mass spectrum, parent peaks at m/e 206 (^{35}Cl, ^{35}Cl), 208 (^{35}Cl, ^{37}Cl), and 210 (^{37}Cl, ^{37}Cl).

Anal. Calcd for $C_9H_{12}Cl_2O$: C, 51.1; H, 5.79. Found: C, 51.52; H, 5.73.

2-Bromo-2-chloro-4-isopropylidene-3,3-dimethylcyclobutanone (V). Bromochloroketene and tetramethylallene yielded the cycloadduct at 85° (0.10 mm): mol wt (theory), 251.5; mass spectrum, parent peaks at m/e 250 (^{35}Cl, ^{79}Br), 252 (^{35}Cl, ^{81}Br; ^{37}Cl, ^{79}Br), and 254 (^{37}Cl, ^{81}Br).

4-Isopropylidene-2,3,3-trimethylcyclobutanone (VII). The cycloadduct of methylketene and tetramethylallene was prepared in a 20% yield at 40° (0.25 mm): mol wt (theory), 152; mass spectrum, parent peak at m/e 152.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.51. Found: C, 78.79; H, 10.54.

10,10-Dichlorobicyclo[7.2.0]undec-1-en-11-one (X). The cycloadduct of dichloroketene and 1,2-cyclononadiene was prepared in 75% yield at 108° (0.005 mm): nmr δ 1.5 (m, 8 H), 2.35 (m, 4 H), 3.3 (m, 1 H), and 6.7 (m, 1 H).

Anal. Calcd for $C_{11}H_{14}Cl_2O$: Cl, 30.47. Found: Cl, 30.64.

10-Chloro-10-methylbicyclo[7.2.0]undec-1-en-11-one (XI). The methylchloroketene and 1,2-cyclononadiene cycloadduct was prepared in 73% yield at 98–100° (0.005 mm): nmr δ 1.5 (m, 9 H), 2.0 (m, 4 H), 2.3 (m, 2 H), 2.85 (2 d, 1 H), and 6.4 (m, 1 H).

Anal. Calcd for $C_{12}H_{17}ClO$: Cl, 16.70. Found: Cl, 16.52.

Cycloaddition of Methylchloroketene and 1-Methyl-1,2-cyclononadiene (XII). The cycloaddition of this unsymmetrical allene with methylchloroketene produced both the isomers of the cycloadduct in a ratio of 2:1 with the least substituted cycloadduct predominating in a 70% yield: bp 105° (0.005 mm); ir 1770 (C=O) and 1670 cm^{-1} (C=O); nmr δ 1.5 (m, 12 H), 2.05 (m, 4 H), 2.3 (m, 2 H, allyl protons), 2.85 [(2 d for methinyl proton of one isomer) and 6.4 (t for vinyl proton of second isomer)] (1 H). The ratio of methinyl proton to vinyl proton is 2:1.

Anal. Calcd for $C_{13}H_{19}ClO$: Cl, 15.68. Found: Cl, 16.01.

2-Chloro-4-isopropylidene-3,3-dimethylcyclobutanone (VI). A 0.075-mol portion of chloroacetyl chloride was added with stirring to a solution of 0.075 mol of triethylamine in 100 ml of dry pentane at −78°. After the addition was complete, a pentane solution of 0.10 mol of tetramethylallene was added. The mixture was allowed to warm slowly to room temperature overnight. After filtration and solvent evaporation, the filtrate was vacuum distilled to yield the cycloadduct (25%): bp 75° (0.15 mm); mol wt (theory), 172.5; mass spectrum, parent peaks at m/e 172 (^{35}Cl) and 174 (^{37}Cl).

4-Isopropylidene-2,3,3-trimethyl-2-phenylcyclobutanone VIII). Equimolar amounts of phenylmethylketene and tetramethylallene were combined and stirred for 30 hr at 50°, bp 92 (0.05 mm).

2-Ethyl-4-isopropylidene-3,3-dimethyl-2-phenylcyclobutanone (IX). Equimolar quantities of phenylethylketene and tetramethylallene were combined and stirred for 30 hr at 50°, bp 105° (0.05 mm).

Acknowledgments. The authors wish to express appreciation to the Robert A. Welch Foundation and the North Texas State University Faculty Research Fund for support of this investigation.

Registry No. I, 42915-13-9; II, 42915-14-0; III, 42915-15-1; IV, 42915-16-2; V, 42915-17-3; VI, 42915-18-4; VII, 42915-19-5; VIII, 42915-20-8; IX, 42915-21-9; X, 42915-22-0; XI, 42915-23-1; XIIA, 42915-24-2; XIIB, 42915-25-3; methylchloroketene, 13363-86-5; tetramethylallene, 1000-87-9, methylbromoketene, 29264-45-7; ethylchloroketene, 29264-44-6; dichloroketene, 4591-28-0; bromochloroketene, 42915-26-4; methylketene, 6004-44-0; 1,2-cyclononadiene, 1123-11-1; 1-methyl-1,2-cyclononadiene, 42915-27-5; chloroacetyl chloride, 79-04-9; phenylmethylketene, 3156-07-8; phenylethylketene, 20452-67-9.

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Addition of Sulfonyl Iodides to Allenes[1]

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Received January 18, 1973

Sulfonyl iodides add rapidly to allenes to give 1:1 adducts. The addition of sulfonyl iodides to 1,2-propadiene yields a mixture of products, including the two 1:1 adducts resulting from attack by the sulfonyl radical on both the central and terminal positions of the allenic unit. Complete kinetic control has probably not been achieved under the conditions of these additions. In contrast, the addition of sulfonyl iodides to phenylallene and 3-methyl-1,2-butadiene proceeds rapidly and in excellent yield to give only the products resulting from central attack by the sulfonyl radical, *i.e.*, $R_1R_2C{=}C(SO_2R)CH_2I$. The addition of *p*-toluenesulfonyl iodide to 2,3-pentadiene behaves in a similar fashion, giving a moderate yield of 1:1 adduct resulting from central attack. The structures of the adducts were proven by zinc–acid reduction to the unsaturated sulfones.

Although the chemistry of sulfonyl halides has been extensively investigated, most of the work has concentrated on the chemistry of the readily available sulfonyl chlorides. Much less work has been done with the relatively stable, but less readily available sulfonyl bromides, and relatively few of the highly reactive, very unstable sulfonyl iodides have been prepared.

The sulfur–halogen bond of sulfonyl halides has been found to be particularly susceptible to homolytic cleavage; consequently, the free-radical reactions of sulfonyl halides comprise a large portion of their chemistry. Much of the work in this area of date has involved the free-radical addition of sulfonyl halides to olefins,[2-10] the following chain mechanism being generally accepted.

$$RSO_2X \xrightarrow{h\nu} RSO_2\cdot + X\cdot$$

or (1)

$$RSO_2X + In\cdot \longrightarrow RSO_2\cdot + InX$$

$$RSO_2\cdot + RCH{=}CH_2 \longrightarrow R\dot{C}HCH_2SO_2R \qquad (2)$$

$$R\dot{C}HCH_2SO_2R + RSO_2X \longrightarrow R\underset{\substack{|\\X}}{C}HCH_2SO_2R + RSO_2\cdot \qquad (3)$$

Step 1 is the chain-initiating step, which may be effected by either irradiation or the addition of an initiator (In·) such as a peroxide.

Perhaps the most extensive work with sulfonyl iodides has been carried out by Truce and Wolf,[11] who prepared a series of sulfonyl iodides and found that these would readily add to acetylenes to give the iodovinyl sulfones. Yields were generally very good, and the reaction conditions were mild.

Although the sulfonyl iodides are clearly a highly reactive, potentially useful class of compounds, relatively little is known of their chemistry. Brief investigations in these laboratories[12,13] had previously shown that *p*-toluenesulfonyl iodide could be added to three allenes to give 1:1 adducts.[14] Examination of the literature revealed that the position of initial attack of free radicals on allene has been a point of considerable controversy. Although there are relatively few examples of free-radical additions to allenes, recent studies have somewhat clarified the situation, and the general area of addition reactions of allenes has been recently reviewed.[15]

Since the π bonds of allenes are orthogonal, the initially formed radical resulting from central attack on allene resembles a primary radical rather than an allylic one, a rotation of 90° being required before full allylic stabilization is achieved.[16] Thus, it is reasonable that the isomeric vinylic radical intermediate $CH_2{=}\dot{C}{-}CH_2X$ is similar in energy to the nonplanar allylic radical intermediate $CH_2{=}C(X)\dot{C}H_2$, and Heiba[17] has indeed shown that the activation energies for forming $CH_2{=}\dot{C}{-}CH_2SPh$ and $CH_2{=}C(SPh)\dot{C}H_2$ from allene and PhS· differ only by 1.1 kcal/mol. However, $\cdot CF_3$, $\cdot CCl_3$, and $\cdot CH_3$ have been reported to add exclusively to the terminal position of allene,[15,17-20] while $(CH_3)_3Sn\cdot$, Br·, and PhS· give varying amounts of central attack.[15,17,21-23] The factors governing the orientation of addition are not well understood, but clearly polar factors cannot be a major factor owing to the difference in polarity between $\cdot CH_3$ and $\cdot CF_3$.

Considering the lack of a good theoretical explanation for the observed orientations of addition, it was desirable to examine carefully the light-initiated addition of a series of sulfonyl iodides to allenes. Besides the interest in the theoretical aspects of the orientation of addition and the expansion of knowledge of the behavior of sulfonyl iodides, the resulting 1:1 adducts contain several functional groups and might prove to be valuable synthetic intermediates.

Results

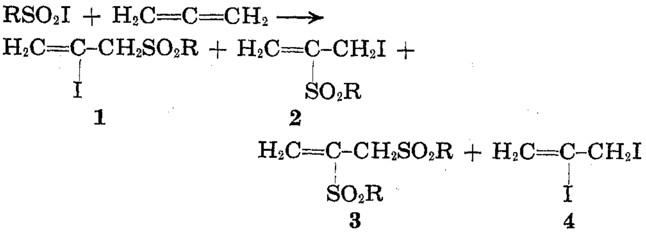
We have added five sulfonyl iodides to 1,2-propadiene. Nmr analysis (60 MHz) of the crude products indicated that a mixture of four products was produced in the addition of all five sulfonyl iodides to allene. In order to positively identify the reaction products, the crude reaction mixtures were separated by either elution chromatography or fractional crystallization. Table I illustrates the generality of the reaction and lists the isolated yields.

The 2,3-diiodopropene (**4**) was isolated and found to be a very unstable oil which liberated iodine vapors upon standing for a short time at room temperature. Considering the instability of this product, it is not surprising that occasionally this material was lost to decomposition during work-up.

A more serious problem, however, was presented by the relative instability of the allylic iodides **2a–e**. These allylic iodides were generally much less stable than the vinyl iodides **1a–e** and could be lost during lengthy column chromatography. Clearly the isolated yields are not reproducible and hence no conclusions concerning ratios of central *vs.* terminal attack can be drawn from the data in Table I. These data should therefore be considered as being representative of what might be accomplished from a synthetic viewpoint.

In order to determine the true product ratios, all five reactions were repeated under identical conditions (using benzene as a solvent) and the crude products obtained by removal of solvent at reduced pressure were analyzed immediately by nmr using a Varian XL-100 (100 MHz) instrument. The results of this analysis are shown in Table II.

Table I
Addition of Sulfonyl Iodides to Allene



$$RSO_2I + H_2C{=}C{=}CH_2 \longrightarrow \underset{\mathbf{1}}{H_2C{=}\underset{I}{C}{-}CH_2SO_2R} + \underset{\mathbf{2}}{H_2C{=}\underset{SO_2R}{C}{-}CH_2I} + \underset{\mathbf{3}}{H_2C{=}\underset{SO_2R}{C}{-}CH_2SO_2R} + \underset{\mathbf{4}}{H_2C{=}\underset{I}{C}{-}CH_2I}$$

1–4	R	Product isolated yield, %[d]			
		1	2	3	4
a	CH_3	32	20	0 (18)[c]	22
b	CH_3CH_2	25	12	28	31
c	$(CH_3)_2CH$	4	33	52	17
d	C_6H_5	46	0[b]	14	Trace
e	p-$CH_3C_6H_4$[a]	60	0[b]	16	0[b]

[a] Reaction run in ether. [b] Present by nmr, but not isolated from this reaction. [c] Isolated in a second trial by fractional crystallization. [d] Per cent yields of **3** and **4** are based on a theoretical yield of one half the number of moles of sulfonyl iodide used.

Table II
Nmr Analysis of the Addition of Sulfonyl Iodides to Allene

$$RSO_2I + H_2C{=}C{=}CH_2 \longrightarrow \mathbf{1} + \mathbf{2} + \mathbf{3} + \mathbf{4}$$

1–4	R	Material recovery, %	Product, mol % of product mixture			
			1	2	3	4
a	CH_3	94	35	34	17	15
b	CH_3CH_2	83	28	42	17	13
c	$(CH_3)_2CH$	37	11	66	15[b]	8
d	C_6H_5	99[a]	46	29	11	14
e	p-$CH_3C_6H_4$	100	47	28	13	12

[a] Average of two separate trials. [b] Incomplete resolution in the nmr reduces the accuracy of this figure.

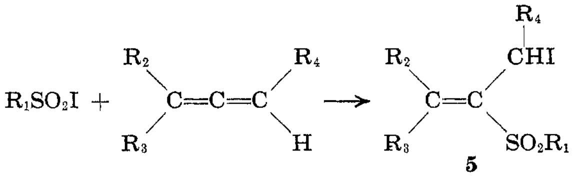
We have also added sulfonyl iodides to phenylallene, 3-methyl-1,2-butadiene, and 2,3-pentadiene, and have found that addition occurs rapidly and in generally high yield. The results of these additions are tabulated in Table III.

Note that yields were generally excellent. In all cases the only isomer observed was the internal olefin resulting from iodine abstraction by the terminal position and from central attack of the sulfonyl radical. No evidence of isomers resulting from terminal attack of the sulfonyl radical was observed in the nmr spectra of crude material. The products of the addition of sulfonyl iodides to phenylallene also seemed to be only one stereoisomer, which was tentatively assigned as β-(alkyl/arylsulfonyl)-*cis*-β-(iodomethyl)styrene, *i.e.*, a trans relationship between the aromatic ring and the sulfonyl group as expected. However, this would also probably be the most thermodynamically stable isomer in every case, and therefore a postisomerization cannot be ruled out.

Discussion

The possible mechanistic pathways involved in the addition of a sulfonyl iodide to 1,2-propadiene are outlined in Scheme I. Careful examination of these pathways reveals that *a priori* there are indeed at least four products of reaction possible. The initiation step involving the

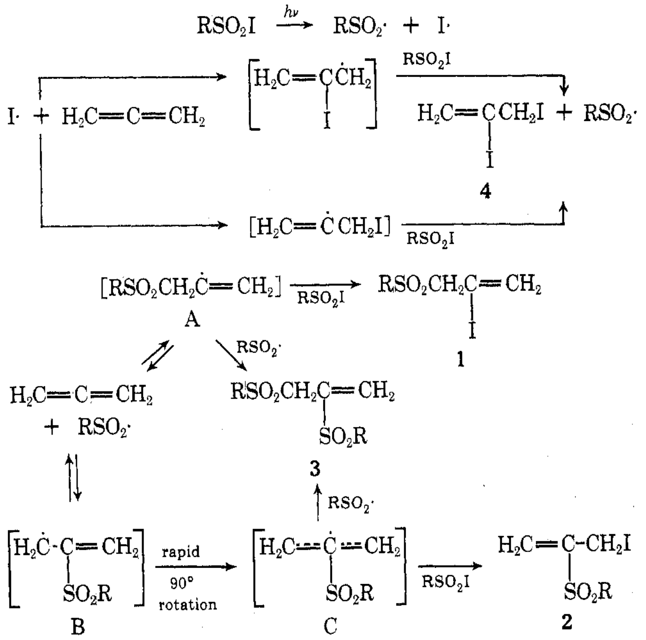
Table III
Addition of Sulfonyl Iodides to Substituted Allenes



1-4	R_1	R_2	R_3	R_4	Yield, %
a	CH_3	C_6H_5	H	H	93
b	CH_3CH_2	C_6H_5	H	H	92
c	$(CH_3)_2CH$	C_6H_5	H	H	43[a]
d	C_6H_5	C_6H_5	H	H	94
e	p-$CH_3C_6H_4$	C_6H_5	H	H	80
f	CH_3	CH_3	CH_3	H	100
g	CH_3CH_2	CH_3	CH_3	H	96
h	C_6H_5	CH_3	CH_3	H	100
i	p-$CH_3C_6H_4$	CH_3	CH_3	H	97
j	p-$CH_3C_6H_4$	CH_3	H	CH_3	45

[a] Separated from remaining phenylallene by elution chromatography.

Scheme I
Diagram of the Addition of a Sulfonyl Iodide to Allene



homolytic cleavage of the sulfur–iodine bond not only produces a chain-initiating sulfonyl radical, but also produces a free iodine atom. In the presence of excess allene, the free iodine atom will undoubtedly add to the allene molecule to give either of the two possible intermediate radicals shown. Either of these radicals should rapidly abstract an iodine atom from another molecule of the sulfonyl iodide to give 2,3-diiodopropene (4) and another sulfonyl radical.[24] Note that to this point two chain-initiating sulfonyl radicals have been produced while the two iodine atoms have been consumed. Therefore, even if all of the rest of the molecules of sulfonyl iodide are consumed in the production of the two 1:1 adducts, two sulfonyl radicals must be left to attack allene and form the 2,3-bis(alkyl/arylsulfonyl)propene (3). This analysis indicates that products 3 and 4 should be formed in equimolar amounts.

The results obtained in Table II were generally as expected, *i.e.*, the calculated yields of allylic iodides **2a–e** were higher in every case than the isolated yields of Table I. Perhaps most striking was the detection by nmr of the allylic iodides **2d** and **2e**, which were not isolated from the crude reaction mixtures represented in Table I, apparently owing to substantial decomposition during fractional crystallization and/or chromatography.

From Table II, the calculated yield of adduct **1e** is slightly less than 47%, while previously in Table I the isolated, purified yield of **1e** was listed as 60%. This discrepancy may be due to a solvent effect, since the reaction listed in Table I was run in ether, while the reaction listed in Table II was run in benzene. No valid conclusion may be drawn, however, since this is the only addition to allene which was performed in ether.

The low material balance obtained in the addition of 2-propanesulfonyl iodide may be due to decomposition of the intermediate sulfonyl radical according to the following scheme.

$$(CH_3)_2CHSO_2\cdot \longrightarrow SO_2\uparrow + (CH_3)_2\dot{C}H \xrightarrow{(CH_3)_2CHSO_2I} (CH_3)_2CHI + (CH_3)_2CHSO_2\cdot$$

The biting odor of sulfur dioxide was occasionally noted above the crude reaction mixture prior to removal of solvent at reduced pressure. The solvent removal would, of course, also remove any isopropyl iodide produced during the course of the reaction. Since the extrusion of sulfur dioxide from the 2-propanesulfonyl radical would yield a relatively stable secondary radical, this decomposition is likely to occur. Other sulfonyl halides are known to undergo this type of decomposition; for example, benzyl iodide is produced in high yield from α-toluenesulfonyl iodide upon irradiation,[25] and a similar decomposition has been reported for *tert*-butylsulfonyl chloride.[26] Such destruction of the sulfonyl iodide would have no effect on the product ratios, however.

From the data in Table II, the composition of the 1:1 adducts may be calculated to show more clearly the relative ratios of products resulting from central and terminal attack of the intermediate sulfonyl radical. These data are shown in Table IV. The two aromatic sulfonyl iodides add to allene to give very nearly the same ratio of products, the difference being within experimental error. The ratios of 1:1 adducts obtained from the alkanesulfonyl iodides, however, are markedly different from each other and from the ratio obtained for the aromatic sulfonyl iodides. The trend seems to be toward more central attack as the electron-donating power of the alkyl/aryl group increases. Steric factors apparently do not play a major role in determining the orientation of attack, since 2-propanesulfonyl iodide gives a much greater amount of central attack than the arylsulfonyl iodide although the steric requirements would be expected to be similar.

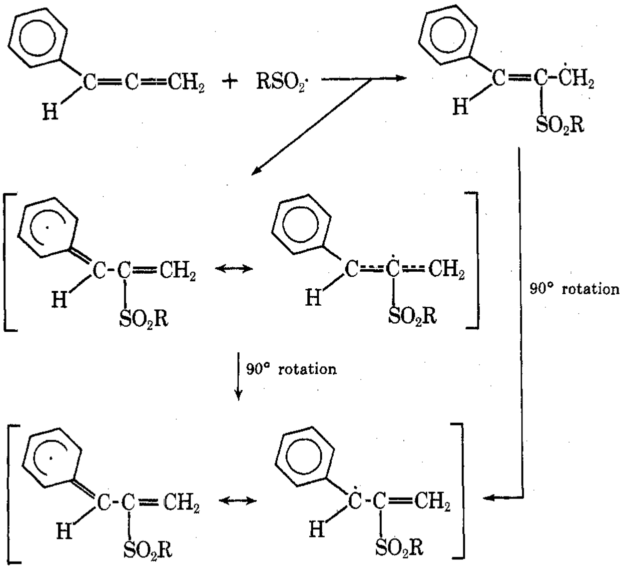
The question of greatest theoretical importance, however, is whether the observed product distribution may be directly related to the selectivity of free-radical attack, *i.e.*, whether the products are formed under strictly kinetic control. By using an excess of the sulfonyl iodide in two cases the product ratios were shifted toward increased terminal attack, indicating that in fact complete kinetic control has probably not been reached. Thus definite conclusions regarding the selectivity of attack of sulfonyl radicals on allene cannot be drawn from these data.

While the vinylic radical resulting from terminal attack of the sulfonyl radical may be comparable in energy to the nonplanar allylic radical derived from central attack, clearly any substitution on the allenic unit will upset this balance. Substitution on the allenic unit would be expected to heavily favor central attack by lowering the activation energy, and therefore should also activate the allene toward free-radical addition. The scheme for phenylallene

Table IV
Composition of the 1:1 Adducts Obtained from the Addition of Sulfonyl Iodides to Allene

Sulfonyl iodide RSO_2I	Product, % 1 (terminal attack)	2 (central attack)
CH_3SO_2I	51	49
$CH_3CH_2SO_2I$	40	60
$(CH_3)_2CHSO_2I$	14	86
$C_6H_5SO_2I$	62	38
p-$CH_3C_6H_4SO_2I$	62	38

Scheme II
Possible Intermediates Involved in the Attack of a Sulfonyl Radical on the Central Carbon of Phenylallene



shown in Scheme II, however, *implies that attack at the central carbon occurs preferentially at one of the two π bonds, i.e.*, the π bond which would yield an incipient benzylic radical rather than an incipient primary radical. Rotation in either case would give the same intermediate radical and the same products, however. The rate of rotation about single bonds is much larger (by a factor of *ca.* 10^8)[27] than chain transfer, and therefore the intermediate radical is almost certainly fully delocalized.

If chain transfer now occurs, *a priori* the iodine may be abstracted at two different positions. The preference for either of these two positions would seem to depend upon steric factors, the relative odd-electron density at the two sites, and the relative stabilities of the final products. From these considerations, the most likely point of attachment of iodine would seem to be at the terminal position. This would seem to be best from a steric point of view, since the terminal position should be more open to attack; the final product also would have the double bond in conjugation with the aromatic ring. The alternative structure [$PhC(I)HC(SO_2R){=}CH_2$] would seem to be less likely to be observed.

Since the final product is $PhCH{=}C(SO_2R)CH_2I$ as expected, then the question of stereochemistry of the product arises. If preferential attack on one of the π bonds occurs, then the 90° rotation to achieve allylic stabilization can occur in either direction to give either a cis or a trans final product. Given the rather large size of the sulfonyl grouping, the rotation would be expected to occur to place the aromatic ring and the sulfonyl group trans. We believe that this explanation involving the relief of steric strain during the 90° rotation is preferable to the recent suggestion[28] that sulfonyl radicals are selective in the direction of approach.

Similar arguments apply to the addition of other substituted allenes such as 3-methyl-1,2-butadiene and 2,3-pentadiene.

From the experimental results the theoretical picture seems to be reasonable. Certainly substitution on the allenic unit brings about a dramatic shift in products and is the overriding factor. The addition of sulfonyl iodides to allenes would seem to be a useful method of making certain iodine-containing sulfones which could be synthetically useful intermediates. The reaction would be of greatest synthetic utility when substituted allenes are employed, since they are more reactive and, in the substituted ones just described, give a single product in very high yield.

One potential use for the 1:1 adducts is in the synthesis of various unsaturated sulfones. Although further details will be reported later, we would like to report that we have successfully replaced the iodine atom by hydrogen in both the vinyl iodides and the allylic iodides by treatment with zinc-acetic acid. This reduction also served as a proof of the assigned structure, since the reduced adducts could be readily distinguished by their nmr spectra. For example, although the nmr spectrum of **1a** [$H_2C{=}C(I)CH_2SO_2CH_3$] is similar to that of **2a** [$H_2C{=}C(SO_2CH_3)CH_2I$], the nmr spectra of the corresponding reduced adducts [$H_2C{=}CHCH_2SO_2CH_3$ and $H_2C{=}C(SO_2CH_3)CH_3$] are quite different.

Experimental Section

All melting points and boiling points are uncorrected. The 60-MHz nmr spectra were recorded on a Varian A-60A and the 100-MHz nmr spectra were recorded on a Varian XL-100. Infrared spectra were recorded on a Beckman IR-33. The nmr spectral data are reported in chemical shift from TMS (δ 0), with s, d, t, q, and m referring to singlet, doublet, triplet, quartet, and multiplet, respectively.

Microanalyses were performed by Dr. C. S. Yeh and staff of this department. Sodium benzensulfinate and sodium *p*-toluenesulfinate were purchased from Aldrich Chemical Co. Methane- and ethanesulfonyl chloride were purchased from Aldrich and Eastman, respectively, while 2-propanesulfonyl chloride had to be prepared from Eastman's sodium 2-propanesulfonate. Allene was purchased from J. T. Baker, 3-methyl-1,2-butadiene was obtained from Chemical Samples Co., and 2,3-pentadiene was obtained as a National Bureau of Standards sample (no. 558-5s). Phenylallene was prepared by the method of Skattebøl and Solomon.[32] All sulfonyl iodide addition reactions, unless otherwise stated, were carried out in a flame-dried apparatus using spectral grade benzene as solvent, under the influence of a 250-W General Electric sun lamp, and were performed under nitrogen.

Alternate Preparation of 2,3-Diiodopropene (4). Allene was bubbled into a benzene solution of iodine under illumination from a General Electric sun lamp. The dark purple color of the iodine solution was rapidly discharged and the solution became colorless. Removal of solvent under vacuum gave 2,3-diiodopropene (**4**), a very unstable oil which liberated iodine upon standing at room temperature, nmr ($CDCl_3$) δ 4.34 (d, 2, $J \cong$ 1 Hz), 5.8 (d, 1, $J \cong$ 2 Hz), 6.47 (m, 1).

Preparation of 2-Propanesulfonyl Chloride. Thionyl chloride (59.50 g, 0.50 mol) was added over a period of 1 hr to a solution of sodium 2-propanesulfonate monohydrate (24.62 g, 0.15 mol) in 150 ml of DMF, the temperature of the mixture rising to approximately 50° during the addition. The mixture was allowed to stir at ambient temperature, then poured onto 300 g of ice. An additional 500 ml of water was added and the aqueous mixture was extracted with ether. The combined ether extracts were dried over $MgSO_4$ and the solvent was removed under vacuum, to give 10.4 g (48.4%) of 2-propanesulfonyl chloride of greater than 95% purity by nmr, nmr ($CDCl_3$) δ 1.58 (d, 6, J = 6 Hz), 3.83 (septet, 1, J = 6 Hz).

General Procedure for the Preparation of the Sodium Salts of the Sulfinic Acids. The appropriate sulfonyl chloride and sodium bicarbonate were added alternately in small portions to a stirred solution of sodium sulfite in water. The additions were carried out over a period of 30 min and unless stated otherwise the reaction temperatures were maintained at 75–95° throughout the addition. (Caution: In all of these reductions the gas evolution upon addition of sodium bicarbonate was very vigorous after an initial induction period. The bicarbonate must be added in very small portions to prevent much foaming.) The solution was stirred for an additional 30 min and checked to ensure that the solution was mildly basic, and the solvent was removed under reduced pressure. The resulting solid was dried, stirred with boiling absolute ethanol, and filtered. Removal of the solvent from the filtrate under reduced pressure, followed by drying of the white solid product in a vacuum desiccator, gave the sulfinic acid salt.

Sodium methanesulfinate, sodium ethanesulfinate, and sodium 2-propanesulfinate were prepared in this manner in yields ranging from 70 to 72%.

General Procedure for the Preparation of the Sulfonyl Iodides. *p*-Toluenesulfonyl iodide was prepared by adding an equivalent quantity of a concentrated ethanolic solution of iodine to a very dilute solution of the sodium arylsulfinate in water. The sulfonyl iodide precipitated from solution, and was collected and recrystallized from carbon tetrachloride. The sulfonyl iodide began to darken and decompose in a few hours at room temperature, but could be stored for several days at −10°.

The remaining sulfonyl iodides were not isolated, but were used as freshly prepared benzene solutions. When a benzene solution of iodine was vigorously mixed with an aqueous solution containing an excess of the sodium sulfinate, the intense purple color of the iodine rapidly faded and was replaced by the bright yellow-orange color of the sulfonyl iodide. When no further color change was evident, the benzene layer was separated, dried briefly over $MgSO_4$, and filtered to give a clear, yellow-orange solution of the sulfonyl iodide. Delay in using this dried sulfonyl iodide solution or exposure to strong light produced considerable decomposition of the sulfonyl iodide and darkening of the benzene solution. Hence, the solutions were used immediately and were protected from the light until the appropriate allene was present.

Preparation of *p*-Toluenesulfonyl Iodide. A solution of iodine (25.0 g, 0.0985 mol) in approximately 300 ml of absolute ethanol was added with vigorous stirring to a solution of sodium *p*-toluenesulfinate (17.8 g, 0.10 mol) in 1500 ml of water. A flocculent yellow solid rapidly precipitated and was collected and recrystallized from carbon tetrachloride. After this dried in a vacuum desiccator for 30 min, 23.5 g (84.5%) of the sulfonyl iodide was obtained as bright yellow crystals, mp 88–90° dec (lit.[29] mp 90–91° dec).

The *p*-toluenesulfonyl iodide could also be prepared by the above procedure in 74.5% yield by the use of iodine monochloride instead of iodine.

General Procedure for the Addition of the Sulfonyl Iodides to Allenes. The addition reactions were carried out at room temperature in benzene solution with the exception of the *p*-toluenesulfonyl iodide additions, which could be carried out in either benzene or ether.

When 1,2-propadiene was used as the substrate, the gaseous allene was bubbled into the freshly prepared sulfonyl iodide solution at an undetermined rate until allene was being returned by a Dry Ice condenser and the allene was certainly in excess. At this point the solution was exposed to light from a 250-W General Electric sun lamp until the solution became colorless, usually within 15 min. Removal of solvent under reduced pressure gave the crude product.

When the liquid allenes were used as substrates, an equivalent quantity of the allene was added to the sulfonyl iodide solution and the flask was subsequently exposed to illumination until the solution became colorless, usually within 5 min. Removal of solvent at reduced pressure gave the crude product.

Yields of the adducts were generally based on the amount of starting iodine.

General Procedure for the Nmr Analysis of the Addition of Sulfonyl Iodides to 1,2-Propadiene. The additions of sulfonyl iodides to allene were repeated using benzene as solvent in all cases and the crude products obtained were analyzed immediately by nmr to determine the true product ratios. Nmr analysis of the crude products using a Varian A-60A (60 MHz) instrument indicated that in every case 2,3-diiodopropene (**4**) and 2,3-bis(alkyl/arylsulfonyl)propene (**3a–e**) were present in nearly equimolar quantities, as evidenced by the fact that the overall integration of the various regions of the spectrum was nearly perfect for 1:1 adduct. [For example, an equimolar mixture of 2,3-bis(methanesulfonyl)propene and 2,3-diiodopropene would integrate as follows: vinyl region:methylene region:methyl region as 2:2:3 which would be the same as for 2-iodo-3-methanesulfonylpropene (**1a**) or 2-methanesulfonyl-3-iodopropene (**2a**).]

The samples were then further analyzed using a Varian XL-100 (100 MHz) instrument. The scale was expanded to 100 Hz and each area of the spectrum was examined in turn. Peak assignments were based on appearance and chemical shift as determined from the spectra of products which had previously been isolated. Comparison of peak areas on a per hydrogen basis gave the appropriate product ratios. Averages were calculated where appropriate.

Addition of Methanesulfonyl Iodide to Allene. Treatment of methanesulfonyl iodide (0.05 mol) with excess allene afforded 9.1 g of crude product. Purification by elution chromatography using a silica gel column and 1:1 ether–hexane as eluent afforded 2-methanesulfonyl-3-iodopropene (**2a,** 0.4 g, 3.3%), nmr ($CDCl_3$) δ 3.1 (s, 3), 4.27 (d, 2), 6.43 (m, 1), 6.57 (m, 1); 2-iodo-3-methanesulfonylpropene (**1a,** 3.8 g, 30.9%), mp 51–52° or 57–58°, nmr ($CDCl_3$) δ 3.03 (s, 3), 4.20 (s, 2), 6.27 (d, 1, $J \cong 2$ Hz), 6.6 (m, 1); and 2,3-diiodopropene (**4**, 1.5 g, 10.2% based on available iodine), nmr ($CDCl_3$) δ 4.34 (d, 2, $J \cong 1$ Hz), 5.8 (d, 1, $J \cong 2$ Hz), 6.47 (m, 1). A second trial also yielded 9.1 g of crude product. Addition of a small amount of dry ether to this material precipitated 0.9 g (18.2% based on 0.025 mol possible) of 2,3-bis(methanesulfonyl)propene (**3a**), mp 90–91°, nmr ($CDCl_3$) δ 3.04 (s, 3), 3.07 (s, 3), 4.20 (s, 2), 6.47 (m, 1), 6.70 (m, 1).

In a third trial **1a** was isolated in 31.8% yield, **2a** in 19.5% yield, and **4** in 21.5% yield. Thus, the isolated yields of products are not reproducible.

Anal. Calcd for $C_4H_7IO_2S$ (**1a**): C, 19.52; H, 2.87; I, 51.57. Found: C, 19.74; H, 3.00; I, 51.44.

Nmr Analysis of the Addition of Methanesulfonyl Iodide to Allene. Treatment of methanesulfonyl iodide with excess allene, followed by removal of solvent under vacuum, gave a crude product whose 100-MHz nmr spectrum indicated the presence of 2-iodo-3-(methanesulfonyl)propene (**1a**), 2-methanesulfonyl-3-iodopropene (**2a**), 2,3-bis(methanesulfonyl)propene (**3a**), and 2,3-diiodopropene (**4**). The product ratios were calculated from the integration of the vinyl region (*ca.* δ 5.7–6.8) of the spectrum. The results of two separate trials may be tabulated as follows.

Trial	CH_3SO_2I, mol	Crude product, g	Material recovery, %	Product, mol % of product mixture			
				1a	2a	3a	4
1	0.03	6.90	93.5	34.5	30.9	17.6	17.0
2	0.01	2.30	93.5	35.1	36.8	15.8	12.3
Average			93.5	34.8	33.8	16.7	14.7

A third trial in which the sulfonyl iodide was always in excess gave somewhat different results. In this trial the allene was slowly bubbled into the solution under illumination until the solution became colorless. The results are tabulated as follows.

Trial	CH_3SO_2I, mol	Crude product, g	Material recovery, %	Product, mol % of product mixture			
				1a	2a	3a	4
3	0.01	2.20	89.5	46.2	22.9	17.6	13.2

Addition of Ethanesulfonyl Iodide to Allene. Ethanesulfonyl iodide (0.05 mol), when treated with excess allene, yielded 9.75 g of crude product. Purification by elution chromatography using a silica gel column with 1:1 ether–hexane as eluent afforded 3.22 g (24.8%) of 2-iodo-3-ethanesulfonylpropene (**1b**), nmr ($CDCl_3$) δ 1.37 (t, 3, $J = 7.7$ Hz), 3.13 (q, 2, $J = 7.7$ Hz), 4.17 (s, 2), 6.25 (m, 1), 6.60 (m, 1); 1.51 g (11.6%) of 2-ethanesulfonyl-3-iodopropene (**2b**), nmr ($CDCl_3$) δ 1.33 (t, 3, $J = 8$ Hz), 3.22 (q, 2, $J = 8$ Hz), 4.27 (s, 2), 6.42 (s, 2); 1.55 g (27.4% based on 0.025 mol theoretical yield) of 2,3-bis(ethanesulfonyl)propene (**3b**), mp 40–43°, nmr ($CDCl_3$) δ 1.32 (t, 3, $J = 8$ Hz), 1.42 (t, 3, $J = 8$ Hz), 3.2 (q, 4, $J = 8$ Hz), 4.17 (s, 2), 6.57 (s, 1), 6.65 (s, 1); 2.3 g (31.3% based on 0.025 mol theoretical yield) of 2,3-diiodopropene (**4**).

Nmr Analysis of the Addition of Ethanesulfonyl Iodide to Allene. Treatment of ethanesulfonyl iodide (0.01 mol) with excess allene afforded 2.15 g (82.7%) of crude material. The product ratios were calculated from the integration of the vinyl region of the 100-MHz nmr spectrum using a sweep width of 100 Hz. The mixture was found to be composed of 27.9 mol % 2-iodo-3-ethanesulfonylpropene (**1b**), 41.8 mol % 2-ethanesulfonyl-3-iodopropene (**2b**), 17 mol % 2,3-bis(ethanesulfonyl)propene (**3b**), and 13.3 mol % 2,3-diiodopropene (**4**).

Addition of 2-Propanesulfonyl Iodide to Allene. When 2-propanesulfonyl iodide (0.01 mol) was treated with excess allene, 2.3 g of a crude oil was obtained. Purification by elution chromatography using a silica gel column with 1:1 ether–hexane as eluent afforded 0.9 g (32.8%) of 2-(2-propanesulfonyl)-3-iodopropene (**2c**), nmr (CDCl$_3$) δ 1.34 (d, 6, J = 7 Hz), 3.1–3.6 (m, 1), 4.23 (s, 2), 6.4 (s, 2); 0.1 g (3.6%) of 2-iodo-3-(2-propanesulfonyl)propene (**1c**), nmr (CDCl$_3$) δ 1.43 (d, 6, J = 7 Hz), 3.10–3.57 (m, 1), 4.13 (s, 2), 6.26 (d, 1, $J \cong$ 2 Hz), 6.63 (m, 1); 0.66 g (52% based on 0.005 mol theoretical yield) of 2,3-bis(2-propanesulfonyl)propene (**3c**), nmr (CDCl$_3$) δ 1.36 (d, 6, $J \cong$ 7 Hz), 1.44 (d, 6, $J \cong$ 7 Hz), 3.07–3.63 (m, 2), 4.10 (s, 2), 6.61 (m, 2); 0.25 g (17% based on 0.005 mol theoretical yield) of 2,3-diiodopropene (**4**).

Nmr Analysis of the Addition of 2-Propanesulfonyl Iodide to Allene. Treatment of 2-propanesulfonyl iodide (0.01 mol) with excess allene gave 1.0 g (36.5%) of crude product. The product ratios were calculated from the integration of the vinyl region of the 100-MHz nmr spectrum using a sweep width of 100 Hz. The relative amount of 2,3-bis(2-propanesulfonyl)propene (**3c**) was less accurately determined owing to incomplete resolution; the relative ratio of 1:1 adducts are the most accurate calculations. The product was found to be composed of 10.6 mol % **1c**, 65.7 mol % **2c**, 15.4 mol % **3c**, and 8.3 mol % **4**.

Addition of Benzenesulfonyl Iodide to Allene. Benzenesulfonyl iodide (0.05 mol), when treated with excess allene, afforded a crude oil whose nmr spectrum showed the presence of 2-iodo-3-benzenesulfonylpropene (**1d**), 2-benzenesulfonyl-3-iodopropene (**2d**), 2,3-diiodopropene (**4**), and 2,3-bis(benzenesulfonyl)propene (**3d**). Addition of a small amount of ethanol induced crystallization; recrystallization from absolute ethanol produced crystals, mp 80–88°. Nmr analysis showed this to be a mixture of **1d** and **3d**. The entire product was recovered from the mother liquors by evaporation under vacuum and combined with the crystals to again obtain a crude oil. Purification of this crude oil by elution chromatography using a silica gel column with 1:1 ether–hexane as eluent afforded 7.0 g (45.5%) of **1d**, mp 89.5–92°, nmr (CDCl$_3$) δ 4.24 (s, 2), 6.08 (d, 1), 6.27 (m, 1), 7.4–8.07 (m, 5); and 1.1 g (13.7% based on 0.025 mol theoretical) of **3d**, mp 129–130°, nmr (CDCl$_3$) δ 4.12 (s, 2), 6.47 (s, 1), 6.67 (s, 1), 7.3–7.83 (m, 10).

Nmr Analysis of the Addition of Benzenesulfonyl Iodide to Allene. Treatment of benzenesulfonyl iodide (0.01 mol) with excess allene gave 3.05 g (99%) of crude product. Product ratios were calculated from the integration of the vinyl region of the 100-MHz nmr spectrum using a sweep width of 100 Hz. The product mixture was found to be composed of 46.2 mol % **1d**, 29.1 mol % **2d**, 10.8 mol % **3d**, and 14.0 mol % **4**. While **2d** had not been isolated from the addition of benzenesulfonyl iodide to allene, the product was visible in the 100-MHz nmr spectrum, nmr (CDCl$_3$) vinyl H *ca.* δ 6.28 (1, overlapped with **1d**) and 6.65 (m, 1). The integration of the vinyl region was consistent with this assignment, which is based solely on the nmr evidence.

Addition of *p*-Toluenesulfonyl Iodide to Allene. When an ethereal solution of *p*-toluenesulfonyl iodide (16.92 g, 0.06 mol) was treated with excess allene, a white solid precipitated from the solution. The solution was concentrated and filtered to give 1.7 g (16.2% based on 0.03 mol possible) of 2,3-bis(*p*-toluenesulfonyl)propene (**3e**): mp 155.5–157°; nmr (CDCl$_3$) δ 2.40 (s, 6), 4.06 (s, 2), 6.47 (m, 1), 6.63 (m, 1), 7.42 (q, 8).

Anal. Calcd for C$_{17}$H$_{18}$O$_4$S$_2$: C, 58.26; H, 5.18; S, 18.30. Found: C, 57.99; H, 4.88; S, 18.52.

The remaining ethereal solution was evaporated to dryness and the residue was crystallized from absolute ethanol to give 11.65 g (60.4%) of 2-iodo-3-(*p*-toluenesulfonyl)propene (**1e**): mp 77–80°; nmr (CDCl$_3$) δ 2.43 (s, 3), 4.17 (s, 2), 6.05 (d, 1), 6.23 (m, 1), 7.58 (q, 4).

Anal. Calcd. for C$_{10}$H$_{11}$IO$_2$S: C, 37.28; H, 3.44; I. 39.39; S, 9.95. Found: C, 37.47; H, 3.69; I, 39.30; S, 10.09.

Nmr Analysis of the Addition of *p*-Toluenesulfonyl Iodide to Allene. Treatment of *p*-toluenesulfonyl iodide (0.01 mol) with excess allene gave 3.20 g (99.5%) of crude product. Product ratios were calculated from the integration of the vinyl region of the 100-MHz nmr spectrum using a sweep width of 100 Hz. The product was found to be a mixture of 46.7 mol % **1e**, 28.2 mol % **2e**, 13.3 mol % **3e**, and 11.8 mol % **4**. While **2e** had not been isolated from the addition of *p*-toluenesulfonyl iodide to allene, the product was clearly visible in the 100-MHz nmr spectrum, nmr (CDCl$_3$) vinyl H *ca.* δ 6.26 (1, overlapped with **1e**) and 6.61 (d, 1). The integration of the nmr spectra was consistent with this assignment, which is based solely on the nmr evidence. Use of a limited quantity of allene produced a mixture of 1:1 adducts composed of 82.7% **1e** and 17.3% **2e** (as well as some **3e** and **4**).

Addition of Methanesulfonyl Iodide to Phenylallene. Treatment of methanesulfonyl iodide (0.01 mol) with phenylallene (1.16 g, 0.01 mol) afforded 3.0 g (93.2%) of β-(methanesulfonyl)-β-(iodomethyl)styrene (**5a**), which by nmr was found to be the only product of this reaction. The product was recrystallized from ethanol to give needles, mp 110–111°, nmr (CDCl$_3$) δ 3.22 (s, 3), 4.47 (s, 2), 7.4–7.8 (m, 6).

Addition of Ethanesulfonyl Iodide to Phenylallene. Treatment of ethanesulfonyl iodide (0.01 mol) with phenylallene (1.16 g, 0.01 mol) afforded 3.1 g (92.2%) of β-(ethanesulfonyl)-β-(iodomethyl)styrene (**5b**), which by nmr was found to be the only product of this reaction. The product was further purified by recrystallization from absolute ethanol to give pale yellow-white needles: mp 129–130°; nmr (CDCl$_3$) δ 1.37 (t, 3, J = 7 Hz), 3.34 (q, 2, J = 7 Hz), 4.45 (s, 2), 7.33–7.83 (m, 6). In a second trial, the yield of 1:1 adduct increased slightly to 3.15 g (93.7%) of material which was found to be pure by nmr.

Addition of 2-Propanesulfonyl Iodide to Phenylallene. Treatment of 2-propanesulfonyl iodide (0.01 mol) with phenylallene (1.16 g, 0.01 mol) afforded a mixture of phenylallene and β-(isopropylsulfonyl)-β-(iodomethyl)styrene (**5c**). Purification of this crude product by elution chromatography using a silica gel column with 1:1 ether–hexane as eluent yielded 1.5 g (42.8%) of **5c**, which was further purified by recrystallization from ethanol to give crystals: mp 90.5–92°; nmr (CDCl$_3$) δ 2.40 (d, 6, J = 7 Hz), 3.20–3.90 (m, 1), 4.43 (s, 2), 7.33–7.67 (m, 6).

Addition of Benzenesulfonyl Iodide to Phenylallene. Treatment of benzenesulfonyl iodide (0.01 mol) with phenylallene (1.16 g, 0.01 mol) afforded 3.62 g (94.3%) of pure (by nmr) β-(benzenesulfonyl)-β-(iodomethyl)styrene (**5d**). Recrystallization from absolute ethanol gave crystals: mp 92–93°; nmr (CDCl$_3$) δ 4.28 (s, 2), 7.33–7.73 (m, 8), 7.83–8.10 (m, 3).

Addition of *p*-Toluenesulfonyl Iodide to Phenylallene. Treatment of an ethereal solution of *p*-toluenesulfonyl iodide (11.28 g, 0.04 mol) with phenylallene (4.65 g, 0.04 mol) gave a crude solid product which was recrystallized from ethanol–water to give 12.77 g (80.0%) of β-(*p*-toluenesulfonyl)-β-(iodomethyl)styrene (**5e**): mp 119–120°; nmr (CDCl$_3$) δ 2.35 (s, 3, C$_6$H$_4$CH$_3$), 4.21 (s, 2, CH$_2$I), 7.20–8.00 (m, 10, C$_6$H$_5$C**H** and C$_6$H$_4$).

Anal. Calcd. for C$_{16}$H$_{15}$IO$_2$S: C, 48.25; H, 3.80, I, 31.86; S, 8.05. Found: C, 48.23; H, 4.06; I, 31.66; S, 7.99.

Addition of Methanesulfonyl Iodide to 3-Methyl-1,2-butadiene. Treatment of methanesulfonyl iodide (0.01 mol) with 3-methyl-1,2-butadiene (1.02 g, 0.015 mol) afforded a quantitative yield of 1-iodo-2-methanesulfonyl-3-methyl-2-butene (**5f**), recrystallized from absolute ethanol: mp 81.5–82.5°; nmr (CDCl$_3$) δ 1.95 (s, 3), 2.23 (s, 3), 3.08 (s, 3), 4.33 (s, 2).

Anal. Calcd for C$_6$H$_{11}$IO$_2$S: C, 26.29; H, 4.05; I, 46.29. Found: C, 26.48; H, 4.35, I. 46.02.

Addition of Ethanesulfonyl Iodide to 3-Methyl-1,2-butadiene. Treatment of ethanesulfonyl iodide (0.01 mol) with 3-methyl-1,2-butadiene (1.02 g, 0.015 mol) afforded 2.75 g (95.5%) of pure (by nmr) crystalline 1-iodo-2-ethanesulfonyl-3-methyl-2-butene (**5g**). Attempts to recrystallize this adduct from ethanol or hexane failed, as the adduct decomposed very readily. The nmr spectrum was found to be free of other possible 1:1 adducts and to be consistent with the assigned structure: nmr (CDCl$_3$) δ 1.38 (t, 3, J = 7 Hz), 1.97 (s, 3), 2.23 (s, 3), 3.16 (q, 2, J = 7 Hz), 4.33 (s, 2).

Addition of Benzenesulfonyl Iodide to 3-Methyl-1,2-butadiene. Treatment of benzenesulfonyl iodide (0.01 mol) with 3-methyl-1,2-butadiene (1.02 g, 0.015 mol) afforded a quantitative yield of 1-iodo-2-benzenesulfonyl-3-methyl-2-butene (**5h**): nmr (CDCl$_3$) δ 1.80 (s, 3), 1.98 (s, 3), 4.35 (s, 2), 7.37–7.70 (m, 3), 7.80–8.13 (m, 2). Attempts to recrystallize this material from ethanol or hexane–ethanol failed, substantial decomposition occurring during each attempt.

Addition of *p*-Toluenesulfonyl Iodide to 3-Methyl-1,2-butadiene. Treatment of *p*-toluenesulfonyl iodide (5.64 g 0.02 mol) with 3-methyl-1,2-butadiene (1.5 g, 0.0221 mol) afforded a mixture of 6.8 g (97.4%) of 1-iodo-2-(*p*-toluenesulfonyl)-3-methyl-2-butene (**5i**) and 0.34 g of residual benzene solvent (by nmr). No other products were detected by nmr. Recrystallization from absolute ethanol gave 5.75 g (82.2%) of pure product: mp 66–67° (lit.[28,30] mp 77–80°); nmr (CDCl$_3$) δ 1.83 (s, 3), 2.02 (s, 3), 2.38 (s, 3), 4.35 (s, 2), 7.58 (q, 4).

Addition of *p*-Toluenesulfonyl Iodide to 2,3-Pentadiene. Equivalent quantities (0.0496 mol) of the allene and the sulfonyl iodide were combined in ether. After 30 min, the solution was very dark red-orange in color. Solvent removal and recrystallization of the residue from ethanol-water gave 7.88 g (45%) of 3-(*p*-toluenesulfonyl)-4-iodo-2-pentene (**5j**): mp 114-115° dec; nmr ($CDCl_3$) δ 1.91 (m, 6, $CH_3CH{=}C$ and $CHICH_3$), 2.42 (s, 3, $C_6H_4CH_3$), 4.99 (q, 1, $CHICH_3$), 6.99-7.82 (m, 6, C_6H_4 and $CH_3CH{=}C$).

Anal. Calcd for $C_{12}H_{15}IO_2S$: C, 41.15; H, 4.32; I, 36.24; S, 9.16. Found: C, 41.35; H, 4.51; I, 36.15; S, 9.40.

Zinc-Acid Reduction of β-(*p*-Toluenesulfonyl)-β-(iodomethyl)styrene (5e). The allylic iodide **5e** (1.99 g, 0.005 mol) was dissolved in a mixture of acetic acid (1.5 ml), water (1.5 ml), dioxane (5 ml), and ether (30 ml). Zinc dust (0.654 g, 0.01 mol) was added. Heat was evolved and vigorous bubbling occurred. The mixture was stirred for 2 hr and then poured into water. The aqueous mixture was extracted with ether, the ether layer was dried over $MgSO_4$, and the solvent was removed under vacuum to give the crude solid product. Recrystallization from absolute ethanol gave platelets, mp 116-118°. These platelets were again recrystallized from ethanol and could be induced to crystallize as white needles, mp 119-120°. This material was found by nmr, ir, and mixture melting point to be identical with β-(*p*-toluenesulfonyl)-*cis*-β-methylstyrene, which was alternately prepared from *trans*-β-methylstyrene and *p*-toluenesulfonyl chloride by a method used by Goralski[31] for the synthesis of similar compounds. The nmr coupling constant for trans $HC{=}CCH_3$, $J = 1.5$ Hz, supported the stereochemical assignment. The yield of reduced product was 74%.

Alternate Synthesis of β-(*p*-Toluenesulfonyl)-*cis*-β-methylstyrene. *trans*-β-Methylstyrene (10.0 g, 0.085 mol), *p*-toluenesulfonyl chloride (16.2 g, 0.085 mol), anhydrous cupric chloride (0.11 g, 0.00085 mol), and triethylamine hydrochloride (0.175 g, 0.00127 mol) were combined in 3.4 g of acetonitrile. The mixture was heated to 110° (reflux) under nitrogen for 2.5 hr and then cooled. Methanol (35 ml) was added and the resulting solution was cooled, but no product crystallized. Removal of solvents under vacuum left a clear, viscous, yellow oil. This oil was dissolved in dry benzene, triethylamine (12.87 g, 0.127 mol) was added, and the mixture was stirred at room temperature overnight. Triethylamine hydrochloride was removed by filtration and aqueous extraction, the benzene layer was dried over $MgSO_4$, and the solvent was removed under vacuum to give a solid residue. This residue was recrystallized from absolute ethanol to yield 16.8 g (72.7%) of β-(*p*-toluenesulfonyl)-*cis*-β-methylstyrene: mp 119.5-121°; nmr ($CDCl_3$) δ 2.09 (d, 3, $J \cong 1.5$ Hz), 2.38 (s, 3), 7.17-7.50 (m, 7), 7.70-7.97 (m, 3).

Acknowledgment. We thank the National Science Foundation for financial support in the form of Grant GP-12326.

Registry No. **1a**, 42790-58-9; **1b**, 42790-59-0; **1c**, 42790-60-3; **1d**, 42790-61-4; **1e**, 35890-15-4; **2a**, 42790-63-6; **2b**, 42790-64-7; **2c**, 42790-65-8; **3a**, 42790-66-9; **3b**, 42790-67-0; **3c**, 43790-68-1; **3d**, 2525-55-5; **3e**, 35925-44-1; **4**, 39557-29-4; **5a**, 42790-72-7; **5b**, 42790-73-8; **5c**, 42790-74-9; **5d**, 42790-75-0; **5e**, 42790-76-1; **5f**, 42790-77-2; **5g**, 42790-78-3; **5h**, 42790-79-4; **5i**, 35890-17-6; **5j**, 42790-81-8; methanesulfonyl iodide, 42790-82-9; allene, 463-49-0; ethanesulfonyl iodide, 42790-83-0; 2-propanesulfonyl iodide, 42790-84-1; benzenesulfonyl iodide, 1950-77-2; *p*-toluenesulfonyl iodide, 1950-78-3; phenylallene, 2327-99-3; 3-methyl-1,2-butadiene, 598-25-4; 2,3-pentadiene, 591-96-8; *trans*-β-methylstyrene, 873-66-5; β-(*p*-toluenesulfonyl)-*cis*-β-methylstyrene, 42790-87-4.

References and Notes

(1) Presented in part at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972; abstracted in part from the Ph.D. Thesis of D. L. Heuring, Purdue University, Lafayette, Ind., 1972; abstracted in part from the Ph.D. Thesis of G. C. Wolf, Purdue University, Lafayette Ind., 1970.

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