Table III. Products from Substitution Reactions of **1a**

Reagent	Solvent	T, °C	Time, hr	Yield, %	Product (mp (°C))	Calcd C	Calcd H	Found C	Found H
$C_6H_5SO_2Na$	DMF	100	15	80	**5a** (206–207)	58.60	4.63	58.46	4.61
$C_6H_5S^-Et_3NH^+$	C_6H_6[a]	80	8	88	**5b** (137.5–139)	64.53	5.10	64.65	5.23
C_6H_5SK	MeOH[a]	65	13	55	**5b**, 45% of **4**				
NaCN	10% (v/v) DMF–EtOH	*b*	20	42	**5c** (177–178)	61.77[c]	4.75	61.62[c]	4.71
LiN_3	DMF	65	8	*d*	**5d** (122–124 dec)	52.99	4.85	52.98	4.55

[a] Flushed with nitrogen. [b] At reflux. [c] Calcd: N, 6.00. Found: N, 5.83. [d] A mixture of **5d** and **10** (or **11**) in a proportion of 68:32%; pure **5d** was obtained by fractional crystallization.

Anal. Calcd for $C_{11}H_{12}O_2Br_2S$: C, 35.89; H, 3.29. Found: C, 35.71; H, 3.23.

Dehydrobromination with excess pyridine by refluxing in benzene for 4 hr gave 0.71 g (90%) of **1b**: mp 149–150°; nmr δ 2.14 (s, 6 H), 6.56 (s, 1 H), 7.65 (m, 4 H); ir essentially identical with that of **1a**.[2a]

Anal. Calcd for $C_{11}H_{11}O_2BrS$: C, 46.00; H, 3.86. Found: C, 45.93; H, 3.95.

Substitution Reactions of 3-(α-Chloro-α-methylethyl)benzo[*b*]thiophene 1,1-Dioxide (1a). These are summarized in Table III.

Deuterium Exchange Experiments. Complete exchange of the protons in the α positions of **5a**, **5b**, and **5c** was effected under the following conditions: **5a**, 0.001 *M* NaOD in 80% (v/v) dioxane–D_2O for 3 min at 25°; **5b**, 0.005 *M* NaOMe in MeOD at 25° for 20 sec; **5c**, 0.01 *M* NaOMe in MeOD at 25° for 20 min. Under comparable conditions the vinyl protons in enamine **3**, 3-(1-thiophenylmethylene)-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide (**6**), or C_6H_5-$C(CH_3)$=$CHSO_2C_6H_5$ (**7**) failed to exchange to any appreciable extent.

Formation of 3,4-Dimethylbenzo[*b*]thiacyclohex-3-ene 1,1-Dioxide (9) from 2-Cyano-3-isopropylidene-2,3-dihydrobenzo[*b*]thiophene 1,1-Dioxide (5c). A 0.5-g (2 mmol) sample of **5c** was hydrolyzed by refluxing with 0.2 *M* KOH in aqueous ethanol for 4 days to give 0.44 g of carboxylic acid (oil). An amide, mp 244–245°, was isolated from another experiment stopped after 1 day. The acid and amide had nmr spectra consistent with those expected for hydrolysis products of **5c**. Decarboxylation of the acid by refluxing in dry quinoline under a nitrogen atmosphere for 2.5 days gave 0.4 g of **9**: mp 229–231° (from EtOH); nmr δ 2.0 (t, J = 1.5 Hz, 3 H), 2.4 (t, J = 2.0 Hz, 3 H), 3.9 (br s, 2 H), 7.6 (m, 5 H); ir (μ) 3.45 (m), 6.06 (m), 6.27 (w), 6.8 (m), 6.9 (m), 7.25 (m), 7.8 (s), 8.68 (s), 8.8 (s), 8.86 (s), 9.4 (s), 13.02 (s), 13.8 (s), 14.1 (s), 15.32 (s).

Anal. Calcd for $C_{11}H_{12}O_2S$: C, 63.48; H, 5.81. Found: C, 63.18; H, 5.77.

Attempts to rearrange **4** to **9** by heating with *t*-BuOK in pyridine at 200° for 3 days gave recovered **4**.

Catalytic hydrogenation of **9** in EtOH using Pd/C gave a dihydro derivative: mp 127–128°; nmr δ 1.11 (d, J = 6 Hz, 3 H), 1.32 (d, J = 6 Hz, 3 H), 2.0–2.6 (m, 2 H), 3.2 (m, 2 H), 7.6 (m, 4 H).

Similar hydrogenation of **4** gave an oil: nmr δ 0.82 (d, J = 7 Hz, 3 H), 1.08 (d, J = 7 Hz, 3 H), 2.2–2.7 (m, 2 H), 3.4 (m, 2 H), 7.6 (m, 4 H).

Nucleophilic Substitutions in Allylic Systems. Further Evidence against the Existence of the Concerted SN2′ Mechanism

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Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received October 8, 1971*

Abstract: Attempts to discover systems susceptible to SN2′ reactions have led to the synthesis of *exo*- and *endo*-2-chloro-2-phenylsulfonyl-3-methylenebicyclo[2.2.1]hept-5-enes (**2a** and **2b**) and γ-*p*-tolylsulfonylallyl, -α-methylallyl, and -α,α-dimethylallyl halides (or methanesulfonates) (**5**, **4**, and **3**, respectively). Halides **2a** and **2b** proved to be relatively inert to nucleophilic attack. Halides **5** and **4** underwent SN2 displacement, usually accompanied by tautomerism of the starting halide or product. Halides (or mesylate) **3** underwent SN2-type displacements with protic solvents (Table I) or nucleophiles (Table II) accompanied by small amounts of elimination reactions. Despite the incorporation of structural features that should favor SN2′ displacements, none such were observed. The results cast further doubt concerning the existence of concerted SN2′ reactions.

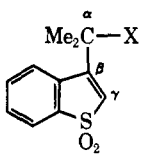
A variety of nucleophiles have been shown to initiate attack at the γ position of tertiary allylic halides in the benzo[*b*]thiophene 1,1-dioxide series (**1**) leading to addition–elimination reactions.[2] Although it is difficult to rule out the (concerted) SN2′ mechanism for these reactions, we favor a mechanism (SN2′-like) involving reversible formation of an ion-pair intermediate.[2b] In fact, we have come to question the very existence of the concerted SN2′ mechanism.[3] The successful attack of nucleophiles at the C=C bond in **1** is no doubt due to: (a) the relative electron deficiency of the C=C bond caused by electron withdrawal from both the γ and β positions by the sulfonyl group, and (b) stabilization of the negative charge in the β position in the intermediate (or transition state) by delocalization to the sulfonyl group. It was of interest to examine the behavior toward nucleophiles of analogous systems where activation by the sulfonyl group is restricted to the α position (**2**)

(1) National Institutes of Health Predoctoral Fellow, 1968–1971.

(2) (a) F. G. Bordwell and D. A. Schexnayder, *J. Org. Chem.*, **33**, 3240 (1968). (b) F. G. Bordwell and T. G. Mecca, *J. Amer. Chem. Soc.*, **94**, 5825 (1972).

(3) F. G. Bordwell, *Accounts Chem. Res.*, **3**, 281 (1970).

or γ position (**3**). Here activation toward SN2′ (or SN2′-like) displacements by the sulfonyl group is limited to its inductive effect which, by electron withdrawal, makes the C=C bond more susceptible to nucleophilic attack than in ordinary allylic halides.[4] The sulfonyl group in systems **2** and **3** cannot directly



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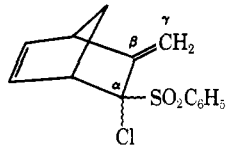
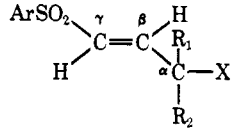


2a and **2b**
(*exo* and *endo*)

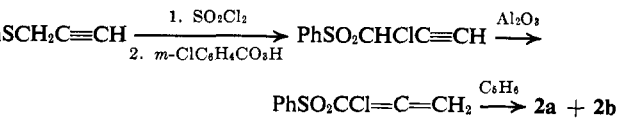


3, $R_1 = R_2 = Me$; X = Cl, Br, OMs
4, $R_1 = H$; $R_2 = Me$; X = Cl, Br
5, $R_1 = R_2 = H$; X = Br, OMs

stabilize a β carbanion intermediate (or transition state), as it does in **1**, but one would expect it to promote *concerted* SN2′ displacements by virtue of its inductive effect. At the same time the sulfonyl group should strongly discourage the formation of carbonium-type reactions which, in our opinion, account for the formation of "abnormal" substitutions in most, if not all, reactions that have been given the SN2′ mechanistic label.[3] For example, **4** (X = Cl) is an analog of α-methylallyl chloride, the most popular substrate eliciting supposed SN2′ reactions.[2a] In **4** one of the γ-hydrogen atoms of α-methylallyl chloride has been replaced by an arylsulfonyl group, which should enhance the tendency of the molecule to react by the SN2′ mechanism.[4] We will see, however, that this expectation is not realized.

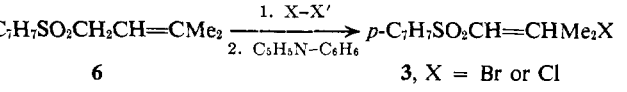
Results

1-Chloro-1-phenylsulfonylpropadiene was prepared by isomerization of 1-phenylsulfonyl-1-chloropropyne using the method of Stirling.[8] Diels–Alder condensation of this allene with cyclopentadiene gave the *exo*- and *endo*-2-chloro-2-phenylsulfonyl-3-methylenebicyclo[2.2.1]hept-5-enes (**2a** and **2b**). These isomeric α-chloro sulfones (separated by chromatography on silica gel) had remarkably different nmr spectra with respect to splitting patterns and chemical shifts of the vinylic protons and the methylene bridge protons. The spectra were consistent with the **2a** and **2b** structures shown, but a definite assignment of exo and endo structures was not possible.



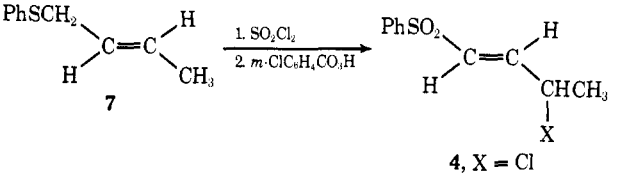
Both **2a** and **2b** proved to be inert to the action of nucleophiles. The unreacted and unisomerized α-chloro sulfones were recovered after treatment for 2 days at 50° with excess 0.6 *M* lithium azide in DMF and after treatment for 2 days with excess 0.625 *M* sodium thiophenoxide in refluxing methanol. Treatment for 2 days in refluxing benzene with excess 0.625 *M* triethylammonium thiophenoxide or excess 0.5 *M* piperidine also failed to evoke a reaction, as did treatment with excess 0.5 *M* piperidine in refluxing methanol. (Reactions with **1** or with α-methylallyl chloride would be complete under these conditions in a far shorter reaction time.[2])

The tertiary halides (**3**, X = Br or Cl) were prepared by addition of bromine or iodine chloride to 3-*p*-tolylsulfonyl-2-butene (**6**) followed by dehydrohalogenation.



The methanesulfonate (mesylate, X = OMs) derivative of **3** was obtained by epoxidation of **6**, eliminative rearrangement with Et_3N–EtOH to form **3** (X = OH),[9] and esterification with methanesulfonyl chloride according to the method of Crossland and Servis.[10]

The secondary chloride (**4**, X = Cl) was prepared by chlorination of 1-thiophenyl-2-butene (**7**) followed by oxidation.



Chlorination of **7** presumably proceeds by way of a chlorosulfonium salt, an ylide intermediate, and α-chloro sulfide **8**.[11] Dissociation of **8** to carbonium–sulfonium ion **8a** should be facile,[12] setting up an equilibrium **8** ⇄ **9**, wherein **9** would be expected to be the more stable partner (PhS conjugated with C=C). About 20% of a chloro sulfone that may correspond in structure to **8** was obtained as a by-product in the synthesis of **4** from **7**.

Primary bromide **5**, $C_6H_5SO_2CH{=}CHCH_2X$ (X = Br) was obtained as before,[9] and mesylate **5** (X = OMs) was prepared from the alcohol[13] using the method of Crossland and Servis.[10]

Essentially quantitative yields of SN2 products were obtained when primary bromide **5** was treated with MeOH, $PhSO_2Na$ in DMF, or KSCN in acetone. The product from the reaction of the (more basic) nucleo-

(4) A nucleophile must overcome a sizable energy barrier in attacking an ordinary C=C bond, judging from the difficulty experienced by even the most powerful bases, including isopropyllithium,[5] solvated electrons,[6] or dimsyl ion ($DMSO^-$)[7] in adding to unconjugated C=C bonds.

(5) J. E. Mulvaney and Z. G. Gardlund, *J. Org. Chem.*, **30**, 917 (1965); J. A. Landgrebe and J. D. Shoemaker, *J. Amer. Chem. Soc.*, **89**, 4465 (1967).

(6) R. A. Benkeser, *J. Org. Chem.*, **38**, 1094 (1963), and references cited therein.

(7) C. Walling and L. Bollyky, *ibid.*, **29**, 2698 (1964).

(8) C. J. M. Stirling, *J. Chem. Soc.*, 5856 (1964).

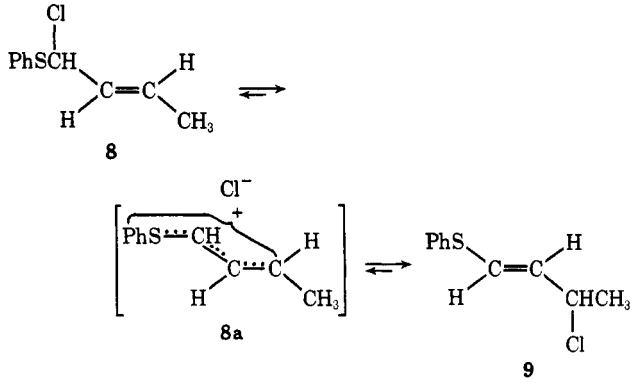
(9) F. G. Bordwell, P. E. Sokol, and J. D. Spainhour, *J. Amer. Chem. Soc.*, **82**, 2881 (1960).

(10) R. K. Crossland and K. Servis, *J. Org. Chem.*, **35**, 3195 (1970).

(11) F. G. Bordwell and B. M. Pitt, *J. Amer. Chem. Soc.*, **77**, 572 (1955). For a recent discussion of sulfide chlorination mechanisms see D. L. Tuleen and T. B. Stevens, *J. Org. Chem.*, **34**, 31 (1969).

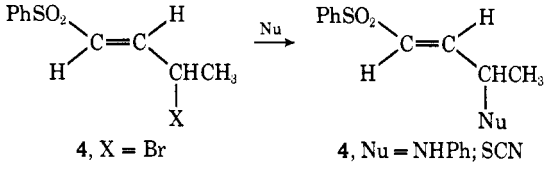
(12) F. G. Bordwell, G. D. Cooper, and H. Morita, *J. Amer. Chem. Soc.*, **79**, 376 (1957).

(13) C. C. J. Culvenor, W. Davies, and W. E. Savige, *J. Chem. Soc.*, 2198 (1949).



phile LiN_3 reacting in either MeOH or DMF was the tautomer, $PhSO_2CH_2CH{=}CHN_3$, of the initially formed product ($PhSO_2CH{=}CHCH_2N_3$).

Secondary chloride **4** gave tautomerized starting material ($PhSO_2CH_2CH{=}CMeCl$, a mixture of cis–trans isomers) when treated in MeOH with basic nucleophiles such as NaOMe, Et_3N, or piperidine. Reaction with methanol in the absence of other nucleophiles or with lithium bromide in acetone gave high yields of SN2 products. Secondary bromide **4** gave high yields of SN2 products with aniline in MeOH or with KSCN in acetone. The product from LiN_3 in MeOH was tautomerized to the extent of *ca.* 80%.



No evidence for the formation of "abnormal" allylic substitution (SN2′) products or products from nucleophilic addition to the C=C bond was obtained in any of these reactions.

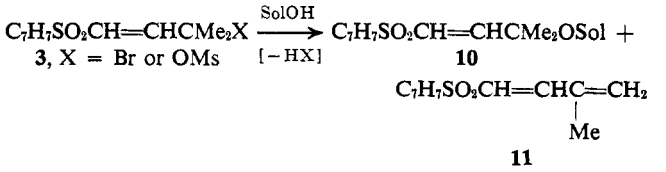
Reactions of the tertiary systems **3** were free of the complications of tautomerism experienced with **4** and **5**. The products formed on solvolysis of **3** are summarized in Table I.

Table I. Products from the Solvolysis of γ-*p*-Tolylsulfonyl-α,α-dimethylallyl Bromide and Methanesulfonate (OMs), *p*-$C_7H_7SO_2CH{=}CHCMe_2X$(RX)

X	Solvent	*T*, °C	Products,[a] % R-OSol	Elim
Br	MeOH	65	78	22
OMs	MeOH	25	90	10
OMs	HOAc	25	52	48
Br	70% (v/v) dioxane–water	70	56	44
Br	60% (v/v) MeOH–H_2O	65	74[b]	26

[a] Analysis by nmr integration. [b] Mixture of the *tert*-methyl ether and tertiary alcohol corresponding roughly to the MeOH–H_2O mole fraction.

Examination of Table I shows that methanolyses of *tert*-bromide **3** and *tert*-mesylate **3** gave similar results. [The larger amount of elimination product (diene **11**) obtained from the bromide is probably a consequence primarily of the higher temperature used.] Similar results were obtained on solvolysis of bromide **3** in 60% (v/v) MeOH–H_2O (Table I) and on methanolysis of the β-methyl derivative of the bromide, *p*-$C_7H_7SO_2CH{=}CMeCMe_2Br$. A larger amount of elimination was observed for **3** in acetic acid and in aqueous dioxane (Table I).



Products formed in the reaction of *tert*-bromide **3** and mesylate **3** with a number of nucleophiles are summarized in Table II.

Table II. Products from the Reactions of γ-*p*-Tolylsulfonyl-α,α-dimethylallyl Bromide and Methanesulfonate (OMs), *p*-$C_7H_7SO_2CH{=}CHCMe_2X$ (RX), with Nucleophiles

X	Nucleophile[b]	Solvent	Products, %[c] R-Nu	R-OMe (**10**)	Elim (**11**)
Br	Et_3N	MeOH	0	5	95
OMs	Et_3N	MeOH	0	90	10
Br	Piperidine	MeOH	0	0	88[d]
OMs	Piperidine	MeOH	0	90	10
Br	$PhNH_2$	MeOH	80	20	0
OMs	$PhNH_2$	MeOH	0	90	10
Br	LiN_3	MeOH	>98	<2	0
Br	LiN_3	DMF	>98		0
OMs	LiN_3	MeOH	83	17	0
OMs	LiN_3	DMF	98		2
Br	PhSK	MeOH	30	0	70[e]
Br	$PhSO_2Na$	MeOH	10	51	39[d]
OMs	$PhSO_2Na$	MeOH	<2	*Ca.* 90	*Ca.* 8
Br	$PhSO_2Na$	DMF	80		20[d]
OMs	$PhSO_2Na$	DMF	23		77[d]
Br	$Et_4N^+Cl^-$	Acetone	25		75
Br	$Et_4N^+Cl^-$	DMF	25		75
OMs	$Et_4N^+Cl^-$	Acetone	25		75
Br	LiCl	MeOH	10	59	31
OMs	LiCl	MeOH	16	70	14
Br	KSCN	Acetone	95[f]	0	5
Br	KSCN	MeOH	43[g]	36	21
OMs	KSCN	Acetone	75[h]	0	25

[a] Concentrations in the range 0.05–0.1 *M*. [b] Concentration *ca.* 1 *M*. [c] Relative product yields were determined by nmr; R–Nu is the SN2 substitution product, R–OMe is *tert*-methyl ether (**10**), and Elim refers to diene **11**. [d] Product is the 1,4 adduct of the nucleophile to diene **11** (see text). [e] 70% diene **11** and 30% 1,4 adduct. [f] Mixture of RSCN–RNCS = 1.3:1.0. [g] Mixture of RSCN–RNCS = 0.3:1.0. [h] Mixture of RSCN–RNCS = 1.3:1.0 in 0.5 hr (1.8:1.0 after 4 hr).

Discussion

From the results just described we see that α-phenylsulfonyl allylic chlorides, as exemplified by the norbornenyl systems **2a** and **2b**, are remarkably resistant to nucleophilic attack. This is perhaps not surprising since attack at the α position would be expected to be retarded in view of the inertness of α-halo sulfones to SN2 reactions,[14] and an SN2′-like attack at the γ position would require formation of a norbornadienyl ring system, which is known to be highly strained.[15]

On the other hand, we have seen that the γ-*p*-tolylsulfonyl allylic halides (or mesylates) **3**, **4**, and **5** react

(14) F. G. Bordwell and G. D. Cooper, *J. Amer. Chem. Soc.*, **73**, 5184 (1951); F. G. Bordwell and B. B. Jarvis, *J. Org. Chem.*, **33**, 1182 (1968).

(15) R. B. Turner, W. R. Meador, and R. E. Winkler, *J. Amer. Chem. Soc.*, **79**, 4116 (1957).

readily with nucleophiles. The substitution products were all of the normal, SN2 type. In no instance was there any indication of the formation of an "abnormal" (SN2′-type) substitution product. The reactions of the secondary and primary halides **4** and **5** were complicated, however, by tautomerisms occurring with the starting halides or products. Perhaps the most clearcut evidence indicating that an SN2′-type reaction is unfavorable in these systems is the failure of secondary bromide **4** to rearrange to the "abnormal" product, **12**, even after prolonged treatment with lithium bromide in acetone.

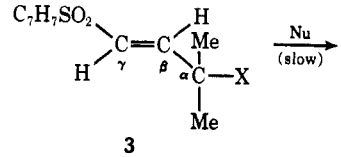
$$\underset{\mathbf{4},\ X = Br}{PhSO_2CH{=}CHCHMeBr} + LiBr \xrightarrow[\text{acetone}]{////} PhSO_2CHBrCH{=}CHMe$$

12

If bromide **12** were formed one would expect it to be stable at equilibrium, relative to **4**,[2b] or to tautomerize further to $PhSO_2CBr{=}CHCH_2Me$. It follows that SN2′ attack by bromide ion on **4** in acetone must be very slow. This does not agree with the conclusion of England that SN2′ attack on $CH_2{=}CHCHMeBr$ is only *ca.* 60 times slower than SN2 attack.[16]

Most of the claims for successful SN2′ reactions have been made for α-methylallyl chloride.[2a] Here the steric effect of the α-methyl group is presumed to retard SN2 reactions to the point where SN2′ reactions can emerge with certain nucleophiles in certain solvents. A second α-methyl substituent should be even better in this regard, but unfortunately its presence, as in α,α-dimethylallyl chloride, strongly accelerates SN1 reactions, and a second-order rate component is seldom, if ever, observed with nucleophiles. This difficulty is obviated with *tert*-bromide **3**, which undergoes methanolysis *ca.* 10^{10} times slower than does $CH_2{=}CH\text{-}CMe_2Br$.[17] In fact, system **3** appears to be an ideal candidate for SN2′ reactions on many counts: (1) SN2 attack at the α position is inhibited sterically by the presence of the two methyl groups, (2) Br and OMs, as well as Cl, can be used as leaving groups, (3) the electron-withdrawing $ArSO_2$ group inhibits SN1 or SNi reactions, (4) the $ArSO_2$ group decreases the electron density at the C=C bond and thereby promotes attack at the γ position,[4] and (5) the transition state for attack at the γ position in a concerted SN2′ reaction would be favored by both relief of ground-state repulsive forces[18] and by conjugation with the two methyl groups. Despite the presence of all of these favorable features, substitutions at the γ position (SN2′ reactions) were not observed with any of the nucleophiles used in either protic or dipolar aprotic solvents (Tables I and II). Although this is negative evidence, we believe that, when considered in light of the paucity of positive evidence for the concerted SN2′ mechanism (as distinct from carbonium ion processes),[3] it accentuates the doubts already expressed concerning the reality of the concerted mechanism.[3]

It is, of course, possible to offer other explanations for the failure of **3** to form "abnormal" substitution products. One alternative explanation is that an SN2′ reaction does indeed occur, but that the abnormal product **13** thus formed rearranges rapidly to give the (observed) normal product **14**.



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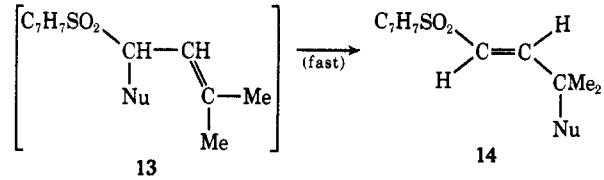


13 **14**

This seems most unlikely since: (a) **13** would be expected to be more stable than **14**,[2b,18] and (b) rearrangements such as **13** ⇄ **14** usually proceed by carbonium ion mechanisms, which are strongly retarded in the present system. Nevertheless, a test of this mechanism was made by studying the behavior of **3** (X = Br) reacting with $PhSO_2Na$ in DMF and of $PhSO_2\text{-}CH{=}CHCMe_2Br$ reacting with *p*-$C_7H_7SO_2Na$. If the two substitutions go by the SN2′-rearrangement path shown for **3**, *i.e.*, **3** → **13** → **14**, they should give a common intermediate, $C_7H_7SO_2CH(SO_2Ph)CH{=}CMe_2$ (**13** with Nu = $PhSO_2$). Since the migratory aptitudes of $C_7H_7SO_2$ and $PhSO_2$ should be similar, a mixture of products ($C_7H_7SO_2CH{=}CMe_2SO_2Ph$ and $PhSO_2CH{=}CMe_2SO_2C_7H_7$) would be expected in each substitution. In practice it was found that in each instance a *single* substitution product was formed, namely, that where substitution had occurred at the tertiary center.

Another possible route from **3** to **14** is elimination to form diene **11**, followed by nucleophilic addition to the diene to give **14**. Products from this elimination–addition sequence were indeed obtained with some of the more basic nucleophiles. These products did not, however, have structure **14**, but an isomeric structure. Isomeric structure **15** is expected from nucleophilic 1,4 addition to diene **11**. This route was examined by preparing diene **11** from bromide **3** (or mesylate **3**) by treatment with triethylamine in acetonitrile. 1,4-Additions to **11** forming **15** were realized in high yields with piperidine in methanol, sodium benzenesulfinate in DMF, and lithium azide in methanol.

$$\underset{\text{or OMs}}{\mathbf{3},\ X = Br} \xrightarrow[CH_3CN]{Et_3N} \underset{\mathbf{11}}{C_7H_7SO_2CH{=}CHCMe{=}CH_2} \xrightarrow[DMF]{PhSO_2Na} C_7H_7SO_2CH_2CH{=}CMeCH_2Y$$

15, Y = SO_2Ph

The evidence is conclusive, then, that nucleophilic attack on **3** by $PhSO_2Na$ occurs by direct substitution at the tertiary center. It seems safe to conclude that this is true also for the other nucleophiles producing **14** (Table II).

The failure of nucleophilic attack at the C=C bond in **3** (SN2′ reaction) could conceivably be caused by steric hindrance originating in the sulfonyl group.[19] This possibility was rendered unlikely by the observa-

(16) B. D. England, *J. Chem. Soc.*, 1615 (1955).
(17) F. G. Bordwell and T. G. Mecca, *J. Amer. Chem. Soc.*, **94**, 2119 (1972).
(18) D. E. O'Connor and W. I. Lyness, *ibid.*, **86**, 3840 (1964).
(19) This is a possible explanation for the inertness of α-halo sulfones to nucleophilic attack.[14] It is less reasonable for **3** since an sp^2 center is less susceptible to steric screening.

tion that an allylic halide in which the $ArSO_2$ group had been replaced by cyano, *i.e.*, $N{\equiv}CCH{=}CHCMe_2Br$ (**16**), reacted with methanol, lithium azide in methanol, and sodium benzenesulfinate in DMF to give substitution at the tertiary center in a manner completely analogous to that of **3**.

The question next arises as to the mechanism of the nucleophilic substitution at the tertiary centers of **3** and **16**. Examples of nucleophilic attack at tertiary centers to form high yields of substitution products are rare. The only general example of which we are aware is nucleophilic substitution at the tertiary center of *p*-nitrocumyl halides and related compounds.[20] In an elegant study Kornblum and his students have demonstrated convincingly that the reactions of *p*-nitrocumyl systems occur by radical-anion processes.[20] The nitro group appears to be greatly superior to other electron-withdrawing groups in initiating such radical-anion reactions.[20] For this reason radical-anion processes are not likely with **3** and **16**. Furthermore, attempts to inhibit or change the course of reactions of **3** with nucleophiles by use of radical traps such as *m*-dinitrobenzene, oxygen, or galvinoxyl, which have proved successful in Kornblum's reactions,[20] were unsuccessful. Finally, kinetic studies showed that **3** and **16** reacted with nucleophiles in MeOH or DMF by clean second-order processes, first order in substrate and first order in nucleophile.[17] It seems unlikely that a radical-anion process would conform to such a simple kinetic scheme. We conclude, therefore, that these are not radical-anion substitutions, but SN2 reactions. The problem has thus been narrowed down to one of deciding where substitutions of **3** (and **16**) fit in the mechanistic classification of substitution at saturated carbon. Despite the fact that several books have been written on the subject,[21] this is not easy to do. After using a number of experimental probes we have concluded that the reactions are occurring by ion-pair SN2 mechanisms.[17]

Ion-Pair SN2′ Mechanisms and Concerted SN2′ Mechanisms for Allylic Systems. As a result of the studies just described and a critical analysis of the literature, we have come to the conclusion that the *concerted* SN2′ mechanism is a myth, and that reactions previously described as proceeding by this mechanism occur, instead, by ion-pair SN2′ mechanisms or other alternative mechanisms.[3] We can perhaps best document our case against the concerted SN2′ mechanism with the aid of Table III, which summarizes all of the supposed examples of this mechanistic class that have come to our attention for which supporting kinetic data have been provided.

An SNi′ type of rearrangement (catalyzed by Li^+) has already been suggested[22] as an alternative mechanism for the (slow) formation of "abnormal" bromides in the reactions of the two bromides listed in Table III, namely, the reactions of $CH_2{=}CHCHMeBr$ and $MeCH{=}CHCH_2Br$ with LiBr* in acetone.[16] (Most workers have avoided bromides in such studies because of their known susceptibility to such internal rearrangements.) In a recent careful extension of this study Hemmingson and England have shown that the rearrangement of the corresponding chlorides is catalyzed by Cl^- (and not by Et_4N^+) of $Et_4N^+Cl^-$.[23] They have assigned an SN2′ mechanism (presumably concerted) to this isomerization and state, without discussion, that the alternative mechanisms we suggested "are not consistent with the experimental data." This is not true since the ion-pair SN2′ mechanism would accommodate the data. The elegant study of Lesnini, Buckley, and Noyes in an analogous system indicates, however, that the situation is probably more complex than this.[24] The latter investigation of the cis–trans isomerization, isotopic exchange (of chloride ion), and racemization of 5-methyl-2-cyclohexenyl chloride, as catalyzed by $Et_4N^+Cl^-$, led to the conclusion that both trans and cis concerted SN2′ reactions are unimportant.[24] The deduction that the cis chloride undergoes racemization more rapidly than exchange led to the postulate of a sandwich-type intermediate for this reaction.[24] Their mechanism can be considered to be a variation (or elaboration) of the ion-pair SN2′ mechanism.

Table III. Types of Substrates Claimed to Give SN2′ Reactions[a]

Secondary allylic systems
9 chlorides (6 with R_2NH)
1 bromide
5 2,6-dichlorobenzoates (3 with R_2NH)
Primary and tertiary systems
1 primary ($MeCH{=}CHCH_2Br$ + LiBr* in acetone)
1 tertiary
Other
2 $CH_2{=}CHCHCl_2$ and 2 $CH_2{=}CMeCCl_3$
Total 21

[a] For a list with rate data and references see F. G. Bordwell and D. A. Schexnayder, *J. Org. Chem.*, **33**, 3240 (1968).

Tertiary allylic halides ordinarily solvolyze so rapidly that a second-order component in the rate is not observed even when good nucleophiles are present. This is true of the one tertiary halide listed in Table III, $H_2C{=}CHCMe_2Cl$, which solvolyzes at a rate *ca.* 10^4 times that of *t*-BuCl. Azide ion does not affect the rate of solvolysis in 80% acetone, although appreciable quantities of azide product are formed because of the high selectivity of the $[H_2C{-}{=}CH{=}{-}CMe_2]^+$ cation for azide ion.[25] In view of the demonstration that $H_2C{=}CHCMe_2Cl$ reacts by a Lim mechanism under these conditions,[25] the claim of a concerted SN2′ reaction of this chloride with PhSK in EtOH[26] needs to be further documented before being accepted. Originally we suggested[3] that the SNi′–SN2 mechanism had not been ruled out for this example. Recently de la Mare and Vernon have presented convincing counter arguments in this regard.[27] On the other hand, their arguments

(20) N. Kornblum and F. W. Stuchal, *J. Amer. Chem. Soc.*, **92**, 1804 (1970), and references cited therein. We are indebted to Professor Kornblum for helpful discussions, particularly with respect to his unpublished results.

(21) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962; C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier, New York, N. Y., 1963; E. R. Thornton, "Solvolysis Mechanisms," Ronald Press, New York, N. Y., 1964.

(22) R. H. DeWolfe and W. G. Young, *Chem. Rev.*, **56**, 753 (1956).

(23) J. A. Hemmingson and B. D. England, *J. Chem. Soc. B*, 1347 (1971).

(24) D. G. Lesnini, P. D. Buckley, and R. M. Noyes, *J. Amer. Chem. Soc.*, **90**, 668 (1968).

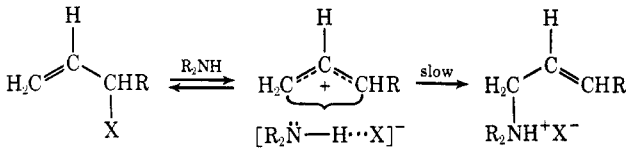
(25) R. A. Sneen, J. V. Carter, and P. S. Kay, *ibid.*, **88**, 2594 (1966).

(26) P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 3555 (1953).

(27) P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc. B*, 1699 (1971).

against the ion-pair SN2′ mechanism, which we suggested as another alternative, are not convincing.[28]

It is perhaps significant that 9 of the 21 claims listed in Table III have been for reactions involving secondary amines in hydrocarbon solvents such as benzene. Under these reaction conditions it seems likely that hydrogen bonding between the attacking amine and the leaving group may provide an important driving force for the reaction.[29] For this reason Ingold has classified these reactions as SNi′, rather than SN2′.[30] Ingold's SNi′ rearrangement is essentially an ion-pair SN2′ reaction, *i.e.*



Three presumed SN2′ reactions of secondary allylic chlorides in EtOH solvent have been recorded. Two of these, where diethyl sodiomalonate is the nucleophile, give only minor amounts of "abnormal" products (10% from CH_2=CHCHMeCl and 20% from CH_2=CHCHEtCl). An ion-pair SN2′ mechanism has not been ruled out as a route to the abnormal products; O-allylation followed by SNi′ rearrangement has also been suggested as an alternative mechanism.[31] (These alternative mechanisms are also possibilities for the reaction of diethyl sodiomalonate with 4-alkyl-3-cyclohexenyl 2,6-dichlorobenzoates in BuOH, although strong arguments against the Dewar mechanism can be made.[32]) One example of abnormal substitution using NaOEt as a nucleophile is known [with CH_2=CHCH(*t*-Bu)Cl],[33] but here the rate has a second-order component only at high concentrations of sodium ethoxide.[33] The possibility that this acceleration in rate is caused by a salt effect does not appear to have been ruled out and, of course, the ion-pair SN2′ mechanism remains as a possibility.

Reactions of NaOEt, NaOPh, or NaSPh in EtOH with CH_2=$CHCHCl_2$ in each instance give about equal amounts of $NuCH_2CH$=CHCl (cis and trans) and CH_2=$CHCH(Nu)_2$ products; the first Cl^- is lost in a second-order process.[34] These results have been interpreted as indicating that SN2 and SN2′ reactions proceed at comparable rates in each of these reactions.[32] Arguments against the alternative SNi′–SN2 mechanism have been presented recently,[27] but an ion-pair SN2′ mechanism or reaction of the nucleophile with a carbene intermediate (CH_2=$CH\ddot{C}Cl \leftrightarrow :\bar{C}H_2CH{=}C^+Cl$) appears to remain as a reasonable alternative to the concerted SN2′ mechanism. For abnormal substitutions of CH_2=$CHMeCCl_3$ with NaOEt and PhSNa in EtOH[35] alternatives to the concerted SN2′ mechanism include an ion-pair SN2′ mechanism and an addition–elimination mechanism (nonconcerted SN2′ reaction involving a carbanion intermediate).

One final, general argument for the likelihood of ion-pair SN2′ mechanisms can be made in that secondary allylic chlorides, and the like, show either SN1 or borderline mechanistic behavior in solvolysis reactions. They are, therefore, susceptible to carbonium ion type reactions. Furthermore, it turns out the tertiary bromide **3** undergoes methanolysis at about the same rate as for secondary allylic chlorides. If then, our interpretation that **3** is reacting with nucleophiles by ion-pair SN2 mechanisms[17] is accepted, it follows that ion-pair SN2 and ion-pair SN2′ mechanisms are likely for the secondary allylic systems listed in Table III.

Our conclusion is that, in instances where SN2′ mechanisms have been suggested, alternative mechanisms can serve at least as well. In view of the relative unattractiveness of attack of a nucleophile on an unactivated C=C bond,[4] and indications that for reactions of this type bond making may not be of much assistance to bond breaking,[3] it seems doubtful to us that the *concerted* SN2′ mechanism ever has been or ever will be realized.

Experimental Section

***exo*- and *endo*-2-Chloro-2-phenylsulfonyl-3-methylenebicyclo[2.2.1]hept-5-enes (2a and 2b).** 1-Chloro-1-phenylsulfonylpropyne was prepared from 1-phenylthiopropyne by successive chlorination and oxidation, as described below for the preparation of 3-chloro-1-phenylsulfonyl-1-butene: nmr δ 3.0 (d, J = 3 Hz, 1 H), 5.45 (d, J = 3 Hz, 1 H), 7.7 (m, 5 H). Isomerization[8] of a 2.1-g sample was effected by absorption on a 4 × 40 cm column packed with Woelm's Grade II basic alumina, and then eluting as quickly as possible with 50% (v/v) ether–hexane. The resulting viscous reddish oil had nmr resonances at 5.74 (s, 2 H) and 7.8 (m, 5 H), and ir bands at 3.27 (w), 3.35 (w), 5.08 (w), 6.91 (m), 7.5 (s), 8.63 (s), 9.19 (s), 11.06 (m), 13.21 (m), 13.8 (s), 14.54 (s). A solution containing 1.07 g (5 mmol) of this allene and 1.3 g (20 mmol) of freshly prepared cyclopentadiene in 100 ml of dry benzene was held at reflux for 75 min. Chromatography on a 2 × 20 cm column packed with Woelm Grade II neutral alumina (elution with 50-ml fractions of 1.5% EtOAc–hexane) gave 0.6 g of colorless solid in fraction 2: mp 81–82° (crystallization from MeOH); nmr δ 1.72 (d of t, J = 9 Hz, 1 H, bridgehead proton), 2.75 (br d, J = 9 Hz, 1 H, bridgehead proton), 3.4 (br s, 2 H, bridge protons), 6.45 (s, 2 H, *exo*-CH_2), 6.18 (d of d, 6, J = 3 Hz, 1 H, CH=CH), 6.5 (d of d, 6, J = 3 Hz, 1 H, CH=CH), 7.86 (m, 5 H).

Anal. Calcd for $C_{14}H_{13}O_2ClS$: C, 59.89; H, 4.67. Found: C, 59.98; H, 4.72.

Fractions 3 and 4 were mixtures; fractions 5 and 6 contained 0.3 g of an oil: nmr δ 1.84 (br d, J = 9 Hz, 1 H, bridgehead proton), 2.14 (br d, J = 9 Hz, 1 H, bridgehead proton), 2.98 (br s, 1 H, bridge proton), 3.39 (br s, 1 H, bridge proton), 5.39 (s, 1 H), 5.67 (s, 1 H), 6.31 (br s, 2 H), and 7.7 (m, 5 H).

1-*p*-Tolylsulfonyl-3-methyl-2-butene (6) was obtained in 88% yield from the reaction of 8.5 g (57 mmol) of 1-bromo-3-methyl-2-butene[36] and 14 g (77 mmol) of sodium *p*-toluenesulfinate in 300 ml of absolute ethanol: mp 80–81°; nmr δ 1.34 (s, 3 H), 1.70 (s, 3 H), 2.39 (s, 3 H), 3.75 (d, J = 8 Hz, 2 H), 5.11 (t, J = 8 Hz, 1 H), 7.6 (m, 4 H).

1-*p*-Tolylsulfonyl-3-bromo-3-methyl-1-butene (3, X = Br). Bromine (6.6 g, 37 mmol) was added dropwise to a solution of 8.1 g (36 mmol) of **6** in 70 ml of CH_2Cl_2 at 0°. The crude, unstable dibromide (no ir absorptions at 5.9–6.3 μ) was refluxed in 70 ml of dry benzene containing 3 g (38 mmol) of pyridine for 6 hr. Crystalliza-

(28) In a footnote the authors state that their usage of the terms "concerted" or "synchronous" does not necessarily imply a one-stage process, and that "the intervention of unstable intermediates on either side of the rate-limiting transition state is neither precluded nor assumed." In essence this statement defines the SN2′ reaction as any second-order reaction of an allylic halide with a nucleophile to form an abnormal product *irrespective of mechanism*. This begs the question we are asking. The point we are concerned with is whether or not reactions as complex as abnormal nucleophilic allylic substitutions, where two bonds are formed and two are broken, ever occur by one-stage mechanisms with bond making aiding bond breaking.[3]

(29) W. G. Young, I. D. Webb, and H. L. Goering, *J. Amer. Chem. Soc.*, 73, 1076 (1951).

(30) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, pp 859–860.

(31) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, 18, C43 (1951).

(32) G. Stork and W. N. White, *J. Amer. Chem. Soc.*, 78, 4609 (1956).

(33) P. B. D. de la Mare, E. D. Hughes, P. C. Merriman, L. Pichet, and C. A. Vernon, *J. Chem. Soc.*, 2563 (1958).

(34) P. B. D. de la Mare and C. A. Vernon, *ibid.*, 3325, 3331 (1952).

(35) P. B. D. de la Mare and C. A. Vernon, *ibid.*, 3628 (1952).

(36) Prepared by the reaction of hydrobromic acid with 2-methyl-3-buten-2-ol (Aldrich).

Table IV. Nuclear Magnetic Parameters[a] for *trans*-*p*-$MeC_6H_4H_IC{=}CH_{II}CMe_2X$

X	H_I[b]	H_{II}[b]	$C(CH_3)_2$	*p*-CH_3	Aromatic	Other
Cl	6.5 (d)	7.13 (d)	1.70 (s)	2.45 (s)	7.5 (q)	
Br	6.5 (d)	7.13 (d)	1.87 (s)	2.45 (s)	7.5 (q)	
OSO_2CH_3	6.48 (d)	7.0 (d)	1.72 (s)	2.43 (s)	7.6 (q)	3.0 (s, OSO_2CH_3)
OH	6.6 (d)	7.0 (d)	1.35 (s)	2.44 (s)	7.6 (q)	2.55 (s, -OH)
OCH_3	6.4 (d)	6.81 (d)	1.28 (s)	2.45 (s)	7.55 (q)	3.14 (s, OCH_3)
OAc	6.34 (d)	6.98 (d)	1.53 (s)	2.44 (s)	7.6 (q)	2.0 (s, $COCH_3$)
N_3	6.5 (d)	6.84 (d)	1.40 (s)	2.45 (s)	7.6 (q)	
NHPh	6.4 (d)	6.9 (d)	1.37 (s)	2.40 (s)	7.5 (m)	7.5, 4.45 (s, NH)
SPh	5.8 (d)	6.98 (d)	1.35 (s)	2.49 (s)	7.4 (m)	7.4
SO_2Ph	6.3 (d)	7.0 (d)	1.49 (s)	2.49 (s)	7.6 (m)	7.6
SO_2Ph-*p*-Me	6.3 (d)	7.0 (d)	1.49 (s)	2.49 (s), 2.39 (s)	7.6 (m)	
SO_2Ph-*p*-Me	6.3 (d)	7.0 (d)	1.49 (s)	2.38 (s)	7.6 (m)	
SC≡N	6.4 (d)	6.92 (d)	1.63	2.4 (s)	7.6 (m)	
N=C=S	6.55 (d)	6.88 (d)	1.53	2.42 (s)	7.6 (q)	

[a] Chemical shifts are reported in δ values measured in parts per million (ppm) relative to TMS. [b] Doublet, J = 15 Hz.

Table V. Nuclear Magnetic Resonance Parameters[a] for $PhSO_2CH_I{=}CH_{II}CH_{III}(CH_3)X$

X	H_I (d)[b]	H_{II} (d of d)[c]	H_{III} (qu)[b]	CH_3 (d)[e]	Aromatic	Other
Cl	6.75	7.06	4.73	1.68	7.8	
Br	6.59	7.0	4.67	1.82	7.8	
OCH_3	6.75	6.96	4.0	1.24	7.8	3.28 (OCH_3)
NHPh	6.5	6.98	4.1	1.30	7.8	3.36 (NH)
SCN	6.6	6.98	4.06	1.62	7.8	

[a] Chemical shifts are reported in δ values measured in parts per million (ppm) relative to TMS. [b] Doublet; $J_{I,II}$ = 15 Hz. [c] Doublet of doublets; $J_{I,II}$ = 15 Hz, $J_{II,III}$ = 7.5 Hz. [d] Overlapping doublet of quartets to give a quintet; $J_{II,III} = J_{III,CH_3}$ = 7.5 Hz. [e] Doublet, J = 7.5 Hz.

tion from 95% EtOH gave 10 g (91%) of material, mp 81–83°. Pure **3** (X = Br) melted at 84–84.8°: nmr, Table IV; uv (MeOH) 238 nm (ϵ 1.77 × 10^4).

1-*p*-Tolylsulfonyl-3-chloro-3-methyl-1-butene (3, X = Cl) was prepared in a similar manner from a reaction of **6** with iodine monochloride in CH_2Cl_2 (0°, 12 hr) followed by a 2-day dehydroiodination at 25°: mp 68.2–68.8°; nmr, Table IV.

1-*p*-Tolylsulfonyl-3-hydroxy-3-methyl-1-butene (3, X = OH) was prepared from **6** by epoxidation with *m*-$ClC_6H_4CO_3H$ in CH_2Cl_2 (0°, 3 hr; 25°, 4 hr) followed by eliminative rearrangement[9] using Et_3N in 95% EtOH (12-hr reflux): yield 84%; mp 101.9–102.4°; nmr, Table IV.

1-*p*-Tolylsulfonyl-3-methyl-3-buten-1-yl Methanesulfonate (3, X = OSO_2CH_3). This ester was prepared from alcohol **3** using the method of Crossland and Servis,[10] as described for preparation of the ester of alcohol **5** (see below): yield 95%; mp 48–50° dec; nmr, Table IV; ir (μ) 3.2 (w), 6.05 (w), 6.25 (m), 6.9 (m), 7.2 (m), 7.6 (vs), 8.4 (s), 8.52 (s), 8.7 (s), 8.85 (s), 9.19 (s), 10.1 (m), 10.35 (s), 10.6 (s), 10.9 (s), 12.35 (s), 12.69 (s), 15.2 (s). Attempts at further purification led to decomposition. The dry powder was stable at 0° for periods of 1–3 weeks.

3-Chloro-1-phenylsulfonyl-1-butene (4, X = Cl). 1-Phenylthio-2-butene, bp 80–82° (1.2 mm), was prepared in 60% yield from the reaction of 22.5 g (0.25 mol) of crotyl chloride with 0.25 mol of sodium thiophenoxide in EtOH: nmr δ 1.4 (d, J = 7 Hz, CH_3 one isomer, 30%), 1.67 (d, J = 4 Hz, CH_3 second isomer, 70%), 3.55 (m, 2 H), 5.6 (m, 2 H), 7.36 (m, 5 H). A 4.6-g (28 mmol) sample of this sulfide in 60 ml of dry CCl_4 was purged with nitrogen and treated (under reflux), by dropwise addition, with 4.25 g (31 mmol) of sulfuryl chloride in 30 ml of CCl_4. After 1 hr the solution was cooled to 0° and 14.3 g (71 mmol) of 85% *m*-chloroperoxybenzoic acid in CH_2Cl_2 was added slowly. After work-up a 2-g sample of the product, a viscous yellow oil, was chromatographed on silica gel, eluting with ether–hexane (75-ml fractions). Fractions 13–18 contained 0.4 g of an unidentified oil containing chlorine and sulfur: nmr δ 1.6 (d, J = 6 Hz, 3 H), 5.0 (br, 1 H), 6.0–6.5 (m, 2 H), 7.8 (m, 5 H); ir (μ) 3.25 (m), 3.35 (m), 5.78 (w), 6.11 (m), 6.3 (w), 6.75 (w), 6.9 (s), 7.31 (m), 7.6 (s), 8.65 (s), 9.2 (s), 12.8 (s), 13.5 (b), 14.55 (s). These spectra are consistent with the structure 1-chloro-1-phenylsulfonyl-2-butene. Fractions 22–30 contained 1.4 g of **4** (X = Cl), a viscous oil: uv $\lambda_{max}^{95\%\ EtOH}$ 259 nm (ϵ 8.8 × 10^2), 273 (ϵ 8.35 × 10^2), 266 (ϵ 1.03 × 10^3); ir (μ) 3.25 (w), 6.12 (m), 6.9 (s), 7.6 (s), 8.7 (s), 9.18 (s), 9.85 (m), 10.3 (m), 11.95 (s), 12.75 (m), 13.25 (s), 13.8 (s), 14.5 (s); nmr, Table V.

Reactions of 1-Phenylsulfonyl-3-methyl-3-but-1-enyl Halides and Mesylate 3. (See Tables I and II product distributions.) **(a) With Triethylamine.** Reaction of bromide **3** with a threefold excess of Et_3N in refluxing dry acetonitrile for 8 hr gave 67% of 1-*p*-tolylsulfonyl-3-methyl-1,3-butadiene (**11**): mp 62–63°; nmr δ 1.89 (br s, 3 H), 2.4 (s, 3 H), 5.41 (br s, 2 H), 6.34 (d, J = 15 Hz, 1 H), 7.36 (d, J = 15 Hz, 1 H), 7.6 (m, 4 H); ir (μ) 3.23 (w), 3.32 (w), 3.4 (w), 6.15 (w), 6.23 (m), 6.85 (m), 7.6 (vs), 8.7 (s), 9.14 (s), 12.3 (s), 13.12 (m), 14.15 (m), 15.08 (s); uv (95% EtOH) 252 nm (ϵ 5.8 × 10^4). Another experiment using mesylate **3** with excess 1 *M* Et_3N in CH_3CN also gave **11**.

(b) With Methanol. After a 24-hr reflux of bromide **3** (or mesylate **3**) in MeOH the solvent was removed under reduced pressure. Diene **11** (22% by nmr) was removed by refluxing for 5 hr with methanolic $PhSO_2Na$. Vacuum distillation at 100° (0.15 mm) gave 1-*p*-tolylsulfonyl-3-methoxy-3-methyl-1-butene (**3**, X = OMe); nmr, Table IV.

(c) With Lithium Azide. Treatment of bromide **3** with a 15-fold excess of LiN_3 in MeOH at reflux for 30 min gave >98% of azide as a viscous yellow oil (<2% of methyl ether by nmr): nmr, Table IV. Reaction with Pd/H_2 (2 atm) in 95% EtOH gave 95% of amine as a waxy solid: nmr δ 1.07 (s, 6 H), 1.8 (m, 4 H), 2.4 (s, 3 H), 3.3 (m, 2 H), 7.6 (q, J = 8 Hz, 4 H); benzoyl derivative; mp 111.5–112.5°; nmr δ 1.34 (s, 6 H), 2.2 (m, 2 H), 2.4 (s, 3 H), 3.12 (m, 3 H), 6.0 (s, 1 H), 7.5 (m, 9 H).

Anal. Calcd for $C_{19}H_{23}O_3NS$: C, 66.06; H, 6.71. Found: C, 65.99; H, 6.80.

Treatment of the amide, mp 111.5–112.5°, with NaOMe–MeOD at 25° for 13 hr caused disappearance of the δ 6.0 signal (NH).

(d) With Piperidine. Reaction of bromide **3b** with piperidine (3:1 molar amounts) in MeOH at reflux for 12 hr gave 88% of 1-piperidino-2-methyl-4-*p*-tolylsulfonyl-3-butene (**15**, Y = $C_5H_{10}N$): mp 92.5–93.5°; nmr, Table VI). An identical product was obtained by reaction of piperidine with diene **11** in MeOH (3-hr reflux).

Reaction with 0.01 *M* NaOMe–MeOD at 25° for 1 hr caused the δ 3.8 doublet (CH_2 α to SO_2) to disappear and the δ 5.35 triplet to collapse to a broad singlet.

Mesylate **3** (1 mmol) in 10 ml of 1 *M* piperidine in MeOH at 25° for 1 hr gave 90% of methyl ether **3** and 10% of diene **11** (nmr).

(e) With Sodium Benzenesulfinate. Reaction of bromide **3** with a fivefold excess of $PhSO_2Na$ in DMF at 50° for 3 hr gave (nmr analysis) 80% of 1-*p*-tolylsulfonyl-3-phenylsulfonyl-3-methyl-1-butene (**3**, X = $PhSO_2$) and 20% of **15** (Y = SO_2Ph). Two crys-

Table VI. Nuclear Magnetic Resonance Parameters[a] for p-$CH_3C_6H_4SO_2(CH_2)^dCH_b{=}C(CH_3)(CH_2)^aX^c$

X	CH_2^a	CH_2^d	$H_bC{=}$	$(CH_3)^c$	p-CH_3	Aromatic	Other
NC_5H_{10}	3.8 (s)	4.85 (d, 8)	5.4 (t, 8)	1.47 (s)	2.46 (s)	7.6 (q, 8)	2.2, 1.5 (m, piperidine)
OCH_3	3.8 (s)	3.9 (d, 8)	5.0 (t, 8)	1.40 (s)	2.46 (s)	7.6 (q, 8)	2.33 (s, $-OCH_3$)
N_3	3.64 (s)	3.79 (d, 8)	5.47 (t, 8)	1.44 (s)	2.45 (s)	7.6 (q, 8)	
$O_2SC_6H_5$	3.8 (s)	3.76 (d, 8)	5.26 (t, 8)	1.57 (s)	2.44 (s)	7.5 (m)	
SC_6H_5	3.51 (s)	3.68 (d, 8)	5.36 (t, 8)	1.54 (s)	2.44 (s)	7.4 (m)	

[a] Chemical shifts are reported in δ values measured in parts per million. The multiplicity and coupling constants (Hz) are given in parentheses following the chemical shift.

Table VII. Nuclear Magnetic Resonance Parameters[a] for $PhSO_2CH_2CH{=}CXR$

R	X	HC=	$-CH_2-$	R	Aromatic
H	N_3	4.88 (t, 7.3)	3.88 (d, 7.3)	6.4 (d, 7.3)	7.7 (m)
CH_3	Cl	5.58 (t, 8, 1.2)[b]	4.0 (d, 8, 1.2)[c]	2.04 (q, 1.2)	7.7 (m)
CH_3	Br	5.80 (t, 8, 1.2)[b]	4.0 (d, 8, 1.2)[c]	2.05 (q, 1.2)	7.7 (m)
CH_3	N_3	4.79 (t, 8.0, 1.2)[b]	3.78 (d, 8, 1.0)[c]	1.96 (q, 1.0)	7.7 (m)

[a] Chemical shifts are reported in δ values measured in parts per million (ppm) relative to TMS. The multiplicity and coupling constants (Hz) are given in parentheses following the chemical shift. [b] Triplet of quartets. [c] Doublet of quartets.

tallizations from 95% EtOH and two from MeOH gave pure **3**: mp 168.5–169.3°; nmr, Table IV.

Reaction of mesylate **3** with a saturated solution of $PhSO_2Na$ in DMF (2 hr at 25° and 3 hr at 50°) gave 23% of **3** (X = $PhSO_2$) and 77% of **15** (Y = SO_2Ph) as indicated by nmr analysis. Reaction of diene **11** (0.27 mmol) with a $PhSO_2Na$ (1.2 mmol) and $Et_3NH^+Br^-$ (0.3 mmol) in DMF at 50° for 4 hr gave 95% of 1-*p*-tolylsulfonyl-4-phenylsulfonyl-3-methyl-2-butene (**15**, Y = SO_2Ph): mp 143.5–144.5°; nmr, Table VI.

(f) With Potassium Thiophenoxide. Reaction of bromide **3** with a sixfold excess of PhSK under nitrogen in MeOH at reflux for 2.5 hr gave a mixture containing 30% of phenyl sulfide **3** (X = SPh), 50% of diene **11**, and 20% of the 1,4 adduct of PhSH to **11** (nmr analysis).

1-*p*-Tolysulfonyl-3-phenylthio-3-methyl-1-butene (**3**, X = SPh) was separated from the other components of the mixture by thick-layer chromatography: mp 119–120.5°; nmr (Table IV) ir (μ) 3.4 (w), 6.2 (w), 6.26 (w), 7.7 (s), 8.74 (s), 9.21 (m), 11.94 (s), 13.22 (s), 14.9 (s); λ_{max}^{MeOH} 229 nm (ϵ 1.6 × 10^4). Oxidation with *m*-chloroperoxybenzoic acid gave sulfone **3** (X = $PhSO_2$).

(g) With Aniline. Reaction of bromide **3** with an 18-fold excess of aniline in MeOH at reflux for 24 hr gave 80% of amine **3** (X = NHPh) and 20% of methyl ether **3** (X = OMe). The amine was too easily oxidized to allow purification: nmr, Table IV; the benzamide was obtained as an oil [ir absorptions at 5.6 (s), 5.74 (s), 6.12 (s), 6.2 (s), 6.3 (m)].

(h) With Tetraethylammonium Chloride. Reaction of bromide **3** with a 15-fold excess of $Et_4N^+Cl^-$ in acetone at reflux for 44 hr gave 25% of chloride **3** (nmr, Table IV) and 75% of diene **11** (nmr analysis).

(i) With Potassium Thiocyanate. A solution of 0.5 g (1.6 mmol) of mesylate **3** and 2 g (20 mm) of KSCN in 20 ml of acetone was stirred at ambient temperature for 4 hr. Processing gave 25% of diene **11** and 75% of a mixture of isomeric tertiary substitution products of **3**, RSCN and RNCS, in a ratio of 1.8:1.0 (nmr). Separation was accomplished by thick-layer chromatography using silica gel and eluting with 40% (v/v) chloroform–hexane. For thiocyanate **3**, the following spectral data were observed: ir (μ) 3.27 (w), 2.4 (m), 4.64 (sh), 5.8 (m), 6.26 (m), 6.84 (m), 7.17 (w), 7.55 (s), 7.73 (s), 8.68 (s), 8.93 (m), 9.18 (s), 11.9 (b), 12.3 (s), 15.06 (s); nmr, Table IV; note the *gem*-dimethyl resonance at δ 1.63. For isothiocyanate **3**, the following spectral data were observed: ir (μ) 3.28 (w), 3.4 (m), 4.85 (vs), 5.8 (w), 6.26 (m), 6.9 (m), 7.57 (s), 7.78 (s), 8.71 (s), 9.19 (s), 10.25 (m), 12.65 (v br), 13.15 (s), 15.2 (s); nmr, Table IV; note the *gem*-dimethyl resonance at δ 1.53.

A pure sample of thiocyanate **3** was converted completely to isothiocyanate **3** (ir and nmr analysis) by refluxing in acetonitrile for 60 hr.

Reaction of bromide **3** with excess 1 *M* KSCN in acetone at reflux for 13 hr gave 5% of diene **11** and 95% of a mixture of RSCN and RNCS isomers **3** in a ratio of 1.3:1.0. A comparable experiment in methanol gave 36% of methyl ether **3**, 21% of diene **11**, and 43% of the RSCN and RNCS mixture (ratio *ca.* 0.3:1.0).

Reactions of 4 (X = Cl, Br). (a) With Lithium Bromide. Reaction of chloride **4** with a tenfold excess of LiBr in refluxing acetone for 48 hr gave 92% of bromide **4** as a slightly yellow oil. An analytical sample was prepared by thick layer chromatography on silica gel: nmr, Table V.

(b) With Methanol. Bromide **4** was refluxed in MeOH for 10 days to give 1-phenylsulfonyl-3-methoxy-1-butene (**4**, X = OMe). The oil was purified by molecular distillation at 100° (0.1 mm): nmr, Table V.

(c) With Bases. Refluxing chloride **4** in benzene with excess Et_3N for 15 hr gave 98% of the tautomer 1-chloro-3-phenylsulfonyl-1-butene (**4a–4b**) as a yellow solid: mp 69.5–70.5° after crystallization from MeOH; the nmr spectrum (Table VII) indicated that it is a mixture of cis–trans isomers. Reactions of chloride **4** with NaOMe in MeOH and with piperidine in benzene also gave the **4a–4b** mixture.

(d) With Lithium Azide. Reaction of chloride **4** with a tenfold excess of LiN_3 in DMF at 0° for 4 hr gave a brownish oil with an nmr spectrum (Table VII) strikingly similar to that of mixture **4a–4b**. Two vinyl methyl resonances at δ 1.96 and 1.54 (ratio 1.0:0.49) are believed to be due to *trans*- and *cis*-1-azido-3-phenylsulfonyl-1-butenes, respectively. A third component (*ca.* 18% of the total) had an nmr resonance centered at δ 1.36 (d, J = 7 Hz). Assignment of the structure of the 18% component as 3-azido-1-phenylsulfonyl-1-butene was supported by the observation that when the crude azide was refluxed for 10 min with 0.005 *M* NaOMe in MeOH the δ 1.96 and 1.54 peaks increased in intensity (ratio 1.0:0.47) and the δ 1.36 doublet disappeared.

(e) With Aniline. Reaction of chloride **4** with a fivefold excess of aniline in refluxing MeOH for 3 hr gave 94% of $PhNH_3^+Cl^-$ and 88% of a viscous orange oil identified by nmr (Table V) as 1-phenylsulfonyl-3-anilino-1-butene; the ir showed an N–H stretch at 2.8 μ.

(f) With Potassium Thiocyanate. Reaction of bromide **4** with a tenfold excess of KSCN in refluxing acetone for 2 hr gave 1-phenylsulfonyl-3-but-1-enyl thiocyanate (**4**, X = SCN) as a viscous oil; nmr, Table V. None of the isomeric isothiocyanate was detectable. A sample was purified for analysis by thick-layer chromatography on silica gel.

1-Phenylsulfonyl-3-prop-1-enyl methanesulfonate (5, X = OMs) was prepared from the corresponding alcohol[13] by the method of Crossland and Servis:[10] yield, 95%; mp 93.5–95°; nmr, Table VIII.

Reactions of 5. (a) With Methanol. A solution of **5** (X = Br) in methanol was refluxed for 5 days to give an essentially quantitative yield of 1-phenylsulfonyl-3-methoxy-1-propene **5** (X = OMe): mp 109–110°; nmr, Table VIII.

(b) With Lithium Azide. Bromide **5** was refluxed with a tenfold excess of LiN_3 in MeOH for 30 min to give over 90% of 1-phenylsulfonyl-3-azido-1-propene (**5**, X = N_3): mp 95.5–97°; nmr, Table VIII; $\lambda_{max}^{95\%\ EtOH}$ 241 nm (ϵ 1.21 × 10^4).

(c) With Sodium Benzenesulfinate. Reaction of bromide **5** with a fourfold excess of $PhSO_2Na$ in dry DMF at 25° for 2 hr gave 1,3-

Table VIII. Nuclear Magnetic Resonance Parameters[a] for $PhSO_2CH_I{=}CH_{II}CH_{2III}X$

X	H_I (d)[b]	H_{II} (d of t)[c]	CH_2 (d)[d]	Aromatic	Other
Cl	6.7	7.0	4.2	7.8	
Br	6.64	7.08	3.98	7.8	
OSO_2CH_3	6.7	7.0	4.88	7.8	3.03 (OSO_2CH_3)
OH[e]	5.3	7.0	4.25	7.8	3.4 (OH)
OCH_3	6.62	7.0	2.9	7.8	3.3 (OCH_3)
SO_2Ph	6.4	6.77	3.96	7.8	
SCN	6.72	7.08	3.7	7.8	

[a] Chemical shifts are reported in δ values measured in parts per million (ppm) relative to TMS. [b] All are doublets, $J_{I,II}$ = 15 Hz. [c] All are doublets of triplets, $J_{I,II}$ = 15 Hz, $J_{II,III}$ = 6 Hz. [d] All are doublets, $J_{II,III}$ = 6 Hz. [e] Measured in DMSO-d_6.

Table IX. Microanalyses[a] for Compounds Described in the Experimental Section

Compound	Mol formula	Calcd C	Calcd H	Found C	Found H
6	$C_{12}H_{16}O_2S$	64.25	7.19	64.14	7.18
3, X = Br	$C_{12}H_{13}O_2BrS$	47.52	4.94	47.45	4.94
3, X = Cl	$C_{12}H_{14}O_2ClS$	55.70	5.84	55.68	5.89
3, X = OH	$C_{12}H_{16}O_3S$	59.97	6.71	59.98	6.64
4, X = Cl	$C_{10}H_{11}O_2ClS$	52.06	4.80	51.96	4.89
4, X = Br	$C_{10}H_{11}O_2BrS$	43.65	4.03	43.85	4.11
4, X = OMe	$C_{11}H_{14}O_3S$	58.38	5.24	58.23	6.30
4a–4b	$C_{10}H_{11}O_2ClS$	52.06	4.80	51.82	4.79
4, X = SCN	$C_{11}H_{11}O_2NS_2$	52.15	4.38	51.70	4.49
5, X = OMs	$C_{10}H_{12}O_5S_2$	43.46	4.38	43.42	4.29
5, X = OMe	$C_{10}H_{12}O_3S$	57.15	4.77	57.20	4.69
5, X = N_3	$C_9H_9O_2N_3S$	48.42	4.06	48.50	4.02
5, X = $SO_2C_6H_5$	$C_{15}H_{14}O_4S_2$	55.88	4.38	55.80	4.44
5, X = SCN	$C_{10}H_9O_2NS_2$	50.19	3.80	50.13	3.70
3, X = OMe	$C_{13}H_{18}O_3S$	61.39	7.13	61.36	7.04
11	$C_{12}H_{14}O_2S$	64.83	6.35	64.77	6.47
15, Y = NC_5H_{10}	$C_{17}H_{23}O_2NS$[b]	66.94	8.23	66.84	8.20
3, X = SO_2Ph	$C_{18}H_{20}O_4S_2$	59.32	5.53	59.50	5.60
15, X = SO_2Ph	$C_{18}H_{20}O_4S_2$	59.32	5.53	59.08	5.56
3, X = SPh	$C_{18}H_{20}O_2S_2$	65.02	6.06	64.66	6.08
3, X = NCS	$C_{13}H_{13}O_2NS_2$	55.49	5.37	55.28	5.46
16	C_6H_8BrN	41.41	4.63	41.23	4.65
18	$C_{12}H_{13}O_2NS$	61.25	5.57	61.13	5.64

[a] By Micro Tech, Skokie, Ill. [b] Calcd: N, 4.67. Found: 4.56.

diphenylsulfonylpropene **5** (X = $SO_2C_6H_5$): mp 102.5–103°; nmr, Table VIII.

(d) With Potassium Thiocyanate. Reaction of bromide **5** with a tenfold excess of KSCN in acetone at 25° for 30 min gave 1-phenylsulfonyl-3-prop-1-enyl thiocyanate (**5**, X = SCN): mp 103.5–104.5°; nmr, Table VIII. None of the isothiocyanate could be detected.

1-Cyano-3-bromo-3-methyl-1-butene (16). Reaction of 9 g (60 mmol) of 1-bromo-3-methyl-2-butene with 2.4 g (70 mmol) of powdered NaCN in 350 ml of dry DMF for 2.5 hr at 40° gave 4.5 g (79%) of 4-methyl-3-pentenenitrile: bp 107–109° (75 mm). Bromine addition followed by dehydrobromination (as in the preparation of bromide **3**) gave as a first fraction 14% of 1-cyano-4-methyl-1,4-pentadiene (**17**): bp 35–38° (1.5 mm); nmr δ 1.87 (m, 3 H), 5.39 (br s, 2 H), 5.39 (d, J = 16 Hz, 1 H), 7.1 (d, J = 16 Hz, 1 H). The second fraction was 3.9 g (47%) of **16**: bp 38–40° (0.3 mm); ir (μ) 3.25 (w), 3.34 (w), 4.5 (m), 6.12 (w), 6.87 (m), 7.2 (m), 7.28 (m), 9.06 (s), 10.05 (m), 10.33 (m); nmr δ 1.86 (s, 6 H), 5.52 (d, J = 16 Hz, 1 H), 6.90 (d, J = 16 Hz, 1 H).

Reactions of 16. (a) With Sodium Benzenesulfinate. Reaction of **16** with 2 mol of $PhSO_2Na$ in DMF at 50° for 2 hr gave 1-cyano-3-phenylsulfonyl-3-methyl-1-butene (**18**): mp 108–109°; nmr δ 1.5 (s, 6 H), 5.32 (d, J = 17 Hz, 1 H), 6.73 (d, J = 17 Hz, 1 H), 7.65 (m, 5 H).

(b) With Lithium Azide. Reaction of **16** with LiN_3 in MeOH at reflux for 45 min gave over 98% of the corresponding tertiary azide: nmr δ 1.38 (s, 6 H), 5.63 (d, J = 17 Hz, 1 H), 6.72 (d, J = 17 Hz, 1 H). Reduction with H_2/Pd gave an amine: nmr δ 1.2 (s, 6 H), 1.8 (m, 2 H), 2.4 (m, 2 H), 2.78 (s, br, 2 H). The benzamide was an oil: nmr δ 1.4 (s, 6 H), 2.26 (s, 4 H), 6.16 (s, br, 1 H), 7.6 (m, 5 H). Treatment of the amide with 0.2 *M* NaOMe in MeOH for 2 days at 25° caused the δ 2.26 nmr resonance to disappear.

(c) With Methanol. Methanolysis of **16** at reflux for 14 hr gave 30% of diene **17** and 70% of tertiary methyl ether, 4-methoxy-4-methyl-2-pentenenitrile (nmr analysis).

Reactions of 7,8-Disilabicyclo[2.2.2]octa-2,5-dienes. Evidence for the Transient Existence of a Disilene[1]

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Abstract: Three 7,8-disilabicyclo[2.2.2]octa-2,5-dienes (**1**, **2**, and **3**) were prepared and found to thermally decompose to give an intermediate containing a silicon–silicon double bond. The intermediate was trapped by dienes and found to rearrange in the absence of a trap. A mass spectral study of **1**, **2**, and **3** supported the postulated pathway of decomposition.

Evidence has recently been found for the existence of highly reactive species containing multiple (p–π) bonds to silicon.[2,3] Gusel'nikov and Flowers[2] have shown that 1,1-dimethyl-1-silacyclobutane, when

(1) (a) Taken in part from the Ph.D. Thesis of D. N. R., University of Alberta, 1970. (b) For a preliminary account of this work, see G. J. D. Peddle, D. N. Roark, A. M. Good, and S. G. McGeachin, *J. Amer. Chem. Soc.*, **91**, 2807 (1969).

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