Synthesis and Properties of 1-Substituted-2-(phenylsulfonyl)-3-phenyl-2-propenes[1]

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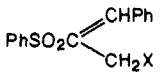
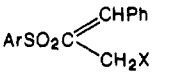
The regiospecific photolytic addition of benzenesulfonyl bromide to 1-phenylpropene served as a key step in the synthesis of 2-(phenylsulfonyl)-1-phenyl-1-propene (**1a**). The propenyl substrate **1a** was brominated with *N*-bromosuccinimide in refluxing carbon tetrachloride to yield 2-(phenylsulfonyl)-3-bromo-1-phenyl-1-propene (**1b**). Reaction of **1b** with *tert*-butylamine, diisopropylamine, glycine methyl ester, serine methyl ester, and piperidine yielded mixtures of substitution–rearrangement (S_N2') and direct substitution and (S_N2) products, **2** and **3**, respectively. The $S_N2':S_N2$ ratio ranged from approximately 20:1 for reaction of piperidine with **1b** to 1:9 for reaction of **1b** with diisopropylamine. *N*-Alkylamine hydrochloride promoted substitution–rearrangement (S_N2') and substitution (S_N2) reactions of *N,N*-diisopropyl-1-amino-2-(phenylsulfonyl)-3-phenyl-2-propene (**3b**) were investigated in chloroform and methanol solutions. Amine hydrochloride catalysis of the rearrangement of *N-tert*-butyl-1-amino-2-(phenylsulfonyl)-1-phenyl-2-propene (**2a**) to its isomer **3a** was investigated also.

Introduction

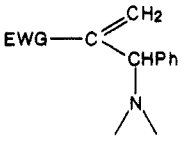
In a previous report, substitution–rearrangement reactions of 2-[(*o*-nitrophenyl)sulfonyl]allyl bromide (**4a**) were described.[1] Additionally, aminotropic rearrangements in the [2-(arylsulfonyl)allyl]amino and the 2-(aroylally)amino substrates (**5a** and **5b**, respectively) are documented in the literature.[2,3] Solvent effects on product distributions ($S_N2:S_N2'$ ratios) were observed, although these effects were not understood clearly. In a very recent report, two stereospecific S_N2' reactions of 2-(phenylsulfonyl)allyl substrates were utilized in key steps of a triply convergent total synthesis of prostaglandins.[4] We report here the chemistry of 1-substituted 2-(phenylsulfonyl)-3-phenyl-2-propenyl systems (**1b**, **2**, and **3**), analogs of the previously studied 2-[(*o*-nitrophenyl)sulfonyl]allyl substrates (**4** and **5a**). Product distributions for reactions of **1b** with primary and secondary amines are compared with those for the previously studied analogue, **4a**. The role of dissolved *N*-alkylamine hydrochloride on product distributions and on the ease of aminotropic rearrangement is described.



1a, X = H
1b, X = Br



4a, X = Br
4b, X = N<
Ar = *o*-nitrophenyl

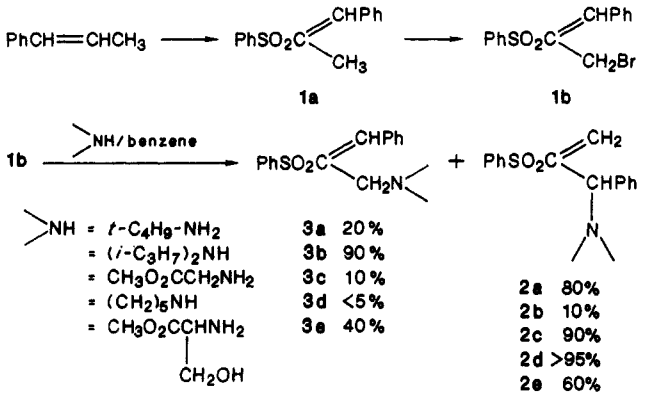


5a, EWG = SO_2Ar
5b, EWG = COAr

Results and Discussion

The regiospecific photolytic addition of benzenesulfonyl bromide to 1-phenyl-1-propene followed by dehydrobromination gave 2-(phenylsulfonyl)-1-phenyl-1-propene (**1a**) in high yield (96%).[5] The reaction of **1a** with *N*-bromosuccinimide in carbon tetrachloride was sluggish, but upon prolonged heating in the presence of benzoyl peroxide the reaction was forced to completion.[6] The allyl bromide **1b** reacted with a variety of amines to give high yields of substitution–rearrangement products (Scheme I). The substitution–rearrangement/direct substitution ($S_N2':S_N2$) product ratios were higher for reactions of **1b** with the less bulky *N*-alkylamines. The low $S_N2':S_N2$ ratio (1:9) for reaction of **1b** with diisopropylamine (compared to a 5:1 $S_N2':S_N2$ ratio for the same reaction of **4a**) indicates that a slight change in the electron-withdrawing capacity of the arylsulfonyl group leads to a large change in product distribution.[1] Since the substitution–rearrangement products (**2b–d**) are thermodynamically less stable than their isomers (**3b–d**), the proportions of **2** represent minima for the S_N2' pathway in these reactions.

Scheme I



Allylamino substrates that contain terminal methylene groups (**2**) react readily with amines or amine hydrohalides to yield rearranged and/or rearrangement–substitution products **3**. A driving force in this reaction (**2** → **3**) is the greater thermodynamic stability of **3** compared to **2**. Thus treatment of **2a** and **2e** with *tert*-butylamine hydrochloride and serine methyl ester hydrochloride yielded **3a** and **3e**, respectively. Also, the *N-tert*-butyl allylamino substrate **2a** reacts readily with piperidine hydrochloride to yield the rearrangement–substitution product (**3d**). In a previous study, we showed that *N,N*-diisopropylallylamino sulfone **4b** [>N = N(*i*-C_3H_7)$_2$] did not rearrange in a benzene

(1) Previous paper in the series on Activated Allylamno Substrates: Doomes, E.; Thiel, P. A.; Nelson, M. L. *J. Org. Chem.* **1976**, *41*, 248. Presented in part at the 187th National Meeting of the American Chemical Society, St. Louis, MO, April 10–13, 1984; Abstr. ORGN 107.

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(3) Maury, G.; Wu, E.-M.; Cromwell, N. H. *J. Org. Chem.* **1968**, *33*, 1900. Cromwell, N. H.; Matsumoto, K.; George, A. D. *J. Org. Chem.* **1971**, *36*, 272.

(4) Donaldson, R. E.; Saddler, J. C.; Byrn, S.; McKenzie, A. T.; Fuchs, P. L. *J. Org. Chem.* **1983**, *48*, 2167.

(5) Cristol, S. J.; Harrington, J. K.; Singer, M. S. *J. Am. Chem. Soc.* **1966**, *88*, 1529.

(6) Substitution of bromine for an allyl hydrogen atom in 2-(methylsulfonyl)-1-phenyl-1-propene occurs readily: Doomes, E.; Overton, B. M. *J. Org. Chem.*, following paper in this issue.

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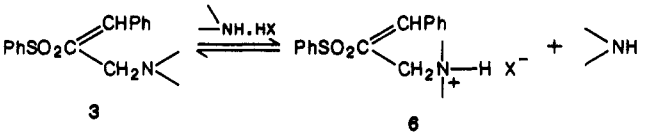
Table I. Summary of Aminotropic Rearrangement and Substitution-Rearrangement Reactions[a,b]

reactant	amine salt	reactn time, h	product(s)	% convn
3b	piperidine·HCl	48	**3d (2d)**	100
3b	piperidine	72	**3d**	20
3b	glycine methyl ester·HCl	48	**3c (2c)**[c,d]	95 (15)[c]
3b	serine methyl ester·HCl	48	**3e (2e)**[c]	75 (20)[c]
2b	diisopropylamine·HBr	48	**3b**	0
2a	*tert*-butylamine·HCl	6	**3a**	100
2e	serine methyl ester·HCl	48	**3e**	95

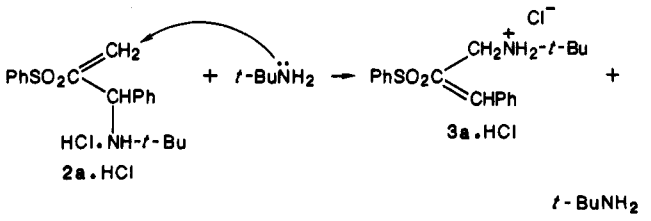
[a] The concentration of allylamino compound was 0.2 M and the concentration of amine salt (or amine) was 0.8 M. [b] Refluxing chloroform was the solvent in each case. [c] Minor products along with the percent of that product in the total conversion are given in parentheses. [d] The product composition was the same when methanol was the solvent.

solution that contained diisopropylamine.[1] additionally, the *N,N*-diisopropylallylamino sulfone **2b** is stable toward rearrangement to **3b** in a refluxing chloroform solution of diisopropylamine hydrobromide. However, less bulky *N*-alkylamine hydrochlorides react with the *N,N*-diisopropylallylamino substrate (**3b**) in refluxing chloroform solution to yield equilibrium mixtures of rearrangement–substitution and direct substitution products (**2** and **3**, respectively). Product distributions for these reactions are summarized in Table I. We propose that these rearrangement reactions occur through the intermediacy of a protonated [2-(phenylsulfonyl)allyl]amino substrate (**6**).[7] Since the thermodynamically less stable isomers (**2c** and **2e**) are detected for two of these reactions, it seems probable that portions of the direct substitution products arise from a slow S_N2' reaction on the protonated allylamine **6**, followed by a second fast S_N2' reaction (**6b** ⇌ **6** → **3c**, **3d**, **3e**). Also, since **3b** reacts with piperidine to give a lower yield of **3d** compared to its reaction iwth piperidine hydrochloride, nucleophilic addition followed by elimination appears improbable.[8] We have shown that allylamino substrates (**2**) that contain terminal methylene groups react readily with *N*-alkylamine hydrohalides to yield S_N2'-type products (see Experimental Section). Since propenyl bromide **1b** yielded mixtures of S_N2 and S_N2' products, it seems reasonable that the two mechanisms would compete in the amine exchange reactions of the analogous *N,N*-diisopropylpropenylamine **3b**. However, the steric bulk of the *N,N*-diisopropylamino group and the fact that it is a poor leaving group (compared to bromide) would favor the S_N2' over the S_N2 mechanism for the amine exchange reactions of **3b**. An 85:15 mixture of **3c** and **2c** was obtained from the reaction of **2b** with glycine methyl ester hydrochloride in chloroform solution. The minor product, **3c**, must have arisen from an S_N2'-type reaction between **2b** and the amine hydrochloride (or from equilibration between **2c** and **3c**). However, a 10:90 mixture of **3c** and **2c** underwent clean conversion to **2c** only when it was treated with glycine methyl ester hydrochloride in refluxing chloroform for 14 h. The latter experiment suggests that **2c** is formed via an S_N2' reaction between **3c** (or its hydrochloride) and glycine methyl ester.



3 **6**

The *tert*-butylamine hydrochloride promoted aminotropic rearrangement of the *N-tert*-butylallylamino substrate **2a** to its isomer **3a** was investigated in three solvents: chloroform-*d*, methanol-d_4, and acetonitrile-d_3. The rearrangement reaction (**2a** → **3a**) was monitored by ^1H NMR spectrometry. A 0.20 M solution of **2a** in chloroform-*d* (saturated with *tert*-butylamine hydrochloride) was greater than 95% rearranged (**2a** → **3a**) in 48 h, while a control sample in chloroform-*d* remained essentially unchanged. After 48 h, 0.20 M solutions of **2a** in acetonitrile-d_3 and methanol-d_4 (that contained dissolved *tert*-butylamine hydrochloride) were 62% and 45% rearranged, respectively. Thus preliminary data suggest specific acid catalysts of the rearrangement reaction since an inverse relationship between the extent of rearrangement and solvent basicity was observed. A reasonable mechanism for the aminotropic rearrangement (**2a** → **3a**) is an S_N2' reaction between the protonated allylamino substrate (**2a**·HCl) and free *tert*-butylamine.

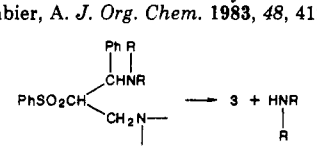


2a·HCl **3a**·HCl

We have shown that amine hydrohalides promote aminotropic rearrangements of the [2-(phenylsulfonyl)allyl]amines (**2** and **3**). Rearrangements in the [2-(phenylsulfonyl)allyl]amino substrates (**2** and **3**) occur with greater ease than rearrangements in the corresponding [2-methylsulfonyl)allyl]amino series.[9] Thus rearrangements and substitutions in activated allylamino substrates are sensitive to the *electron-withdrawing capacity* of the substituent at position-2. The [2-(phenylsulfonyl)allyl]-amino system is less reactive than the analogous (2-benzoylallyl)amino substrates toward amine hydrohalides.[10] Also, the [2-(phenylsulfonyl)allyl]amino system

(7) Two independent observations prompted this investigation. Cromwell and Rebman (*Tetrahedron Lett.* **1965**, *52*, 4833) showed that *N-tert*-butyl-1-amino-2-benzoyl-3-phenyl-1-propene rearranged slowly when allowed to stand in chloroform solution. Also, Doomes and Thiel (unpublished results) showed that *N*-alkyl-1-amino-2-(arylsulfonyl)-1-phenyl-2-propenes rearranged less readily in chloroform solution when amine hydrohalide byproduct was rigorously removed. Amine hydrohalide catalysis was suggested by these observations.

(8) Since the diamino adduct (**7**) was not observed in any of these reactions, rapid formation of **7** followed by a rate-limiting acid-catalyzed elimination of an amine to form **3** is unlikely. See also: Grandclaudon, P.; Lablache-Combier, A. *J. Org. Chem.* **1983**, *48*, 4129.



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(9) Doomes, E.; Overton, B. M. *J. Org. Chem.*, following paper in this issue. Compare the facility of aminmotropic rearrangements of *tert*-butylamino substrates in the 2-(arylsulfonyl) and 2-methylsulfonyl series.

(10) Doomes, E.; Sadeghi, A. G.; Carter, R. Abstracts of Papers, 137th Southwest Regional Meeting of the American Chemical Society, San Antonio, TX, December 9–11, 1981, No. 123. Doomes, E.; Sadeghi, A. G.; Gardner, J. D.; Dillon, B. S.; Green, C. S.; Cromwell, N. H., unpublished results.

(**3b**) does not react with methanol containing *N*-methylpiperidine hydrochloride whereas *N,N*-diisopropyl-1-amino-2-benzoyl-2-propene gives a quantitative yield of the corresponding methoxy derivative with this reagent.[10,11]

Experimental Section

General Procedures. All melting points were obtained with a Mel-Temp melting point apparatus and are uncorrected. Infrared spectra were recorded on a Beckman Microlab 600 MX spectrophotometer. The 60-MHz ^{1}H NMR spectra were determined on a Varian EM-360A NMR spectrometer with tetramethylsilane as an internal standard and are reported in δ units. Low-resoltuion (70 eV) masss spectra were obtained on a Hewlett Packard 5985 GC/MS spectrometer. Elemental analyses were obtained from MicAnal Organic Microanalysis, Tuscon, AZ.

2-(Phenylsulfonyl)-1-phenylpropene (1a). A suspension of 16.4 g (0.10 mol) of sodium benzenesulfinate in 100 mL of benzene was stirred vigorously while 16.0 g (0.10 mol) of bromine was added in small portions.[5] Bromine was added until the reddish bromine color persisted. A small amount of sodium benzenesulfinate was added to remove excess bromine. The solution was filtered and 50 mL of benzene was used to rinse the precipitated sodium bromide. An 11.8-g (0.10 mol) sample of β-methylstyrene was added to the benzene solution of benzenesulfonyl bromide. The solution was irradiated with a clear tungsten light bulb for 18 h. A 10-g (0.10 mol) sample of *N*-methylpiperidine was added to the benzene solution, and the reaction was allowed to proceed for 5 h at room temperature. Water (150 mL) was added to the reaction mixture, and the layers were mixed thoroughly. The aqueous layer was discarded, and the benzene layer was washed with 100 mL of 2% hydrochloric acid. Finally, the organic layer was washed with 100 mL of water and the benzene evaporated under reduced pressure. A brown oil was obtained, which crystallized within 10 min of swirling the flask. Recrystallization of the solid from methanol yielded 24.8 g (96%) of **1a**, mp 89–92 °C, as an off-white crystalline solid: ^{1}H NMR ($CDCl_3$) δ 2.07 (3 H, s), 6.9–8.2 (11 H, m). Anal. Calcd for $C_{15}H_{14}SO_2$: C, 69.74; H, 5.46. Found: C, 69.93; H, 5.50.

2-(Phenylsulfonyl)-3-bromo-1-phenylpropene (1b). A 15.0-g (0.058 mol) sample of **1a** was dissolved in 50 mL of carbon tetrachloride. An 11.4-g (0.064 mol) sample of *N*-bromosuccinimide was added and the mixture was heated to a gentle reflux. Benzoyl peroxide (0.3 g) was dissolved in 25 mL of carbon tetrachloride, and the solution was added to the refluxing mixture in a dropwise manner. Refluxing was continued for a total of 120 h. The solution was filtered while hot and evaporated under reduced pressure to yield a brown oil. Recrystallation of the product from methanol yielded 8.6 g (44%) of **1b**, mp 83–84 °C, as yellow crystals: ^{1}H NMR ($CDCl_3$) δ 5.32 (2 H, s), 6.9–8.3 (11 H, m). Anal. Calcd for $C_{15}H_{13}SO_2Br$: C, 53.42; H, 3.89; Br, 23.69. Found: C, 53.57; H, 3.95; Br, 23.44.

***N,N*-Diisopropyl-1-amino-2-(phenylsulfonyl)-3-phenyl-2-propene (3b).** A 1.0-g (0.030 mol) sample of **1b** was dissolved in 20 mL of benzene. Three molar equivalents (0.90 g, 0.0090 mol) of diisopropylamine were added, and the mixture was allowed to react at room temperature for 138 h. The precipitated diisopropylamine hydrobromide was removed by suction filtration. The solution was diluted with 20 mL of benzene and washed with two 15-mL portions of water. The organic layer was separated, dried ($MgSO_4$), and evaporated under reduced pressure. A brown oil was obtained that gave an ^{1}H NMR spectrum that is consistent with the assigned structure. Crystallization of the oil from an ethyl ether/hexane mixture yielded 0.62 g (58%) of **3b**, mp 95–96 °C: ^{1}H NMR ($CDCl_3$) δ 0.57 (12 H, d), 2.58 (2 H, heptet), 3.67 (2 H, d), 6.7–8.3 (11 H, m); mass spectrum, *m/e* (major peaks) 357, 342, 225. Anal. Calcd for $C_{21}H_{27}NO_2S$: C, 70.55; H, 7.61; N, 3.92. Found: C, 70.41; H, 7.39; N, 3.90.

Analysis of the crude reaction mixture by ^{1}H NMR spectrometry indicated that the S_N2' product (**2b**) was present in less than 15 mol % of the total substitution products.

2-(Phenylsulfonyl)-1-(1-piperidinyl)-3-phenyl-2-propene (3d) and 2-(Phenylsulfonyl)-1-(1-piperidinyl)-1-phenyl-2-propene (2d). A 0.50-g (0.0015 mol) sample of **1b** and 0.30 g (0.0035 mol) of piperidine were dissolved in 25 mL of benzene. The mixture was stirred magnetically and allowed to react for 30 min. The usual workup (see above) yielded a yellow oil that was analyzed by ^{1}H NMR spectrometry. The oil consisted of ~60% of S_N2' product and ~40% of S_N2 product. The reaction mixture was dissolved in 10 mL of chloroform, 0.20 g of piperidine was added, and the mixture was heated at reflux for 2 h. The solution was diluted with 20 mL of chloroform, washed with 25 mL of water, and dried ($MgSO_4$) and the solvent was evaporated. The 1-piperidinyl allyl sulfone **3d** was crystallized from an ether–hexane mixture, 0.39 g (79%), mp 107–108 °C: ^{1}H NMR ($CDCl_3$) δ 1.12, 2.12 (10 H, m's), 3.42 (2 H, s), 7.2–8.3 (11 H, m); mass spectrum, *m/e* (major peaks) 341, 199, 156, 115. Anal. Calcd for $C_{20}H_{23}NO_2S$: C, 70.35; H, 6.79; N, 4.10. Found: C, 70.48; H, 6.84; N, 4.10.

2-(Phenylsulfonyl)-1-(1-piperidinyl)-1-phenyl-2-propene Hydrochloride (2d'). A 1.69-g (0.0050 mol) sample of allyl bromide **1b** and 0.85 g (0.010 mol) of piperidine were mixed thoroughly in 100 mL of benzene and then allowed to react at room temperature for 2 min. The reaction mixture was filtered to remove precipitated piperidine hydrochloride. The clear benzene solution was subjected to a stream of dry hydrogen chloride. An oil separated that crystallized upon standing for 24 h. The white solid was recrystallized from a chloroform–ether mixture to yield 1.23 g (65%) of **2d**, mp 154–155 °C: ^{1}H NMR ($CDCl_3$) δ 1.1–4.2 (11 H, m), 4.49, 5.05 (1 H, d, J = 9 Hz), 6.5–8.3 (12 H, m). Anal. Calcd for $C_{20}H_{24}NO_2SCl$: C, 63.56; H, 6.40; N, 3.71. Found: C, 59.62; H, 6.31; N, 4.04. The hydrochloride **2d'** is contaminated with piperidine hydrochloride (~10% by weight). A 0.50-g sample of **2d'** was dissolved in 25 mL of chloroform and extracted (neutralized) with 25 mL of saturated sodium bicarbonate solution. The chloroform was dried (Na_2SO_4) and evaporated under reduced pressure, and the residue was analyzed by ^{1}H NMR spectrometry. The residue consisted of **2d** only (>95%): ^{1}H NMR ($CDCl_3$) δ 1.47, 2.11 (10 H, m), 4.10 (1 H, s), 6.43 (1 H, s), 6.65 (1 H, s), 6.8–8.2 (10 H, m). The chloroform-*d* solution of **2d** was monitored by ^{1}H NMR spectrometry (the appearance of a signal for allyl protons in **3d** at δ 3.42 was observed). A facile rearrangement of **2d** to **3d** occurred; the rearrangement was 90% complete in 24 h. A 0.20-g sample of **2d** in 1 mL of chloroform-*d* to which 5 mg of piperidine hydrochloride was added was 90% rearranged to **3d** in 2 h. A sample of **3d** was isolated from the chloroform solution that is identical in all respects with a sample of this compound isolated in the previous procedure.

2-(Phenylsulfonyl)-1-(methyl *N*-glycinyl)-1-phenyl-2-propene (2c) and 2-(Phenylsulfonyl)-1-(methyl *N*-glycinyl)-3-phenyl-2-propene (3c). A 0.50-g (0.0018 mol) sample of propenyl bromide **1b**, 0.45 g (0.0036 mol) of glycine methyl ester hydrochloride, and 0.40 g (0.0040 mol) of *N*-methylpiperidine were added to 15 mL of benzene. The mixture was stirred magnetically and allowed to react for 24 h. The solution was diluted with 20 mL of benzene, washed with two 20-mL portions of water, and dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. A pale yellow oil (0.47 g, 92%) was obtained and was analyzed by ^{1}H NMR spectrometry. The reaction product consisted of **2c** and **3c** in a 9:1 ratio. **2c**: ^{1}H NMR ($CDCl_3$) δ 2.13 (1 H, s), 3.30 (2 H, s), 3.66 (3 H, s), 4.63 (1 H, s), 6.25 (1 H, s), 6.57 (1 H, s), 6.9–8.2 (10 H, m).

The oil that consisted of **2c** and **3c** was dissolved in 20 mL of chloroform, a 0.20-g sample of glycine methyl ester hydrochloride was added, and the mixture was heated at reflux for 14 h. The chloroform solution was diluted with 20 mL of chloroform, washed with a 25-mL portion of water, dried (Na_2SO_4), and evaporated under reduced pressure. The residue (quantitative) consisted of **3c** only (>95%), as determined by ^{1}H NMR spectrometry. Recrystallization from methanol yielded **3c** as pale yellow crystals (0.34 g, 67%), mp 106–107 °C: ^{1}H NMR ($CDCl_3$) δ 2.08 (1 H, s), 3.33 (2 H, s), 3.53 (2 H, s), 3.63 (3 H, s), 7.0–8.2 (11 H, m); mass spectrum, *m/e* (major peaks) 345, 314, 203, 144, 115. Anal. Calcd for $C_{18}H_{19}NO_4S$: C, 62.59; H, 5.54; N, 4.06. Found: C, 62.52; H, 5.50; N, 4.04.

(11) *N,N*-Diisopropyl-2-(2-naphthalenylsulfonyl)-1-amino-2-propene has been synthesized. This substance is a better model for comparison of relative activating effects of 2-aroyl- and 2-arylsulfonyl substituents on reactivities of simple allylamino substrates. E. Doomes and B. Tadayoni, unpublished results.

Table II. Rearrangement of *N*-*tert*-Butyl Allylamino Substrate 2a to 3a

solvent	[*tert*-butylamine·HCl]	reactn time, h	% rearranged
CD_3OD	0	0	ca. 20
CD_3OD	0	48	20
CD_3OD	0.20 g/5 mL	0	20
CD_3OD	0.20 g/5 mL	24	33
CD_3OD	0.20 g/5 mL	48	45
$CDCl_3$	0	0	20
$CDCl_3$	0	48	24
$CDCl_3$	0.02 g/mL	24	67
$CDCl_3$	0.02 g/mL	48	95
CD_3CN	0.02 g/mL	25	50
CD_3CN	0.02 g/mL	48	62

2-(Phenylsulfonyl)-1-(methyl *N*-serinyl)-1-phenyl-2-propene (2e) and 2-(Phenylsulfonyl)-1-(methyl *N*-serinyl)-3-phenyl-2-propene (3e). A 0.84-g (0.0025 mol) sample of propenyl bromide **1b**, 0.85 g (0.0054 mol) of serine methyl ester hydrochloride, and 0.82 g (0.0083 mol) of *N*-methylpiperidine were added to 50 mL of dry benzene. The mixture was stirred magnetically at room temperature for 16 h. The reaction mixture was extracted twice with 25-mL portions of water, dried (Na_2SO_4), and evaporated under reduced pressure. Analysis of the tan oil by ^1H NMR spectrometry indicated that the major reaction product was **2e**, a viscous tan oil: ^1H NMR ($CDCl_3$) δ 2.32 (2 H, m), 3.0–4.1 (6 H, complex m), 4.77 (1 H, s), 6.28 (1 H, m), 6.67 (1 H, m), 6.8–8.4 (10 H, m). The tan oil, that consisted of **2e** (~60%) and **3e** (~40%), was dissolved in 25 mL of chloroform, 0.20 g of serine methyl ester hydrochloride was added, and the mixture was heated at reflux for 48 h. ^1H NMR analysis of the mixture after the usual workup (to remove amine salts) indicated that the brown viscous oil consisted of **3e** primarily (~95%); ^1H NMR ($CDCl_3$) δ 2.32 (2 H, m), 3.1–4.1 (8 H, complex m), 6.8–8.2 (11 H, m); mass spectrum, *m/e* (major peaks) 344, 316, 272, 257, 115. Anal. Calcd for $C_{19}H_{21}NO_5S$: C, 60.77; H, 5.68. Found: C, 59.86; H, 5.48.

***N*-*tert*-Butyl-1-amino-2-(phenylsulfonyl)-1-phenyl-2-propene (2a) and *N*-*tert*-Butyl-1-amino-2-(phenylsulfonyl)-3-phenyl-2-propene (3a).** A 1.69-g (0.0050 mol) sample of propenyl bromide **1b** and 0.90 g (0.012 mol) of *tert*-butylamine were dissolved in 50 mL of benzene and allowed to react for 3 h while it was stirred. The usual workup (see above) yielded a pale yellow oil that consisted of **2a** and **3a** in a 4:1 ratio based on ^1H NMR analysis. The crude product was dissolved in 20 mL of chloroform to which 0.20 g of *tert*-butylamine hydrochloride was added, and the mixture was heated at reflux for 14 h. The chloroform solution was diluted with 20 mL of chloroform and washed with two 25-mL portions of water and dried ($MgSO_4$) and the solvent was removed under reduced pressure. Recrystallization of the product from an ether–hexane mixture yielded 1.12 g (68%) of **3a**, mp 99–100 °C: ^1H NMR ($CDCl_3$) δ 1.06 (10 H, s), 3.40 (2 H, s). 6.9–8.3 (11 H, m); mass spectrum, *m/e* (major peaks) 329, 314, 272, 115. Anal. Calcd for $C_{19}H_{23}NO_2S$: C, 69.27; H, 7.04; N, 4.25. Found: C, 68.89; H, 7.09; N, 4.28. **2a**: ^1H NMR ($CDCl_3$) δ 0.98 (10 H, s), 4.80 (1 H, s), 6.51 (1 H, s), 6.71 (1 H, s), 6.9–8.3 (10 H, m).

Aminotropic Rearrangement of *N*-*tert*-Butyl-1-amino-2-(phenylsulfonyl)-2-propene to Its Isomer 3a. A 0.30-g (0.00091 mol) sample of **2a** was dissolved in 1.0 mL of the indicated solvent. The solution was analyzed periodically by ^1H NMR spectrometry. Rearrangement data (obtained by comparing intensities of signals for vinyl protons of **2a** and the signal for allyl protons of **3a**) is summarized in Table II. The original sample contained approximately 80% **2a** and 20% **3a**. The chloroform-*d* and the acetonitrile-d_3 solutions were saturated solutions of the amine hydrochloride.

Amine Hydrohalide Promoted Aminotropic Rearrangements and Substitutions. The substituted 1-amino-2-(phenylsulfonyl)allyl substrate (**3b**, **2b** or **2a**) was dissolved in 20 mL of chloroform and 0.008 mol of amine hydrohalide was added. The mixture was heated at reflux temperature for periods that ranged from 6 to 72 h. The usual workup (see procedure above) gave a crude product that was analyzed by ^1H NMR spectrometry. Results are summarized in Table I. The reaction products were crystallized from appropriate solvents as described in the Experimental Section.

1-Methoxy-3-phenyl-2-(phenylsulfonyl)-2-propene (1c). A 0.50-g (0.0015 mol) sample of propenyl bromide **1b** was added to 10 mL of anhydrous methanol, and the mixture was allowed to react at reflux temperature for 5 days. Evaporation of the solvent yielded a brown oil that crystallized upon standing. ^1H NMR analysis of the product indicated that solvolysis was complete; **1c** was the only product detected. The propenyl bromide **1b** was stable with respect to methanolysis when stirred magnetically in methanol for 24 h at room temperature. The methanolysis product, **1c**, was obtained as a yellow crystalline solid from ethyl ether (0.18 g, 42%), mp 70–71 °C: ^1H NMR ($CDCl_3$) δ 3.17 (3 H, s), 4.25 (2 H, s), 7.1–8.3 (11 H, m). Anal. Calcd for $C_{16}H_{16}SO_3$: C, 66.64; H, 5.59. Found: C, 66.58; H, 5.54.

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Registry No. **1a**, 60012-86-4; **1b**, 107271-67-0; **1c**, 107271-68-1; **2a**, 107271-69-2; **2c**, 107271-70-5; **2d**, 107271-71-6; **2d**·HCl, 107271-72-7; **2e**, 107271-73-8; **3a**, 107271-74-9; **3b**, 107271-75-0; **3c**, 107271-76-1; **3d**, 107271-77-2; **3e**, 107271-78-3; $PhCH{=}CHCH_3$, 637-50-3; $t\text{-}C_4H_9NH_2$, 75-64-9; $(i\text{-}C_6H_7)_2NH$, 108-18-9; $H_3CO_2C\text{-}CH_2NH_2\cdot HCl$, 5680-79-5; $L\text{-}H_3CO_2CCH(NH_2)CH_2OH$, 5680-80-8; $t\text{-}C_4H_9NH_2\cdot HCl$, 10017-37-5; sodium benzenesulfinate, 873-55-2; benzenesulfonyl bromide, 2297-65-6; piperidine, 110-89-4; piperidine hydrochloriole, 6091-44-7.