Rearrangement–Substitution Reactions of a 2-(Arylsulfonyl)allyl System[1]

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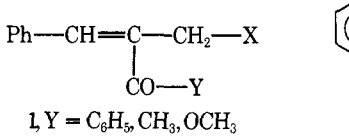
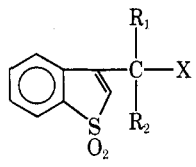
A synthetic route to substituted 2-(arylsulfonyl)allyl bromides (8) is reported. Reaction of allyl bromides 8 with primary and secondary amines in protic and aprotic solvents yielded rearrangement–substitution products (10). The product distribution and stability depend upon the steric requirement of the attacking alkylamine. When the kinetically favored amino sulfones (10, except for the *N,N*-diisopropylamino derivative) were allowed to stand in aprotic solvents of low polarity, rearrangement to the thermodynamically more stable isomeric amino sulfones (11) occurred. The aminotropic rearrangement was facilitated by added alkylamine, and a facile amine-exchange reaction occurred when **10d** was treated with morpholine in aprotic solvents. Reaction of 8 with 2,4-dimethylimidazole yields the direct substitution product (**11e**) only. The significance of these observations with regard to the effect of polar substituents and structure of attacking amine on the mode of reaction of allyl systems is discussed.

There are few reports in the literature regarding rearrangement–substitution reactions of allyl systems bearing polar functional groups.[3] Cromwell and co-workers[4] showed that the 2-aroylallyl system 1 (Y = C_6H_5) reacts with primary and secondary amines in aprotic solvents to yield rearrangement–substitution products by a bimolecular mechanism. Rearrangement–substitution products were observed in two additional 2-carboallyl systems.[5,6] These observations constitute the only reported examples of SN2′-type product formation from primary allyl halides and amines. For this system (1) the product distribution is controlled by the *electron-withdrawing effect* of the carbonyl group.[7] Bordwell and Mecca[8] demonstrated that benzothiophene derivative **2** reacts via a bimolecular mechanism with a variety of nucleophiles, including charged ones, to yield SN2′-type products. It was shown that neither an α- nor γ-arylsulfonyl group (**3a** and **3b**, respectively) is sufficient to promote rearrangement–substitution.[9]



1, Y = C_6H_5, CH_3, OCH_3



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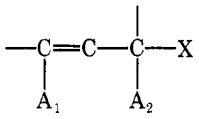


3a, A_1 = H; A_2 = SO_2Ar

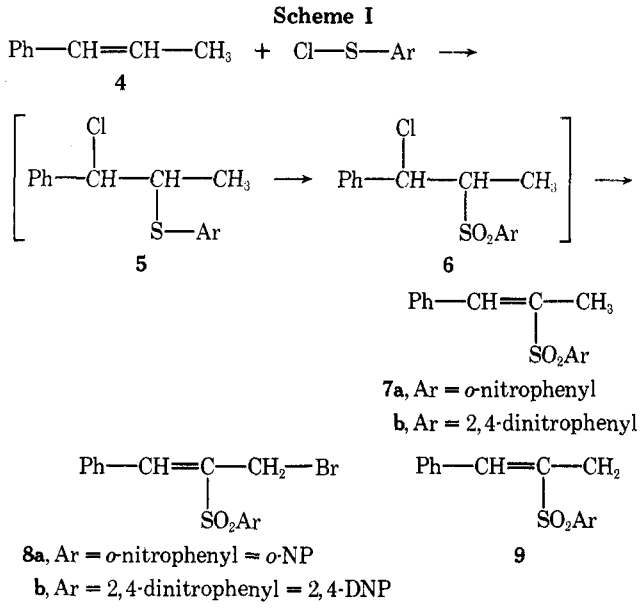
b, A_1 = SO_2Ar; A_2 = H

Thus, Bordwell concluded that an important effect of the sulfonyl group in promoting SN2′-type reactions of **2** is indirect electron withdrawal through the aromatic ring at the β position of the allyl chain. As part of a general program designed to elucidate factors that influence the reactivity of allyl systems, reactions of 2-(arylsulfonyl)allyl bromides (8) with amines were investigated. This report deals with the influence of the β-arylsulfonyl group on product distributions for nucleophilic substitution on the relatively simple allyl system **8**. Allyl bromide **8** is analogous to Cromwell's β-aroylallyl system (1) and allows a comparison of the effectiveness of a β-arylsulfonyl vs. a β-aroyl substituent in promoting SN2′-type reactions.

Results and Discussion

Allyl bromides **8** were synthesized according to Scheme I. Thus treatment of 1-phenylpropene with an arenesulfenyl chloride yielded β-chloro sulfide **5**.[10] The β-chloro sulfide

Scheme I



was oxidized to the corresponding β-chloro sulfone (**6**) with *m*-chloroperoxybenzoic acid in dichloromethane. Dehydrochlorination of **6a** with *N*-methylpiperidine in benzene gave alkene **7a** in 86% yield, wherein an arylsulfonyl group has been substituted for hydrogen (i.e., **4** → **7a**). Alkene **7b** was synthesized via the same sequence of reactions. The alkenes **7** were brominated with *N*-bromosuccinimide in refluxing carbon tetrachloride in the presence of benzoyl peroxide to yield the desired allyl bromides (**8**). This reaction was very slow and could be forced to completion only after prolonged heating, probably reflecting the strong electron-withdrawing effect of the 2-arylsulfonyl group in destabilizing the intermediate free radical **9**. Thus carbonium ion type reactions of **8** would be expected to be inhibited by a similar mechanism during nucleophilic substitution.

8a, Ar = *o*-nitrophenyl ≈ *o*-NP

b, Ar = 2,4-dinitrophenyl = 2,4-DNP

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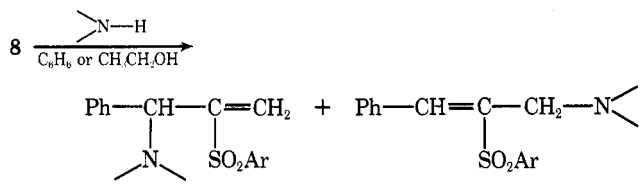
Treatment of **8a** with morpholine, *tert*-butylamine, and diisopropylamine in benzene or ethanol yielded rearrangement–substitution products (**10a**, **10b**, and **10c**, respectively) along with direct substitution products (**11**) in varying amounts (Table I). When **10a** and **10b** were allowed to stand in deuteriochloroform at room temperature, facile rearrangements to the thermodynamically more stable isomers (**11a** and **11b**, respectively) occurred. It is noteworthy that the time required for quantitative rearrangement of **10a** to **11a** is significantly less than that required for rearrangement of **10b** to **11b**. Also, **10c** and **10d** are stable toward rearrangement in the presence or absence of excess diisopropylamine. Thus **10d** could be recovered after

Table I
Summary of Reactions of 2-(Arylsulfonyl)allyl Bromides 8 with Amines[a]

Registry no.	Nucleophile	Reaction time, hr	Solvent[b]	% 10[d]	% 11
110-91-8	OC_4H_8NH	0.05	Benzene (160)	100	0
	OC_4H_8NH	0.10	Ethanol (40)	100	0
75-64-9	t-$C_4H_9NH_2$	2	Brnzene (40)	80	20
	t-$C_4H_9NH_2$	17	Ethanol (40)	30	70
108-18-9	$[(CH_3)_2CH]_2NH$	24	Benzene (40)[c]	80	20
	$[(CH_3)_2CH]_2NH$	24	Benzene (20)[c]	83	17
	$[(CH_3)_2CH]_2NH$	24	Ethanol (20)[c]	33	67
930-62-1	2,4-Dimethylimidazole	2	Benzene (40)[c]	0	100

[a] Reactions were carried out using ca. 0.5 mmol of allyl bromide (8) and 2 equiv of amine. The first five entries involved 8a as reactant, in the latter three 8b was used. [b] The number in parentheses indicates ml solvent per mmol 8. [c] Unreacted bromide (8) remained. [d] Product ratios were determined by ^{1}H NMR analysis, and one isomer (10 or 11) was isolated and characterized for each reaction, except for entry 5.

standing at room temperature for weeks in deuteriochloroform and in chloroform containing added diisopropylamine. Amino sulfones **10a** and **10b** were relatively stable



10a, >N = OC_4H_8N; Ar = o-NP — 11a

b, >N = t-C_4H_9NH; Ar = o-NP — b

c, >N = $[(CH_3)_2CH]_2N$; Ar = o-NP — c

d, >N = $[(CH_3)_2CH]_2N$; Ar = 2,4-DNP — d

e, >N = 2,4-dimethylimidazolyl; Ar = 2,4-DNP — e

toward rearrangement when traces of free alkylamine were removed from solution, or as their hydrochloride salts. This suggested catalysis of the rearrangement by the free amine that acts as nucleophile (see Experimental Section). The diisopropylamino sulfone **10c** reacted with morpholine in chloroform to give **11a** in excellent yield. The isomeric diisopropylamino sulfone **11c** did not react with morpholine under the same conditions. Excess *tert*-butylamine facilitated the conversion of **10b** to the thermodynamically more stable isomer **11b.** While the 2-(arylsulfonyl)allyl system (8) mimics the behavior of the 2-aroylallyl system (1) in that both systems undergo facile amine exchange and rearrangement reactions, these systems differ in their reactivity toward diisopropylamine. Arylsulfonylallyl bromide **8a** reacts with diisopropylamine in benzene solution to give 80% rearrangement–substitution product **10c,** whereas aroylallyl bromide 1 gives only a trace of the SN2′-type product.[11,12]

We were unable to isolate **10a** or **10b** as crystalline materials. Thus, the structures of **10a** and **10b** were assigned on the basis of ^{1}H NMR spectral analysis of their solutions. The progress of rearrangement of **10** to **11** was followed by observing the sets of signals for **10** decrease with a corresponding increase in signals for **11** (Table II). Upon completion of the rearrangement of **10** to **11,** the amino sulfones **11a** and **11b** were isolated as crystalline substances. The diisopropylamino sulfone **10d** was isolated in 37% yield as bright orange crystals from ether solution. The ^{1}H NMR spectra of isomerically pure compounds (**11a, 11b,** and **10d**) were compared with spectra of the corresponding mixtures

Table II
Summary of Physical Data for Substituted 2-(Arylsulfonyl)allyl Derivatives[a,c]

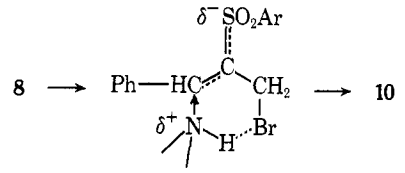
Compd	Mp, °C	H_a	H_b	H_c
7a	151			2.13
7b	155			2.17
8a	131			4.31
8b	144[b]			4.38
10a		6.43	4.09	
11a	152			3.51
10b		6.55	4.88	
11b	109			3.55
10d	138	6.60	5.25	
11d				3.71
11e	169			5.08

[a] H_a represents the vinyl protons of **10**, H_b represents the benzal proton, and H_c represents allyl protons of **7**, **8**, and **11**. The expected absorption bands were observed for the aromatic and alkyl protons of each compound. Chemical shifts are given in δ values relative to tetramethylsilane as internal standard in deuteriochloroform. [b] This sample was conaminated with a trace of **7b**. [c] Satisfactory analytical values (±0.3% for C, H, N) were reported for **7a,b, 8a,b, 11a,b,e,** and **10d**. Ed.

in order to confirm structure assignments and product distributions.

Previous studies have indicated that hydrogen bonding plays a role, of undetermined importance, in rearrangement–substitution reactions of allyl halides with amines in aprotic solvents.[13] In the present work, rearrangement–substitution products (**10**) were obtained from **8** and primary and secondary amines in both benzene and ethanol. The mild reaction conditions and aprotic environment for the reaction in benzene would be expected to favor a bimolecular mechanism.[7] We speculate that the presence of the amino proton provides a relatively low energy path for the rearrangement–substitution reaction, since a quasi-six-membered transition state is available through hydrogen bonding to the leaving bromide ion. The lower SN2′:SN2 product ratio in ethanol may be rationalized in terms of competing hydrogen bonding by solvent, or a faster amine exchange reaction in this solvent. In the case for reaction of 2,4-dimethylimidazole with **8b** an eight-membered transition state would be required (the proton is lost from the remote nitrogen atom), rendering the lower energy path inaccessible. The product distributions can be rationalized if one assumes a bimolecular mechanism; the less bulky amines would be expected to give a higher proportion of nucleophilic attack at the more hindered secondary carbon of the allyl chain (Table I). Thus, the transition state for formation of **10** from reaction of **8** with primary and secondary amines may be represnted by structure **12,** wherein

the arylsulfonyl group absorbs the developing negative charge. An analogous cyclic transition state (13) may be envisioned for the amine exchange reactions. Although the intervention of diamino adducts (14) was considered for



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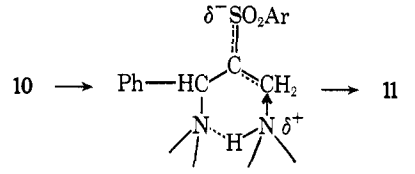

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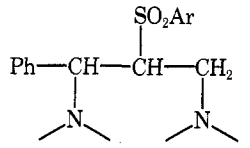

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the latter reaction, no evidence for such intermediates was obtained upon close scrutiny of ^{1}H NMR spectra of reaction mixtures during the rearrangements. The inertness of **10d** toward reaction with diisopropylamine can be rationalized in terms of transition state **13**, since available evidence indicates that the bulky entering and leaving groups would require a cis relationship.[13]

In nonpolar aprotic solvents both **1**[4] and **8** probably react via a "variant of the SN2'" mechanism.[7] Since steric factors in **1** and **8** are practically identical, the difference in product distribution (for reactions in the same solvent) arises from the effect of the β-electron-withdrawing group. Data for reactions involving diisopropylamine (with **1** and **8**)[12] suggest that the β-arylsulfonyl group is more effective than the β-aroyl group in stabilizing the "SN2'-type" transition state for substitution in allyl halides. This parallels Taft σ constants for these substituents.[14] The arylsulfonyl group would be expected to more effectively stabilize a developing negative charge compared to an aroyl group, but the latter group is more effective in stabilizing a carbanion, judging from the relative acidities of ketones and sulfones.[15,16] Thus, we propose that the transition state for substitution in **8** lies along a continuum between a carbanionic intermediate and the classical SN2' model.

Experimental Section[17]

2-(*o*-Nitrophenylsulfonyl)-1-phenylpropene (7a). A 19.0-g (0.10 mol) sample of *o*-nitrophenylsulfenyl chloride was allowed to react with 11.8 g (0.10 mol) of 1-phenylpropene in 200 ml of dichloromethane at room temperature for 24 hr. A 42.0-g (0.22 mol) sample of 85% *m*-chloroperoxybenzoic acid dissolved in 200 ml of dichloromethane was added slowly to the reaction mixture. Following reaction for 24 hr at room temperature, the reaction mixture was washed with saturated aqueous sodium bicarbonate solution, 10% aqueous sodium bisulfite, and again with sodium bicarbonate. The dried ($MgSO_4$) solution was evaporated under reduced pressure to yield a yellow oil. The oil was taken up in 300 ml of benzene and 15 g (0.15 mol) of *N*-methylpiperidine was added. The reaction was allowed to proceed at reflux temperature for 4 hr. The mixture was filtered while hot and washed with 300 ml of water and 300 ml of 1 *N* hydrochloric acid. Evaporation of the solvent yielded a yellow solid. This material was suction filtered with the aid of methanol as transfer agent. The desired product was obtained as an off-white powder, 26 g (86%), mp 142–145°. This compound was reasonably pure on the basis of its ^{1}H NMR spectrum and was used without further purification. The analytical sample was obtained upon several recrystallizations from methanol, mp 151°.

2-(2,4-Dinitrophenylsulfonyl)-1-phenylpropene (7b). The procedure that was used in the preparation of **7a** was applied to 23.5 g (0.10 mol) of 2,4-dinitrobenzenesulfenyl chloride and 11.8 g (0.10 mol) of 1-phenylpropene. Compound **7b** was obtained as a yellow, crystalline material from methanol, 16.3 g (47%), mp 154–155°.

2-(*o*-Nitrophenylsulfonyl)-3-phenylallyl Bromide (8a). A 10.0-g (0.033 mol) sample of **7a** and 7.0 g (0.039 mol) of *N*-bromosuccinimide were added to 150 ml of carbon tetrachloride and the mixture was brought to a gentle reflux. A solution of 0.5 g of benzoyl peroxide in 50 ml of carbon tetrachloride was added dropwise to the refluxing mixture over a 2-hr period. Refluxing was continued for 24 hr and the mixture was filtered while hot to remove suspended solids. Evaporation of the solvent under reduced pressure yielded a yellow oil that consisted of starting material (27%) and the expected allyl bromide **8a** (73%) by ^{1}H NMR analysis. The oil was treated with an additional 6.0-g (0.033 mol) sample of *N*-bromosuccinimide in the manner described above. After a 24-hr reflux period the solution was filtered while hot; a yellow-brown solid separated from the filtrate upon cooling. This solid consisted of the desired allyl bromide and excess *N*-bromosuccinimide, 9.2 g, mp 100–116°. Recrystallization from ethyl acetate yielded 5.6 g (44%) of yellow crystals, mp 130–131°.

2-(2,4-Dinitrophenylsulfonyl)-3-phenylallyl Bromide (8b). The procedure[18] that was used in the preparation of **8a** was applied to 9.3 g (27 mmol) of **7b** (i.e., the same approximate reaction time and reactant and solvent ratios). Compound **8b** was obtained as bright yellow crystals from ethyl acetate, 5.5 g (48%), mp 143–144°.

3-Morpholino-3-phenyl-2-(*o*-nitrophenylsulfonyl)propene (10a) and 3-Morpholino-2-(*o*-nitrophenylsulfonyl)-1-phenylpropene (11a). A 0.24-g (0.63 mmol) sample of **8a** and 0.12 g (1.4 mmol) of morpholine were mixed in 80 ml of benzene and allowed to react with stirring for 5 min. The benzene solution was washed with 50 ml of water and evaporated to dryness under reduced pressure. A ^{1}H NMR spectrum of the residue indicated the presence of direct substitution product **11a** only. This procedure was repeated, except that the reaction was terminated after 2 min by bubbling gaseous HCl into the benzene solution. The salt was removed by suction filtration, taken up in 50 ml of chloroform, and washed with aqueous saturated sodium bicarbonate. The organic phase was washed with water, dried ($MgSO_4$), and evaporated. The ^{1}H NMR spectrum indicated the presence of **10a** only (spectrum obtained approximately 3 hr after mixing of reagents).

A 0.24-g (0.63 mmol) sample of **8a** and 0.12 g (1.4 mmol) of morpholine were allowed to react in 20 ml of absolute ethanol for 10 min. Addition of 75 ml of diehhyl ether and treatment with gaseous HCl led to precipitation of an amine salt.[19] The free base was recovered as described in the preceding paragraph. ^{1}H NMR analysis of the product indicated the presence of **10a** (signals at δ 6.43 and 4.09) and the absence of **11a** (signal at δ 3.51 was absent).

Treatment of a 0.50-g (1.3 mmol) sample of **8a** with 0.26 g (3.0 mmol) of morpholine in 20 ml of benzene for 24 hr gave upon work-up (see above) a yellow oil that was recrystallized from a dichloromethane–petroleum ether mixture, 0.38 g (75%) of **11a**, mp 150–151°.

3-(*N*-*tert*-Butylamino)-2-(*o*-nitrophenylsulfonyl)-1-phenylpropene (11b). A 0.96-g (2.5 mmol) sample of bromide **8a** was added to 20 ml of benzene that contained 0.40 g (5.5 mmol) of *tert*-butylamine and the mixture was allowed to react at room temperature for 1.5 hr. The usual work-up gave an oil that consisted of a 50:50 mixture of **10b** and **11b**. Upon standing for 24 hr the amino sulfone **10a** rearranged to the direct substitution product (**11b**), judging from signals in the ^{1}H NMR spectrum at δ 6.55 and 4.88 for **10b** and at δ 3.55 for **11a**. The latter substance was recrystallized from dichloromethane–petroleum ether, yielding 0.41 g (44%) of bright yellow crystals, mp 108–109°. The proportion of substitution–rearrangement product was increased to 80% by altering reactant concentrations and reaction time (see Table I).

1-(*N*,*N*-Diisopropylamino)-2-(2,4-dinitrophenylsulfonyl)-1-phenylpropene (10d). A 1.0-g (2.6 mmol) sample of **8b** and 3.0 g (30 mmol) of diisopropylamine dissolved in 80 ml of benzene were allowed to react at room temperature for 4 days. The usual work-up gave a light brown oil that consisted of 83% **10d** and 17% **11d**. Crystallization of this material from ether gave 0.39 g (37%) of bright orange crystals of **10d**, mp 137–138°. The ^{1}H NMR spec-

trum ($CDCl_3$) showed peaks at δ 0.55 and 1.13 (d, 6 H, J = 7 Hz), 3.21 (heptet, 2 H, J = 7 Hz), 5.25 (s, 1 H), 6.5–8.5 (m, 10 H).

3-(*N,N*-Diisopropylamino)-2-(*o*-nitrophenylsulfonyl)-3-phenylpropene (10c) and 3-(*N,N*-Diisopropylamino)-2-(*o*-nitrophenylsulfonyl)-1-phenylpropene (11c). To a 0.24-g (0.63 mmol) sample of allyl bromide **8a** in 10 ml of benzene was added 0.13 g (1.4 mmol) of diisopropylamine in 10 ml of the same solvent. The reaction was allowed to proceed at room temperature with stirring for 24 hr. The benzene solution was washed with water and evaporated under reduced pressure to yield a brown, viscous oil. Examination of the ^1H NMR spectrum (signals at δ 6.53 and 5.25 for **10c**, and at δ 3.72 for **11c**) indicated the presence of **10c** and **11c** in a 4:1 ratio, plus starting material (**8a**). The signal for isopropyl protons in **11c** appeared at δ 0.55, while the isopropyl methyls of **10c** were nonequivalent, appearing at δ 0.77 and 1.13 (J = 7 Hz).

Reaction of 0.50 g (1.3 mmol) of **8a** with 1.0 g (9.9 mmol) of diisopropylamine in 20 ml of benzene for 4 days at room temperature gave **10c** and **11c** in a 4:1 ratio. Treatment of this mixture with 0.50 g (5.7 mmol) of morpholine in 20 ml of chloroform for 24 hr at room temperature yielded **11a** and **11c** in a 4:1 ratio (by ^1H NMR analysis). The solvent and excess morpholine were removed under reduced pressure and **11a** was crystallized from carbon tetrachloride, 0.23 g (48%), mp 151°. This compound was identical with **11a** that was obtained from **8a**.

3-(2,4-Dimethyl-1-imidazolyl)-2-(2,4-dinitrophenylsulfonyl)-1-phenylpropene (11e). A 0.50-g (1.3 mmol) sample of **8b** and 0.30 g (3.0 mmol) of 2,4-dimethylimidazole dissolved in 40 ml of benzene were allowed to react at room temperature for 3 days. The benzene layer was diluted to 60 ml and washed with two 50-ml portions of water. The dried ($MgSO_4$) solution was concentrated under reduced pressure. The bright yellow solid that resulted was recrystallized from dichloromethane–hexane, 0.26 g (50%), mp 168–169°. The ^1H NMR spectrum ($CDCl_3$) showed peaks at δ 1.70 (s, 3 H), 2.30 (s, 3 H), 5.07 (s, 2 H), 6.17 (s, 1 H), 7.2–8.5 (m, 8 H).

Aminotropic Rearrangements. A. 3-Morpholino-3-phenyl-2-(*o*-nitrophenylsulfonyl)propene (10a). In the presence of trace amounts of morpholine in benzene solution **10a** readily rearranged to **11a**. See the procedure for the preparation of **11a** and note that a short reaction time led to detection of **11a** only.

B. 3-(*N-tert*-Butylamino)-3-phenyl-2-(*o*-nitrophenylsulfonyl)propene (10b). A 4:1 mixture of **10b** and **11b** (from the reaction of 0.24 g of **8** with 2 equiv of *tert*-butylamine) was dissolved in approximately 2 ml of deuteriochloroform. The solution was divided into equal portions and placed in two ^1H NMR tubes. Into one of the ^1H NMR tubes, a drop of *tert*-butylamine was added. Four hours later, a ^1H NMR spectrum of the material in the tube containing the added amine showed no peaks at δ 6.55 or 4.88 while these absorption bands remained for **10b** in the other ^1H NMR tube. The latter mixture contained ca. 30% of **10b** after 4 hr.

C. 3-(*N,N*-Diisopropylamino)-3-phenyl-2-(2,4-dinitrophenylsulfonyl)propene (10d). A 0.50-g (1.2 mmol) sample of a 83:17 mixture of **10d** and **11d** was treated with 1.0 g (9.9 mmol) of diisopropylamine in 20 ml of 95% ethanol. The mixture was stirred at room temperature for 4 days. The mixture was added to 80 ml of water and extracted with three 50-ml portions of chloroform. The chloroform layer was washed with 50 ml of water, dried ($MgSO_4$), and evaporated under reduced pressure. The characteristic ^1H NMR absorption bands at δ 6.60 and 5.25 for **10d** remained, and comparison with the signal at δ 3.71 for **11d** indicated that the ratio of **10d** to **11d** remained unchanged.

To a ^1H NMR tube containing 0.19 g (0.43 mmol) of **10d** in 1.0 ml of deuteriochloroform was added 0.2 g (2.3 mmol) of morpholine. The contents of the tube were thoroughly mixed and allowed to stand at room temperature for 2 hr. ^1H NMR analysis of the mixture indicated quantitative conversion of **10d** to **11a'** (absence of ^1H NMR signals at δ 6.60 and 5.25 and appearance of a signal at δ 3.52 for the allyl protons of **11a'**).

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Registry No.—**4**, 637-50-3; **7a**, 57109-74-7; **7b**, 57109-75-8; **8a**, 57109-76-9; **8b**, 57109-77-0; **10a**, 57109-78-1; **10b**, 57109-79-2; **10c**, 57109-80-5; **10d**, 57109-81-6; **11a**, 57109-82-7; **11b**, 57109-83-8; **11c**, 57109-84-9; **11d**, 57109-85-0; **11e**, 57109-86-1; *o*-nitrophenylsulfenyl chloride, 7669-54-7; 2,4-dinitrobenzenesulfenyl chloride, 528-76-7; *N*-bromosuccinimide, 128-08-5.

References and Notes

(1) Presented in part at the 9th Great Lakes Regional Meeting of the American Chemical Society, St. Paul, Minn., June 1975.
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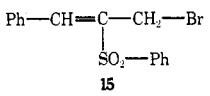
(12) On the basis of our work and data reported by Cromwell and co-workers,[11] the observed diisopropylamino product ratios reflect their kinetic distribution. The *o*-nitro group may play an important role in the reactivity of **8a**, since compound **15** gives only ca. 17% S_N2'-type product



15

upon treatment with diisopropylamine in benzene solution. However, **15** reacts with morpholine and *tert*-butylamine under comparable conditions to give S_N2' products in excellent yield (>80%). J. Neitzel, unpublished results.
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(17) Melting points were determined by the capillary method with a calibrated thermometer. Infrared spectra were obtained on a Beckman IR-5 and ^1H NMR spectra were determined on a Jeolco HL-60 NMR spectrometer. Elemental analyses were obtained from Heterocyclic Chemical Corp., Harrisonville, Mo., and Instranal Laboratory, Inc., Rensselaer, N.Y. A summary of physical data is given in Table II. Reactions were run at room temperature (ca. 25°) unless indicated otherwise.
(18) The authors wish to thank Charlotte Grove for repeating this procedure.
(19) We attempted to isolate and purify the hydrochlorides of amino sulfones **10a** and **10b** but these substances were hygroscopic. The free bases were regenerated after standing for 3 days at room temperature by treatment of the crude salts with dilute sodium bicarbonate solution. For **10b** that was recovered in this manner the product ratio was unchanged (ca. 80% **10b**) and complete rearrangement to **11b** required 3 days, whereas samples obtained by simply washing the benzene layer with water and evaporation required only ca. 24 hr for complete rearrangement under identical conditions.