Copper-Catalyzed Additions of Sulfonyl Iodides to Simple and Cyclic Alkenes

Lilian Kao Liu,* Y. Chi,[1] and Kwan-Yue Jen[2]

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan, Republic of China 300

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A convenient synthesis for various β-iodo sulfones has been developed. The reaction involves additions of alkane- and arenesulfonyl iodides to simple and cyclic alkenes under the catalytic action of copper(II) chloride. The favored stereochemical results for cyclic alkenes have been rationalized in terms of stepwise addition of both portions of the addend from the diaxial direction.

Since Asscher and Vofsi successfully added sulfonyl chlorides to unstrained alkenes with copper catalyst,[3] many additions of sulfonyl halides to various unsaturated systems using redox catalysts or under photolysis conditions have been studied.[3-16] However, the addition of sulfonyl chloride to simple alkenes and cycloalkenes was seldom successful. Evolution of sulfur dioxide was usually observed,[5,11] and no sulfone adducts were obtained. Only in a few cases[3,12] β-chloro sulfones were obtained by heating of the reactants under pressure for a long time. Although sulfonyl iodides have been shown to be the most reactive compounds among various sulfonyl halides,[14] reports concerning their addition to simple alkenes[13,15,16] have seldom appeared in the literature. Conclusive characterization of adducts has not been carried out due to isolation difficulties. We have performed a systematic study and have found that sulfonyl iodides gave good to excellent yields of β-iodo sulfones with mono-, di-, and trisubstituted alkenes and cyclic alkenes in the presence of catalytic amounts of copper(II) chloride. A number of highly unstable unknown adducts deriving from alkanesulfonyl iodides could also be isolated and characterized. No dimerization or disproportionation products[13] were detected under the present conditions. Consequently, isolation of adducts is much easier as compared with other procedures,[13,15,16] and it constitutes a general and simple synthetic method for β-iodo sulfones.

Results and Discussion

Arenesulfonyl Iodides. Reactions were generally carried out under nitrogen and were completed in 2–4 h. Thin-layer chromatography (TLC) and nuclear magnetic resonance spectrometry (NMR) were used to monitor the reaction and the purity of the product. For styrene, 1-hexene, cyclopentene, and 2-methyl-2-butene, excellent yields of a single adduct (**1**–**4**, Table I) were obtained in each case. Cyclohexene gave a mixture of trans (**5** or **7**) and cis (**6** or **8**) adducts with either tosyl iodide (TsI) or benzenesulfonyl iodide (PsI). These mixtures could be separated by chromatography on a silica gel column. 1-Methylcyclohexene gave 66.7% of *trans*-1-iodo-2-tosyl-1-methylcyclohexane (**9**) and 12% of the elimination product, 2-methyl-3-tosyl-1-cyclohexene (**10**). Obviously, the corresponding *cis*-1-iodo-2-tosyl-1-methylcyclohexane was unstable; it lost hydrogen iodide easily under the present reaction conditions or during isolation. For 1-phenylcyclohexene, only elimination product, 2-phenyl-3-tosyl-1-cyclohexene (**11**), was isolated. The results are summarized in Table I.

Though arenesulfonyl iodides undergo spontaneous homolysis[8,13] in aprotic solvents by heating or illumination, additions carried out under these conditions always gave rise to elimination and disproportionation products.[13] The catalytic action of copper(II) chloride can be demonstrated by the fact that no adduct was detected (NMR) when 2-methyl-2-butene was stirred with tosyl iodide in acetonitrile for 2 h at 0 °C, whereas a 92% yield of 2-iodo-2-methyl-3-tosylbutane (**4**) was isolated when minute amounts of copper(II) chloride and triethylaminium iodide were added to the reaction mixture at 0 °C in the dark. Because both the sulfonyl iodides and the adducts were unstable to incident light, better yields would be obtained when reactions were carried out in the dark. Cyclopentene gave 89% of *trans*-1-iodo-2-tosylcyclopentane (**3**) when unprotected, and the yield was 96% by simply wrapping the reaction flask with aluminum foil. It is possible that copper(II) chloride acts only as initiator in the present reactions. Due to the high reactivity of sulfonyl iodides, its transfer step involving iodine undoubtedly is very fast, while in the copper-catalyzed addition of sulfonyl bromides to phenylacetylene, copper(II) bromide was actually involved in the ligand-transfer step.[7]

The exclusive formation of **3** from cyclopentene and the predominant formation of the trans adducts (**5** and **7**) from cyclohexene clearly indicate that stepwise addition of both portions of the addend from the diaxial direction has taken place. In this respect, it is similar to the photoinitiated addition of bromotrichloromethane to cycloalkenes.[17] A

(1) Undergraduate research participant, 1977–1978.
(2) Research assistant on Grant No. NSC-68-0201-02(0311), 1978–1979.
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(14) S. J. Cristol and D. I. Davies, *J. Org. Chem.*, **29**, 1282 (1964).
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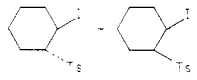
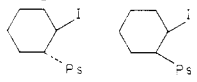
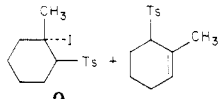
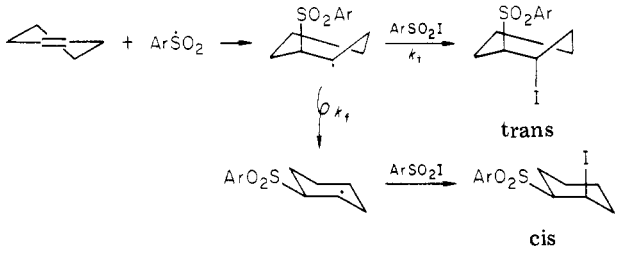
Table I. Products Obtained from Addition of Arenesulfonyl Iodides to Various Alkenes

alkene	Ar in $ArSO_2I$	products isolated	yield, %	mp, °C
styrene	p-$CH_3C_6H_4$	$PhCHICH_2Ts$, 1	93	134 dec
1-hexene	p-$CH_3C_6H_4$	n-$BuCHICH_2Ts$, 2	92	32-32.5
cyclopentene	p-$CH_3C_6H_4$	 3	95.7	51-52
2-methyl-2-butene	p-$CH_3C_6H_4$	$(CH_3)_2ClCH(CH_3)Ts$, 4	92	73-76 dec
cyclohexene	p-$CH_3C_6H_4$	 5 6	68 (trans) 3 (cis)	oil (trans) 144-145 dec
cyclohexene	Ph	 7 8	73.4 (trans) 4.6 (cis)	81 142-144 dec
1-methylcyclohexene	p-$CH_3C_6H_4$	 9 10	66.7 (iodide) 12 (olefin)	86 dec 70-71
1-phenylcyclohexene	p-$CH_3C_6H_4$	 11	44	166.5-168

bridged radical intermediate[18] is unlikely. After initial addition of the arenesulfonyl radical to the cycloalkene, abstraction of iodine from arenesulfonyl iodide by the substituted cycloalkyl radical may occur either before or after ring flipping. In the case of cyclopentene, it will not give products with eclipsed iodo and arenesulfonyl substitutents due to steric reasons. In the case of cyclohexene, both cis and trans adducts are formed. Since the trans adduct (**5** or **7**) was the predominant one with either tosyl iodide or benzenesulfonyl iodide, its formation is favored for stereoelectronic reasons as well as by faster chain transfer (k_t) as compared with ring flipping (k_f).



Structural identifications and configurational assignments were made on the basis of both the spectroscopic data and the structure of the triethylamine-induced elimination product. The 60-MHz NMR spectrum of 1-iodo-2-tosylcyclopentane (**3**) revealed a single absorption for either CHI (H_a) or $CHSO_2Ar$ (H_b), with a coupling constant (J_{ab}) of 3.5 Hz. This small vicinal coupling constant[19] fits better for the trans isomer with a torsional angle close to 120° than for the cis isomer with the vicinal hydrogens substantially eclipsed. The 60-MHz NMR spectrum of the crude adducts obtained from cyclohexene and benzenesulfonyl iodide consisted of two sets of multiplets for either CHI (H_a) or $CHSO_2Ar$ (H_b), indicating it was a mixture of isomers. In fact, both trans (**7**, 73.4%) and cis isomers (**8**, 4.6%) were obtained and were purified. The 60-MHz NMR spectrum of **7** included two unsymmetrical quartets for H_a (δ 5.1) and for H_b (δ 3.3), respectively, with $J_{ab} \simeq J_{ac} \simeq J_{ad} \simeq 3.5$ Hz. A decoupling study confirmed these assignments. Irradiation with a radio frequency of 211 Hz simplified both H_a and H_b to two doublets with $J_{ab} \simeq 3.6$ Hz, while irradiation with a radio frequency of 328 Hz changed H_a to a triplet, with $J_{ac} \simeq J_{ad} = 3.7$ Hz. H_b can also be simplified to a triplet by irradiation with a radio frequency of 453 Hz. In **8**, the unsymmetrical quartet at δ 4.72 was assigned to H_a, and the multiplet at approximately δ 2.5 was assigned to H_b. The cis (**6**) and trans (**5**) isomers obtained from reaction of cyclohexene and tosyl iodide were separated and assigned similarly (see Experimental Section).

To confirm the configurational assignments, we have also carried out the elimination of the adducts with triethylamine.[20] Usually β-iodo sulfones are easily dehydroiodinated when treated with 1.5 equiv of triethylamine in benzene at room temperature, if the leaving groups can fulfill the anti orientation for E2 elimination. Thus compounds **1** and **2** could easily be dehydroiodinated within 15 min to give the corresponding α,β-unsaturated sulfones **12** (87%) and **13** (90%), respectively (Table II). For cyclic β-iodo sulfones, marked differences can be observed be-

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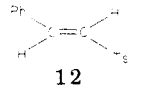
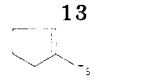
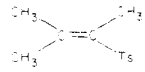
(19) (a) D. A. Nelson, E. H. Wagener, and W. F. Gum, *J. Org. Chem.*, **41**, 155 (1976). These authors observed a similar small coupling constant of 4 Hz (J_{MX}) for the H_M and H_X protons in their cyclopentene–bromodichloronitromethane adduct. (b) See N. O. Brace, *J. Am. Chem. Soc.*, **86**, 665 (1964), and references cited therein. After comparing the proton resonance absorption in CHI with other iodocyclohexanes, Dr. Brace assigned the peak at 300 Hz as that of an equatorial proton in the trans (a,a) conformer. In our study, the CHI absorptions for the trans isomers were 304 Hz (δ 5.05) in **7** and 302 Hz (δ 5) for **5** in the 60-MHz spectra.

(20) Although both Δ^1 and Δ^2 olefins were obtained from the *trans*-1-iodo-2-(perfluoroalkyl)cyclohexanes [N. O. Brace, *J. Am. Chem. Soc.*, **86**, 2428 (1964); *J. Org. Chem.*, **28**, 3090 (1963); **37**, 2429 (1972)], we only obtained the Δ^1 olefins (α,β-unsaturated sulfones) from the cyclic β-iodo sulfones (Table II) under our experimental conditions. The same result was obtained by Waters et al. for 1-iodo-2-tosylcyclohexanes.[13] We also prepared 2-methyl-3-tosyl-1-butene (the β,γ-unsaturated sulfone) by pyrolysis of **4** at 70 °C and then subjected the former to triethylamine in benzene at 35 °C for 3 days. We could not detect any α,β-unsaturated sulfone (**15**, Table II) by NMR. Therefore, β,γ-unsaturated sulfone can not be isomerized to the α,β-unsaturated sulfone by triethylamine.

Table II. Products Obtained from Elimination of HI from β-Iodo Sulfones

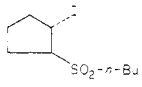
β-iodo sulfone	Et_3N/sulfone ratio (time of elimination)	unsaturated sulfones		
		compd	yield, %	mp (bp), °C
$PhCHICH_2Ts$, 1	1.5 (15 min)	 12	87	120-121
n-$BuCHICH_2Ts$, 2	1.5 (15 min)	 13	90	(148-154 (0.1 torr))
 3	2.5 (4 h)	 14	81	115-116
$(CH_3)_2ClCH(Ts)CH_3$, 4	3 (18 h)	 15	85	66-67
 5	3 (2 days)	 16	76	81-82
 6	1.5 (15 min)	16	77	81-82
 7	3 (2 days)	 17	83	40-42
 8	1.5 (15 min)	17	89	40-42

tween cis and trans isomers. *cis*-1-Iodo-2-phenylsulfonylcyclohexane (8), where both the hydrogen and the iodo groups are in axial positions, was eliminated within 15 min to give 89% of 1-phenylsulfonylcyclohexene (17). But the trans isomer 7 was eliminated much more slowly. It gave 83% of 1-phenylsulfonylcyclohexene (17) only after stirring with 3 equiv of triethylamine for 2 days. Similarly, *cis*-1-iodo-2-tosylcyclohexane (6) was eliminated much faster than the corresponding trans isomer 5. With *trans*-1-iodo-2-tosylcyclopentane (3), where the hydrogen and the iodo groups are trans but are not at exactly anti positions, elimination could be completed but required more drastic conditions. The results of elimination are summarized in Table II.

Alkanesulfonyl Iodides. The scope of the title reaction was also studied with a few alkanesulfonyl iodides. Alkanesulfonyl iodides were so unstable that they should be generated[8] and allowed to react in situ. Both methanesulfonyl and 1-butanesulfonyl iodides and their adducts with alkenes decomposed instantly when exposed to daylight. Addition reactions and the following purifications must be carried out in a darkroom or by wrapping of the reaction flasks and chromatography column with aluminum foil. As with their aromatic analogues, either methanesulfonyl or 1-butanesulfonyl iodide gave single adducts with styrene, 1-hexene, cyclopentene, and 2-methyl-2-butene, respectively. The results were summarized in Table III. Care must be taken with 2-methyl-2-butene to avoid pyrolytic decomposition of the adducts, since the tertiary iodide is apt to eliminate hydrogen iodide even upon gentle warming (~30 °C). It is interesting to note that decomposition always leads to the formation of the β,γ-unsaturated sulfones, whereas base-catalyzed eliminations always give α,β-unsaturated sulfones as products.[20]

Since sulfonyl chlorides added less readily to simple alkenes[7] as compared with acetylenes, β-iodo sulfones are undoubtedly good precursors to the corresponding α,β-unsaturated sulfones. Besides being a class of versatile synthetic intermediates, these β-iodo sulfones are also valuable for nuclear magnetic resonance studies. Preliminary nuclear magnetic resonance results have revealed that *trans*-1-iodo-2-phenylsulfonylcyclohexane (7) contains mainly the diaxial isomer, as was observed for its chloro analogue.[21] Linear adducts also showed evidence of hindered rotation around the single bond due to the presence of vicinal iodo and sulfonyl groups. Further studies in these respects are in progress in our laboratory.

Table III. Products Obtained from Addition of Alkanesulfonyl Iodides to Various Alkenes

alkene	R in RSO_2I	product isolated	yield, %
styrene	CH_3	$PhCHICH_2SO_2CH_3$, 18	57.2
1-hexene	*n*-Bu	*n*-$BuCHICH_2SO_2$-*n*-Bu, 19	85
cyclopentene	*n*-Bu	 20	50.6
2-methyl-2-butene	CH_3	$(CH_3)_2ClCH(CH_3)SO_2CH_3$, 21	50.9

Experimental Section

Materials. Cyclopentene, 1-hexene, and silica gel (Kisselgel G and Kisselgel GF 254) were purchased from Merck. 2-Methyl-2-butene, 1-phenylcyclohexene, 1-methylcyclohexene, *n*-butyl bromide, and tosyl chloride were purchased from Aldrich. Cyclohexene, styrene, copper(II) chloride, and methane- and benzenesulfonyl) chlorides were purchased from Wako Pure

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Chemical Industries Ltd. 1-Butanesulfonyl chloride[9] and all sulfonyl iodides[8] were synthesized by published procedures. Copper(II) chloride was dried at 140 °C to a constant weight before being used.

Boiling points and melting points were uncorrected. The latter were taken on a Mel-Temp instrument. Infrared spectra were recorded on a Perkin-Elmer 337 infrared spectrophotometer. All NMR spectra were obtained on a JEOL C-60 spectrometer, using Me_4Si as an internal standard.[23] The decoupling study was carried out on a JEOL FT-100 100-MHz spectrometer.

General Procedure for the Preparation of Sulfonyl Iodides.[8] Sodium *p*-toluenesulfinate was prepared by heating 97 g of tosyl chloride, 120 g of sodium sulfite, and 84 g of sodium bicarbonate in 480 mL of water at 70–80 °C for 2 h. The yield was 91% (81 g). Similarly, sodium benzenesulfinate (72.2 g, 88%) was prepared from 88.5 g of benzenesulfonyl chloride.

Tosyl iodide was prepared by adding an equivalent amount of a concentrated ethanol solution of iodine to a dilute aqueous solution of sodium *p*-toluenesulfinate. The yellow tosyl iodide precipitated and was collected and recrystallized from carbon tetrachloride; mp 90–95 °C dec (lit.[8] mp 90–95 °C dec). Since it decomposed easily, it was prepared fresh each time before use.

The alkanesulfonyl iodides and benzenesulfonyl iodide were prepared in situ by adding an equimolar quantity of iodine in benzene to a saturated aqueous solution of the corresponding sodium sulfinate under vigorous stirring. The purple color of iodine faded instantly and was replaced by the yellow-orange color of sulfonyl iodide during reaction. The benzene layer was separated and was dried briefly (3–4 h) in a refrigerator over anhydrous magnesium sulfate. The clear yellow-orange filtrate of sulfonyl iodide was used for the addition reactions immediately.

General Procedure for Addition of Sulfonyl Iodides to Alkenes. Equimolar amounts (0.1 mol) of the desired alkene and sulfonyl iodide, 1.5 mmol each of cupric chloride and triethylaminium halide,[22] and 30 mL of acetonitrile were introduced into a 100-mL flame-dried three-necked flask. The flask was equipped with a nitrogen inlet, a reflux condenser, and a magnetic stirrer and was wrapped with aluminum foil. The mixture was stirred magnetically under nitrogen at 0–40 °C for 2–4 h. Methanol (10 mL) was added to the cooled mixture to precipitate the copper salt. Concentration of the filtrate on a rotary evaporator under reduced pressure gave the crude product. Recrystallization or chromatography on silica gel with suitable solvents generally gave the pure product. The adducts obtained from the alkanesulfonyl iodides were very unstable to ordinary light. Filtration and chromatography were carried out in a darkroom to avoid decomposition of the adducts.

General Procedure for Elimination of Hydrogen Iodide. To a saturated solution of the β-iodo sulfone in benzene was added 1.5–3 equiv of triethylamine under magnetic stirring at room temperature. White triethylaminium iodide precipitated immediately. The reaction took from 15 min to 2 days for completion (Table II). At the end of the reaction triethylaminium iodide was filtered off, and the filtrate was diluted with 2 volumes of ether. It was washed first with 5% HCl and then with distilled water. The organic layer was dried over magnesium sulfate and was concentrated via a rotary evaporator at reduced pressure. Recrystallization or vacuum distillation of the resulting solid (or oil) led to the desired α,β-unsaturated sulfones.

1-Iodo-1-phenyl-2-tosylethane (1). Styrene (4.12 g, 0.04 mol) and 11.28 g (0.04 mol) of tosyl iodide at 40 °C afforded 14.6 g of **1** (Table I) as white platelets, mp 134 °C dec (2:1 benzene:chloroform; lit.[13] mp 134 °C dec).

2-Iodo-1-tosylhexane (2). 1-Hexene (6.79 g, 0.082 mol) and 14.1 g (0.05 mol) of tosyl iodide at 40 °C gave 15 g (92%) of **2**: mp 32–32.5 °C (methanol); IR (neat) 1300 (s, SO_2, asym), 1145 cm^{-1} (SO_2, sym); NMR[22] (CCl_4) δ 1 (t, 3 H, CH_3), 1.1–2.1 (m, 6 H, $(CH_2)_3$), 2.4 (s, 3 H, $CH_3C_6H_4$), 3.7 (dd, 2 H, CH_2SO_2), 4.5 (m, 1 H, CHI), 7.3 (d, 2 H, *m*-H), 7.8 (d, 2 H, *o*-H, J_{om} = 8 Hz).

Anal. Calcd for $C_{13}H_{19}O_2SI$: C, 42.63; H, 5.23; S, 8.75; I, 34.65. Found: C, 42.56; H, 5.12; S, 8.99; I, 34.79.

1-Iodo-2-tosylcyclopentane (3). Cyclopentene (4.76 g, 0.07 mol) and 14.1 g (0.05 mol) of tosyl iodide at 40 °C afforded 12.1 g (95.7%) of **3**. Recrystallization gave pure **3** as white platelets; mp 51–52 °C. An analytical sample was obtained by chromatography on silica gel using benzene as eluent: IR (KBr) 1300 (SO_2, asym), 1150 cm^{-1} (SO_2, sym); NMR ($CDCl_3$) δ 1.7–2.3 (m, 6 H, $(CH_2)_3$), 2.5 (s, 3 H, $CH_3C_6H_4$), 3.9 (m, 1 H, $CHSO_2$), 4.6 (m, 1 H, CHI, J_{ab} = 3.5 Hz), 7.3 (d, 2 H, *m*-H), 7.8 (d, 2 H, *o*-H, J_{om} = 8 Hz).

Anal. Calcd for $C_{12}H_{15}SO_2I$: C, 41.16; H, 4.32; S, 9.15; I, 36.23. Found: C, 41.10; H, 4.38; S, 9.49; I, 36.08.

2-Iodo-2-methyl-3-tosylbutane (4). Tosyl iodide (16.92 g, 0.06 mol) and 5.6 g (0.08 mol) of 2-methyl-2-butene at 0 °C gave 19.45 g (92%) of **4**: mp 73–76 °C (methanol); IR ($CHCl_3$) 1300 (SO_2, asym), 1140 (SO_2, sym) cm^{-1}; NMR ($CDCl_3$) δ 1.5 (d, 3 H, CH_3CH), 2.4 (s, 3 H, $CH_3C_6H_4$), 2.2 (s, 3 H, CH_3CI), 2.6 (s, 3 H, CH_3CI), 3.55 (q, 1 H, $CHCH_3$, $J_{3,4}$ = 7 Hz), 7.3 (d, 2 H, *m*-H), 7.75 (d, 2 H, *o*-H, J_{om} = 8 Hz).

***cis*- and *trans*-1-Iodo-2-tosylcyclohexanes.** Cyclohexene (4.1 g, 0.05 mol) and 14.1 g (0.05 mol) of tosyl iodide at 40 °C afforded 13 g of crude product. Chromatography on silica gel with benzene as eluent gave 11.72 g (68%) of the oily trans isomer **5** and 0.51 g (3%) of the cis isomer **6**, mp 144–145 °C dec (hexane–carbon tetrachloride).

5: IR (neat) 1300 (SO_2, asym), 1140 (SO_2, sym) cm^{-1}; NMR ($CDCl_3$) δ 1.2–2.2 (2 m, 8 H, $(CH_2)_4$), 2.4 (s, 3 H, $CH_3C_6H_4$), 3.3 (q, 1 H, $CHSO_2$), 5.1 (q, 1 H, CHI, $J_{ab} \simeq$ 3.3 Hz), 7.3 (d, 2 H, *m*-H), 7.7 (d, 2 H, *o*-H, J_{om} = 8 Hz).

6: IR (KBr) 1300 (SO_2, asym), 1175 (SO_2, sym) cm^{-1}; NMR (CCl_4) 1.2–2.2 (m, 8 H, $(CH_2)_4$), 2.5 (s, 3 H, $CH_3C_6H_4$), 2.55 (br s, 1 H, $CHSO_2$), 4.7 (br s, 1 H, CHI), 7.3 (d, 2 H, *m*-H), 7.9 (d, 2 H, *o*-H, J_{om} = 8 Hz).

***cis*- and *trans*-1-Iodo-2-(phenylsulfonyl)cyclohexanes.** The title compound was obtained as a mixture from reaction of 4.1 g (0.05 mol) of cyclohexene and 13.9 g (0.05 mol) of benzenesulfonyl iodide at 40 °C in benzene. Addition of ethanol to the crude product gave 0.64 g (4.6%) of the cis isomer **8**, mp 142–144 °C dec. The oil left behind was chromatographed on silica gel by using benzene as eluent to give 10.25 g (73.4%) of the trans isomer **7**, mp 81 °C (*n*-C_6H_{14}–CCl_4).

7: IR (KBr) 1310 (SO_2, asym), 1147 (SO_2, sym) cm^{-1}; NMR ($CDCl_3$) δ 1.2–2.6 (2 m, 8 H, $(CH_2)_4$), 3.45 (q, 1 H, $CHSO_2$), 5.1 (q, 1 H, CHI, $J_{ab} \simeq$ 3.5 Hz), 7.4–8.2 (m, 5 H, C_6H_5).

8: IR (KBr) 1280 (SO_2, asym), 1140 (SO_2, sym) cm^{-1}; NMR ($CDCl_3$) δ 1.2–2.2 (m, 8 H, $(CH_2)_4$), 2.55 (m, 1 H, $CHSO_2$), 4.7 (br s, 1 H, CHI), 7.3–8.2 (m, 5 H, C_6H_5).

Anal. Calcd for $C_{12}H_{15}SO_2I$: C, 41.2; H, 4.3; S, 9.3; I, 36.3.

Found: (for **7**) C, 41.19; H, 4.16; S, 9.21; I, 37.9; (for **8**) C, 41.17; H, 4.26; S, 9.43; I, 36.38.

***trans*-1-Iodo-*cis*-1-methyl-2-tosylcyclohexane (9).** 1-Methylcyclohexene (3.84 g, 0.04 mol) and 11.28 g (0.04 mol) of tosyl iodide gave 11.28 g of crude product. Recrystallization with methanol–acetonitrile (5:1) gave 10.4 g (66.7%) of pure **9**, mp 86 °C dec. The mother liquid was washed with 5% aqueous $Na_2S_2O_3$ and recrystallized from ethanol to give 1.23 g (12%) of 2-methyl-3-tosylcyclohexene (**10**), mp 70–71 °C.

9: IR (KBr) 1300 (SO_2, asym), 1130 (SO_2, sym) cm^{-1}; NMR ($CDCl_3$) δ 1.2–2.2 (2 m, 8 H, $(CH_2)_4$), 2.5 (s, 3 H, $CH_3C_6H_4$), 2.6 (s, 3 H, CH_3CI), 3.7 (t, 1 H, $CHSO_2$, $J_{ac} \simeq J_{ad}$ = 3.5 Hz), 7.2 (d, 2 H, *m*-H), 7.6 (d, 2 H, *o*-H, J_{om} = 8 Hz).

10: IR (KBr) 1590 (C=C), 1300 (SO_2, asym), 1140 (SO_2, sym) cm^{-1}; NMR ($CDCl_3$) δ 1.2–2.3 (m, 6 H, $(CH_2)_3$), 2 (s, 3 H, CH_3C=), 2.5 (s, 3 H, $CH_3C_6H_4$), 3.65 (q over br s, 1 H, $CHSO_2$), 5.85 (m over br s, 1 H, HC=), 7.3 (d, 2 H, *m*-H), 7.8 (d, 2 H, *o*-H, J_{om} = 8 Hz).

2-Phenyl-3-tosylcyclohexene (11). The only product isolated from reaction of equimolar amounts (0.021 mol) of 1-phenylcyclohexene (3.34 g) and tosyl iodide (5.91 g) in the usual manner was 2-phenyl-3-tosylcyclohexene (**11**; 2.8 g, 44%): mp 166.5–168 °C (ethanol); IR (KBr) 1600 (C=C), 1280 (SO_2, asym), 1130 (SO_2, sym) cm^{-1}; NMR ($CDCl_3$) δ 1.5–3 (m, 6 H, $(CH_2)_3$), 2.3 (s, 3 H, $CH_3C_6H_4$), 4.3 (br s, 1 H, $CHSO_2$), 6.85 (br s, 1 H, HC=), 7 (d, 2 H, *m*-H), 7.35 (d, 2 H, *o*-H, J_{om} = 8 Hz), 7.1 (s, 5 H, C_6H_5).

(22) Either triethylaminium iodide or triethylaminium chloride could be used in these additions. No difference was observed.

(23) In all tosyl iodide adducts, the aromatic protons appeared as two doublets of the AX pattern. The protons ortho to the solfonyl group are designated as *o*-H, and the other two meta protons are designated as *m*-H.

(*E*)-1-Phenyl-2-tosylethene (12). The title compound was obtained in 87% yield (3.78 g) from dehydroiodination of 6.6 g of **1**; mp 120–121 °C (ethanol; lit.[9] mp 120–121 °C).

(*E*)-1-Tosylhexene (13). Dehydroiodination of 18.3 g of **2** afforded 10.7 g (90%) of **13**: bp 148–153 °C (0.1 torr); IR (neat) 1650 (C=C), 1300 (SO_2, asym), 1140 (SO_2, sym) cm^{-1}; NMR (CCl_4) 0.9 (t, 3 H, CH_3), 1–1.7 (m, 4 H, $(CH_2)_2$), 2.2 (q, 2 H, $=CH_2$, J_{bc} = 6 Hz), 6.3 (dt, 1 H, $=CH_aC(H_c)_2$, J_{ab} = 15 Hz, J_{ac} = 2 Hz), 6.8 (td, 1 H, $=CH_bTs$, J_{ab} = 15 Hz, J_{bc} = 6 Hz), 7.3 (d, 2 H, *m*-H), 7.7 (d, 2 H, *o*-H, J_{om} = 8 Hz).

1-Tosylcyclopentene (14). Dehydroiodination of 5.25 g of 1-iodo-2-tosylcyclopentane (**3**) with 2.5 equiv of triethylamine gave 2.69 g (81%) of **14**, mp 115–116 °C (ethanol; lit.[24] mp 115–116 °C).

2-Tosyl-3-methyl-3-butene (15). Dehydroiodination of 22.75 g of **4** gave 12.3 g (85%) of **15**: mp 66–67 °C (ethanol); IR (KBr) 1650 (C=C), 1300 (SO_2, asym), 1100 (SO_2, sym) cm^{-1}; NMR ($CDCl_3$) δ 1.88 (s, 3 H, CH_3, H_a), 2 (q, 3 H, CH_3, H_c), 2.2 (q, 3 H, CH_3, H_b, J_{bc} = 1.2 Hz), 2.45 (s, 3 H, $CH_3C_6H_4$), 7.37 (d, 2 H, *m*-H), 7.8 (d, 2 H, *o*-H, J_{om} = 7.5 Hz).

1-Tosylcyclohexene (16). The title compound could be obtained from dehydroiodination of either *trans*- or *cis*-1-iodo-2-tosylcyclohexane with triethylamine. The yields were 76% (3.32 g from 6.14 g of **5**) and 77% (99 mg from 196 mg of **6**), respectively, mp 81–82 °C (ethanol; lit.[24] mp 82–83 °C).

1-(Phenylsulfonyl)cyclohexene (17). Dehydroiodination of either **7** (7.7 g) or **8** (379 mg) with triethylamine gave **17** in 83% (4.02 g) or 89% (223 mg) yield, respectively. But the cis isomer **8** reacted much faster than the trans isomer **7**. Recrystallization from ethanol gave pure **17**: mp 40–42 °C; IR (KBr) 1620 (C=C), 1300 (SO_2, asym), 1140 (SO_2, sym) cm^{-1}; NMR ($CDCl_3$) δ 1.65 (m, 4 H, $(CH_2)_2$), 2.3 (t, 4 H, $=C(CH_3)CH_2$), 7.1 (q, 1 H, $=CHCH_3$, J = 2 Hz), 7.7 (m, 5 H, C_6H_5).

1-Iodo-2-(methanesulfonyl)-1-phenylethane (18). Reaction of 2.08 g of styrene (0.02 mol) and 4.12 g (0.02 mol) of methanesulfonyl iodide at 20–25 °C gave 5.62 g (57.2%) of **18**: mp 104–106 °C (3:1 $CHCl_3$:hexane); IR (KBr) 1280 (SO_2, asym), 1120 (SO_2, sym) cm^{-1}; NMR ($CDCl_3$) δ 2.3 (s, 3 H, CH_3SO_2), 4.2 (2 d, 2 H, CH_2SO_2, J = 11 and 6 Hz), 5.45 (dd, 1 H, CHI, J = 11.6 Hz), 7.2 (m, 5 H, C_6H_5).

Anal. Calcd for $C_9H_{11}SO_2I$: C, 34.84; H, 3.55; S, 10.35; I, 40.94. Found: C, 35.11; H, 3.74; S, 10.36; I, 41.06.

1-(*n*-Butanesulfonyl)-2-iodohexane (19). Reaction of 1.68 g of 1-hexene (0.02 mol) and 4.96 g (0.02 mol) of *n*-butanesulfonyl iodide at 20–25 °C gave 5.65 g (85.1%) of **19**. The product was first purified by chromatography on a silica gel column in the dark using benzene as eluent, followed by recrystallization from 3:1 methanol:*n*-hexane to give white crystals of **19**: mp 35–36 °C; IR (neat) 1290 (SO_2, asym), 1100 (SO_2, sym) cm^{-1}; NMR ($CDCl_3$) δ 1 (t, 6 H, CH_3), 1.2–2.2 (m, 10 H, $(CH_2)_3$), 3.15 (2 d, 2 H, CH_2CHI, J = 6 Hz), 3.75 (2 d, 2 H, SO_2CH_2CI, J = 6 and 1 Hz), 4.7 (m, 1 H, CHI).

Anal. Calcd for $C_{10}H_{21}SO_2I$: C, 36.14; H, 6.33; S, 9.64; I, 38.22. Found: C, 36.29; H, 6.08; S, 10.03; I, 37.97.

1-Iodo-2-(*n*-butanesulfonyl)cyclopentane (20). Reaction of equimolar amounts (0.02 mol) of *n*-butanesulfonyl iodide (4.96 g) and cyclopentene (1.36 g) at 30–35 °C gave 3.2 g (50.6%) of **20**. Purification on a silica gel column in the dark with benzene as eluent gave an analytical pure sample: mp 12–13 °C; IR (neat) 1300 (SO_2, asym), 1130 (SO_2, sym) cm^{-1}; NMR ($CDCl_3$) δ 0.95 (t, 3 H, CH_3), 1.1–2.9 (m, 10 H, $(CH_2)_2$ and ring protons), 3 (2 d, 2 H, CH_2SO_2, J = 6 Hz), 3.8 (m, 1 H, $CHSO_2$), 4.7 (m, 1 H, CHI).

Anal. Calcd for $C_9H_{17}SO_2I$: C, 34.29; H, 5.40; S, 11.69; I, 40.29. Found: C, 34.57; H, 5.48; S, 11.76; I, 40.03.

2-Iodo-2-methyl-3-(methanesulfonyl)butane (21). Reaction of equimolar amounts (0.02 mol) of methanesulfonyl iodide (4.12 g) and 2-methyl-2-butene (1.4 g) at 0 °C gave 2.8 g (50.9%) of the title compound. Purification on a silica gel column in the dark with benzene as eluent gave 1.8 g (33%) of pure **21**: IR (neat) 1300 (SO_2, asym), 1180 (SO_2, sym) cm^{-1}; NMR ($CDCl_3$) δ 1.25 (d, 3 H, CH_3CH, J = 6 Hz), 2.0 (s, 3 H, CH_3CI), 2.12 (s, 3 H, CH_3CI), 3.72 (s, 3 H, CH_3SO_2), 4.53 (q, 1 H, $CHSO_2$, J = 6 Hz).

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Titanium Trichloride Reduction of Substituted *N*-Hydroxy-2-azetidinones and Other Hydroxamic Acids

Phillip G. Mattingly and Marvin J. Miller*

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556

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A mild method of reduction of the N–O bond of substituted *N*-hydroxy-2-azetidinones was required to complete a hydroxamic acid mediated synthesis of substituted β-lactams. Of the several reduction methods studied, most either failed to reduce the N–O bond, cleaved the 2-azetidinone ring, or were inefficient and inconvenient. However, buffered titanium trichloride cleanly reduced the N–O bond of the *N*-hydroxy-2-azetidinones under conditions compatible with a peripheral acid-sensitive *tert*-butoxycarbonyl (Boc) group and the base-sensitive chiral center at C_3. These results therefore constitute an efficient synthesis of β-lactams from substituted serinehydroxamic acids. The competitive C–O and N–O reductions of noncyclic hydroxamic acids of various substitution patterns are also described.

During the development of a synthesis of β-lactams from hydroxamic acids,[1] we required a mild method of reduction of the N–O bond of substituted *N*-hydroxy-2-azetidinones (eq 1). A number of efficient methods of N–O reduction

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