild conditions which avoid the stereochemical uncertainties and skeletal rearrangements associated with the conversion of an alcohol to a halide.[1] There are several instances, however, where tosylates resist displacement,[2,3] and a recent paper[4] has noted the failure of a tosylate to undergo γ-elimination. Accordingly, we are prompted to present our observations concerning the anomalous behavior of the tosylate leaving group in elimination reactions.

Table I. Elimination from 3-Phenylpropyl Derivatives[5]

X	type[a]	X	type[a]
I[b]	β	F	γ
Br	β	OTs	γ
Cl	β, γ		

[a] Type of elimination. β elimination is accompanied by alkylation of the salt of propenylbenzene to give diphenylhexenes. [b] Unpublished observations from this laboratory.

Scheme I



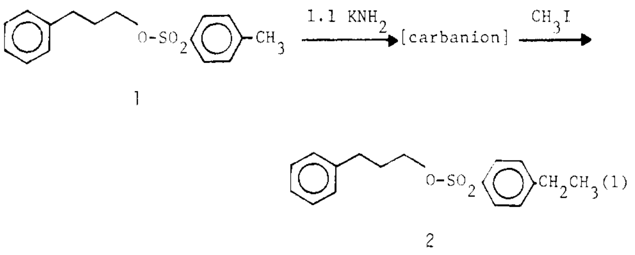
Our interest in tosylate as a "problem" leaving group stems from an investigation of the base-induced elimination reactions of a series of 3-phenylpropyl derivatives (Table I, Scheme I). In moving through the halogen series, we observe a gradual shift from β to γ elimination. As the halogen becomes less polarizable and more tightly bound to the α-carbon, leaving group ability decreases. Since tosylate is generally ranked between bromide and chloride in reactivity,[6] one might expect this ester to undergo predominantly β elimination. It is therefore surprising that tosylate joins the poorer leaving group fluoride in giving γ-elimination (Table I). As a possible rationale for the poor leaving ability of tosylate under these conditions, we speculated that the tosyl methyl protons might be preferentially abstracted by the strong base.[7]

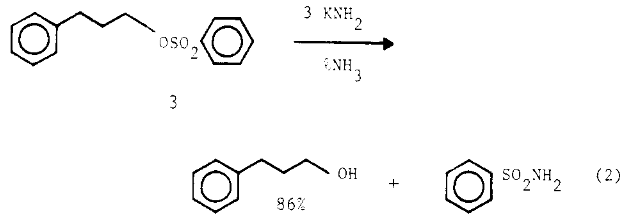
Evidence that this is the case was obtained by quenching a mixture of 3-phenylpropyl tosylate (**1**) and potassium amide with methyl iodide. The recovered ester showed substantial alkylation (70%), providing the ethyl derivative **2**[8] (eq 1); the γ-elimination product, phenylcyclopropane, was isolated in 20% yield (Scheme I). That deprotonation of the tosyl ester alters the reaction pathway can be seen by removal of the suspect methyl group. When the analogous benzenesulfonate (**3**) was subjected to excess potassium amide in liquid ammonia (eq 2), 3-phenyl-1-

---

(1) House, H. O. "Modern Synthetic Reactions", 2nd ed.; Benjamin, W. A.: Menlo Park, CA, 1972; p 531.
(2) (a) Meyers, A. I.; Nabeya, A.; Adicker, H. W.; Politzer, I. R. *J. Am. Chem. Soc.* **1969**, *91*, 763. (b) Still, W. C.; MacDonald, T. I. *Ibid.* **1974**, *96*, 5561.
(3) Seebach, D.; Wilka, E.-M. *Synthesis* **1976**, 476 and references therein.
(4) Chang, Y. H.; Pinnick, H. W. *J. Org. Chem.* **1978**, *43*, 373. The corresponding mesylate also failed to cyclize.
(5) Bumgardner, C. L. *Chem. Commun.* **1965**, 374.
(6) (a) Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry"; Harper and Row: New York, 1976; pp 192, 374–5. (b) Leaving group ability is generally correlated with the strength of the conjugate acid of the leaving group: March, J. In "Advanced Organic Chemistry: Reactions, Mechanism, and Structure", 2nd ed; McGraw-Hill: New York, 1977; p 325. (c) See also: Stirling, C. J. M. *Acc. Chem. Res.* **1979**, *12*, 198.
(7) (a) Rash, F. H.; Hauser, C. R. *J. Org. Chem.* **1967**, *32*, 3379. (b) During the course of this study, benzylic metalation, aryl metalation, and one-electron transfer have been suggested as possible side reactions of tosylates with certain organolithiums.[3] (c) Although benzylic metalation of tosylhydrazones had been suggested as a complicating factor in the Shapiro olefin synthesis, a recent study has shown that metalation is directed ortho to the tosyl sulfonyl: Chamberlain, A. R.; Stemke, J. E.; Bond, F. T. *J. Org. Chem.* **1978**, *43*, 147.
(8) Determined by NMR analysis of the ratio of the tosyl methyl to the A_2X_3 system of the *p*-ethyl derivative. The mass spectrum showed a new molecular ion indicative of the alkylated material.

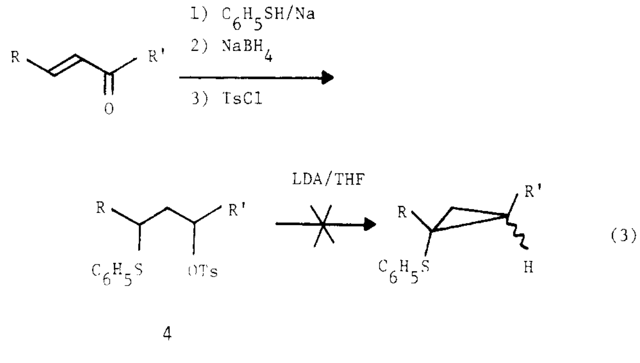
0022-3263/80/1945-0748$01.00/0





propanol and benzenesulfonamide, resulting from cleavage of the oxygen–sulfur bond, were obtained instead of products from β or γ elimination.

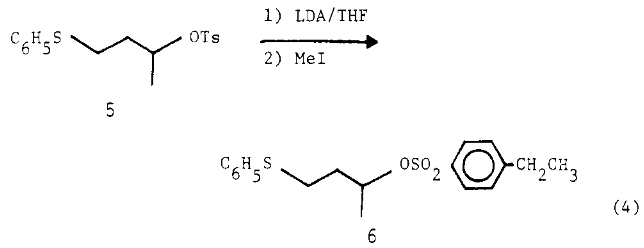
Realizing that deprotonation of the tosyl group affects reactivity under strongly basic reaction conditions, we reexamined a proposed general synthetic route to phenylthiocyclopropanes (eq 3) which was abandoned when



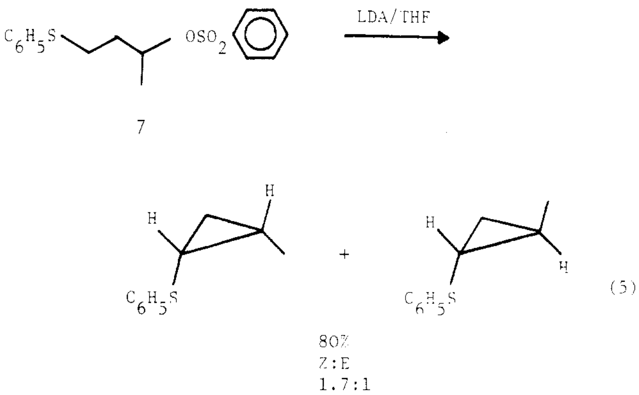
$R = H,\ R' = (CH_2)_8CH_3$

treatment of tosylate 4 with lithium diisopropylamide (LDA) in tetrahydrofuran (THF) did not result in cyclization.[4] Failure of the ring closure was attributed to inadequate carbanion stabilization by the phenylthio group since closure of the corresponding sulfone proceeded under the same conditions.

We observed that addition of methyl iodide to the reaction mixture prepared from a similar ester, 5, and LDA in THF gives the ethyl derivative 6[8] (eq 4) in 80% yield.



This suggested that a successful ring closure might be achieved if the benzenesulfonate were used instead of the tosylate. Indeed, with the benzenesulfonate 7 a mixture of *cis*- and *trans*-2-methylcyclopropyl phenyl sulfide is obtained in high yield (eq 5), demonstrating that LDA will in fact α-metalate alkyl aryl sulfides.[9] With the relatively



hindered base LDA, no complications arise from substitution at the sulfonyl moiety. Interestingly, the isomer distribution obtained (1.7:1 Z/E)[10] complements an alternate route[11] to the 2-methylcyclopropyl phenyl sulfides (1:5 Z/E).

Clearly these facile deprotonations by amide bases must be considered in the design of synthetic schemes and almost certainly may be extrapolated to include mesylates as well as tosylates.[4,12]

Acknowledgment. We are grateful to Professor J. F. Bunnett for stimulating discussions.

Registry No. 1, 3742-75-4; **2**, 72444-53-2; **3**, 72444-54-3; **4**, 72444-55-4; **5**, 72444-56-5; **6**, 72444-57-6; **7**, 72444-58-7; 3-phenylpropyl iodide, 4119-41-9; 3-phenylpropyl bromide, 637-59-2; 3-phenylpropyl chloride, 104-52-9; 3-phenylpropyl fluoride, 2038-62-2; 3-phenyl-1-propanol, 122-97-4; benzenesulfonamide, 98-10-2; *cis*-2-methylcyclopropyl phenyl sulfide, 63365-89-9; *trans*-2-methylcyclopropyl phenyl sulfide, 63365-88-8; phenylcyclopropane, 873-49-4.

---

[9] If the alkyl group is not methyl, more forcing conditions have generally been required: Dolak, T. M.; Bryson, T. A. *Tetrahedron Lett.* **1977**, 1961.

[10] Determined by GLC (20% Carbowax 20M on Chromosorb W at 165 °C). Preparative GLC afforded pure samples of the *Z* and *E* isomers, each of which had spectral data in accord with literature values (see ref 11).

[11] Trost, B. M.; Keeley, D. E.; Arndt, H. C.; Rigby, J. H.; Bogdanowicz, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 3080.

[12] (a) Comparison of the pK_a data for $PhSO_2CH_3$ [pK_a = 29: Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006] to those for $PhSO_2PhCH_3$ [pK_a = 29.8: Bordwell, F. G.; Algrim, D.; Vanier, N. R. *J. Org. Chem.* **1977**, *42*, 1817] supports this extrapolation. (b) The α-lithio derivative of methyl methanesulfonate has been reported: Corey, E. J.; Durst, T. *J. Am. Chem. Soc.* **1966**, *88*, 5656.

Carl L. Bumgardner,* John R. Lever
Suzanne T. Purrington
Department of Chemistry
North Carolina State University
Raleigh, North Carolina 27650

Received October 15, 1979

Oxidative Coupling Reactions Using Silica-Bound Ferric Chloride

Summary: Silica-bound ferric chloride serves as an oxidant for phenols and phenol ethers, leading to coupling of the aromatic rings.

Sir: It has recently been shown that ferric chloride supported on silica gel ($FeCl_3/SiO_2$) can be used for the dehydration and/or rearrangement of alcohols.[1] We re-

---

[1] Keinan, E.; Mazur, Y. *J. Org. Chem.* **1978**, *43*, 1020.

0022-3263/80/1945-0749$01.00/0