5b-OPNB, 61117-28-0; benzonorbornadiene, 4453-90-1; (+)-2-benzonorbornenone, 21159-73-9; p-bromobenzenesulfonyl chloride, 98-58-8; 6,7-dimethoxybenzonorbornadiene, 54576-19-1; 6,7-dimethoxy-2-benzonorbornenone, 54576-22-6; (+)-6,7-dimethoxy-2-benzonorbornenone, 54630-83-0.

References and Notes

(1) (a) D. V. Braddon, G. A. Wiley, J. Dirlam, and S. Winstein, *J. Am. Chem. Soc.*, **90**, 1901 (1968); (b) J. P. Dirlam and S. Winstein, *ibid.*, **91**, 5905 (1969); (c) *ibid.*, 5907 (1969).
(2) (a) H. Tanida, H. Ishitobi, T. Irie, and T. Tsushima, *J. Am. Chem. Soc.*, **91**, 4512 (1969); (b) H. Tanida, T. Irie, and T. Tsushima, *ibid.*, **92**, 3404 (1970).
(3) H. C. Brown and G. L. Tritle, *J. Am. Chem. Soc.*, **90**, 2689 (1968).
(4) H. L. Goering, C.-S. Chang, and D. Masilamani, unpublished work.
(5) H. L. Goering, A. C. Backus, C.-S. Chang, and D. Masilamani, *J. Org. Chem.*, **40**, 1533 (1975).
(6) S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1127 (1952).
(7) P. D. Bartlett and W. P. Giddings, *J. Am. Chem. Soc.*, **82**, 1240 (1960).
(8) Similar large rate-accelerating effects have been observed for the 6-methoxy substituent in solvolysis of the exo chlorides in aqueous acetone. Reference 2a reports an *exo*-**3a**-Cl/*exo*-**2a**-Cl rate ratio of 178 for solvolysis in 70% acetone at 77.6 °C and ref 3 reports a ratio of 210 for 80% acetone at 25 °C.
(9) J. D. Roberts and W. T. Moreland, Jr., *J. Am. Chem. Sc.*, **75**, 2267 (1953).
(10) C. J. Lancelot, D. J. Cram, and P. v. R. Schleyer in "Carbonium Ions", Vol. III, G. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N.Y., 1972, Chapter 27.
(11) S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *J. Am. Chem. Soc.*, **87**, 376 (1965).
(12) J. P. Dirlam, A. Diaz, S. Winstein, W. P. Giddings, and G. C. Hanson, *Tetrahedron Lett.*, 3133 (1969).
(13) Unless indicated otherwise, rotations are for chloroform solutions.
(14) (a) D. J. Sandman, K. Mislow, W. P. Giddings, J. Dirlam, and G. C. Hanson, *J. Am. Chem. Soc.*, **90**, 4877 (1968); (b) H. L. Goering, J. V. Clevenger, and K. Humski, *J. Org. Chem.*, **37**, 3019 (1972).
(15) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1147 (1952).
(16) H. C. Brown and G. L. Tritle, *J. Am. Chem. Soc.*, **88**, 1320 (1966).
(17) S. Ikegami, D. L. Vander Jagt, and H. C. Brown, *J. Am. Chem. Soc.*, **90**, 7124 (1968).
(18) H. L. Goering and H. Hopf, *J. Am. Chem. Soc.*, **93**, 1224 (1971).
(19) H. L. Goering and K. Humski, *J. Org. Chem.*, **40**, 920 (1975).
(20) H. L. Goering and G. N. Fickes, *J. Am. Chem. Soc.*, **90**, 2848, 2856 (1968).
(21) In all cases active samples had IR and NMR spectra that were indistinguishable from those for coresponding authentic samples.
(22) H. L. Goering, C. Brown, S. Chang, J. V. Clevenger, and K. Humski, *J. Org. Chem.*, **34**, 624 (1969).

Preparation and Spectral Properties of the 3-*p*-Tolylsulfenyl- and 3-*p*-Tolylsulfonyl-2-norbornanols

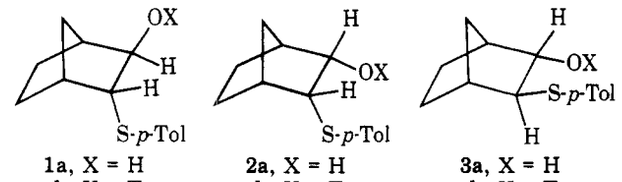
Donald C. Kleinfelter,* Thomas G. Squires, J. Harold Mashburn, Roberta P. Watsky, and S. Bruce Brown

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37916

Received September 28, 1976

The synthetic routes to the four 3-*p*-tolylsulfenyl-2-norbornanols and the four 3-*p*-tolylsulfonyl-2-norbornanols are described. The key reaction is that between the *p*-methylthiophenoxide ion and *exo*-norbornene oxide. The NMR spectra of these alcohols and their tosylate derivatives in the region of the C-2 and C-3 protons are discussed. Infrared studies were carried out on all cis alcohols to determine the extent of intramolecular H bonding in these compounds.

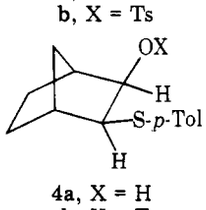
The tosylate derivatives of the four isomeric 3-*p*-tolylsulfenyl-2-norbornanols (**1a–4a**) and the four isomeric 3-*p*-tolylsulfonyl-2-norbornanols (**5a–8a**) were required for two separate mechanistic studies. The 3-*p*-tolylsulfenyl-2-norbornyl tosylates (**1b–4b**) were desired for investigation of neighboring group participation by sulfur in the norbornyl system,[1] whereas the 3-*p*-tolylsulfonyl-2-norbornyl tosylates (**5b–8b**) were desired for investigation of the E1cB mechanism.[2] Because NMR and IR data on these compounds should serve as good models for eclipsed effects of the sulfur and SO_2 groups on vicinal hydrogen, hydroxyl, and tosylate functions, we are reporting their preparations and spectral properties at this time.



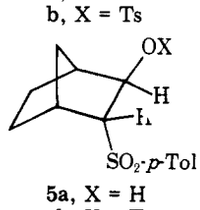
1a, X = H
b, X = Ts

2a, X = H
b, X = Ts

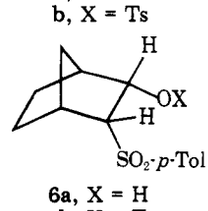
3a, X = H
b, X = Ts



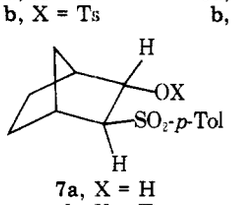
4a, X = H
b, X = Ts



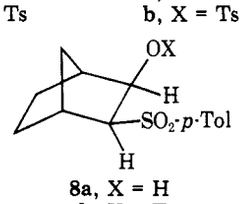
5a, X = H
b, X = Ts



6a, X = H
b, X = Ts



7a, X = H
b, X = Ts

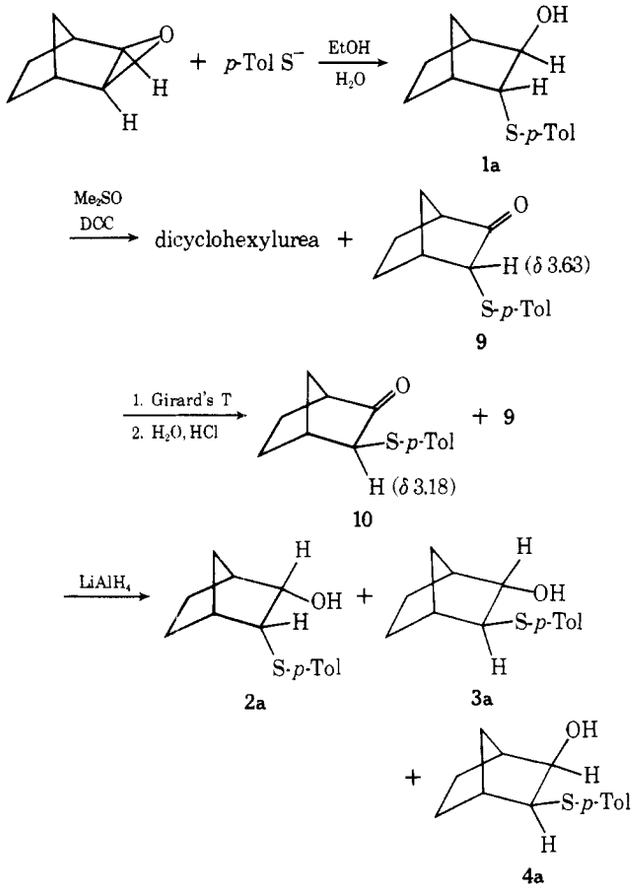


8a, X = H
b, X = Ts

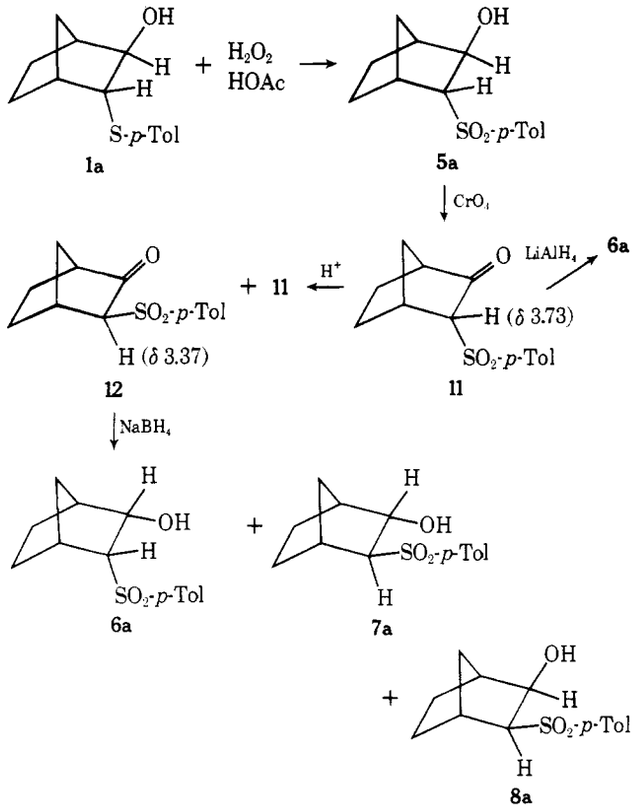
Scheme I illustrates the preparative routes to the 3-*p*-tolylsulfenyl-2-norbornanols. The key reaction in their preparation and the subsequent preparation of the 3-*p*-tolylsulfonyl-2-norbornanols was that of *exo*-norbornene oxide with the sodium salt of *p*-methylthiophenol to give the trans product, **1a**. Most oxirane ring openings of *exo*-norbornene oxide involving Brønsted–Lowry and Lewis acids proceed to give rearrangement products.[3] However, because the reaction with *p*-methylthiophenoxide ion is done in a basic medium, only one product, that of nucleophilic attack from the endo side of the norbornyl system, is obtained.

Attempts to secure 3-*endo*-*p*-tolylsulfenyl-2-norbornanone (**9**) from **1a** by conventional oxidation procedures, e.g., chromic acid, proved unsuccessful because the sulfide is oxidized to the sulfone more readily than the alcohol to the ketone. Consequently, the oxidation of both groups resulted.[4] The reagent mixture that selectively oxidized the alcohol group without affecting the sulfide was *N,N*-dicyclohexylcarbodiimide (DCC) and dimethyl sulfoxide (Me_2SO).[5] Although NMR analysis showed that **9** was formed uncontaminated with any exo isomer (**10**), dicyclohexylurea, formed as a by-

Scheme I. 3-*p*-Tolylsulfenyl-2-norbornanols



Scheme II. 3-*p*-Tolylsulfonyl-2-norbornanols



product of the reaction, was a contaminant that could not be completely removed in this and subsequent reactions. Girard's Reagent T[6] accomplished the desired separation of the ketone from the urea, but the acid-catalyzed hydrolysis of the water-soluble Girard derivative caused ketone epimerization. Integration of the exo proton in **9** at δ 3.63 ($J_{3x,4}$ = 4.0 Hz) and the endo proton in **10** at δ 3.18 ($J_{3n,7a}$ = 3.0 Hz) in the resulting mixture gave a relative ratio of **9** to **10** of 34:66.

Lithium aluminum hydride reduction of this ketone mixture gave 3-*endo*-*p*-tolylsulfenyl-2-*endo*-norbornanol (**2a,** 33%), 3-*exo*-*p*-tolylsulfenyl-2-*endo*-norbornanol (**3a,** 55%), and 3-*exo*-*p*-tolylsulfenyl-2-*exo*-norbornanol (**4a,** 12%), as shown by NMR analysis. Column chromatography separated **2a** and **3a,** but **4a** could only be obtained as a mixture contaminated by 10% of **3a.**

Scheme II illustrates the preparative routes to the 3-*p*-tolylsulfonyl-2-norbornanols. The sulfone group was introduced into the norbornyl system by oxidation of **1a** to **5a** with 30% hydrogen peroxide in glacial acetic acid. Pure 3-*endo*-*p*-tolylsulfonyl-2-norbornanone (**11**) was obtained by Jones reagent oxidation[7] of **5a** in acetone. NMR analysis revealed no contamination by the exo isomer, 3-*exo*-*p*-tolylsulfonyl-2-norbornanone (**12**).

Lithium aluminum hydride reduction of **11** afforded pure 3-*endo*-*p*-tolylsulfonyl-2-*endo*-norbornanol (**6a**). Refluxing **11** in a 1:1 ethanol–water solution containing a small amount of HCl caused ketone epimerization. Integration of the exo proton in **11** at δ 3.73 ($J_{3x,4}$ = 4.3 Hz) and the endo proton in **12** at δ 3.37 ($J_{3n,7a}$ = 3.1 Hz) in the resulting mixture gave a relative ratio of **11** to **12** of 38:62. Sodium borohydride reduction of this mixture of ketones gave **6a** (38%), 3-*exo*-*p*-tolylsulfonyl-2-*endo*-norbornanol (**7a,** 46%), and 3-*exo*-*p*-tolylsulfonyl-2-*exo*-norbornanol (**8a,** 16%). When pure **11** was reduced with sodium borohydride, a mixture of **6a, 7a,** and **8a** was obtained in practically the same relative percentages, indicating that epimerization occurred prior to reduction. Separation of the alcohol mixture was accomplished by column chromatography.

NMR and IR Spectral Analysis. The 3-*p*-tolylsulfenyl-2-norbornanols, the 3-*p*-tolylsulfonyl-2-norbornanols, and their tosylate derivatives (**1b–8b**) were characterized by virtue of their NMR spectra, particularly in the region of the C-2 and C-3 protons. Table I contains the chemical shifts and coupling constants for these protons. Chemical shift data for *exo*- and *endo*-norbornanol are included for comparison purposes.

In analyzing the data from Table I, several general trends may be noted. All the exo-2 and exo-3 protons of the substituted norbornanols and tosylates appear at lower fields than the corresponding endo-2 and endo-3 protons. This trend is consistent with prior observations.[8] However, no apparent constant difference exists between an exo and an endo hydrogen on the same carbon in a given series. The different effects of eclipsed phenyl groups and oxygen atoms have been discussed previously.[9] The effect of eclipsing a sulfide and a sulfone group in the exo and endo positions with hydrogen atoms can be gathered by comparison with the noneclipsed analogues. Table II compares the shielding contributions of these substituents.

Analysis of the data from Table II reveals that sulfide groups, whether exo or endo, shield their corresponding eclipsed hydrogens, with the shielding effect being significantly greater for the endo orientation. A similar effect by exo and endo oxygen atoms has been demonstrated.[10] Because a sulfide group is similar to an oxygen attachment, the same underlying reason presumably operates for both substituents. In contrast to the effect of eclipsed sulfide and oxygen attachments, sulfone groups deshield both eclipsed exo and eclipsed endo hydrogens. Whereas for the alcohols the deshielding of an eclipsed endo hydrogen is considerably less (0.28 − 0.07 = 0.21) than of an eclipsed exo H, their tosylate derivatives show no appreciable difference (0.20 − 0.19 = 0.01) in the desheilding contributions of the eclipsed sulfone groups.

Table I. NMR Spectral Data for Title Compounds[a]

Compd	δ, ppm[b] 2n	2x	3n	3x	J, Hz[c] 2,3	1,2x	3x,4	2n,7a	2n,7a
exo-Norbornanol	3.66								
endo-Norbornanol		4.15							
1a	3.39 (t)[d]			3.13 (m)	~2.0		?	~2.0	
1b	4.08 (t)			3.22 (m)	~2.2		?	~2.2	
2a		4.11 (dp)		3.48 (dp)	9.2	4.0	4.0		
2b		4.90		3.50	9.6	4.2	4.2		
3a		3.88 (dp)	2.69 (t)		3.0	3.6			
3b		4.47	2.76		3.0	3.0			
4a	3.73 (d)		3.17 (dp)		6.2				1.8
4b	4.64		3.26		6.8				2.1
5a	4.24 (dp)			3.17 (t)	~3.6		~3.6	~1.6	
5b	4.90			3.35	~3.6		~3.6	~1.6	
6a		4.32 (dp)		3.37 (dp)	9.6	4.0	4.0		
6b		4.92		3.47	10.0	4.0	4.0		
7a		4.60 (t)	2.70 (dp)		4.4	4.2			2.1
7b		5.11	2.88		4.3	4.3			2.4
8a	4.17 (d)		3.14 (d)		6.4				
8b	4.70		3.23		6.8				

[a] All solid compounds gave satisfactory analyses for C, H, and S. (Alcohols **2a** and **4a** and tosylate **3b** were obtained as oils and were not analyzed.) [b] δ values are correct to ±0.01 ppm. Those for the alcohols are for dilute solutions (less than 1 mol %) in carbon tetrachloride; those for the tosylates are for dilute solutions in chloroform-*d*. [c] *J*'s are precise to ±0.1 Hz except for those labeled ~, which are believed precise to ±0.2 Hz. [d] t = triplet; m = multiplet; dp = doublet pair; d = doublet.

Table II. Shielding Contributions (ppm) for Eclipsed Sulfide and Sulfone Functions

Exo sulfide				Endo sulfide			
Alcohol		Tosylate		Alcohol		Tosylate	
2a	4.11	**2b**	4.90	**4a**	3.73	**4b**	4.64
3a	3.88	**3b**	4.47	**1a**	3.39	**1b**	4.08
	0.23		0.43		0.34		0.56
Exo sulfone				**Endo sulfone**			
Alcohol		Tosylate		Alcohol		Tosylate	
6a	4.32	**6b**	4.92	**8a**	4.17	**8b**	4.70
7a	4.60	**7b**	5.11	**5a**	4.24	**5b**	4.90
	−0.28		−0.19		−0.07		−0.20

The spectral patterns of the C-2 and C-3 protons and the coupling constants obtained are in line with the proposed structures for all the title compounds. The agreement between the alcohols and their tosylate derivatives precludes any possible rearrangement taking place during derivative formation.

Infrared studies were conducted on very dilute solutions of alcohols **1a–8a** to gain information on the ability of the sulfide and sulfone groups to act as proton acceptors in intramolecular hydrogen bonding. The cis compounds, **2a, 4a, 6a,** and **8a,** should be ideal models for such a study, because the dihedral angle between the substituents is ca. 0°, and this arrangement might allow for maximum interaction between the proton and its accepting group. The ability of oxygen to form the O—H- - -O hydrogen bond has been repeatedly established by infrared techniques.[11] However, similar extensive studies on the sulfur atom as a proton acceptor in hydrogen bonding of the O—H- - -S type have not been conducted. On the basis of the O—H spectral shift alone, sulfur atoms in sulfides are relatively strong proton acceptors in intramolecular hydrogen bonding.[12]

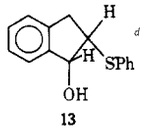
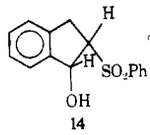
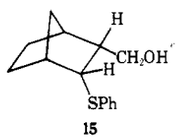
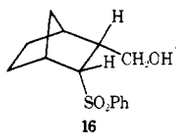
The results of our studies on the cis compounds and relevent data from previous studies by others are listed in Table III. In comparing the ability of ethers vs. sulfides to cause an O–H spectral shift, it is apparent that a greater shift (larger Δν in cm^{-1}) is caused by sulfur. A similar effect is observed when the *cis*-3-*p*-tolylsulfenyl-2-norbornanols are compared with the *cis*-norbornane-2,3-diols.[13,14] The Δν for the exo-cis compound, **4a,** is slightly greater than that for the endo-cis compound, **2a.** The ability of the sulfide group to function as a proton acceptor in hydrogen bonding depends markedly on structural factors. For example, whereas *cis*-2-phenylsulfenylindanol (**13**) shows a large Δν of 120 cm^{-1}, no spectral shift is observed for 3-*endo*-phenylsulfenyl-2-*endo*-hydroxymethylnorbornane (**15**).[15,16]

Oxygen rather than sulfur is the proton accepting atom in sulfones.[16] In the indanol compounds, **13** and **14,** the sulfone group causes a slightly greater O–H spectral shift than the sulfide. This trend is reversed in the cis compounds studied by us. For example, the Δν observed for the exo-cis sulfone, **8a,** is almost 100 cm^{-1} less than that of the corresponding exo-cis sulfide, **4a.** Also, in contrast to the sulfides, **2a** and **4a,** the endo sulfone, **6a,** exhibits a greater spectral shift (103 cm^{-1}) than the exo sulfone, **8a** (78 cm^{-1}). Evidently the degree to which sulfone groups function as proton acceptors in hydrogen bonding is also very sensitive to structural factors.

Experimental Section

Melting points were determined in soft capillary tubes using a Hoover capillary melting point apparatus (Arthur H. Thomas Co.,

Table III. Intramolecular Hydrogen Bonding in Some Sulfur and Oxygen Compounds

Compd	ν_{OH}, free	ν_{OH}, bonded	$\Delta\nu$, cm^{-1}
CH_2OHCH_2OEt[a]	3641	3610	31
CH_2OHCH_2SEt[a]	3617	3527	90
$HO(CH_2)_3OMe$[b]	3641	3554	87
$HO(CH_2)_3SMe$[c]	3640	3502	138
 13	3620	3500	120
 14	3620	3494	126
 15	3640		
 16	3640	3536	104
2a	(3618)[f]	3450	168
4a	3618	3441	177
6a	3613	3510	103
8a	(3614)[g]	3536	78

[a] Reference 12. [b] A. B. Foster, A. H. Haines, and M. Stacey, *Tetrahedron*, 16, 177 (1961). [c] N. Mori, Y. Takahashi, and Y. Tsuzuki, *Bull. Chem. Soc. Jpn.*, 40, 2720 (1967). [d] Reference 15. [e] Reference 16. [f] No free OH peak was observed; the free peak listed is for 3a. However, a shoulder was observed at ca. 3600 cm^{-1} (rel intensity 20% of the peak at 3450 cm^{-1}); this shoulder may be attributed to OH···π bonding. [g] No free OH peak was observed; the free peak listed is for 5a.

Philadelphia, Pa.) and are uncorrected. A Varian A-60 NMR spectrometer, calibrated with tetramethylsilane (δ 0) and chloroform (δ 436.5 Hz), was used for the NMR determinations. Infrared spectra in the OH region were recorded on a Perkin-Elmer Model 257 grating spectrometer calibrated against polystyrene standard. Microanalyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn., and by F. B. Strauss Microanalytical Laboratory, Oxford, England. All ether, ligroin, and chloroform solutions of products were dried over anhydrous sodium sulfate prior to removal of solvent. Ligroin was distilled over potassium permanganate and had bp 40–55 °C. The *p*-toluenesulfonates (tosylates), **1b–8b**, were prepared in the usual manner.[17] Tosylates **1b–4b** were purified by recrystallization from ether–ligroin; tosylates **5b–8b** were purified by recrystallization from chloroform–ligroin.

3-*endo*-*p*-Tolylsulfenyl-2-*exo*-norbornanol (1a). To 150 ml of 1:1 ethanol–water in which sodium hydroxide (12 g) was dissolved was added *p*-thiocresol (26.2 g, 0.211 mol) and then *exo*-norbornene oxide (18.0 g, 0.164 mol), mp 125–126 °C (lit.[18] mp 125–127°C). The mixture was refluxed for 100 h, during which time the solution turned from yellow to amber color. The solution was cooled and extracted repeatedly with chloroform. The extracts were washed twice with 100 ml of 5% sodium hydroxide, once with 50 ml of 5% hydrochloric acid, once with 100 ml saturated sodium bicarbonate, and once with 100 ml of water. The chloroform was removed by flash evaporation, leaving a brown oil that solidified on standing. Recrystallization of the crude sulfide from ligroin gave 25.1 g (65.4%), mp 61–62 °C. The tosylate (**1b**) gave mp 87–88 °C.

3-*endo*-*p*-Tolylsulfenyl-2-norbornanone (9) and 3-*exo*-*p*-Tolylsulfenyl-2-norbornanone (10). To a solution of **1a** (10.3 g, 0.0431 mol), 100 ml of benzene, and 100 ml of dimethyl sulfoxide (Me_2SO) were added 37.1 g of *N,N*-dicyclohexylcarbodiimide (DCC), 4.8 ml of pyridine, and 2.4 ml of trifluoroacetic acid. The mixture was stirred for 48 h after which time 200 ml of benzene was added to effect precipitation of some of the dicyclohexylurea formed during the reaction. The cooled reaction mixture was then filtered to remove the urea, and the filtrate was washed several times with water to remove the Me_2SO. The benzene was removed by flash evaporation leaving a brown oil.

The brown oil was added to 100 ml of 95% ethanol. Cooling the resulting solution caused precipitation of additional urea which was filtered. To the ethanol solution was added 10.3 g of Girard's Reagent T and 10 ml of acetic acid, and the solution was refluxed for 24 h. The cooled solution was poured into a separatory funnel, ether, water, and sodium chloride solution were added, and the mixture was shaken. The ether layer was discarded, and the aqueous portion was treated with 10 ml of concentrated HCl and heated on a steam bath for 2 h. The ketone mixture separated as a yellow oil which was extracted with chloroform. Flash evaporation of the chloroform left a mixture of **9** and **10** (9.00 g, 90.0%), as determined by NMR analysis.

3-*endo*-*p*-Tolylsulfenyl-2-*endo*-norbornanol (2a), 3-*exo*-*p*-Tolylsulfenyl-2-*exo*-norbornanol (4a), and 3-*exo*-*p*-Tolylsulfenyl-2-*endo*-norbornanol (3a). Reduction of a mixture of **9** and **10** (12.0 g, 0.0521 mol) with lithium aluminum hydride (1.8 g, 0.047 mol) in ether in the standard manner[19] gave an oily mixture of **2a, 3a,** and **4a** (11.0 g, 90.2%), as determined by NMR analysis. Chromatography over alumina with ether–ligroin mixtures gave initially pure **2a** (an oil), followed by a mixture of **2a** and **4a,** followed by a mixture of **4a** and **3a,** followed by pure, solid **3a.** Tosylate **2b** gave mp 110–111 °C. Recrystallization of **3a** was accomplished with ligroin to give mp 57–58 °C. Tosylate **3b** is an oil.

Chromatography of those portions containing **4a** was repeated, but no pure **4a** could be obtained. Spectra were run on samples containing about 90% **4a** and 10% **3a.** Tosylate **4b** gave mp 106–107 °C.

3-*endo*-*p*-Tolylsulfonyl-2-*exo*-norbornanol (5a). To a solution of **1a** (16.2 g, 0.0691 mol) in 47 ml of acetic acid was added dropwise 130 ml of 30% hydrogen peroxide. The reaction temperature rose to 60 °C during one-half the addition of the peroxide and afterward dropped to slightly above room temperature. The solution was heated on a steam bath for 30 min and then allowed to cool. White crystals formed which were filtered. The filtrate was poured into ice water to give additional crystals. The combined crystals were washed with cold 2% sodium bicarbonate, then with water, and then dried to give 17.5 g (95.1%) of **5a.** Recrystallization of **5a** was accomplished with 1-propanol or with ether to give mp 145–146 °C. Tosylate **5b** gave mp 144–145 °C.

3-*endo*-*p*-Tolylsulfonyl-2-norbornanone (11). To a solution of **5a** (25.0 g, 0.0938 mol) in 600 ml of acetone was added dropwise 8 N chromic acid until the orange color of the chromic acid persisted. The reaction temperature was maintained at ca. 0 °C during this addition and for 0.5 h afterwards. Cold saturated sodium bisulfite was added until a green color persisted in the solution. The green chromium salts were filtered and washed with acetone. The filtrates were poured into a large volume of ice water to effect crystallization of **11.** The crystals of **11** were washed repeatedly with water and dried to give 23.4 g (94.4%), mp 131–132 °C. Anal. Calcd for $C_{14}H_{16}SO_3$: C, 63.61; H, 6.10; S, 12.13. Found: C, 63.41; H, 6.12; S, 12.32.

Care must be taken during this reaction and workup to maintain a temperature of ca. 0 °C. During several oxidations conducted at 10 °C, a mixture of **11** and 3-*exo*-*p*-tolylsulfonyl-2-norbornanone (**12**) was obtained.

3-*endo*-*p*-Tolylsulfonyl-2-norbornanone (11) and 3-*exo*-*p*-Tolylsulfonyl-2-norbornanone (12). A solution of **11** (10.0 g, 0.0378 mol) in 400 ml of 50% ethanol and 4 ml of concentrated hydrochloric acid was refluxed for 12 h. The cooled solution was added to ice water to attain crystallization. The crystals were washed with water and dried to give a mixture of **11** and **12,** 9.90 g (98.3%), as determined by NMR analysis.

3-*endo*-*p*-Tolylsulfonyl-2-*endo*-norbornanol (6a). Reduction of pure **11** (2.64 g, 0.0100 mol) with lithium aluminum hydride (0.40 g, 0.010 mol) in ether in the standard manner[19] gave **6a,** 2.45 g (92.1%), which could be recrystallized from ether to give mp 111–112 °C. Tosylate **6b** gave mp 195–196 °C.

3-*endo*-*p*-Tolylsulfonyl-2-*endo*-norbornanol (6a), 3-*exo*-*p*-Tolylsulfonyl-2-*exo*-norbornanol (8a), and 3-*exo*-*p*-Tolylsulfonyl-2-*endo*-norbornanol (7a). To a solution of a mixture of **11** and **12** (5.00 g, 0.0189 mol) in 300 ml of 50% ethanol held at 10 °C was added sodium borohydride (1.2 g, 0.032 mol). The mixture was stirred for 4 h and extracted several times with chloroform. The chloroform extracts were washed well with saturated sodium chloride and then dried. Flash evaporation of the chloroform left a mixture of **6a, 7a,** and **8a** (4.47 g, 88.8%), as determined by NMR analysis. Chromatography over alumina with chloroform–ligroin mixtures gave initially

pure **6a**, followed by a mixture of **6a** and **8a**, then pure **8a**, then a mixture of **8a** and **7a**, and finally pure **7a**. The compounds were recrystallized from ether, high-boiling ligroin, or ligroin–chloroform mixtures. Alcohol **7a** and tosylate **7b** gave mp 101–102 and 150–151 °C, respectively; alcohol **8a** and tosylate **8b** gave mp 102–103 and 180–181 °C, respectively.

Registry No.—**1a**, 61348-85-4; **1b**, 61348-86-5; **2a**, 61376-26-9; **2b**, 61376-27-0; **3a**, 61376-28-1; **3b**, 61376-29-2; **4a**, 61376-30-5; **4b**, 61376-31-6; **5a**, 61348-87-6; **5b**, 61348-88-7; **6a**, 61376-32-7; **6b**, 61376-33-8; **7a**, 61376-34-9; **7b**, 61376-35-0; **8a**, 61376-36-1; **8b**, 61376-37-2; **9**, 61348-89-8; **10**, 61348-90-1; **11**, 61348-91-2; **12**, 61348-92-3; *exo*-norbornene oxide, 3146-39-2; *p*-thiocresol, 106-45-6.

References and Notes

(1) S. J. Cristol, R. P. Arganbright, G. D. Brindell, and R. M. Heitz, *J. Am. Chem. Soc.*, **79**, 6035 (1957); W. H. Mueller, *Angew. Chem., Int. Ed. Engl.*, **8**, 482 (1969).
(2) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University Press, Ithaca, N.Y., 1953, pp 420–427; J. Hine, "Physical Organic Chemistry", 2d ed, McGraw-Hill, New York, N.Y., 1962, pp 187–206.
(3) For example, see H. Kwart and W. Vosburgh, *J. Am. Chem. Soc.*, **76**, 5400 (1954); H. M. Walborsky and D. F. Loncrini, *J. Org. Chem.*, **22**, 1117 (1957); S. Winstein and E. T. Stafford, *J. Am. Chem. Soc.*, **79**, 505 (1957); J. Meinwald and B. C. Cadoff, *J. Org. Chem.*, **27**, 1539 (1962); H. Kwart and T. Takeshita, *ibid.*, **28**, 670 (1963).
(4) See M. N. Rerick, "Reduction Techniques and Applications in Organic Synthesis", R. L. Augustine, Ed., Marcel Dekker, New York, N.Y., 1968, p 83.
(5) L. A. Paquette and L. D. Wise, *J. Am. Chem. Soc.*, **89**, 6659 (1967).
(6) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1, Wiley, New York, N.Y., 1967, p 410.
(7) A. Bowers, T. G. Halsall, R. E. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2555 (1953).
(8) J. I. Musher, *Mol. Phys.*, **6**, 93 (1963); L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2d ed, Pergamon Press, Oxford, 1969, p 230.
(9) D. C. Kleinfelter, T. E. Dye, J. E. Mallory, and E. S. Trent, *J. Org. Chem.*, **32**, 1734 (1967).
(10) J. C. Davis, Jr., and T. V. Van Auken, *J. Am. Chem. Soc.*, **87**, 3900 (1965).
(11) E. B. Wilson, Jr., "The Hydrogen Bond", G. C. Pimentel and A. L. McClellan, Ed., W. H. Freeman, San Francisco, Calif., 1960, p 193.
(12) P. v. R. Schleyer and R. West, *J. Am. Chem. Soc.*, **81**, 3164 (1959).
(13) H. Kwart and W. G. Vosburgh, *J. Am. Chem. Soc.*, **76**, 5400 (1954).
(14) Although a hydroxyl oxygen may differ from an ethereal oxygen in its ability to act as a proton acceptor in hydrogen bonding, the known $\Delta\nu$'s for ethylene glycol (32 cm^{-1}) and 1,3-propanediol (79 cm^{-1}) compare favorably with the values for the corresponding ethers in Table III.
(15) H. H. Szmant and J. J. Rigau, *J. Org. Chem.*, **31**, 2288 (1966).
(16) S. Ghersetti, H. Hogeveen, G. Maccagnani, F. Montanari, and F. Tadder, *J. Chem. Soc.*, 3718 (1963).
(17) Reference 6, p 1180.
(18) H. M. Walborsky and D. F. Loncrini, *J. Am. Chem. Soc.*, **76**, 5396 (1954).
(19) W. G. Brown, *Org. React.*, **6**, 469 (1951).

Base-Induced Cycloaddition of Sulfonylmethyl Isocyanides to C,N Double Bonds. Synthesis of 1,5-Disubstituted and 1,4,5-Trisubstituted Imidazoles from Aldimines and Imidoyl Chlorides[1]

Albert M. van Leusen,* Jurjen Wildeman, and Otto H. Oldenziel[2]

Department of Organic Chemistry, The University, Zernikelaan, Groningen, The Netherlands

Received June 9, 1976

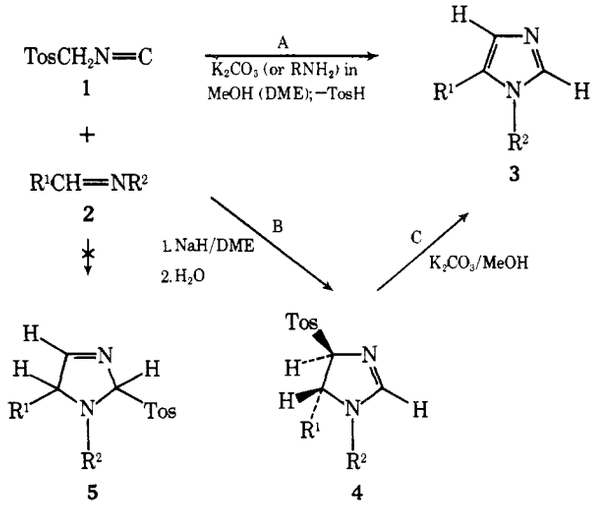
Base-induced cycloaddition of tosylmethyl isocyanide (TosMIC) to aldimines ($R^1CH{=}NR^2$) in protic medium occurs with concomitant elimination of *p*-toluenesulfinic acid to give the otherwise more difficultly accessible 1,5-disubstituted imidazoles (**3**). The influence of R^1 and R^2 on the formation of **3** is analyzed in a qualitative way. α-Tosylbenzyl isocyanide and α-tosylethyl isocyanide, likewise, give 1,4,5-trisubstituted imidazoles (**7**). The cycloaddition of TosMIC to imidoyl chlorides is accompanied by loss of HCl, instead of TosH, and leads to the 1,4,5-trisubstituted imidazoles **11**. Under aprotic conditions a number of *trans*-1,5-diaryl-4-tosyl-2-imidazolines (**4**) have been isolated and identified as the primary cycloadducts of TosMIC and aldimines, leading ultimately to the imidazoles **3**.

TosMIC (tosylmethyl isocyanide, **1**) is a new synthon of considerable utility. In previous communications we have shown its use in novel syntheses of a series of azoles[3] (including oxazoles,[3a] pyrroles,[3c] and 1,2,4-triazoles[3e]), and in the conversion of ketones to cyanides[4a] and to α-hydroxy aldehydes.[4b] The present paper is concerned with the application of TosMIC and some analogues to the synthesis of imidazoles (and 2-imidazolines) from aldimines or imidoyl chlorides.

Substituted imidazoles, many of which play an important role in biologically interesting processes, have been prepared by a variety of synthetic methods.[5] Although most substitution patterns can be realized by these methods, as yet no simple, straightforward synthesis of 1,5-disubstituted imidazoles is reported. A limited number of such 1,5-disubstituted imidazoles has been obtained previously by separation from a mixture of 1,4- and 1,5-disubstituted imidazoles formed by N-alkylation of 4(5)-aryl- or 4(5)-alkylimidazoles.[6]

Synthesis of 1,5-Disubstituted Imidazoles. The TosMIC molecule (**1**), which accommodates a reactive isocyanide carbon and an activated methylene,[7] can cycloadd its $CH_2N{=}C$ moiety to polarized double bonds under basic conditions.[3,4] When applied to aldimines (**2**, Scheme I), this type of reaction results in the formation of imidazoles **3** by

Scheme I. Synthesis of Imidazoles 3 and 2-Imidazolines 4 from Aldimines (2) and TosMIC (1)[a]



[a] For substituents R^1 and R^2 in **3** see Table I; the same abbreviation to a, b, etc., holds for **2**, **4** (and **5**).