(A) Perhydrochromene derivative 29 (30 mg, 4.3%, mp 104 °C, from 95% EtOH): IR ($CHCl_3$) 2940, 1730, 1430, 1165, 1105, 965, 690 cm^{-1}; ^1H NMR δ 0.98 (s, 3 H), 1.08 (s, 3 H), 1.2–1.6 (m, 3 H), 1.7–2.0 (m, 2 H), 2.10–2.60 (m, 2 H), 2.80–3.20 (m, 2 H), 3.30 (br s, 1 H), 3.74 (s, 3 H), 3.89 (dd, J = 8 Hz, 4.4 Hz, 1 H), 7.40 (m, 3 H), 7.75 (m, 2 H); ^{13}C NMR δ 23.02 (q), 23.42 (t), 27.43 (t), 29.52 (t), 33.90 (q), 35.68 (s), 39.67 (t), 50.58 (d), 51.28 (s), 51.38 (q), 67.00 (t), 78.95 (d), 125.82 (s), 128.81 (d), 129.06 (d), 138.74 (d), 172.92 (s).

Anal. Calcd for $C_{19}H_{26}O_3Se$: C, 59.84; H, 6.87; Se, 20.70. Found: C, 59.82; H, 6.90; Se, 20.59.

(B) Spiro[tetrahydrofuran-2(3*H*),1′-[4′,4′-dimethyl-2′-(phenylseleno)cyclohexane]]-3-carboxylic acid, methyl ester (28) (340 mg, 48.3%, liquid): IR ($CHCl_3$) 2940, 1730, 1575, 1475, 1430, 1360, 1160, 1070, 990, 740, 690 cm^{-1}; ^1H NMR δ 0.88 (s, 3 H), 0.94 (s, 3 H), 1.0 (six-line m, 1 H), 1.31 (six-line m, 1 H), 1.62 (six-line m, 1 H), 1.79 (d, J = 8 Hz, 2 H, $C_{3'}$ protons), 2.04 (six-line m, 1 H), 2.30 (m, 2 H, C_4 protons), 3.30 (dd, J = 7 Hz, 6 Hz, 1 H, C_3 proton), 3.70 (t, J = 8 Hz, 1 H, $C_{2'}$ proton), 3.71 (s, 3 H, ester methyl group), 3.94 (m, 2 H, C_5 protons), 7.3 (m, 3 H), 7.65 (m, 2 H); ^{13}C NMR δ 25.17 (q), 31.33 (t), 31.66 (s, C_4), 32.15 (q), 32.55 (t), 35.79 (t), 45.14 (t), 48.31 (d, $C_{2'}$), 51.60 (q), 52.16 (d, C_3), 66.95 (t, C_5), 87.76 (s, C_2), 127 (d), 128.9 (d), 130.53 (s), 133.57 (d), 174.36 (s, C=O).

Anal. Calcd for $C_{19}H_{26}O_3Se$: C, 59.84; H, 6.87; Se, 20.70. Found: C, 59.94; H, 6.97; Se, 20.52.

8c (200 mg, 48.1%) also was isolated.

Spiro[tetrahydrofuran-2(3*H*),1′-4′,4′-dimethylcyclohex-2′-ene]-3-carboxylic acid, methyl ester (24b), prepared by reaction of **28** (192 mg, 0.5 mmol) with H_2O_2 (30%, 0.07 mL, 0.75 mmol) by the procedure described for conversion of **9** into **10a**. Preparative HPLC (ethyl acetate–hexanes, 1:9) afforded **24b** (95 mg, 84%) as a colorless oil: IR (neat) 2940, 1730, 1355, 1160, 1040, 890, 750 cm^{-1}; ^1H NMR δ 0.94 (s, 3 H), 1.02 (s, 3 H), 1.34 (m, 1 H), 1.66 (m, 3 H), 2.21, 2.41 (two m, 1 H each, C_4 protons), 2.88 (t, J = 8 Hz, C_3 proton), 3.70 (s, 3 H), 3.95 (m, 2 H, C_5 protons), 5.60 (q, J = 10 Hz, 2 H, vinyl protons); ^{13}C NMR δ 2.70 (t), 27.68 (q), 28.84 (s, $C_{4'}$), 29.59 (q), 31.68 (t), 33.62 (t), 51.63 (q), 53.33 (d), 65.68 (t), 80.81 (s, C_2), 127.75 (d), 141.62 (d), 172.70 (s).

Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 9.01. Found: C, 69.65; H, 9.01.

Acknowledgment. This work was supported by the National Institute of General Medical Science (GM 26568). Portions of the early phase of this project were discussed at the NSF Sponsored 13th Workshop on Organic Synthesis and Natural Products Chemistry. NMR spectra were recorded on a Varian XL-200 instrument purchased with funds provided, in part, by a National Science Foundation Department Instrumentation Grant.

Registry No. **5**, 96-48-0; **6a**, 61097-33-4; **6b**, 89908-76-9; **6c**, 89908-77-0; **7a**, 32591-07-4; (*R**,*R**)-**7b**, 89908-78-1; (*R**,*S**)-**7b**, 89908-79-2; **7c**, 89908-80-5; **8a**, 89908-81-6; (*R**,*R**)-**8b**, 89908-82-7; (*R**,*S**)-**8b**, 89908-83-8; **8c**, 89908-84-9; **9**, 89908-85-0; **10a**, 89908-86-1; **10b**, 89908-91-8; **11**, 89908-87-2; **12a**, 89908-88-3; **12b**, 89908-89-4; **12c**, 89908-90-7; **13**, 89908-93-0; **14a**, 89908-92-9; **14b**, 89922-00-9; **15a**, 89908-94-1; **15b**, 89908-95-2; **20**, 89908-96-3; **23**, 89908-97-4; **24a**, 89908-98-5; **24b**, 89909-06-8; **25**, 89908-99-6; **26**, 89909-00-2; **27a**, 89909-01-3; **27b**, 89909-02-4; **27c**, 89909-03-5; **28**, 89909-04-6; **29**, 89909-05-7; **30**, 89908-57-6; **31**, 89955-28-2; **32**, 89908-56-5; **33**, 89908-58-7; PhSeCl, 5707-04-0; cyclohexanone, 108-94-1; 4-methylcyclohexanone, 589-92-4; 4,4-dimethylcyclohexanone, 4255-62-3.

Reaction Manifolds of Alkenes with [Hydroxy(tosyloxy)iodo]benzene: Stereospecific *syn*-1,2-Ditosyloxylation of the Carbon–Carbon Double Bond and Other Processes

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The treatment of various alkenes with [hydroxy(tosyloxy)iodo]benzene (**1**) in CH_2Cl_2 gives moderate yields of the corresponding *vic*-bis(tosyloxy)alkanes (**2**). When *cis*- and *trans*-2-butenes, *cis*- and *trans*-2-pentenes, *cis*-3-hexene, *cis*-4-octene, and cyclohexene are reactants, the tosyloxy ligands are introduced with syn stereospecificity. With *cis*- and *trans*-stilbenes, however, a mixture of *meso*- and *dl*-1,2-diphenyl-1,2-bis(tosyloxy)ethanes results from either alkene. Some alkenes react with **1** in a different way. Thus, *trans*-3-hexene and *trans*-4-octene with **1** give low yields of 2,5-bis(tosyloxy)-3-hexene and 3,6-bis(tosyloxy)-4-octene, respectively. Evidence is presented that the formation of the bis(tosyloxy)alk*enes* proceeds via initial oxidation of the trans alkenes by **1** to conjugated dienes and subsequent conjugate ditosyloxylation of the dienes. In a few cases, molecular rearrangements occur. Thus, norbornene with **1** gives 2,7-bis(tosyloxy)norbornane, among other products, while 1,1-diphenylethylene gives deoxybenzoin (major product) and (β,β-diphenylethenyl)phenyliodonium tosylate. The reaction of styrene with **1** depends on the medium; when CH_2Cl_2 is present, the product is 1-phenyl-1,2-bis(tosyloxy)ethane, but in the absence of solvent, the product is 1,1-bis(tosyloxy)-2-phenylethane. Most alkenes react with **1** to give *p*-toluenesulfonic acid as a byproduct, and, in rare instances, (iodoxy)benzene is obtained. A mechanism for the *vic*-ditosyloxylation of alkenes by **1**, consistent with the observed syn stereospecificity, is proposed.

We recently described the reactions of several alkenes and alkynes with [hydroxy(tosyloxy)iodo]benzene (**1**),[1] a readily available, crystalline organoiodine(III) compound.[2-4] Particularly relevant is the observation that cyclohexene, 2,3-dimethyl-2-butene, styrene, and *cis*- and *trans*-stilbenes were converted directly by **1** to the corresponding *vic*-bis(tosyloxy)alkanes (**2**) (eq 1); in the case of cyclohexene, only the *cis*-1,2-bis(tosyloxy)cyclohexane was isolated.

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(3) Koser, G. F.; Wettach, R. H. *J. Org. Chem.* **1977**, *42*, 1476.
(4) Koser, G. F.; Wettach, R. H. *J. Org. Chem.* **1980**, *45*, 1542.

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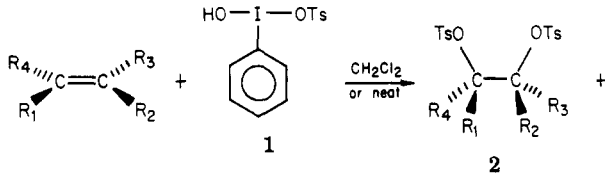


1 2 PhI + H_2O (1)

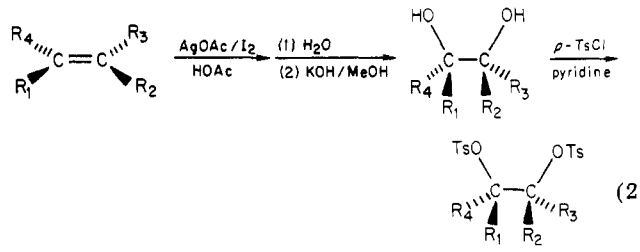
We have since investigated the action of **1** on a variety of alkenes and have found the ditosyloxylation of the carbon–carbon double bond to be a moderately general process. Furthermore, the introduction of the tosyloxy ligands proceeds with high syn stereospecificity. We now report the results of this study, including descriptions of some rather unexpected "side" reactions.

Results

Acyclic and Exocyclic Alkenes. Various acyclic alkenes of general formula C_nH_{2n} reacted with [hydroxy(tosyloxy)iodo]benzene to give moderate yields of *vic*-bis(tosyloxy)alkanes (**2**). Experimental conditions and yields for nine such alkenes are presented in Table I. The reactions were conducted by mixing **1** with the alkene in CH_2Cl_2 ($CHCl_3$ in one case), the time and temperature depending to some extent on the nature of the alkene. [Hydroxy(tosyloxy)iodo]benzene is largely insoluble in CH_2Cl_2 and gradually disappears as it is consumed to give reaction mixtures typically consisting of a solution phase containing an insoluble scum or oil or some particulate matter. *p*-Toluenesulfonic acid was a nearly ubiquitous byproduct. A typical workup involved initial extraction of the mixture with water (to remove *p*-TsOH) followed by isolation, drying, and concentration of the organic phase. The crude bis(tosyloxy)alkanes were usually oils which could be crystallized by treatment with an appropriate solvent. The bis(tosyloxy)alkanes were characterized by spectral and elemental analysis. For example, the ^1H NMR spectrum ($CDCl_3$) of the crystalline ditosylate from *cis*-2-butene exhibits a doublet at δ 1.18 (CH_3 at C-2 and C-3), a singlet at 2.41 (CH_3 of -OTs), a complex multiplet at 4.46 (methine), and an AA'XX' multiplet centered at 7.41.

The stereochemical course of the ditosyloxylation reaction was probed with the aid of four cis and trans pairs of alkenes: *cis*- and *trans*-2-butene, *cis*- and *trans*-2-pentene, *cis*- and *trans*-3-hexene, and *cis*- and *trans*-4-octene. *trans*-3-Hexene and *trans*-4-octene failed to yield *vic*-bis(tosyloxy)alkanes with **1**, but the remaining six alkenes reacted in stereospecific fashion to give *vic*-bis(tosyloxy)alkanes arising via the syn introduction of the tosyloxy ligands. The stereochemistry of the products was established by spectral comparisons (IR, ^1H NMR) and by mixed melting points with authentic compounds synthesized by treatment of the appropriate diols with *p*-toluenesulfonyl chloride in pyridine, the diols having been prepared by the method shown in eq 2.[5,6] *dl*-4,5-Octanediol was synthesized by acid-catalyzed hydrolysis of *cis*-4-octene oxide.[7]

The extent of *p*-toluenesulfonic acid formation was determined by titration of aqueous extracts of reaction mixtures with standard aqueous sodium hydroxide or by direct isolation; see Table II.



(2)

R_1	R_2	R_3	R_4
Me	Me	H	H
Me	Et	H	H
Me	H	Et	H
Et	Et	H	H
Et	H	Et	H
n-Pr	*n*-Pr	H	H

Not all of the acyclic alkenes afforded isolable *vic*-bis(tosyloxy)alkanes. 2-Methyl-2-butene (**3**) gave an oil of

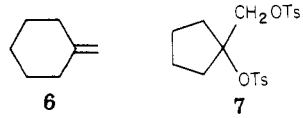
$(CH_3)_2C{=}CHCH_3$ **3**

$CH_3C(OTs)HCH{=}CHC(OTs)HCH_3$ **4**

$CH_3CH_2C(OTs)HCH{=}CHC(OTs)HCH_2CH_3$ **5**

apparently complex composition, and two of the *trans*-alkenes reacted differently than their cis congeners. Thus, while *cis*-3-hexene and *cis*-4-octene were converted by **1** into *meso*-3,4-bis(tosyloxy)hexane (51%) and *meso*-4,5-bis(tosyloxy)octane (48%), respectively, the trans analogues gave low yields of unstable solids exhibiting ^1H NMR spectra consistent with 2,5-bis(tosyloxy)-3-hexene (**4**) (8% yield) and 3,6-bis(tosyloxy)-4-octene (**5**) (15% yield).

The action of [hydroxy(tosyloxy)iodo]benzene with exocyclic alkenes was also studied to a limited extent. Methylenecyclohexane (**6**) gave an oil of complex composition,



6 **7**

but methylenecyclopentane gave an unstable solid, the ^1H NMR spectrum of which is consistent with the *vic*-bis(tosyloxy)alkane (**7**) (26% yield). Both alkenes gave moderate yields (~30%) of *p*-toluenesulfonic acid.

Cycloalkenes. [Hydroxy(tosyloxy)iodo]benzene reacted with cyclohexene, either neat or in the presence of CH_2Cl_2, to give *cis*-1,2-bis(tosyloxy)cyclohexane (Table I). The cis geometry was confirmed by comparisons of spectra (IR, ^1H NMR) and melting points with authentic *cis*- and *trans*-1,2-bis(toxyloxy)cyclohexanes: the authentic *cis*-ditosylate was prepared by the method of eq 2, and the authentic *trans*-ditosylate was synthesized by the treatment of cyclohexene sequentially with (1) HOCl, (2) NaOH, (3) H^+/H_2O, and (4) *p*-TsCl/pyridine.[8,9]

The *cis*-1,2-bis(tosyloxy)cyclohexane from reactions of cyclohexene with **1** was isolated in two polymorphs: α, mp 115–117 °C; β, mp 128–130 °C. A solidified melt of the α-polymorph showed slight decomposition and remelted at 125–127 °C. The IR (KBr) spectra of the two polymorphs are virtually identical with one another and with that of authentic *cis*-1,2-bis(tosyloxy)cyclohexane but

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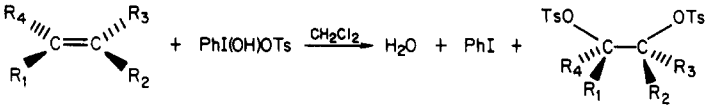
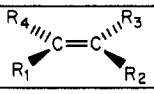
Table I. *vic*-Bis(tosyloxy)alkanes[a] from Alkenes and [Hydroxy(tosyloxy)iodo]benzene



alkene					PhI(OH)OTs,	reaction conditions			bis(tosyloxy)alkane		
R_1	R_2	R_3	R_4	mmol	mmol	CH_2Cl_2, mL	time	temp	isomer	yield, %	mp, °C
Me	Me	H	H	45.5	10.0	15	12 h	room	meso	48	92–93.5
Me	H	Me	H	60.4	10.0	10	1.5 h	room	dl	28	80–81.5
Me	H	H	Me	62.5	10.0	30	36 h	0 °C		54	
Me	Et	H	H	23	10.0	20	28 h	3 °C	dl-erythro	45	82–83
Me	H	Et	H	27	10.0	20	5 h	3 °C → room	dl-threo	19	87–89
				27	10.0	15	2 h	room	dl-threo	48	
n-Pr	H	H	H	27	10.0	20[b]	13 h	reflux		70	
Et	Et	H	H	20.2	10.0	25	11 h	room	meso	51	100.5–102[d]
n-Pr	*n*-Pr	H	H	16	10.0	25	24 h	room	meso	48	80.5–82[d]
Me	Me	Me	Me	29.0	10.0	55	0.5 h	*c*		18	
$(CH_2)_3$		H	H	34	10.0	20	3.5 h	3 °C → room		16[e]	
$(CH_2)_4$		H	H	247	9.94	0	1.5 h	room	cis	38	
				89	29.98	50	4 days	room	cis	69	
H	$(CH_2)_4$		H	15	10.0	20	1 h	~3 °C		26	
Ph	H	H	H	10.4	10.1	35	12.5 h	room		63	
Ph	Ph	H	H	10.1	10.1	50	2 weeks	room	meso	26	
									dl	32	
Ph	H	Ph	H	10.0	9.95	50	2 weeks	room	meso	24	
									dl	27	

[a] All the *vic*-bis(tosyloxy)alkanes gave the expected C,H analysis except two: 2,3-dimethyl-2,3-bis(tosyloxy)butane (thermally unstable) gave a poor analysis, and the ditosylate from methylenecyclopentane, also thermally unstable, was not submitted for analysis. [b] Chloroform was used. [c] The alkene solution at room temperature was added dropwise to a mixture of 1 and CH_2Cl_2 at 3 °C. [d] The melting points of dl-3,4-bis(tosyloxy)hexane and dl-4,5-bis(tosyloxy)octane are 122.6–125 °C and 91 °C, respectively. [e] The stereochemistry was not established.

Table II. Yields of *p*-Toluenesulfonic Acid from Reactions of Alkenes with [Hydroxy(tosyloxy)iodo]benzene



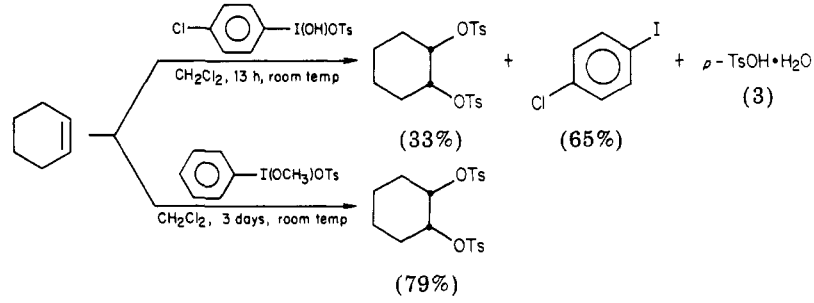
					yield of *p*-TsOH, %	
R_1	R_2	R_3	R_4	reaction conditions	by isolation[a]	by titration[b]
Me	Me	H	H	0 °C, 24 h, CH_2Cl_2		10.7
				room temp, 12 h, CH_2Cl_2	15	
Me	H	Me	H	0 °C, 27 h, CH_2Cl_2		14.3
				room temp, 1.5 h, CH_2Cl_2		24.4
n-Pr	H	H	H			~0
Me	Et	H	H	room temp, 1.5 h, CH_2Cl_2		20.0
Me	H	Et	H	room temp, 4 days, CH_2Cl_2		24.4
Et	Et	H	H	room temp, 11 h, CH_2Cl_2		22.8
Et	H	Et	H	room temp, 7.5 h, CH_2Cl_2		49.0
n-Pr	*n*-Pr	H	H	room temp, 11 h, CH_2Cl_2		45.3
n-Pr	H	*n*-Pr	H	room temp, 4 h, CH_2Cl_2		48.8
				0 °C, 20 days, CH_2Cl_2		52.4
Me	Me	Me	H		61	
Me	Me	Me	Me	see Table I		57.7
n-Pr	H	H	Me	0 °C, 3 days, CH_2Cl_2		14.5
H	$(CH_2)_4$		H	3 °C, 1 h, CH_2Cl_2		34.2
H	$(CH_2)_5$		H	0 °C, 12 h, CH_2Cl_2		32.2
$(CH_2)_3$		H	H	0 °C, 20 h, CH_2Cl_2		22.7
$(CH_2)_4$		H	H	room temp, 1.5 h, neat	10	
				room temp, 4 days, CH_2Cl_2		0.8
$(CH_2)_4$		Me	H	0 °C, 20 h, CH_2Cl_2		69.3
norbornene				reflux, 1 d, CH_2Cl_2		~0
Ph	Ph	H	H	room temp, 2 weeks, CH_2Cl_2	21	
Ph	H	Ph	H	room temp, 2 weeks, CH_2Cl_2	17	
Ph	H	H	H	room temp, 5 min, neat	10	
Ph	H	H	Ph		69	

[a] Determined by isolation of the *p*-toluenesulfonic acid after evaporation of aqueous extracts of reaction mixtures to dryness. Monohydrate assumed, although higher hydrates may have been obtained. [b] *p*-Toluenesulfonic acid assumed to be the only acid in solution.

different from the IR spectrum of the authentic *trans*-ditosylate.

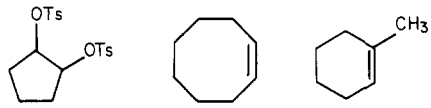
trans-1-Hydroxy-2-(tosyloxy)cyclohexane was obtained in low yield from the reaction of 1 with cyclohexene in CH_2Cl_2, and its structure was confirmed by spectral (IR, ^1H NMR) and melting point comparisons with authentic material.

cis-1,2-Bis(tosyloxy)cyclohexane was also isolated from



cyclohexene with either [methoxy(tosyloxy)iodo]benzene[10] or *p*-[hydroxy(tosyloxy)iodo]chlorobenzene;[4] eq 3.

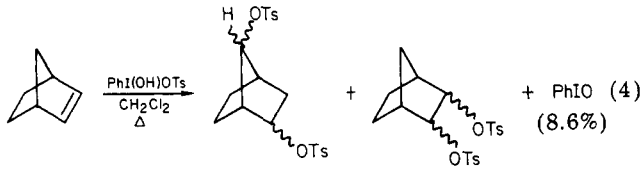
When cyclopentene was treated with **1**, 1,2-bis(tosyloxy)cyclopentane (**8**) was obtained in 15.6% yield, along with a moderate yield of *p*-toluenesulfonic acid. Isolation



8 **9** **10**

of the ditosylate requires careful control of the reaction temperature. Neither cyclooctene (**9**) nor 1-methylcyclohexene (**10**) gave *vic*-bis(tosyloxy)alkanes with **1**; in the case of **10**, the yield of *p*-toluenesulfonic acid was high (69%).

When norbornene was heated with **1** in CH_2Cl_2 under reflux, two bis(tosyloxy)alkanes were isolated, along with iodoxybenzene, one crystalline and the other an oil which could not be purified; eq 4. The crystalline material was

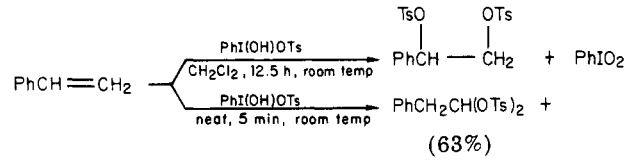


(28%)

shown by its elemental composition and NMR (^1H, ^{13}C) spectra to be 2,7-bis(tosyloxy)norbornane, a product of skeletal rearrangement. The ^{13}C NMR spectrum ($CDCl_3$) is consistent with a mixture of two diastereomers and clearly reveals the unsymmetrical placement of the tosyloxy ligands on the norbornane skeleton; i.e., the carbon atoms bound to the tosyloxy groups are nonequivalent: δ 80.60, 84.26 (major diastereomer) and δ 82.59, 85.11 (minor diastereomer). The ^1H NMR spectrum of the impure oil is consistent with 2,3-bis(tosyloxy)norbornane contaminated with a hydrocarbon, but this structural assignment must be regarded as equivocal.

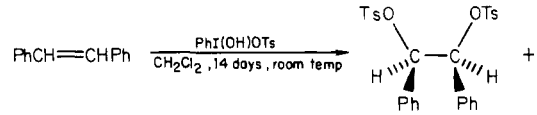
The formation of iodoxybenzene and the *absence* of *p*-toluenesulfonic acid in this reaction is noteworthy. The two byproducts may be mutually exclusive. Thus, the reaction of **1** with 1-pentene likewise gave iodoxybenzene (33%) but did not afford *p*-toluenesulfonic acid.

Phenyl-Substituted Alkenes. The reaction of styrene with **1** showed a rather remarkable solvent effect. When the reactants were mixed in the presence of CH_2Cl_2, 1-phenyl-1,2-bis(tosyloxy)ethane was obtained in 62.5% yield, and some iodoxybenzene was formed, but in the absence of solvent the products were 1,1-bis(tosyloxy)-2-phenylethane (63%) and *p*-toluenesulfonic acid (eq 5). The ^1H NMR spectra ($CDCl_3$) of the vicinal and geminal ditosylates are quite distinct. In particular, the spectrum of the geminal isomer exhibits a triplet at δ 6.26 (1 H) and

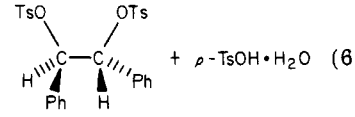


a doublet at δ 3.07 (2 H) for the side chain hydrogen atoms while that of the vicinal isomer exhibits an apparent triplet at δ 5.45 (1 H) and an AB multiplet at δ ~4.07 (2 H).

The direct attachment of phenyl groups to the carbon–carbon double bond destroys the stereospecificity of ditosyloxylations with **1**. Thus, either *trans*- or *cis*-stilbene reacted *slowly* with **1** in CH_2Cl_2 to give a mixture of *meso*- and *dl*-1,2-bis(tosyloxy)-1,2-diphenylethanes in comparable yields (eq 6, Table I). The products, which could be



cis 26%
trans 24%

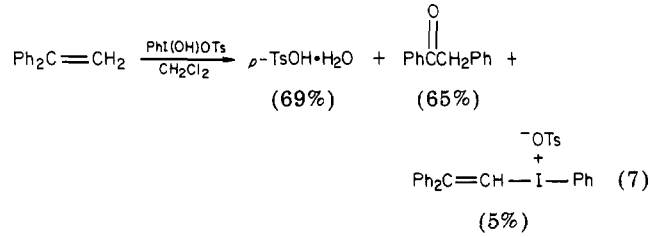


dl

cis	32%	21%
trans	27%	17%

separated easily by virtue of their differential solubilities in 3-pentanone, were identified by IR spectral comparisons with the authentic diastereomers (they could not be distinguished by ^1H NMR or by melting point comparisons). The authentic ditosylates were obtained from the appropriate diols with *p*-toluenesulfonyl chloride in pyridine, *dl*-stilbenediol having been prepared as shown in eq 2 and *meso*-stilbenediol by the sodium borohydride reduction of benzil.[11]

1,1-Diphenylethylene reacted with [hydroxy(tosyloxy)-iodo]benzene in an entirely different way (eq 7). Besides



(10) Koser, G. F.; Wettach, R. H. *J. Org. Chem.* **1980**, *45*, 4988.

(11) Fieser, L. F. "Experiments in Organic Chemistry", 3rd ef. revised; D.C. Heath: Boston, 1955, 1957; p 175.

a considerable yield of *p*-toluenesulfonic acid, there were obtained deoxybenzoin, a product of oxidative rearrangement, and a low yield of (β,β-diphenylethenyl)phenyliodonium tosylate.

Scope of the Reaction. There seems to be an inherent electronic limitation of the successful isolation of *vic*-bis(tosyloxy)alkanes from reactions of alkenes with **1**. If the olefinic component is too electron rich (e.g., EtOCH=CH_2), the products may be oils or dark colored tars of complex compositions. This does not necessarily imply that ditosylates will not be formed, but, if formed, they may be subject to facile thermal decomposition. If, on the other hand, the olefinic component is too electron poor, it may not react with **1** at all. For example, maleic anhydride is somewhat unreactive to **1**.

We have, however, obtained a ditosylate from chalcone, despite the presence of the electron-withdrawing benzoyl function on the carbon–carbon double bond (eq 8).

$$\mathrm{PhCH{=}CHC(=O)Ph} \xrightarrow[\mathrm{CH_2Cl_2,\ 44\ h,\ reflux}]{\mathrm{PhI(OH)OTs}} \underset{(57\%)}{\mathrm{PhC(OTs)HC(OTs)HC(=O)Ph}} \quad (8)$$

Discussion and Additional Results

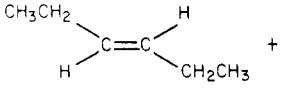
General Remarks on Stoichiometry. The most obvious stoichiometry for the ditosyloxylation of alkenes by [hydroxy(tosyloxy)iodo]benzene is shown in eq 9: 1 mol

$$\mathrm{R_1R_4C{=}CR_2R_3 + 2PhI(OH)OTs \rightarrow R_1R_4C(OTs)C(OTs)R_2R_3 + PhI + PhIO + H_2O} \quad (9)$$

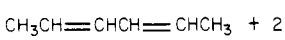
of alkene would require 2 mol of **1** to give 1 mol each of *vic*-bis(tosyloxy)alkane, iodobenzene, iodosobenzene, and water. The role of **1** is apparently 2-fold: 1 mol of **1** to serve as an oxidant for the alkene and to provide one tosylate ligand, and 1 mole of **1** to donate the *elements* of *p*-TsOH to appropriate intermediates, the tosylate "portion" being utilized in the production of the bis(tosyloxy)alkane and the hydrogen "ion" in the production of water. In a quantitative conversion, *p*-TsOH would *not* be an end product; however *p*-TsOH is a significant byproduct in most such reactions, and iodosobenzene has not been obtained. The ditosyloxylation process is far from quantitative (see Table I), and there is substantial evidence that *p*-TsOH originates in competitive and secondary reaction pathways. The fate of any iodosobenzene is more difficult to ascertain. The presence of iodosobenzene as an *end* product can be ruled out for any reaction in which *p*-TsOH is an end product, since iodosobenzene would be converted immediately back to **1** by *p*-TsOH. We can only conclude that, in most of the reactions studied, iodosobenzene is either not formed or, if it is, there exists some mechanism for its ultimate reduction to iodobenzene.

Competitive Oxidation of Alkenes to Dienes; A Source of *p*-Toluenesulfonic Acid. The isolation of 2,5-bis(tosyloxy)-3-hexene and 3,6-bis(tosyloxy)-4-octene from the reactions of *trans*-3-hexene and *trans*-4-octene with **1** reveals an alternate mode of oxidation of alkenes by **1**. The two-electron oxidation of an alkene to a conjugated diene coupled with the two-electron reductive decomposition of **1** to give 1 mol of *p*-TsOH per mole of **1** in addition to 1 mol each of water and iodobenzene is proposed. Subsequent 1,4-ditosyloxylation of the diene by **1** would give a bis(tosyloxy)alk*ene*; (eq 10 and 11).

This suggestion is supported by the identification (by gas chromatography) of *cis,trans*-2,4-hexadiene and *trans,trans*-2,4-hexadiene from a reaction of *trans*-3-hexene with PhI(OH)OTs in CH_2Cl_2 in 2.0% and 3.4% yields, respectively.[12] In another experiment, authentic *trans*,-

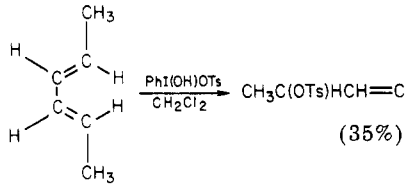


$$\mathrm{CH_3CH{=}CHCH{=}CHCH_3 + PhI + \textit{p}\text{-}TsOH + H_2O} \quad (10)$$



$$\mathrm{CH_3C(OTs)HCH{=}CHC(OTs)HCH_3 + PhI + PhIO + H_2O} \quad (11)$$

trans-2,4-hexadiene was treated with **1** in CH_2Cl_2 at 0–5 °C to give 2,5-bis(tosyloxy)-3-hexene (34.9% yield) as a white crystalline solid (eq 12). The compound is some-



(12)

what unstable at room temperature, but it can be stored at −20 °C.[13] The ^{1}H NMR spectrum (CD_2Cl_2) of the product is similar to that of the ditosylate from *trans*-3-hexene (in $CDCl_3$). The spectra of both products exhibit a 6 H doublet, a 6 H singlet, two 2 H multiplets (methine and vinyl hydrogens) and an AA′XX′ multiplet. It seems likely that the mixture of isomeric 2,4-hexadienes from the oxidation of *trans*-3-hexene would afford a more complex mixture of 2,5-bis(tosyloxy)-3-hexene diastereomers than that arising from pure *trans,trans*-2,4-hexadiene, especially if the conjugate ditosyloxylation reaction is stereospecific.

Other Sources of *p*-Toluenesulfonic Acid. Other than the oxidation of alkenes by **1** to conjugated dienes, primary sources of *p*-TsOH have been difficult to define. The origin of *p*-TsOH in the reaction of **1** with 1,1-diphenylethylene is obvious since the major product, deoxybenzoin, would be generated via the formal removal of an oxygen atom from the iodine reagent. The situation with the stilbenes is not so clear, and, although one might speculate on the capture of intermediate stilbene radical–cations with water as a proton source, the appropriate products have not been isolated and identified.

In some cases, *p*-TsOH may arise in a secondary reaction involving the decomposition of a first formed *vic*-bis(tosyloxy)alkane (or a transient bis(tosyloxy)alkene; see foregoing discussion). Indeed, the crystalline ditosylate of 2,3-dimethyl-2-butene gradually decomposes on standing at room temperature, either in the solid state or in CH_2Cl_2 solution, to give at 96% yield of *p*-TsOH and a yellow oil of complex composition. The ditosylate of methylenecyclopentane has also been observed to decompose within 0.5 h at room temperature to an acidic gray solid.

Reported anodic oxidation potentials for various alkenes in CH_3CN *decrease* with increased substitution at the carbon–carbon double bond,[14-17] and there is at least a *crude* inverse relationship between those potentials and

(12) The dienes were identified by GLC comparisons with authentic samples. *cis,cis*-2,4-Hexadiene was not in our possession, and we cannot be certain that it would have been separated from either the cis,trans or the trans,trans isomer under the conditions that we employed. We can say, however, that the total yield of surviving dienes was 5.4%.

(13) Because the bis(tosyloxy)alkenes from *trans,trans*-2,4-hexadiene, *trans*-3-hexene and *trans*-4-octene are unstable at room temperature, they were not submitted for C,H analysis. The assigned structures are based on their ^{1}H NMR spectra.

(14) Fleischmann, M.; Pletcher, D. *Tetrahedron Lett.* **1968**, 6255.

(15) Shono, T.; Ikeda, A. *J. Am. Chem. Soc.* **1972**, *94*, 7892.

(16) Shono, T.; Matsumura, Y.; Nakagawa, Y. *J. Am. Chem. Soc.* **1974**, *96*, 3532.

(17) Gassman, P. G.; Yamaguchi, R.; Koser, G. F. *J. Org. Chem.* **1978**, *43*, 4392.

the *p*-TsOH yields for those alkenes where both measurements have been made: e.g., alkene ($E_{1/2}$, V, % TsOH) $Me_2C{=}CMe_2$ (1.48, 58%), MeCH=CHMe (2.26, 11–24%), $CH_3CH_2CH_2CH{=}CH_2$ (2.78, ~0%), and 1-methylcyclohexene (1.70, 69%), cyclopentene (2.03 or 1.96, 23%), cyclohexene (2.05 or 2.14, 0.7% and 10%).

Stoichiometry in the Reaction of 1-Pentene with 1. Among the acyclic alkenes, the behavior of 1-pentene appears to be unique. Thus, *p*-TsOH was not generated as a endproduct, but iodoxybenzene was obtained (eq 13).

$$\underset{(27.4\ \text{mmol})}{CH_2{=}CHCH_2CH_2CH_3} + \underset{(10.0\ \text{mmol})}{PhI(OH)OTs} \xrightarrow[13\ \text{h, reflux}]{CHCl_3} \underset{(3.06\ \text{mmol})}{C(OTs)H_2C(OTs)HCH_2CH_2CH_3} + \underset{(1.47\ \text{mmol})}{PhIO_2} + \underset{(8.68\ \text{mmol})}{PhI} \quad (13)$$

The formation of iodoxybenzene under the reaction conditions ($CHCl_3$, reflux) is not surprising since iodosobenzene, the expected byproduct, is known to disproportionate on heating to iodobenzene and iodoxybenzene.[18] A 3.06-mmol yield of 1,2-bis(tosyloxy)pentane would require the consumption of 6.12 mmol of [hydroxy(tosyloxy)iodo]benzene and would be accompanied by the production of 3.06 mmol of iodosobenzene. This corresponds to a 1.53 mmol yield of iodoxybenzene, close to the observed yield of 1.47 mmol. The yield of iodobenzene (by GLC) was 8.68 mmol, again close to the expected yield of 8.47 mmol if all of the original [hydroxy(tosyloxy)iodo]benzene were converted to either iodobenzene or iodoxybenzene. We cannot, however, explain how the 3.88 mmol of 1 not involved in the ditosyloxylation reaction could give iodobenzene without also giving 3.88 mmol of *p*-TsOH.

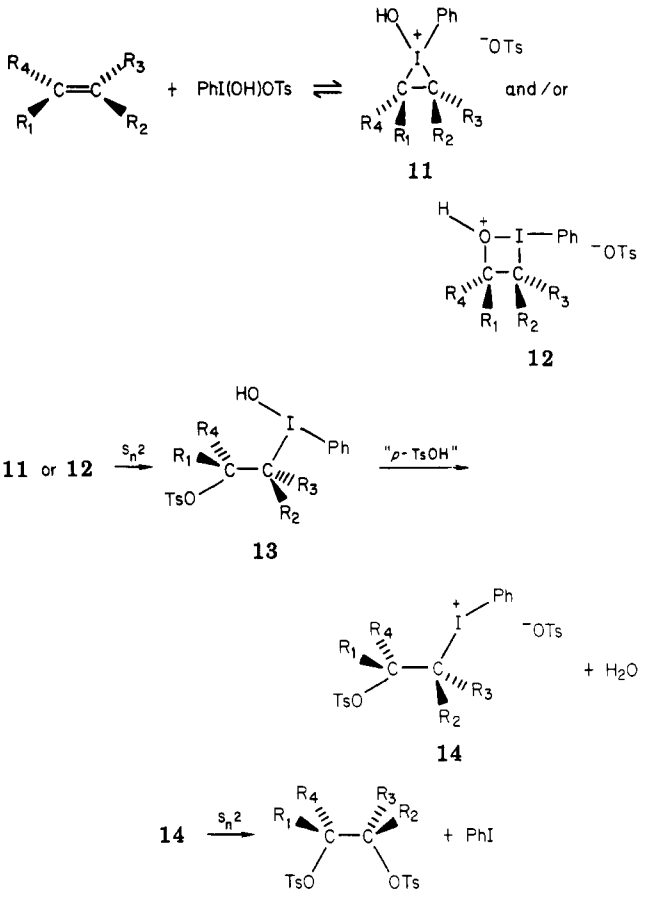
Mechanism. The mechanism for the conversion of alkenes by 1 into *vic*-bis(tosyloxy)alkanes must account for the cis introduction of the tosyloxy ligands into the carbon–carbon double bond. This stereochemical constraint is consistent with a *cyclic* organoiodine intermediate. Two likely structures (**11** and **12**) for such an intermediate are given in Scheme I, both of which might be expected to arise via electrophilic addition of the phenyl(hydroxy)iodonium ion to the double bond of the alkene. Nucleophilic collapse of either **11** or **12** to the hydroxyiodinane **13** with inversion of configuration at carbon followed by dehydration of **13** with *p*-toluenesulfonic acid, or its formal equivalent, to give the phenyl[(β-tosyloxy)alkyl]iodonium tosylate (**14**) is proposed. Nucleophilic displacement of iodobenzene by the tosylate ion in **14** with inversion of configuration at carbon would give a *vic*-bis(tosyloxy)alkane, an overall syn ditosyloxylation.

Several features of the proposed mechanism warrant further discussion.

(1) The suggested electrophilic behavior of **1** is supported by its known reactions with various thiophenes and activated arenes (e.g., anisole) to give phenyl(α-thienyl)iodonium tosylates[3,19] and arylphenyliodonium tosylates.[2,19]

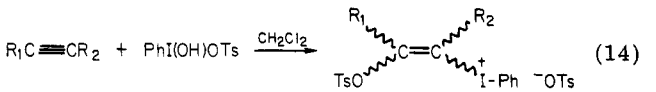
(2) A single-crystal X-ray study of [hydroxy(tosyloxy)iodo]benzene has shown the I–OTs bond to be substantially elongated (2.473 Å) relative to the sum of the oxygen and iodine covalent radii (1.99 Å) and the three sulfur–oxygen bonds of the tosyloxy group to be nearly equal in length (i.e., 1.467 Å, 1.453 Å, and 1.436 Å.[20] Thus the I–OTs bond of crystalline **1** appears to be partially ionic.

Scheme I



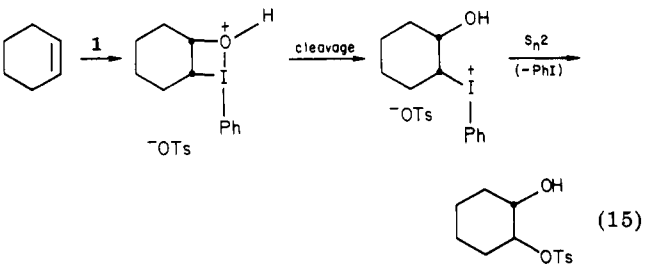
(3) The displacement of iodobenzene from sp^3 carbon by the tosylate ion, depicted in the last step, finds ample precedent in the known reactivity of dialkylhalonium ions, R–X^+–R′, toward a variety of weak nucleophiles (alkenes, ethers, etc.).[21]

(4) Finally, the existence of such iodonium species as **14** is consistent with the known reactions of **1** with various alkynes to afford stable phenyl((β-tosyloxy)vinyl)iodonium tosylates (eq 14).[1]



(14)

Besides providing a rationale for the syn introduction of tosyloxy ligands into the π-bond of alkenes, the proposed cyclic iodine(III) intermediate **12** is consistent with other processes that have been observed, for example, the formation of *trans*-1-hydroxy-2-(tosyloxy)cyclohexane (3.8% yield) from cyclohexene and **1** in CH_2Cl_2 (eq 15).



(15)

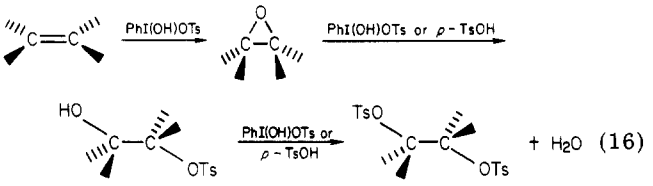
Deoxybenzoin, isolated in 65% yield from the reaction of **1** with 1,1-diphenylethylene, might also originate from

(18) For example, see: Lucas, H. J.; Kennedy, E. R. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. III, p 483.
(19) Koser, G. F.; Margida, A. J., unpublished results.
(20) Koser, G. F.; Wettach, R. H.; Troup, J. M.; Frenz, B. A. *J. Org. Chem.* **1976**, *41*, 3609.
(21) Olah, G. A. "Halonium Ions"; Wiley-Interscience: New York, 1975; Chapter 3.

a cyclic iodine(III) species by iodine–oxygen bond cleavage and subsequent pinacol rearrangement.

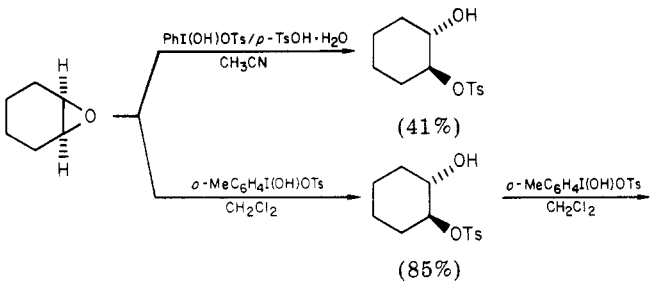
We emphasize, however, that the formation of a vinylphenylidonium tosylate (5% yield) from 1 and 1,1-diphenylethylene, a process which requires a β-proton elimination, and the loss of stereospecificity in reactions of 1 with *cis*- and *trans*-stilbenes suggests the possible intervention of "open" carbenium ions along the reaction coordinate, at least for those alkenes with phenyl substituents on the carbon–carbon double bond.

The initial formation of epoxides from alkenes and 1 and their conversion to the observed *vic*-bis(tosyloxy)alkanes (eq 16) seems unlikely, since such a process should proceed



+ H_2O (16)

with anti ditosyloxylation. Furthermore, when authentic cyclohexene oxide was treated with 1 and *p*-TsOH·H_2O in acetonitrile (a better solvent than CH_2Cl_2 for *p*-TsOH·H_2O) for 17 days at room temperature, *trans*-1-hydroxy-2-(tosyloxy)cyclohexane was obtained in 41% yield; eq 17.



no bis(tosyloxy)cyclohexanes (17)

Similar treatment of the epoxide with *o*-[hydroxy(tosyloxy)iodo]toluene in CH_2Cl_2 (6 days, room temperature) gave an 85% yield of the same product. Finally, when *trans*-1-hydroxy-2-(tosyloxy)cyclohexane was treated with *o*-[hydroxy(tosyloxy)iodo]toluene (CH_2Cl_2, 5 days, room temperature), there was no evidence (TLC analysis) for bis(tosyloxy)cyclohexane formation.

Historical Perspective. The ditosyloxylation of alkenes by 1 finds analogy in the diacetoxylation of *trans*-anethole and cyclopentadiene with (diacetoxyiodo)arenes, $ArI(OAc)_2$,[22] and in the stereoselective, *cis*-ditrifluoroacetoxylation of a variety of alkenes with tris(trifluoroacetoxy)iodine.[23,24] In the latter study, *gem*-bis(trifluoroacetoxy)alkanes were obtained as minor products from all methyl-substituted ethylenes except 2,3-dimethyl-2-butene, and as the major product from styrene. The oxidative rearrangement of 1,1-diphenylethylene to deoxybenzoin by 1 is similar to conversions of various 1,1-diarylethylenes by (difluoroiodo)arenes, $ArIF_2$, to the corresponding 1,1-difluoro-1,2-diarylethanes.[25-28] Finally, the formation of 2,7-bis(tosyloxy)norbornane from 1 and norbornene is analogous to the conversion of norbornene by (difluoroiodo)benzene to 2,7-difluoronorbornane.[29]

(22) Criegee, R.; Beucker, H. *Liebigs Ann. Chem.* **1939**, *541*, 218.
(23) Buddrus, J. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 163.
(24) Buddrus, J.; Plettenberg, H. *Chem. Ber.* **1980**, *113*, 1494.
(25) Carpenter, W. *J. Org. Chem.* **1966**, *31*, 2688.
(26) Zupan, M.; Pollak, A. *J. Chem. Soc., Chem. Commun.* **1975**, 715.
(27) Gregorcic, A.; Zupan, M. *Bull. Chem. Soc. Jpn.* **1976**, *50*, 517.
(28) Patrick, T. B.; Scheibel, J. J.; Hall, W. E.; Lee, Y. H. *J. Org. Chem.* **1980**, *45*, 4492.

Experimental Section

General Methods. 60-MHz ^1H NMR spectra were recorded on a Varian Model EM-360 spectrometer. Chemical shifts are expressed relative to internal Me_4Si, and the number of "protons" reported for a given multiplet is based on the combined integrations of all resonances in a spectrum (except for those of minor impurities) divided by the total number of "protons" in the molecule under consideration. The ^{13}C NMR spectrum of 2,7-bis(tosyloxy)norbornane was recorded on a Varian Model FT-80A spectrometer, chemical shifts being expressed relative to internal Me_4Si. IR spectra were recorded on a Perkin-Elmer Model 597 spectrophotometer and were calibrated against polystyrene (1603 cm^{-1}). IR samples were generally prepared as KBr pellets, and, usually, only the peaks between 600 and 1600 cm^{-1} are reported. GLC analyses were performed on a Hewlett-Packard Model 5750 gas chromatograph, equipped with a Model 3380A integrator, in the FID mode. Elemental compositions were determined by Galbraith Laboratories Inc., Knoxville, TN. Melting points, decomposition points, and boiling points are uncorrected. In workups involving the concentration of solutions under aspirator vacuum, a Büchi Rotavapor was employed.

Reactions of Alkenes with [Hydroxy(tosyloxy)iodo]benzene (1). Summaries of experimental conditions for reactions of 1 with those alkenes that gave *vic*-bis(tosyloxy)alkanes are given in Table I. The reaction mixtures typically consisted of a solution phase containing an insoluble component (i.e., a scum, oil, or solid), *sometimes* identified as either iodoxybenzene or *p*-toluenesulfonic acid. In a few instances, workup was preceeded by dilution or filtration steps, but not usually. In the initial stage of workup, the reaction mixtures were extracted with H_2O, dried, and concentrated to a residual oil. The oils were then crystallized by treatment with an appropriate solvent or combination of solvents (e.g., Et_2O, pentane, Et_2O–pentane, MeOH, ketone), often at low temperature (i.e., 0 °C, −20 °C). The *vic*-bis(tosyloxy)alkanes, thus obtained, were identified by spectral and elemental (C,H) analysis and, in some cases, by spectral comparisons and mixed melting points with authentic compounds.

One representative experimental procedure is given below and is followed by brief descriptions of the crystallization stage of workup for all reactions given in Table I. *Complete experimental details, including spectral and analytical (C,H) information, are given in the microfilm edition of this journal.* Experimentals for reactions of 1 with those alkenes that gave products other than *vic*-bis(tosyloxy)alkanes are fully described herein.

***cis*-2-Pentene.** A mixture of 1 (3.92 g, 10.0 mmol), *cis*-2-pentene (2.5 mL, 1.6 g, 23 mmol), and CH_2Cl_2 (20 mL) was allowed to stand for 28 h at 3 °C. A slightly yellow solution containing a clear, floating scum resulted. This was washed with H_2O (2 × 20 mL), dried (Na_2SO_4), and concentrated, under aspirator vacuum, to a yellow oil. The oil was washed with pentane (15 mL) and crystallized from MeOH (6 mL)/pentane (3 mL) at −20 °C to give 0.827 g (40%) of *erythro*(*dl*)-2,3-bis(tosyloxy)pentane: mp 82–83 °C. The pentane wash, upon cooling at 0 °C, returned an additional 0.092 g of product: mp 81.5–83.5 °C; combined yield 0.918 g (44.5%); IR (KBr) 1600, 1487, 1455, 1400, 1360, 1300, 1215, 1193, 1109, 1090, 1040, 1020, 1000, 960, 937, 910, 880, 860, 829, 790, 772, 750, 711, 683, 627 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.78, 1.19 and 1.33–1.90 (closely spaced "distorted" t, d and m with five major peaks, 8.5 H, CH_3 and CH_2CH_3), 2.42 (s, 5.9 H, CH_3 of OTs), 4.49 (*ca.* symmetric complex m, 1.8 H, CH's), 7.47 (AA'XX' m, lower two lines "split", 7.9 H).

Anal. Calcd for $C_{19}H_{24}S_2O_6$: C, 55.31; H, 5.88. Found: C, 55.27; H, 6.07.

In another experiment conducted similarly, except for a reaction time of 67 h, the product was obtained in 56% yield; mp 80–82 °C.

The stereochemistry was confirmed by melting points of 50:50 mixtures of the reaction product with authentic *erythro*(*dl*)- and *threo*(*dl*)-2,3-bis(tosyloxy)pentanes: authentic erythro (mp 81.5–83 °C); authentic threo (mp 88–89 °C); reaction product/authentic erythro (mp 80–81.5 °C); reaction product/authentic threo (mp 66–78 °C).

(29) Gregorcic, A.; Zupan, M. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1446.

***cis*-2-Butene.** The clear, viscous oil was crystallized from Et_2O (20 mL):pentane (30 mL) at −20 °C to give 0.958 g (48%) of *meso*-2,3-bis(tosyloxy)butane, mp 92–93.5 °C.

***trans*-2-Butene.** The clear, colorless oil was washed with pentane (2 × 10 mL) and crystallized from Et_2O (5 mL):pentane (7 mL) to give 0.57 g (28%) of *dl*-2,3-bis(tosyloxy)butane, mp 80–81.5 °C.

2-Methylpropene. The white solid was triturated with Et_2O (2 × 20 mL) to give 1.07 g (54%) of 1,2-bis(tosyloxy)-2-methylpropane, mp 87 °C dec.

1-Pentene. The clear oil was washed twice with pentane (25 mL):Et_2O (3 mL) and solidified on standing; the yield of 1,2-bis(tosyloxy)pentane was 1.44 g (70%), mp 48.5–52.5 °C.

***trans*-2-Pentene.** The clear oil was washed with pentane (2 × 5 mL) and allowed to stand under pentane (1 h at room temperature, 24 h at 0 °C) whereupon it crystallized: yield, 0.384 g. The original pentane washings, upon treatment with Et_2O (0.5 mL) and cooling at 0 °C, returned 0.109 g more of crystalline material. The combined solids were recrystallized form MeOH (3 mL):pentane (3 mL) at −20 °C to give 0.386 g (18.7%) of *threo*(*dl*)-2,3-bis(tosyloxy)pentane, mp 87–89 °C.

***cis*-3-Hexene.** A solution of the clear oil in MeOH (20 mL) was cooled to −20 °C to give 0.88 g (41%) of *meso*-3,4-bis(tosyloxy)hexane, mp 100.5–102 °C. The mother liquor was concentrated to a brown oil which was dissolved in CH_2Cl_2 (25 mL), treated with charcoal, and reconcentrated to a yellow oil. The yellow oil, upon dissolution in warm pentane (15 mL):Et_2O (5 mL) and cooling to 0 °C, gave 0.20 g more of product, mp 96–99 °C.

***cis*-4-Octene.** The light brown, viscous oil was dissolved in Et_2O (40 mL):pentane (10 mL), and the solution was stored for 24 h at −20 °C to give light brown crystals. These were washed with pentane and identified as *meso*-4,5-bis(tosyloxy)octane: yield, 1.10 g (48%). Recrystallization of 0.5 g of the "crude" product from ligroin (50 mL) returned 0.48 g of white needles, mp 78–81 °C. A second recrystallization returned 0.40 g of product, mp 80.5–82 °C.

2,3-Dimethyl-2-butene. The clear oil was triturated with pentane to give 0.376 g (18%) of 2,3-dimethyl-2,3-bis(tosyloxy)butane, mp 68 °C dec.

Cyclopentene. The yellow oil was washed twice with pentane (17 mL):Et_2O (3 mL) and dissolved in Et_2O (5 mL). The solution was cooled for 12 h at −20 °C to give 0.321 g (15.6%) of 1,2-bis(tosyloxy)cyclopentane, mp 65–70 °C. Recrystallization from Et_2O (1.5 mL):pentane (5 drops) returned 0.230 g of product, mp 68–72 °C.

Cyclohexene (Neat). A solution of the clear, viscous oil in warm Et_2O (70 mL), after standing for 16 h at room temperature, 4 h at 0 °C, and 4 h at −20 °C, gave 0.7979 g (38%) of *cis*-1,2-bis(tosyloxy)cyclohexane: mp (α-form) 115–117 °C; mp (β-form) 128–130 °C.

Cyclohexene (CH_2Cl_2). A solution of the clear, viscous oil in warm Et_2O (50 mL) was cooled for 1 day at 0 °C to give 4.40 g of *cis*-1,2-bis(tosyloxy)cyclohexane. Evaporation of the mother liquor left a crystalline residue which was washed with pentane and recrystallized from Et_2O (4 mL):CH_2Cl_2 (1 mL) to give 0.31 g (3.8%) of *trans*-1-hydroxy-2-(tosyloxy)cyclohexane, mp 94–95.5 °C [lit.[30] mp 93–95 °C].

Methylenecyclopentane. The "dirty" yellow oil was dissolved in warm pentane (15 mL):Et_2O (3 mL), and, after 2 h at room temperature, the solution yielded 0.445 g (21%) of 1-((tosyloxy)methyl)-1-(tosyloxy)cyclopentane. Upon cooling at −20 °C, the mother liquor gave 0.12 g more of product: combined yield, 0.56 g (26%); mp 50–52 °C dec.

Styrene. Iodoxybenzene was removed from the reaction mixture, and the CH_2Cl_2 filtrate was washed with H_2O, dried, and concentrated to a volume of 1.5 mL. Pentane (90 mL) was then added, slowly and with stirring, to the concentrate whereupon a solid separated. The solid was washed with pentane, dissolved in CH_2Cl_2 (20 mL), and reprecipitated with pentane to give 1.44 g (62.5%) of 1,2-bis(tosyloxy)-1-phenylethane, mp 116–118 °C.

***cis*-Stilbene.** The light brown oil was dissolved in boiling 3-pentanone (30 mL), and the solution was allowed to stand at room temperature whereupon 0.682 g (26%) of *meso*-1,2-diphenyl-1,2-bis(tosyloxy)ethane separated; mp range 116–131 °C dec. The mother liquor was concentrated to 10 mL, mixed with Et_2O (10 mL) and cooled at 0 °C to give 0.834 g (32%) of *dl*-1,2-diphenyl-1,2-bis(tosyloxy)ethane, mp range 116–131 °C.

***trans*-Stilbene.** Same workup as that for *cis*-stilbene.

Chalcone. A solution of the yellow oil in 2-butanone was cooled for 30 h at −20 °C to give 0.995 g of 1,2-diphenyl-2,3-bis(tosyloxy)-1-oxopropane. Concentration of the mother liquor followed by the addition of hot MeOH (10 mL) gave 0.581 g more of product: combined yield, 1.576 g (57%); mp 136–138 °C dec.

***trans*-4-Octene.** A mixture of 1 (3.92 g, 10.0 mmol), *trans*-4-octene (3.0 mL, 2.14 g, 19.1 mmol), and CH_2Cl_2 (20 mL) was allowed to stand for 20 days at 0 °C. The reaction mixture was then washed with H_2O (2 × 10 mL), dried (Na_2SO_4), and concentrated, under aspirator vacuum, to a yellow oil. The oil was taken up in ~13 mL of Et_2O/pentane (7:5 v/v), and the resulting solution was cooled at −20 °C whereupon some solid material began to separate. More pentane (5 mL) was added, over a period of 3 h, and the mixture was cooled at −70 °C for 1.5 h. The solvent was then removed by decantation, and the slush that remained was washed with cold pentane (2 × 20 mL), pumped under aspirator vacuum, and subjected to a quick N_2 purge. The slushy brown solid finally obtained was identified by ^1H NMR analysis as 3,6-bis(tosyloxy)-4-octene: yield, 0.35 g (15%); ^1H NMR ($CDCl_3$) δ 0.52–1.78 (closely spaced m's including a distorted t, a d and an apparent q, 10.4 H), 2.41 (s, 5.9 H), 4.70 (m, some fine structure, 1.8 H), 5.37 (m, some fine structure, 1.9 H), 7.47 (AA'XX' m, 7.9 H); impurities.

The product readily decomposed to an acidic black tar and was not submitted for elemental analysis. Titration of the aqueous extracts from the above workup with standardized aqueous NaOH indicated a 52.4% yield of *p*-TsOH.

***trans*-3-Hexene.** A mixture of 1 (1.96 g, 5.00 mmol), CH_2Cl_2 (10 mL), and *trans*-3-hexene (1.20 mL, 0.813 g, 9.66 mmol) was stirred as the temperature was gradually allowed to raise, over a 7-h period, from 3 °C to 24 °C. The reaction mixture was subsequently washed with H_2O (2 × 20 mL), dried (Na_2SO_4), and concentrated, under aspirator vacuum, to a clear oil. The oil was washed with pentane and dissolved in Et_2O (4 mL):pentane (3 mL). Upon cooling at 0 °C, the solution yielded 0.093 g of a solid precipitate identified as 2,5-bis(tosyloxy)-3-hexene: ^1H NMR ($CDCl_3$) δ 1.17 (d, 6.2 H), 2.38 (s, 6.1 H), 4.76 (poorly resolved m, 1.9 H), 5.31 (poorly resolved m, 1.8 H), 7.38 (AA'XX' m, 8.0 H), 3.41 (m, impurity).

The solid rapidly decomposed to an acidic black tar and was not submitted for elemental analysis. Titration of the aqueous extracts from the above workup with standardized aqueous NaOH indicated a 49% yield of *p*-TsOH.

Styrene (Neat). 1 (3.94 g, 10.04 mmol) was added to 15 mL of styrene, and the mixture was stirred at room temperature. Within 5 min, a clear solution mixed with a small quantity of solid matter was obtained. This was diluted with CH_2Cl_2 (65 mL), washed with H_2O (2 × 20 mL), dried ($MgSO_4$), and concentrated, under aspirator vacuum, to a clear viscous oil. The oil was dissolved in CH_2Cl_2 (10 mL), and the solution was treated with hexane (120 mL) whereupon a white solid precipitated. After the mixture was stirred for 0.5 h, the solid was isolated and identified as 1,1-bis(tosyloxy)-2-phenylethane: yield, 1.402 g (63%); mp 92.5–95.5 °C; ^1H NMR ($CDCl_3$) δ 2.33 (s, 6.0 H), 3.07 (d, $J \sim 6$ Hz, 1.8 H), 6.26 (t, $J \sim 6$ Hz, 1.05 H), 6.73–7.69 (Ar m, 13.2 H).

Anal. Calcd for $C_{22}H_{22}S_2O_6$: C, 59.18; H, 4.97. Found: C, 59.04; H, 5.14.

The aqueous extracts, upon evaporation, gave 0.194 g (10%) of *p*-TsOH·H_2O (^1H NMR).

1,1-Diphenylethylene. A solution of 1,1-diphenylethylene (1.906 g, 10.6 mmol) in CH_2Cl_2 (20 mL) was added dropwise over 1 h to a cold (~3 °C), stirred mixture of 1 (3.96 g, 10.1 mmol) and CH_2Cl_2 (40 mL). A solution mixed with undissolved *p*-TsOH·H_2O was obtained. After filtration, the CH_2Cl_2 solution was extracted with H_2O (2 × 20 mL), dried ($MgSO_4$), and concentrated, under aspirator vacuum, to a yellow slush. This was dissolved in CH_2Cl_2 (10 mL), and the solution was treated with Et_2O (75 mL), slowly and with stirring, whereupon (β,β-diphenylethenyl)phenyliodonium tosylate separated: yield, 0.295 g (5.3%); mp 112–113 °C dec; ^1H NMR (Me_2SO-d_6) δ 2.23 (s, 3.2

(30) Roberts, R. M.; Corse, J.; Boschan, R.; Seymour, D.; Winstein, S. *J. Am. Chem. Soc.* **1958**, *80*, 1247.

H), 6.87–7.80 (complex m, 18.7 H), 8.03 (s, 1.1 H), 4.16 (s, H_2O in solvent).

Anal. Calcd for $C_{27}H_{23}ISO_3$: C, 58.49; H, 4.18; I, 22.89. Found: C, 58.07; H, 4.25; I, 23.29.

The Et_2O/CH_2Cl_2 mother liquor was concentrated, under aspirator vacuum, to a yellow oil. The oil was dissolved in 40 mL of boiling $MeOH/H_2O$ (87:13 v/v), and the resulting solution was cooled at −20 °C whereupon deoxybenzoin crystallized: yield, 1.28 g (65%); mp 54–56 °C (from $MeOH/H_2O$). The identity of the product was confirmed by spectral (IR, ^1H NMR) comparisons with authentic deoxybenzoin.

Norbornene. A mixture of 1 (3.92 g, 10.0 mmol), norbornene (2.08 g, 22.1 mmol), and CH_2Cl_2 (20 mL) was stirred and heated under reflux for 23 h. A clear solution containing a fine, white precipitate resulted. The solid component was isolated, washed with CH_2Cl_2, and identified as iodoxybenzene: yield, 0.2025 g (8.6%); mp ~250 °C explosive. The CH_2Cl_2 solution was washed with H_2O (2 × 20 mL), dried (Na_2SO_4), and concentrated, under aspirator vacuum, to a clear oil. The oil was subjected to further vacuum pumping (~2 mm, 1.5 h, room temperature) and subsequently triturated with Et_2O (10 mL) to give a solid material identified as 2,7-bis(tosyloxy)norbornane: yield, 0.1971 g; mp 125.5–127 °C. The Et_2O solution, upon dilution with Et_2O to 50 mL and cooling at −20 °C, gave a second fraction of 2,7-bis(tosyloxy)norbornane: yield, 0.218 g; mp 122–125.5 °C; combined yield, 0.405 g (28%); ^1H NMR ($CDCl_3$) δ 0.79–2.56 (closely spaced br m's and s at 2.44, 14.2 H), 4.23 (t) and 4.39–4.66 (unsymmetrical m) [combined areas, 1.8 H], 7.37 (overlapping AA′XX′ m's, 8.0 H, lower two lines "split"); ^{13}C NMR ($CDCl_3$) *carbons of norbornane skeleton* (major diastereomer) δ 24.81, 36.11, 37.92, 44.85, 80.60, and 84.26, (minor diastereomer) δ 23.42, 37.01, 38.92, 43.85, 82.59, and 85.11, *carbons of tosyloxy groups* 21.28, 21.55, 127.57, 127.70, 129.70, 129.86, 133.55, and 133.95.

Anal. Calcd for $C_{21}H_{24}S_2O_6$: C, 57.77; H, 5.55. Found: C, 57.66; H, 5.57.

The Et_2O mother liquor was concentrated, under aspirator vacuum, and the residual oil, when subjected to a vacuum (~2 mm, room temperature) in a "microstill", yielded iodobenzene (collected in receiver cooled to −70 °C). The oil that remained was washed with pentane (2 × 10 mL) leaving 0.64 g of impure 2,3-bis(tosyloxy)norbornane: ^1H NMR ($CDCl_3$) δ ~0.63–2.17 (complex m's of little fine structure including a br, intense resonance at 1.23 and two, somewhat narrow, peaks at 1.73 and 1.92, 17.1 H), 2.40 (s, 6.0 H, CH_3's), 4.37 (br apparent s, hint of splitting, 1.8 H, CH(OTs)), 7.43 (AA′XX′ m, 8.0 H).

The oil eluded attempts at further purification by column chromatography (40 g silica gel, Et_2O), vacuum pumping, and trituration.

Synthesis of Authentic Bis(tosyloxy)alkanes and *trans*-1-Hydroxy-2-(tosyloxy)cyclohexane. Authentic *vic*-bis(tosyloxy)alkanes of known stereochemistry were prepared by treatment of appropriate diols with an excess of *p*-toluenesulfonyl chloride in pyridine. Most of the diols were synthesized by the method reported in the literature for the cis hydroxylation of cyclohexene, i.e., by treatment of an alkene sequentially with (1) $AgOAc/I_2/HOAc$, (2) H_2O, and (3) $KOH/MeOH$.[5,6] Brief summaries are given below. *dl*-4,5-Octanediol, *trans*-1,2-cyclohexanediol, and *meso*-stilbenediol were synthesized by other methods (see below).

***meso*-2,3-Bis(tosyloxy)butane.** From *cis*-2-butene (ca. 2.07 g, 37.5 mmol) was obtained 1.01 g (30%) of crude *meso*-2,3-butanediol; vacuum distillation of the yellow oil (0.74 g) returned 0.57 g of a clear, colorless liquid: n^{20}_D 1.4347 [lit.[31,32] n^{25}_D 1.4366; mp 34.4 °C]. Treatment of the diol (0.354 g, 3.93 mmol) with *p*-TsCl (3.02 g) in pyridine (ca. 10 mL) gave crude *meso*-2,3-bis(tosyloxy)butane as a wet solid purified by trituration with Et_2O: yield, 0.484 g (31%); mp 92–95 °C.

Anal. Calcd for $C_{18}H_{22}S_2O_6$: C, 54.25; H, 5.58. Found: C, 54.44; H, 5.83.

***erythro*(*dl*)-2,3-Bis(tosyloxy)pentane.** From *cis*-2-pentene (2.92 g, 41.6 mmol) was obtained 3.53 g (81%) of crude *erythro*(*dl*)-2,3-pentanediol; vacuum distillation of 1.10 g returned 1.00 g: n^{20}_D 1.4413 [lit.[33] n^{20}_D 1.4431]. Treatment of the crude diol (0.52 g, 5.0 mmol) with *p*-TsCl (3.81 g, 20 mmol) in pyridine (10 mL) gave 1.32 g (64%) of *erythro*(*dl*)-2,3-ditosyloxypentane, mp 81.5–83 °C (ligroin).

Anal. Calcd for $C_{19}H_{26}S_2O_6$: C, 55.32; H, 5.88. Found: C, 55.33; H, 5.96.

***threo*(*dl*)-Bis(tosyloxy)pentane.** From *trans*-2-pentene (4.50 mL, 2.92 g, 41.6 mmol) was obtained 3.41 g (79%) of crude *threo*(*dl*)-2,3-pentanediol; vacuum distillation of 1.85 g returned 0.75 g: n^{20}_D 1.4334 [lit.[33] n_D 1.4320]. Treatment of the diol (0.52 g, 5.0 mmol) with *p*-TsCl (3.81 g, 20.0 mmol) in pyridine (10 mL) gave crude *threo*(*dl*)-2,3-bis(tosyloxy)pentane as a clear oil crystallized from Et_2O:pentane: yield, 1.24 g (60%); mp 88–89 °C.

Anal. Calcd for $C_{19}H_{24}S_2O_6$: C, 55.31; H, 5.88. Found: C, 55.50; H, 5.96.

***meso*-3,4-Bis(tosyloxy)hexane.** From *cis*-3-hexene (5.15 mL, 3.50 g, 41.6 mmol) was obtained 2.62 g (53%) of crude *meso*-3,4-hexanediol; recrystallization from CCl_4 (10 mL) returned 1.76 g, mp 88–89 °C [lit.[34] mp 88 °C]. Treatment of the diol (0.59 g, 5.0 mmol) with *p*-TsCl (3.81 g, 20.0 mmol) in pyridine (10 mL) gave crude *meso*-3,4-bis(tosyloxy)hexane as a clear oil crystallized from Et_2O (20 mL) with pentane (10–15 mL): yield, 1.37 g (64%); mp 102–103 °C.

Anal. Calcd for $C_{20}H_{26}S_2O_6$: C, 56.31; H, 6.16. Found: C, 56.21; H, 6.03.

***dl*-3,4-Bis(tosyloxy)hexane.** From *trans*-3-hexene (2.67 g, 31.8 mmol) was obtained 0.807 g (72%) of crude *dl*-3,4-hexanediol as a thick, yellow oil.

Treatment of the *crude* diol (0.58 g, 4.92 mmol) with *p*-TsCl (3.81 g, 20.0 mmol) in pyridine (11 mL) gave 1.52 g (72%) of *dl*-2,3-bis(tosyloxy)hexane as a near white powder with a sweet odor, mp 122.6–125 °C.

Anal. Calcd for $C_{20}H_{26}S_2O_6$: C, 56.31; H, 6.16. Found: C, 56.31; H, 6.36.

***meso*-4,5-Bis(tosyloxy)octane.** From *cis*-4-octene (4.67 g, 41.7 mmol) was obtained 5.44 g of crude *meso*-4,5-octanediol; recrystallization from cyclohexane (900 mL) returned 3.00 g, mp 122–123 °C [lit.[35] mp 123.5–124.5 °C]. Treatment of the diol (1.56 g, 10.0 mmol) with *p*-TsCl (7.60 g, 40.0 mmol) in pyridine (20 mL) gave crude *meso*-4,5-bis(tosyloxy)octane as a clear oil crystallized from ligroin (300 mL): yield, 2.63 g (58%); mp 81–83 °C.

Anal. Calcd for $C_{22}H_{30}S_2O_6$: C, 58.12; H, 6.66. Found: C, 58.33; H, 6.85.

***cis*-1,2-Bis(tosyloxy)cyclohexane.** From cyclohexene (3.42 g, 41.6 mmol) was obtained 1.46 g (30%) of crude *cis*-1,2-cyclohexanediol: mp 85–93 °C; recrystallization from CCl_4 (30 mL) gave mp 93–95 °C [lit.[5] mp 97–98 °C]. Treatment of the diol (0.58 g, 5.0 mmol) with *p*-TsCl (3.81 g, 20.0 mmol) in pyridine (10 mL) gave 1.71 g of crude *cis*-1,2-bis(tosyloxy)cyclohexane as an oil. Crystallization of 0.82 g from 55 mL of Et_2O/CH_2Cl_2 (10:1 v/v) returned 0.48 g, mp 128–130 °C.

Anal. Calcd for $C_{20}H_{24}S_2O_6$: C, 56.58; H, 5.70. Found: C, 56.56; H, 5.70.

***dl*-1,2-Diphenyl-1,2-bis(tosyloxy)ethane.** From *trans*-stilbene (3.60 g, 20.0 mmol) was obtained 0.54 g (13%) of *dl*-1,2-dihydroxy-1,2-diphenylethane, mp 116–118 °C (after recrystallization from ethanol at −78 °C) [lit.[36] mp 122–123 °C]. Treatment of the diol (0.40 g, 1.87 mmol) with *p*-TsCl (1.48 g, 7.77 mmol) in pyridine (~11.5 mL) gave crude *dl*-1,2-diphenyl-1,2-bis(tosyloxy)ethane as a wet solid purified by trituration with Et_2O: yield, 0.476 g (48.6%); mp 97–104 °C dec.

Anal. Calcd for $C_{28}H_{26}S_2O_6$: C, 64.35; H, 5.01. Found: C, 64.27; H, 5.33.

***meso*-1,2-Diphenyl-1,2-bis(tosyloxy)ethane.** *meso*-Stilbenediol was prepared from benzil according to Fieser.[11] Benzil (5.01 g, 23.8 mmol) upon treatment with $NaBH_4$ (0.98 g, 25.9 mmol) in 95% EtOH (50 mL) gave, after workup, 3.28 (64%) of

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(34) Wiemann, J.; Trillat, J.-J.; Barbezat, S. *C.R. Hebd. Seanses Acad. Sci.* **1954**, *238*, 585.
(35) Young, W. G.; Levanas, L.; Jasaitis, Z. *J. Am. Chem. Soc.* **1936**, *58*, 2274.
(36) "CRC Handbook of Chemistry and Physics", 50th ed.; The Chemical Rubber Co.: Cleveland, OH, 1969–1970; p C-289.

the *meso*-diol, mp 134.8–136.6 °C [lit.[37] mp 137.5–138 °C]. Treatment of the diol (1.07 g, 5.0 mmol) with *p*-TsCl (3.81 g, 20.0 mmol) in pyridine (~16 mL) yielded 0.46 g of a fibrous, white solid, mp 173–174 °C dec; recrystallization of 0.39 g from CH_3CN (~30 mL) returned 0.28 g (10.7%) of *meso*-1,2-diphenyl-1,2-bis(tosyloxy)ethane as a cottony, white solid: mp 131.5–132.5 °C dec: mp 132.5–134 °C dec.

Anal. Calcd for $C_{28}H_{26}S_2O_6$: C, 64.35; H, 5.01. Found: C, 64.44; H, 5.15.

***trans*-1,2-Bis(tosyloxy)cyclohexane.** *trans*-1,2-Cyclohexanediol was prepared according to Winstein.[9] From cyclohexene (24.5 g, 0.3 mol) was obtained 11.3 g (37%) of cyclohexene oxide. Hydrolysis of the epoxide (33 mL H_2O, 1 drop of 70% $HClO_4$) gave *trans*-1,2-cyclohexanediol: yield (after recrystallization from benzene), 10.8 g; mp 102–104 °C [lit.[9] mp 103–104 °C]. Treatment of the diol (2.63 g, 22.6 mmol) with *p*-TsCl (7.68 g) in pyridine (50 mL) gave *trans*-1,2-bis(tosyloxy)cyclohexane: yield (after recrystallization from 60 mL of Et_2O/CH_2Cl_2 (5:1 v/v) at 0 °C), 3.20 g (37.8%); mp 108–110.5 °C.

Anal. Calcd for $C_{20}H_{24}S_2O_6$: C, 56.58; H, 5.70. Found: C, 56.79; H, 5.60.

***dl*-4,5-Bis(tosyloxy)octane.** *cis*-4-Octene oxide was prepared by the method of Bissing and Speziale.[7] From *cis*-4-octene (5.0 g, 45 mmol) and *m*-chloroperoxybenzoic acid (9.0 g, 45 mmol) in $CHCl_3$ (75 mL) was obtained 3.51 g (61%) of the *cis*-epoxide, bp 76 °C (41 mm) [lit.[7] bp 69 °C (32 mm)].

A mixture of *cis*-4-octene oxide (1.28 g, 10.0 mmol) and 5 mL of acidified H_2O (2 drops 70% $HClO_4$/50 mL H_2O) was heated for 5 h under reflux. The reaction mixture was subsequently neutralized (10% aqueous NaOH) and concentrated to a slushy material. Distillation (microstill) of the slush yielded 0.53 g (36%) of *dl*-4,5-octanediol, n^{24}_D 1.4419 [lit.[35] $n^{24.5}_D$ 1.4419]. Treatment of the diol (0.53 g, 3.6 mmol) with *p*-TsCl (2.76 g, 14.5 mmol) in pyridine (7 mL) gave 1.00 g (61%) of *dl*-4,5-bis(tosyloxy)octane, mp 91 °C (after treatment of the crude product, an oil, with ligroin 100 mL).

Anal. Calcd for $C_{22}H_{30}S_2O_6$: C, 58.12; H, 6.66. Found: C, 58.30; H, 6.86.

***trans*-1-Hydroxy-2-(tosyloxy)cyclohexane.** A solution of *trans*-1,2-cyclohexanediol (0.527 g, 4.54 mmol) and *p*-TsCl (0.858 g, 4.50 mmol) in pyridine (8 mL) was allowed to stand for 2 days at room temperature whereupon a pink solution mixed with needles of pyridine hydrochloride was obtained. The mixture was poured into 75 g of cracked ice/H_2O and extracted with CH_2Cl_2 (2 × 25 mL). The CH_2Cl_2 layer was washed with aqueous HCl (1:1 concentrated HCl/H_2O, 2 × 20 mL) followed by H_2O (20 mL), dried (Na_2SO_4), and concentrated, under aspirator vacuum, to an oil. Crystallization of the oil from pentane (20 mL)/Et_2O (5 mL) gave crude *trans*-1-hydroxy-2-(tosyloxy)cyclohexane: yield, 0.990 g (81%); mp 82–90 °C. Recrystallization of the crude product from pentane (30 mL)/CH_2Cl_2 (4 mL) at −20 °C returned 0.926 g, mp 86–92 °C. A 0.613-g portion of the recrystallized material was subjected to preparative TLC (silica gel, CH_2Cl_2); 0.45 g of product was recovered, and this was recrystallized from pentane (20 mL)/Et_2O (5 mL) to give 0.348 g of pure *trans*-1-hydroxy-2-(tosyloxy)cyclohexane, mp 95–96 °C [lit.[30] mp 93–95 °C].

Reaction of Cyclohexene with *p*-[Hydroxy(tosyloxy)iodo]chlorobenzene. A mixture of *p*-[hydroxy(tosyloxy)iodo]-chlorobenzene (3.99 g, 9.35 mmol), cyclohexene (3.0 mL, 2.4 g, 29 mmol), and CH_2Cl_2 (16 mL) was stirred for 13 h at room temperature. A light green solution with a floating scum resulted. The mixture was extracted with H_2O (2 × 25 mL), dried ($MgSO_4$), and concentrated, under aspirator vacuum, to a viscous, yellow oil. The oil was taken up in warm Et_2O (30 mL), and the resulting solution was cooled to 0 °C to give 0.6558 g (33%) of *cis*-1,2-bis(tosyloxy)cyclohexane. The mother liquor was concentrated to an oil, and the oil was heated at 36–50 °C and 2 mm pressure in a sublimation apparatus, whereupon 1.54 g (65%) of *p*-chloroiodobenzene was obtained: ^1H NMR ($CDCl_3$) 7.20 (AA'XX' m).

Titration of the aqueous extracts with standard aqueous sodium hydroxide was consistent with a 15.5% yield of *p*-TsOH.

(37) Kuhn, R.; Rebel, O. *Chem. Ber.* **1927**, *60*, 1565.

Treatment of Cyclohexene Oxide with a Mixture of 1 and *p*-TsOH·H_2O. A mixture of 1 (1.16 g, 2.95 mmol), *p*-TsOH·H_2O (0.56 g, 2.95 mmol), cyclohexene oxide (0.30 mL, 0.29 g, 2.95 mmol, from cyclohexene and *m*ClPBA), and MeCN (10 mL) was allowed to stand for 17 days at room temperature. The slightly yellow solution that resulted was then concentrated, under aspirator vacuum, to a yellow oil. The oil was taken up in CH_2Cl_2 (20 mL), and the CH_2Cl_2 solution was washed with H_2O (2 × 25 mL), dried (Na_2SO_4), clarified with charcoal, and reconcentrated. The residual oil was crystallized from 14 mL of pentane:Et_2O (8:6) at −20 °C to give 0.25 g of *trans*-1-hydroxy-2-(tosyloxy)cyclohexane. Concentration of the mother liquor and a second crystallization of the residual oil from 7 mL of pentane:Et_2O (5:2) returned 0.090 g of additional product, combined yield, 0.34 g (41%). The structure of the product was confirmed by IR and ^1H NMR spectral comparisons with authentic *trans*-1-hydroxy-2-(tosyloxy)cyclohexane.

Titration of the aqueous extracts from the workup with standardized aqueous NaOH indicated the presence of 3.60 mmol of *p*-TsOH.

Reaction of Cyclohexene Oxide with *o*-[Hydroxy(tosyloxy)iodo]toluene. A solution of cyclohexene oxide (0.35 mL, 0.34 g, 3.5 mmol) and *o*-[hydroxy(tosyloxy)iodo]toluene (1.20 g, 2.0 mmol) in CH_2Cl_2 (20 mL) was allowed to stand for 6 days at room temperature during which time an insoluble gelatinous solid was formed. The solid was isolated by filtration, and the filtrate was concentrated, under aspirator vacuum, to an oil. Treatment of the oil with CH_2Cl_2:Et_2O (3 mL:7 mL) gave a second crop of the insoluble solid: yield, 0.23 g; mp 225 °C explosive—probably *o*-$MeC_6H_4IO_2$. Concentration of the remaining CH_2Cl_2:Et_2O solution and treatment of the residual material first with Et_2O (10 mL) and then with pentane (15 mL, slow addition) effected the precipitation of *trans*-1-hydroxy-2-(tosyloxy)cyclohexane: yield, 0.56 g; mp 87–92 °C. Evaporation of the mother liquor to 2 mL yielded a second crop of product: yield, 0.13 g; mp 90–92 °C; combined yield, 0.69 g (85%). The structure was confirmed by spectral (IR, ^1H NMR) comparisons with authentic material.

Mass Balance in the Reaction of [Hydroxy(tosyloxy)iodo]benzene with 1-Pentene. A mixture of 1 (3.92 g, 10.0 mmol), 1-pentene (3.0 mL, 1.6 g, 23 mmol), and $CHCl_3$ (20 mL) was stirred and heated under reflux for 13 h. A clear solution mixed with a white solid resulted. The solid, iodoxybenzene, was isolated by filtration and washed with CH_2Cl_2, yield, 0.348 g (1.47 mmol). The $CHCl_3$ solution was washed with H_2O (2 × 20 mL), dried (Na_2SO_4), and concentrated on a rotary evaporator to a clear oil; the "distillate" was collected. The aqueous extracts were found to be neutral to Alkocid test ribbon and to contain only a trace of unreacted 1. The oil was passed through a column of silica gel (50 g) with CH_2Cl_2 as the elution solvent in order to separate any iodobenzene. The first 60-mL fraction was collected and combined with the distillate from the concentration step. GLC analysis of this solution [6 ft × $^1/_8$ in. column of 5% SP-1200–1.75% Bentone 34 on 100/120 Supelcoport, air as carrier gas, 10 mL min^{-1}, column temperature, 130 °C] with bromobenzene as an internal standard revealed only iodobenzene, yield, 8.68 mmol. The silica gel column was finally "washed" with 200 mL of CH_2Cl_2/CH_3OH (160:40 v/v) followed by 50 mL of CH_2Cl_2/CH_3OH (1:1 v/v). The fractions were combined and concentrated to give 1.26 g (3.06 mmol) of 1,2-bis(tosyloxy)pentane.

GLC Identification of 2,4-Hexadienes in the Reaction of [Hydroxy(tosyloxy)iodo]benzene with *trans*-3-Hexene. A mixture of 1 (1.96 g, 5.00 mmol), *trans*-3-hexene (1.00 mL, 0.677 g, 8.06 mmol), and CH_2Cl_2 (10 mL) was stirred for 3 h at room temperature. The reaction mixture was subsequently washed with H_2O (2 × 15 mL), dried (Na_2SO_4), and transferred to a 50-mL volumetric flask. Cyclohexane (0.65 mL, 0.5 g) was added (as an internal standard), and the solution was diluted with CH_2Cl_2 to 50.0 mL and subjected to GLC analysis: 6 ft × $^1/_6$ in. column of 5% SP-1200–1.75% Bentone 34 on 100/120 Supelcoport; carrier gas, air at a flow rate of 10 mL min^{-1}; column temperature, 24 °C. Both *trans,trans*-2,4-hexadiene (retention time, 6.31 min) and *cis,trans*-2,4-hexadiene (retention time, 7.00 min) were identified by comparison of retention times of those of authentic dienes (Aldrich) and by peak enhancement with authentic dienes: yields (based on the cyclohexane peak area), *cis,trans* (2.0%), *trans,trans* (3.4%). Iodobenzene was detected in substantial

quantity, retention time, 31.78 min at 50 °C. *cis,cis*-2,4-Hexadiene was not in our possession.

Reaction of *trans,trans*-2,4-Hexadiene with [Hydroxy(tosyloxy)iodo]benzene. To a mixture of 1 (8.00 g, 20.4 mmol) and CH_2Cl_2 (~50 mL), cooled to 3 °C, was added a solution of *trans,trans*-2,4-hexadiene (2.167 g, 26.4 mmol) in CH_2Cl_2 (~5 mL); an additional 5 mL of CH_2Cl_2 was used for rinsing purposes and added to the reaction mixture (temperature after mixing, ~4.5 °C). The reaction mixture was stirred for 1 h at ice-bath temperature and allowed to stand for ca. 1 day at 0–1 °C. A straw colored solution mixed with some crystals of *p*-toluenesulfonic acid resulted. This was extracted with H_2O (2 × 35 mL), dried (Na_2SO_4), and concentrated, under aspirator vacuum, to a light brown slush. Trituration of the slush with Et_2O left a white, crystalline solid which was isolated, washed with Et_2O, and identified as 2,5-bis(tosyloxy)-3-hexene: yield, 1.509 g (34.9%); mp 75–76 °C (rapid decomposition to black tar, darkening at 72 °C); ^1H NMR (CD_2Cl_2) δ 1.18 (d, 5.8 H), 2.41 (s, 5.8 H), 4.58–5.14 (complex m, 2.0 H), 5.23–5.49 (complex, well resolved m centered at ~5.35, 2.3 H), 7.48 (AA'XX' m, 8.2 H).

Thermal Decomposition of 2,3-Dimethyl-2,3-bis(tosyloxy)butane. 1. Solid State. 2,3-Dimethyl-2,3-bis(tosyloxy)-butane (0.334 g, 0.783 mmol) was allowed to stand for 15 days in the dark at room temperature. Decomposition to a black tar occurred within 10 days. The tar was mixed with CH_2Cl_2 (15 mL), and the resulting solution/slurry was extracted with H_2O (2 × 20 mL). The aqueous extracts were combined and titrated with standard aqueous NaOH; the yield of *p*-TsOH was 96%. The CH_2Cl_2 solution was dried (Na_2SO_4), treated with charcoal, and concentrated, under aspirator vacuum, to a yellow oil, the ^1H NMR spectrum of which exhibits only a complex pattern in the aliphatic region.

2. In CH_2Cl_2. A solution of 2,3-dimethyl-2,3-bis(tosyloxy)-butane (0.368 g, 0.863 mmol) in CH_2Cl_2 (10 mL) was allowed to stand for 15 days in the dark at room temperature. Within 7 days, the originally clear solution had turned into a reddish-black mixture. The reaction mixture was extracted with H_2O (2 × 25 mL). The aqueous extracts were combined and titrated with standard, aqueous NaOH; the yield of *p*-TsOH was 1.65 mmol (96%). The CH_2Cl_2 solution was dried (Na_2SO_4), treated with charcoal, and concentrated, under aspirator vacuum, to a yellow oil, the ^1H NMR spectrum of which exhibits only a complex pattern in the aliphatic region.

Reaction of Cyclohexene with [Methoxy(tosyloxy)iodo]-benzene. A solution of [methoxy(tosyloxy)iodo]benzene (2.42 g, 5.96 mmol) and cyclohexene (3.5 mL, 2.8 g, 34 mmol) in CH_2Cl_2 (15 mL) was allowed to stand for 3 days at room temperature and subsequently concentrated, under aspirator vacuum, to an oil. The oil was dissolved in Et_2O (10 mL), and the resulting solution was cooled at 0 °C to give 0.91 g of crude *cis*-1,2-bis(tosyloxy)-cyclohexane. Concentration of the mother liquor, dissolution of the residual oil in pentane (10 mL), and cooling at −20 °C gave 0.09 g more of product: combined yield, 1.00 g (79%); clean by ^1H NMR assay. Recrystallization of the crude product from Et_2O (10 mL)/CH_2Cl_2 (a few drops) returned two fractions: 0.74 g (mp 115–117 °C); 0.064 g (mp 114–117 °C, obtained at −20 °C).

Registry No. *dl*-**1**, 27126-76-7; *dl*-**1** (*p*-chloro derivative), 73178-07-1; *dl*-**1** (*o*-methyl derivative), 73177-97-6; *dl*-**1** (methoxy derivative), 75067-08-2; *meso*-**2** ($R_1 = R_2 = Me$, $R_3 = R_4 = H$), 90026-01-0; *meso*-**2** ($R_1 = R_2 = Me$, $R_3 = R_4 = H$, diol), 5341-95-7; *dl*-**2** ($R_1 = R_3 = Me$, $R_2 = R_4 = H$), 90026-02-1; **2** ($R_1 = R_4 = Me$, $R_2 = R_3 = H$), 89959-72-8; *dl-erythro*-**2** ($R_1 = Me$, $R_2 = Et$, $R_3 = R_4 = H$), 89959-73-9; *dl-erythro*-**2** ($R_1 = Me$, $R_2 = Et$, $R_3 = R_4 = H$, diol), 61828-35-1; *dl-threo*-**2** ($R_1 = Me$, $R_3 = Et$, $R_2 = R_4 = H$), 89959-74-0; *dl-threo*-**2** ($R_1 = Me$, $R_3 = Et$, $R_2 = R_4 = H$, diol), 61828-36-2; *dl*-**2** ($R_1 = n$-Pr, $R_2 = R_3 = R_4 = H$), 89959-76-2; *meso*-**2** ($R_1 = R_2 = Et$, $R_3 = R_4 = H$), 89959-77-3; *meso*-**2** ($R_1 = R_2 = Et$, $R_3 = R_4 = H$, diol), 22520-39-4; *dl*-**2** ($R_1 = R_3 = Et$, $R_2 = R_4 = H$, diol), 22520-19-0; *meso*-**2** ($R_1 = R_2 = n$-Pr, $R_3 = R_4 = H$), 89959-78-4; *meso*-**2** ($R_1 = R_2 = n$-Pr, $R_3 = R_4 = H$, diol), 22520-41-8; *dl*-**2** ($R_1 = R_3 = n$-Pr, $R_2 = R_4 = H$, diol), 22520-40-7; **2** ($R_1 = R_2 = R_3 = R_4 = Me$), 79069-18-4; *dl*-**2** ($R_1 = Ph$, $R_2 = R_3 = R_4 = H$), 90026-03-2; *meso*-**2** ($R_1 = R_2 = Ph$, $R_3 = R_4 = H$), 36439-55-1; *meso*-**2** ($R_1 = R_2 = Ph$, $R_3 = R_4 = H$, diol), 579-43-1; *dl*-**2** ($R_1 = R_3 = Ph$, $R_2 = R_4 = H$), 36528-58-2; *dl*-**2** ($R_1 = R_3 = Ph$, $R_2 = R_4 = H$, diol), 655-48-1; **4**, 89959-82-0; **5**, 89959-81-9; **7**, 89959-80-8; **8**, 89959-79-5; (*Z*)-MeCH=CHMe, 590-18-1; (*E*)-MeCH=CHMe, 624-64-6; $Me_2C=CH_2$, 115-11-7; (*Z*)-MeCH=CHEt, 627-20-3; (*E*)-MeCH=CHEt, 646-04-8; *n*-PrCH=CH_2, 109-67-1; (*Z*)-EtCH=CHEt, 7642-09-3; (*E*)-EtCH=CHEt, 13269-52-8; (*Z*)-*n*-PrCH=CHPr-*n*, 7642-15-1; (*E*)-*n*-PrCH=CHPr-*n*, 14850-23-8; $Me_2C=CMe_2$, 563-79-1; PhCH=CH_2, 100-42-5; (*Z*)-PhCH=CHPh, 645-49-8; (*E*)-PhCH=CHPh, 103-30-0; $Ph_2C=CH_2$, 530-48-3; (*E,E*)-MeCH=CHCH=CHMe, 5194-51-4; (*E,Z*)-MeCH=CHCH=CHMe, 5194-50-3; $Ph_2C=CH\text{-}I^+\text{-}Ph\ ^-OTs$, 79069-21-9; *cis*-1,2-cyclohexanediol ditosylate, 5433-22-7; *cis*-1,2-cyclohexanediol, 1792-81-0; *dl-trans*-1,2-cyclohexanediol ditosylate, 89959-86-4; *dl-trans*-1,2-cyclohexanediol, 54383-22-1; *dl-trans*-1-hydroxy-2-(tosyloxy)cyclohexane, 89959-75-1; 1,2-diphenyl-2,3-bis(tosyloxy)-1-oxopropane, 89959-83-1; 1,1-bis(tosyloxy)-2-phenylethane, 79069-22-0; deoxybenzoin, 451-40-1; 2,7-bis(tosyloxy)norbornane, 89959-84-2; 2,3-bis(tosyloxy)norbornane, 89959-85-3; cyclopentene, 142-29-0; cyclohexene, 110-83-8; methylenecyclopentane, 1528-30-9; chalcone, 94-41-7; norbornene, 498-66-8; *cis*-4-octene oxide, 1439-06-1; cyclohexene oxide, 286-20-4.

Supplementary Material Available: Experimental details for the preparation of *vic*-bis(tosyloxy)alkanes from alkenes and PhI(OH)OTs; NMR data for *vic*-bis(tosyloxy)alkanes (13 pages). Ordering information is given on any current masthead page.

Novel Rearrangement of 1,4-Ylidic Thiaanthracenes

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A novel rearrangement of 10-alkyl-9-aryl-10-thiaanthracenes is described. 9-Mesityl-10-methyl-10-thiaanthracene (**8a**) generated by proton abstraction of 9-mesityl-10-methylthioxanthenium perchlorate (**7a**) with sodium hydride in THF underwent thermal rearrangement to afford 3-methyl-9-mesitylthioxanthene (**9a**). Similarly, the 9-bulky aryl group substituted 10-alkyl-10-thiaanthracenes **7b–f** were decomposed thermally to give the corresponding 3-alkyl-9-arylthioxanthenes **9b–f** in 63–67% isolated yields. It is discussed that these abnormal alkyl rearrangements were caused by the steric effect of the bulky substituents at the 9-position of the thiaanthracenes, which prevent the normal 1,4-sigmatropic rearrangement of the 10-alkyl group to the 9-position.

It is reported[1] that 9,10-disubstituted 10-thiaanthracenes **2a**, which are generated by treatment of the corresponding thioxanthenium salts **1a** with base, undergo thermal six-electron 1,4-rearrangement of 10-substituents to give the

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