by J. Radhakrishnan, Postdoctoral Research Associate (1977), Jeffery A. Naus, B.S. Honors Thesis, University of Connecticut (1977), and C. L. Rossiter, IV, B.S. Honors Thesis, University of Connecticut (1982). W.R.V. gratefully acknowledges financial support for several summers in the course of this investigation from the University of Connecticut Research Foundation.

Registry No. (±)-**3**, 87554-07-2; (−)-**3**–cinchonidine, 87583-08-2; (−)-**3**, 87554-08-3; (±)-**4**, 87494-97-1; (±)-**5**, 87494-95-9; (+)-**5**–cinchonidine, 87508-86-9; (+)-**5**, 87494-96-0; (±)-**5** ethyl ester, 87495-00-9; (±)-**6**, 87494-98-2; (±)-**17**, 87494-99-3; triethyl phosphonoacetate, 867-13-0.

Nucleophilic Substitutions of Unactivated Vinyl Halides with Alkanethiolate Anions in Hexamethylphosphoramide[1]

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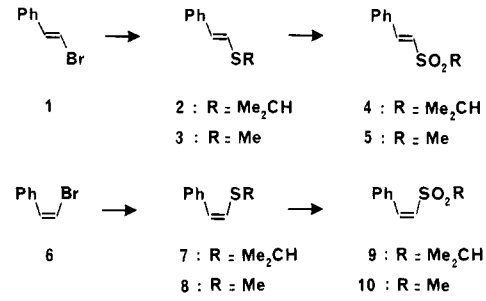
The reactions of unactivated vinyl halides with the sodium salts of alkanethiols in HMPA gave vinyl alkyl sulfides in high yields. These reactions occur with complete retention of configuration. With di-, tri-, and tetrachloroethylenes all the chlorine atoms are substituted by alkylthio groups. By treatment with alkanethiolates the vinyl sulfides are dealkylated to give the sodium salts of the ene thiols. By reaction with sodium all the alkylthio groups present in the molecule suffer fragmentation to give the sodium salts of the corresponding mercaptoethylenes.

Alkenyl sulfides are valuable synthetic precursors of several organic compounds,[2,3] and various methods have therefore been described for their synthesis. Several procedures, which include Wittig-type reactions,[4] dehydration of β-hydroxy thioacetals,[5] and dehydrochlorination of chloro sulfides,[6] use carbonyl compounds as starting products. Carbonyl compounds can afford alkenyl sulfides also by treatment with the lithium salts of (alkylthio)- or (arylthio)(trimethylsilyl)methane.[7] Another useful synthesis of alkenyl sulfides consists of the addition of thiolate anions to acetylenic compounds.[8] Other systems use alkenyl halides as starting materials. These can be transformed into the alkenylmagnesium halides and treated with methyl sulfinate esters to produce alkenyl sulfoxides, which are then reduced to the sulfides.[9] Direct displacement of vinylic halogens by thiolate anions can be effected in activated substrates,[10,11] i.e., in ethylenic compounds of the type YCH=CHX where Y is an electron-withdrawing group and X the halogen atom. Nucleophilic vinylic substitutions on unactivated substrates do not generally take place. The few examples reported in the literature represent special cases in which mechanisms different from those proposed for activated systems are operating. Thus displacement of vinylic halogens by copper alkane thiolates has been described.[12] This reaction takes place with β-bromostyrene only at 200 °C; however with dibromoethylene the product obtained was the (alkylthio)acetylene deriving from the elimination of HBr. (*Z*)-Dichloroethylene reacts with arenethiolates in ethanol, in the presence of sodium ethoxide, to give the (*Z*)-bis(arylthio)ethylenes; this reaction however proceeds through an elimination–addition mechanism and in fact the (*E*)-dichloroethylene does not give any reaction product under the same experimental conditions.[13] Successful stereospecific substitutions of vinyl halides by the lithium salts of alkane- and arenethiols have been recently described; these reactions however require the use of tetrakis(triphenylphosphine)palladium as catalyst in order to activate the substitution process.[3]

Scheme I



We have recently reported that sodium alkanethiolates easily react with unactivated aryl halides[14] and with polyhalogenoarenes[15] to give aryl alkyl sulfides and poly(alkylthio)arenes in high yields when the reactions are carried out in HMPA. We now report that this procedure can be successfully applied to the vinyl halides to effect a stereospecific and very efficient synthesis of vinyl alkyl sulfides. Owing to the easy availability of the starting compounds and to the extremely simple experimental

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(2) H. Okumara, M. Miura, and H. Takei, *Tetrahedron Lett.*, 43 (1979) and references cited therein.
(3) S. I. Murahashi, M. Yamamura, K. Yanagisawa, N. Mita, and K. Kondo, *J. Org. Chem.* **44**, 2408 (1979) and references cited therein.
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(14) P. Cogolli, F. Maiolo, L. Testaferri, M. Tingoli, and M. Tiecco, *J. Org. Chem.*, **44**, 2642 (1979); L. Testaferri, M. Tingoli, and M. Tiecco, *Tetrahedron Lett.*, **21**, 3099 (1980).
(15) L. Testaferri, M. Tingoli, and M. Tiecco, *J. Org. Chem.*, **45**, 4376 (1980).

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conditions employed, the present procedure represents one of the best methods to obtain the alkenyl sulfides. Moreover the reactions described in this paper also have a considerable mechanistic importance since they represent examples of nucleophilic vinylic substitution reactions occurring on unactivated substrates.

Results and Discussion

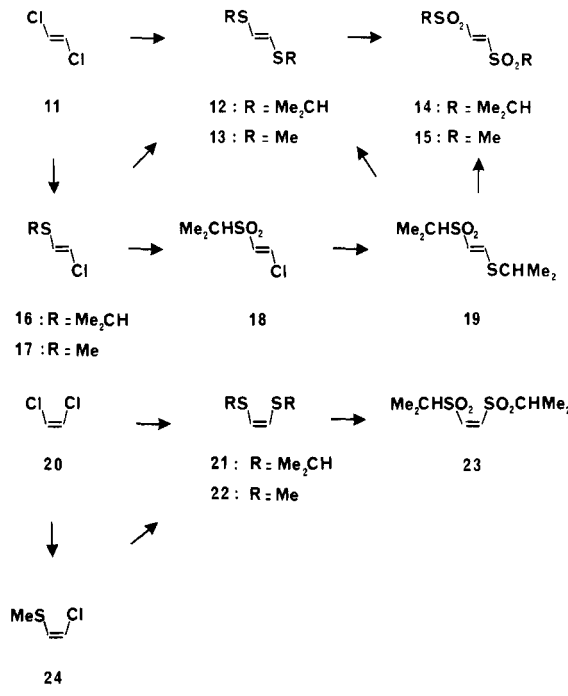
The reactions of (*E*)-β-bromostyrene (0.01 mol) (1) with 1.5 equiv of Me_2CHSNa or MeSNa in HMPA (25 mL) occurred smoothly at room temperature (0.5 h) to give (*E*)-β-(isopropylthio)styrene (2) or (*E*)-β-(methylthio)-styrene (3) in 95% and 96% yields, respectively, after purification by column chromatography. GLC and NMR analysis of the reaction mixture before purification showed that the amount of the *Z* isomers was lower than 2%. Oxidation with hydrogen peroxide in acetic acid gave the corresponding sulfones 4 and 5. Similarly, (*Z*)-β-bromostyrene (6), under the same experimental conditions, afforded compounds 7 and 8 in 95% and 98% yields, respectively. In this case also the *E* stereoisomers were present in less than 5%. Oxidation afforded the sulfones 9 and 10 (Scheme I). Similar good yields were also obtained from the reactions of 1 and 6 with MeSNa in Me_2SO or in DMF. In these cases, however, the reactions were not completely stereospecific, a mixture of 3 and 8 being obtained in 9:1 and 2:8 ratios starting from 1 and 6, respectively. When the reaction medium was completely changed and ethanol was used as the solvent, the *Z*-isomer, 6, afforded compounds 7 and 8 (70% and 45% yields, respectively) only after prolonged reaction times (15 h) and at higher temperatures (80 °C). Under these conditions (*E*)-β-bromostyrene (1) was instead recovered completely unchanged. These findings seem to indicate that in ethanol the substitution reaction takes place through an elimination–addition mechanism as already suggested by W. E. Truce and co-workers.[13] On the contrary, when the reactions were run in HMPA both the isomers 1 and 6 react stereospecifically with almost complete retention of configuration.

The (*E*)- and (*Z*)-dichloroethylenes (11 and 20) reacted, 1 h at room temperature, with an excess of the sodium isopropanethiolate and methanethiolate to give the corresponding (*E*)- and (*Z*)-bis(alkylthio)ethylenes 12, 13 and 21, 22, respectively. Reaction yields were of the order of 90% in every case. Sulfones 14, 15, and 23 were prepared in the usual way (Scheme II).

In every case the reaction mixtures were analyzed by GLC and NMR and the reactions were found to be almost completely stereospecific (less than 5% of the undesired stereoisomer was present). The *E* configuration of compounds 14 and 15 was confirmed by X-ray analysis.[16]

A more detailed investigation was carried out in the case of the reactions of 11 with Me_2CHSNa and MeSNa and of the reaction of 20 with MeSNa. By working at lower temperature (−5 °C) and with an insufficient quantity of the alkanethiolates, the reactions could be stopped at the monosubstitution step and the products 16, 17, and 24 were isolated. The *E* configuration of 16 and 17 and the *Z* configuration of 24 could now be demonstrated by NMR, the coupling constant of the two ethylenic protons being 13.5 Hz in the first two cases and 6.0 Hz in the case of 24. These three chloro(alkylthio)ethylenes, when treated with the appropriate sodium alkanethiolate, gave a quantitative

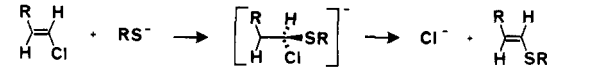
Scheme II



yield of the corresponding bis(alkylthio)ethylenes, namely 12 from 16, 13 from 17, and 22 from 24. Oxidation of 16 afforded the (*E*)-1-(isopropylsulfonyl)-2-chloroethylene (18); reaction of 18 with Me_2CHSNa gave the (*E*)-1-(isopropylsulfonyl)-2-(isopropylthio)ethylene (19). Oxidation of 19 afforded the disulfone 14 identical with that obtained from the oxidation of 12.

An interesting result was obtained when 18 was treated with an excess of Me_2CHSNa, the only reaction product being in this case the bis(alkylthio)ethylene 12. This indicates that the initially formed sulfide sulfone 19 is eventually transformed into 12 and this was also confirmed independently by treating 19 with Me_2CHSNa. It is evident from these results that a stereospecific vinylic substitution occurs also when the leaving group is an alkyl sulfonyl substituent.

The reaction sequences described above and depicted in Scheme II give a clear chemical demonstration that the bis(alkylthio)ethylenes 12 and 13 and 21 and 22 are formed from 11 and 20 through two consecutive reactions which are both stereospecific with almost complete retention of configuration. The reactions of sodium alkanethiolates with the dichloroethylenes 11 and 20, with the chloro(alkylthio)ethylenes 16, 17, and 24, and with the β-bromostyrenes 1 and 6 represent examples of nucleophilic vinylic substitution occurring on unactivated substrates. The success of these reactions is very likely due to the use of HMPA, a solvent which greatly enhances the reactivity of the nucleophile by specific solvation of the cation. The mechanistic details of the nucleophilic substitutions at vinylic carbon atoms have been deeply discussed in two excellent reviews by Modena[10] and Rappoport[11] and need not to be repeated here. On the basis of the observed stereochemical course we suggest that the reactions described in this paper can be seen as bimolecular substitutions which involve nucleophilic attack at the vinylic carbon atom holding the leaving halogen atom (eq 1). The



(1)

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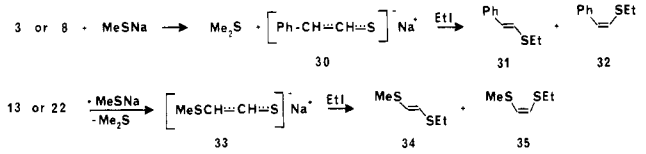
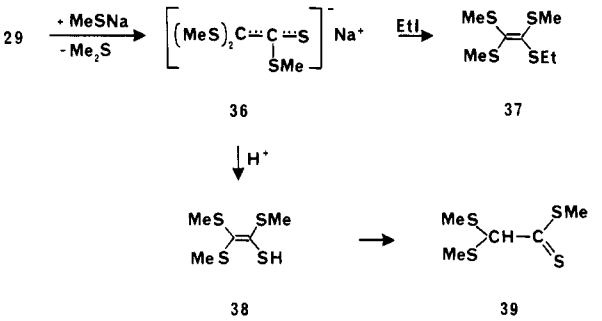
(16) The structural X-ray work (see Experimental Section) was kindly done at the Istituto di Mineralogia, University of Perugia, Italy, by Prof. P. F. Zanazzi, to whom correspondence should be addressed for further details.

Scheme III

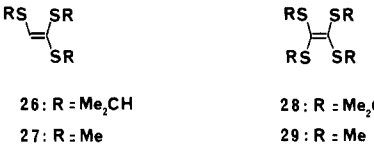


Scheme IV



scarce mechanistic information available so far does not justify any speculation about the problem of whether this substitution can be considered as a single- or a multistep process, i.e., whether **25** is only a transition state or whether it is an intermediate.[11] We think that the reactions reported in the present paper represent particular and interesting examples of nucleophilic vinylic substitutions which merit further mechanistic investigations.[17]

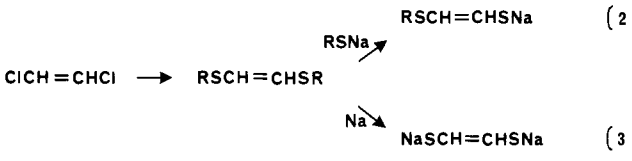
When the same reactions were applied to the trichloro- and the tetrachloroethylene complete displacement of all the chlorine atoms present in the molecule by the isopropylthio or the methylthio groups was obtained. The tris(alkylthio)ethylenes **26** and **27** and the tetrakis(alkylthio)ethylenes **28** and **29** were obtained in 85–95% yields.



26: R = Me_2CH **28**: R = Me_2CH

27: R = Me **29**: R = Me

All the (alkylthio)ethylenes obtained as described above can be easily dealkylated to give solutions of the sodium salts of the enethiols. These reactions can be effected in the same medium and it is therefore possible to realize a one-pot synthesis of enethiols starting from unactivated vinyl halides. The dealkylation process can be effected in two ways and it is possible to obtain the mono(mercapto)- (eq 2) or the poly(mercapto)ethylenes (eq 3) depending on the procedure employed.



The monodealkylation reaction is effected with sodium alkanethiolates and occurs with (methylthio)- and (ethylthio)ethylenes. The polydealkylation is instead effected by treatment with sodium and occurs with all the alkyl vinyl sulfides. The two procedures are similar to those described in our previous works for the dealkylation of the aryl alkyl sulfides.[14,15,18–21] The monodealkylation of methyl vinyl sulfides by sodium methanethiolate occurs easily at 90 °C, in HMPA, and it is the result of a nucleophilic aliphatic substitution.[15,19] Thus, when a solution of (*E*)-β-(methylthio)styrene (**3**) (0.01 mol) and of MeSNa (2 equiv) in HMPA (25 mL) was stirred at 90 °C under nitrogen, for 8 h, a solution of the sodium salt of β-(mercapto)styrene **30** was obtained. This solution was cooled to 0 °C and treated with excess ethyl iodide. A 90% yield of a 2:1 mixture of the (*E*)- **31** and (*Z*)-β-(ethylthio)styrene (**32**) was obtained. (Scheme III). The same mixture of **31** and **32** (90%) was obtained when the dealkylation reaction was carried out on the (*Z*)-β-(methylthio)styrene (**8**). These results indicate that the dealkylation of **3** and **8** gives rise to the same anion **30** and that the treatment with EtI gives the kinetically controlled β-(ethylthio)-styrenes **31** and **32** deriving from alkylation at the sulfur atom. Independent experiments showed that **31** and **32** do not isomerize under the experimental conditions employed and therefore the ratio of **31**:**32** should reflect the ratio of their rates of formation from **30**. As expected, similar results were obtained when the same reactions were carried out on the two isomeric bis(methylthio)ethylenes **13** and **22**. In this case the (*E*)-**34** and (*Z*)-1-(methylthio)-2-(ethylthio)ethylene (**35**) were formed (85% yield) in a 2.4:1 ratio. If the solutions of **33** were instead treated with MeI, a mixture of the disulfides **13** and **22** in a 1.5:1 ratio was obtained in 85% yield.

The dealkylation of the tetrakis(methylthio)ethylene (**29**) afforded the anion **36** (Scheme IV). Treatment with ethyl iodide gave the kinetically controlled product **37** in 91% yield. On the contrary, when the solution was treated with acid, the thioenol **38** was not observed and the only product isolated was the dithioester **39** in 91% yield. Thus, in the present case, the tautomeric equilibrium is completely shifted towards the thioketonic form. This result confirms a previous observation made by Brandsma:[22] in the alkenethiols the tautomeric equilibrium lies towards the enethiol form when the α-position is unsubstituted and towards the thioketonic form when a substituent is linked to the α-carbon atom. Unfortunately this interesting aspect of the chemistry of these compounds could not be studied in more detail in the present case because the treatment with acid of the solution of **30** and **33** gave rise to complex mixtures of products.

Results identical with those described above and collected in Schemes III and IV were obtained when the β-bromostyrenes **1** and **6**, the dichloroethylenes **11** and **20**, and tetrachloroethylene were directly treated with an excess of MeSNa at 90 °C. This procedure thus allows the one-pot synthesis of the sodium ene thiolates **30**, **33**, and **36** from the vinyl halides. This method is identical to that previously described by us to effect a convenient synthesis of aromatic thiols from unactivated aryl halides.[14,23]

If the solutions of the vinyl alkyl sulfides in HMPA are treated with excess sodium at 90 °C fragmentation occurs

(17) The use of sodium methoxide as the nucleophile was also investigated. The reactions of (*Z*)- and (*E*)-β-bromostyrenes with excess MeONa in HMPA gave rise to similar reaction mixtures consisting of phenylacetylene and of (*E*)- and (*Z*)-β-methoxystyrene in a 2:1 ratio. In this case therefore the reaction mechanism is different from that observed with the thiolates. Very likely the reaction proceeds via the elimination–addition route. This is strongly supported by the isolation of the phenylacetylene and from the identical ratio in which the two isomeric methoxystyrenes are formed in both cases. Further evidence came from an independent experiment in which phenylacetylene was allowed to react with MeONa in HMPA; a 2:1 mixture of the (*E*)- and (*Z*)-methoxystyrenes was obtained in this case also.

(18) F. Maiolo, L. Testaferri, M. Tiecco, and M. Tingoli, *J. Org. Chem.*, **46**, 3070 (1981).

(19) M. Tiecco, M. Tingoli, L. Testaferri, D. Chianelli, and F. Maiolo, *Synthesis*, 478 (1982).

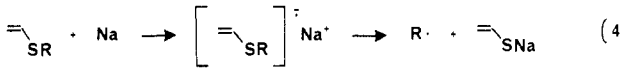
(20) L. Testaferri, M. Tiecco, M. Tingoli, D. Chianelli, and F. Maiolo, *Tetrahedron*, **38**, 2721 (1982).

(21) L. Testaferri, M. Tiecco, M. Tingoli, D. Chianelli, and M. Montanucci, *Tetrahedron*, **38**, 3687 (1982).

(22) L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, **89**, 593 (1970).

(23) M. Tiecco, L. Testaferri, M. Tingoli, D. Chianelli, and M. Montanucci, *Synthesis*, 751 (1983).

at all the alkyl–sulfur bonds present in the molecule to give the sodium salts of the poly(mercapto)ethylene. The cleavage occurs selectively at the sulfur–alkyl bond confirming previous observations made by Brandsma[22] and by Truce and Breiter,[24] who used alkali metals in liquid ammonia or methylamine. As already suggested in the case of aromatic compounds,[18,20,21] these reactions very likely proceed through radical anion intermediates (eq 4).



Thus, the reactions of the tetrakis(isopropylthio)ethylene **28** and of the tris(isopropylthio)ethylene **26** with excess sodium afforded the sodium salts **40** and **41**, which

on treatment with methyl iodide gave tetrakis(methylthio)ethylene (**29**) and tris(methylthio)ethylene (**27**) in 85% and 88.5% yields, respectively.

When the reactions with sodium were carried out on (*E*)-(**3**) or (*Z*)-β-(methylthio)styrene (**8**) the final reaction mixtures contained the anion **30** (Scheme III) and in fact treatment with EtI at 0 °C gave again a mixture of **31** and **32** in the ratio of 2:1 (80% and 86% yields from the *E* or the *Z* isomer, respectively).

On the basis of these results one should expect that the fragmentation of (*E*)-**13** and (*Z*)-bis(methylthio)ethylene (**22**) should afford the sodium salt **42** and that the treatment of this salt with MeI, at 0 °C, should give the intermediate **33**, identical with that obtained from the reaction of **13** and **22** with MeSNa (Scheme III). The further reaction of **33** with MeI should then give rise to a mixture of **13** and **22** in the ratio of 1.5:1 (eq 5). Indeed, when the

reaction was carried out on the (*E*)-isomer, **13** and **22** were obtained (82% yield) in the ratio of 2:1. On the contrary, when the same reaction was carried out on the *Z* isomer, **22**, the dealkylation occurred smoothly and the starting product was completely consumed, but on treatment with MeI at 0 °C the only product obtained was the (*Z*)-bis-(methylthio)ethylene (**22**) (80% yield). Identical results were obtained starting from (*E*)-**12** and (*Z*)-bis(isopropylthio)ethylene (**21**): on dealkylation with sodium followed by alkylation with MeI, **12** gave a mixture of **13** and **22** in a 1.5:1 ratio (75% yield), whereas the (*Z*)-isomer, **21**, afforded only the (*Z*)-bis(methylthio)ethylene (**22**) (78% yield). However, if the solutions deriving from the dealkylation of **13** and **22** were treated with 2-propyl iodide, at 0 °C, an identical mixture of (*E*)-**12** and (*Z*)-bis(isopropylthio)ethylene (**21**) in a 6:1 ratio was obtained in both cases in 82% and 78% yield, respectively. Thus the only unexpected result remains that of the reactions of the *E* isomers **12** and **13** with sodium and methyl iodides; clearly these reactions cannot proceed through the intermediates **42** and **33** as indicated in eq 5.[25] At present we do not have convincing evidence to explain this unpredictable behavior and its rationalization must await further experimental results.

Identical results were obtained when the β-bromostyrenes, the tri- and tetrachloroethylene, and the 1,2-dichloroethylenes were treated with the alkanethiolates and sodium was directly added to the resulting reaction mixtures. Thus, this procedure represents a one-pot synthesis of the sodium salts of poly(mercapto)ethylenes from polychloroethylenes.

Experimental Section[26]

Commercial HMPA was used without further purification. (*Z*)- and (*E*)-Dichloroethylenes, (*E*)-β-bromostyrene (98% isomeric purity), trichloroethylene, and tetrachloroethylene were commercial products. (*Z*)-β-bromostyrene,[27] sodium 2-propanethiolate[15] and sodium methanethiolate[15] were prepared as described in the literature. Reaction products were identified by ^{1}H NMR spectroscopy and elemental analyses. Sulfones were obtained by oxidation with H_2O_2 in acetic acid solutions and were purified by crystallization from ethanol or by distillation.

Reactions of Vinyl Halides with Sodium Alkanethiolates in HMPA. General Procedure. A solution of the vinyl halide (0.01 mol) and of MeSNa or Me_2CHSNa (1.5 equiv for each halogen atom present in the molecule of the vinyl halide) in HMPA (25 mL) was stirred under nitrogen, at room temperature, for 0.5–1 h. The progress of the reaction can be monitored by GLC or TLC. The reaction mixture was poured on water and extracted with ether; the ether was washed with water, dried, and evaporated. The residue was analyzed by GLC and NMR. Purification was effected by column chromatography on silica gel with light petroleum as eluant. The following products[28] were obtained in this way, with the yields indicated in parentheses, starting from the corresponding halides, as reported in the Results and Discussion section:

(*E*)-β-(Isopropylthio)styrene (2): 95%; bp 62–63 °C (1.5 × 10^{-2} mm); NMR δ 7.5–7.0 (m, 5 H), 6.75 (d, *J* = 15.5 Hz, 1 H), 6.5 (d, *J* = 15.5 Hz, 1 H), 3.15 (spt, 1 H), 1.3 (d, 6 H). Anal. Calcd for $C_{11}H_{14}S$: C, 74.09; H, 7.93; S, 17.98. Found: C, 73.97; H, 8.01; S, 17.65.

Sulfone 4: bp 115 °C (3 × 10^{-2} mm); NMR δ 7.7–7.15 (m, 5 H), 7.55 (d, *J* = 16 Hz, 1 H), 6.85 (d, *J* = 16 Hz, 1 H), 3.1 (spt, 1 H), 1.35 (d, 6 H). Anal. Calcd for $C_{11}H_{14}O_2S$: C, 62.82; H, 6.72; S, 15.24. Found: C, 62.62; H, 6.57; S, 15.31.

(*E*)-β-(Methylthio)styrene (3): 96%; oil; NMR δ 7.6–7.0 (m, 5 H), 6.8 (d, *J* = 15.5 Hz, 1 H), 6.35 (d, *J* = 15.5 Hz, 1 H), 2.35 (s, 3 H).

Sulfone 5: mp 76–78 °C (lit.[29] 78–79 °C); NMR δ 7.7–7.35 (m, 5 H), 7.7 (d, *J* = 15.5 Hz, 1 H), 7.0 (d, *J* = 15.5 Hz, 1 H), 3.05 (s, 3 H).

(*Z*)-β-(Isopropylthio)styrene (7): 95%; bp 65–68 °C (1.5 × 10^{-2} mm); NMR δ 7.65–7.0 (m, 5 H), 6.4 (d, *J* = 10.5 Hz, 1 H), 6.2 (d, *J* = 10.5 Hz, 1 H), 3.0 (spt, 1 H), 1.3 (d, 6 H). Anal. Calcd for $C_{11}H_{14}S$: C, 74.09; H, 7.93; S, 17.98. Found: C, 73.95; H, 8.05; S, 18.11.

Sulfone 9: mp 57–59 °C; NMR δ 7.8–7.3 (m, 5 H), 7.15 (d, *J* = 11.5 Hz, 1 H), 6.3 (d, *J* = 11.5 Hz, 1 H), 3.05 (spt, 1 H), 1.35 (d, 6 H). Anal. Calcd for $C_{11}H_{14}O_2S$: C, 62.82; H, 6.72; S, 15.24. Found: C, 62.75; H, 6.58; S, 15.44.

(*Z*)-β-(Methylthio)styrene (8): 97%; oil (lit.[29] 101.5 °C/5 mm); NMR δ 7.6–7.0 (m, 5 H), 6.4 (d, *J* = 10.5 Hz, 1 H), 6.1 (d, *J* = 10.5 Hz, 1 H), 2.2 (s, 3 H).

Sulfone 10: mp 64.5–66 °C (lit.[29] 66–67 °C); NMR δ 7.6–7.45 (m, 2 H), 7.35–7.15 (m, 3 H), 7.0 (d, *J* = 11.5 Hz, 1 H), 6.35 (d, *J* = 11.5 Hz, 1 H), 2.8 (s, 3 H).

(*E*)-Bis(isopropylthio)ethylene (12): 95%; bp 40 °C (2 × 10^{-2} mm); NMR δ 6.25 (s, 1 H), 3.05 (spt, 1 H), 1.3 (d, 6 H). Anal.

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(25) In order to investigate the effect of the counterion the fragmentation of **22** was also effected with potassium. The treatment of the reaction mixture with MeI at 0 °C gave the isomer **22** which was only contaminated by traces of **13**.

(26) NMR spectra were recorded ($CDCl_3$ solutions) at 90 MHz on a Varian EM 390 instrument. GLC analyses were performed on a Hewlett-Packard 5830 chromatograph with a 20 in., 10% UCW 982 column. C, H, and S elemental analyses were carried out on a Carlo Erba Elemental Analyzer Model 1106.

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(28) The vicinal coupling constant in the ethyl and isopropyl groups was 7.5 Hz in every case.

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Calcd for $C_8H_{16}S_2$: C, 54.48; H, 9.16; S, 36.36. Found: C, 54.45; H, 9.12; S, 36.43.

Disulfone 14: mp 153–155 °C; NMR δ 7.4 (s, 1 H), 3.2 (spt, 1 H), 1.4 (d, 6 H). Anal. Calcd for $C_8H_{16}O_4S_2$: C, 39.97; H, 6.72; S, 26.68. Found: C, 40.05; H, 6.66; S, 26.77.

(*E*)-Bis(methylthio)ethylene (13): 85%; bp 74 °C (18 mm) (lit.[30] 50–52 °C (2–3 mm)); NMR δ 6.0 (s, 1 H), 2.25 (s, 3 H).

Disulfone 15: mp 252–254 °C (lit.[30] 249 °C); NMR δ 7.75 (s, 1 H), 3.25 (s, 3 H). Anal. Calcd for $C_4H_8O_4S_2$: C, 26.07; H, 4.38; S, 34.80. Found: C, 26.45; H, 4.21; S, 35.00.

(*Z*)-Bis(isopropylthio)ethylene (21): 95%; bp 48–49 °C (6 × 10^{-2} mm); NMR δ 6.2 (s, 1 H), 3.15 (spt, 1 H), 1.35 (d, 6 H). Anal. Calcd for $C_8H_{16}S_2$: C, 54.48; H, 9.16; S, 36.36. Found: C, 54.50; H, 9.08; S, 36.59.

Disulfone 23: mp 131–133 °C; NMR δ 7.0 (s, 1 H), 3.85 (spt, 1 H), 1.4 (d, 6 H). Anal. Calcd for $C_8H_{16}O_4S_2$: C, 39.97; H, 6.72; S, 26.68. Found: C, 40.01; H, 6.83; S, 26.78.

(*Z*)-Bis(methylthio)ethylene (22): 89%; bp 83–85 °C (18 mm) (lit.[30] 55–56 °C (2.4 mm)); NMR δ 5.95 (s, 1 H), 2.35 (s, 3 H).

Tris(isopropylthio)ethylene (26): 84%; bp 66–67 °C (5 × 10^{-3} mm); NMR δ 6.8 (s, 1 H), 3.45 (spt, 1 H), 3.25 (spt, 1 H), 3.15 (spt, 1 H), 1.3 (d, 6 H), 1.25 (d, 6 H), 1.2 (d, 6 H). Anal. Calcd for $C_{11}H_{22}S_3$: C, 52.74; H, 8.87; S, 38.39. Found: C, 52.98; H, 8.63; S, 38.41.

Tris(methylthio)ethylene (27): 98%; bp 57–59 °C (4 × 10^{-2} mm); NMR δ 6.45 (s, 1 H), 2.35 (s, 3 H), 2.3 (s, 3 H), 2.25 (s, 3 H).[31]

Tetrakis(isopropylthio)ethylene (28): 85%; mp 83–84 °C; NMR δ 3.55 (spt, 1 H), 1.3 (d, 6 H). Anal. Calcd for $C_{14}H_{28}S_4$: C, 51.79; H, 8.71; S, 39.50. Found: C, 51.65; H, 8.80; S, 39.54.

Tetrakis(methylthio)ethylene (29): 94%; mp 59–60 °C (lit.[31] 60 °C); NMR δ 2.4 (s).

The results of the reactions of **1** and **6** with MeSNa in Me_2SO and in DMF and of the reactions of **1** and **6** with MeSNa and Me_2CHSNa in ethanol are reported under the Results and Discussion section.

In order to obtain the chloro(alkylthio)ethylenes described below, the dichloroethylenes **11** and **20** were allowed to react with 0.5 equiv of RSNa at −5 °C for 0.5 h. The reaction mixtures were then worked up as described above. Also present in these reactions were the unreacted starting compounds and some bis(alkylthio)ethylenes. Reaction yields are based on the amount of the RSNa employed.

(*E*)-1-(Isopropylthio)-2-chloroethylene (16): 55%; bp 45 °C (18 mm); NMR δ 6.5 (d, *J* = 13.5 Hz, 1 H), 6.15 (d, *J* = 13.5 Hz, 1 H), 3.05 (spt, 1 H), 1.3 (d, 6 H). Anal. Calcd for C_5H_9ClS: C, 43.94; H, 6.65; S, 23.47. Found: C, 44.00; H, 6.49; S, 23.51.

Sulfone 18: bp 48 °C (5 × 10^{-3} mm); NMR δ 7.4 (d, *J* = 13.5 Hz, 1 H), 6.75 (d, *J* = 13.5 Hz, 1 H), 3.15 (spt, 1 H), 1.4 (d, 6 H). Anal. Calcd for $C_5H_9ClO_2S$: C, 35.61; H, 5.39; S, 19.01. Found: C, 35.51; H, 5.49; S, 18.92. The reaction of **16** with 1.5 equiv of Me_2CHSNa afforded **12** in quantitative yields.

(*E*)-1-(Methylthio)-2-chloroethylene (17): 45%; bp 29–30 °C (18 mm); NMR δ 6.45 (d, *J* = 13.5 Hz, 1 H), 5.85 (d, *J* = 13.5 Hz, 1 H), 2.25 (s, 3 H).[32] The reaction of this compound with 1.5 equiv of MeSNa afforded **13** in quantitative yields.

(*Z*)-1-(Methylthio)-2-chloroethylene (24): NMR δ 6.3 (d, *J* = 6 Hz, 1 H), 6.0 (d, *J* = 6.0 Hz, 1 H), 2.35 (s, 3 H).[32] This compound was not isolated. The NMR data were obtained from the spectrum of the reaction mixture. Complete transformation into **22** was obtained by adding MeSNa to the reaction mixture.

(*E*)-1-(Isopropylsulfonyl)-2-(isopropylthio)ethylene (19), 68%. This compound was obtained from the reaction of **18** (2 mmol) with Me_2CHSNa (1.5 equiv); bp 60–61 °C (5 × 10^{-3} mm); NMR δ 7.65 (d, *J* = 15 Hz, 1 H), 6.1 (d, *J* = 15 Hz, 1 H), 3.3 (spt, 1 H), 3.05 (spt, 1 H), 1.4 (d, 6 H), 1.35 (d, 6 H). Anal. Calcd for $C_8H_{16}O_2S_2$: C, 46.11; H, 7.75; S, 30.77. Found: C, 46.05; H, 7.91; S, 30.83. Also present in this reaction was the disulfide **12**. Oxidation of **19** afforded the disulfone **14**. The reaction of **19** with excess Me_2CHSNa (at room temperature for 3 h) afforded **12** in 75% yield. Similar results were obtained by directly treating **18** with an excess of Me_2CHSNa.

Dealkylation of Vinyl Alkyl Sulfides with MeSNa. General Procedure. A solution of the vinyl alkyl sulfide (0.01 mol) and MeSNa (2 equiv) in HMPA (25 mL) was stirred under nitrogen, at 90 °C, for 6–8 h. The progress of the reaction can be monitored by GLC or TLC. When all the starting product has been consumed, the reaction mixture was poured on ice and hydrochloric acid and extracted with ether. The ether was washed, dried, and evaporated. The residue was analyzed by GLC, TLC, and NMR, and the reaction products were isolated and purified by column chromatography on silica gel with light petroleum as eluant. Alternatively, the reaction mixture was cooled at 0 °C in a thermostat and an excess (2.1 mol) of methyl or ethyl iodide was added dropwise. The mixture was stirred at 0 °C for 2 h and then poured on water and extracted with ether. The ether was washed with water, dried, and evaporated. The reaction mixture was analyzed and purified as described above.

The reactions carried out according to the general procedure reported above are described in the Results and Discussion section. The physical and the NMR data of the products obtained in this way are reported below.

(*E*)-β-(Ethylthio)styrene (31): oil; NMR δ 7.3–6.95 (m, 5 H), 6.6 (d, *J* = 15 Hz, 1 H), 6.3 (d, *J* = 15 Hz, 1 H), 2.75 (q, 2 H), 1.3 (t, 3 H). Anal. Calcd for $C_{10}H_{12}S$: C, 73.11; H, 7.38; S, 19.52. Found: C, 73.22; H, 7.45; S, 19.61.

Sulfone: mp 65–67 °C (lit.[33] 66–67 °C); NMR δ 7.45 (d, *J* = 15 Hz, 1 H), 7.45–7.15 (m, 5 H), 6.75 (d, *J* = 15 Hz, 1 H), 3.05 (q, 2 H), 1.35 (t, 3 H). Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.19; H, 6.17; S, 16.33. Found: C, 61.15; H, 6.28; S, 16.46.

(*Z*)-β-(Ethylthio)styrene (32): oil (lit.[34] bp 85–86 °C (1 mm)); NMR δ 7.55–6.95 (m, 5 H), 6.3 (d, *J* = 10.5 Hz, 1 H), 6.15 (d, *J* = 10.5 Hz, 1 H), 2.7 (q, 2 H), 1.3 (t, 3 H).[3]

(*E*)-1-(Methylthio)-2-(ethylthio)ethylene (34): bp 76 °C (18 mm); NMR δ 6.2 (d, *J* = 14.5 Hz, 1 H), 5.9 (d, *J* = 14.5 Hz, 1 H), 2.65 (q, 2 H), 2.25 (s, 3 H), 1.3 (t, 3 H). Anal. Calcd for $C_5H_{10}S_2$: C, 44.72; H, 7.52; S, 47.76. Found: C, 44.57; H, 7.38; S, 47.61.

Disulfone: mp 145–147 °C; NMR (Me_2SO-d_6) δ 7.9 (d, *J* = 15 Hz, 1 H), 7.75 (d, *J* = 15 Hz, 1 H), 3.4 (q, 2 H), 3.3 (s, 3 H), 1.25 (t, 3 H). Anal. Calcd for $C_5H_{10}O_4S_2$: C, 30.29; H, 5.09; S, 32.34. Found: C, 30.15; H, 5.21; S, 32.28.

(*Z*)-1-(Methylthio)-2-(ethylthio)ethylene (35): bp 81–83 °C (18 mm); NMR δ 6.05 (s, 2 H), 2.7 (q, 2 H), 2.3 (s, 3 H), 1.3 (t, 3 H). Anal. Calcd for $C_5H_{10}S_2$: C, 44.72; H, 7.52; S, 47.76. Found: C, 44.60; H, 7.63; S, 47.61.

Disulfone: NMR δ 7.05 (d, *J* = 11.5 Hz, 1 H), 6.85 (d, *J* = 11.5 Hz, 1 H), 3.45 (q, 2 H), 3.3 (s, 3 H), 1.4 (t, 3 H). Anal. Calcd for $C_5H_{10}O_4S_2$: C, 30.29; H, 5.09; S, 32.34. Found: C, 30.33; H, 5.16; S, 32.20.

1,1,2-Tris(methylthio)-2-(ethylthio)ethylene, (37): bp 77–79 °C (1.5 × 10^{-2} mm); NMR δ 2.85 (q, 2 H), 2.4 (s, 6 H), 2.35 (s, 3 H), 1.25 (t, 3 H). Anal. Calcd for $C_7H_{14}S_4$: C, 37.13; H, 6.24; S, 56.63. Found: C, 37.18; H, 6.29; S, 56.58.

Methyl Bis(methylthio)dithioacetate (39): bp 64–66 °C (1.5 × 10^{-2} mm); NMR δ 5.05 (s, 1 H), 2.7 (s, 3 H), 2.25 (s, 6 H).[31]

Compounds **31**, **32**, **34**, **35**, **37**, and **39** were also obtained, with similar yields, from the reactions of (*E*)- or (*Z*)-β-bromostyrene, (*E*)- or (*Z*)-dichloroethylene, and tetrachloroethylene with an excess of MeSNa (3.5, 5, and 8 equiv, respectively) at 90 °C for 6–8 h. The reactions were followed by GLC and TLC and then worked up as described above.

Dealkylation of Vinyl Alkyl Sulfides with Sodium. General Procedure. To a solution of the vinyl alkyl sulfide (0.01 mol) in HMPA (25 mL), stirred under nitrogen at 90 °C, small pieces of sodium (1.3 atoms for each alkyl thio group present in the molecule) were gradually added. Stirring was continued until all the sodium was dissolved and the starting product was consumed (2–6 h). The progress of the reaction was monitored by TLC and GLC. The reaction mixture was cooled at 0 °C in a

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thermostat and an excess of methyl, ethyl, or 2-propyl iodide (see Results and Discussion section) was added dropwise. The mixture was stirred at 0 °C for 2 h and then poured on water and extracted with ether. The ether was washed with water, dried, and evaporated. The reaction mixture was analyzed by GLC, TLC, and NMR, and the reaction products were isolated and purified by column chromatography on silica gel with light petroleum as eluant.

The results of the reactions carried out according to this procedure are described in the Results and Discussion section. The physical and NMR data of the products **13**, **22**, **27**, **29**, **31**, and **32**, obtained in this way, are reported above. These compounds were also obtained, with similar yields, starting from the β-bromostyrenes and the di-, tri-, and tetrachloroethylenes by reaction with MeSNa or Me_2CHSNa and then with sodium. Reaction conditions were identical with those described above for the vinylic substitutions and for the dealkylations of the vinyl alkyl sulfides with sodium.

Single-Crystal X-ray Work. Crystals of compounds **14** and **15** were mounted on a Philips PW 1100 automatic diffractometer, equipped with graphite monochromatized Mo Kα radiation. Compound **14** resulted to be monoclinic, space group $P2_1/n$ (from systematic extinctions), with lattice parameters a = 11.150 (3) Å, b = 10.294 (3) Å, c = 5.216 (3) Å, β = 91.54 (2)°. Assuming two molecules in the cell, the calculated density is 1.332 g·cm^{-3}, in agreement with the empirical value of 1.30 g·cm^{-3}, which can be computed according to the method of Immirzi and Perini.[35] Since the multiplicity of the general position in the space group is four, the molecule must lie on the inversion center, i.e., it must have the *E* configuration. Further structural work was deemed unnecessary.

Crystals of compound **15** are orthorhombic, acentric, space group $Pca2_1$, with cell constants a = 9.429 (3) Å, b = 5.928 (3) Å, c = 13.848 (3) Å; the calculated density is 1.578 g·cm^{-3} for four molecules in the unit cell, in agreement with the experimental value of 1.55 g·cm^{-3} obtained by flotation method. The intensity data of 503 independent reflections were measured; 377 of these, having $I \geq 3\sigma(I)$, were considered as "observed" and used in subsequent calculations. After the usual corrections, the structure was solved by direct multisolution method with the program MULTAN[36] and refined isotropically by the least-squares method to an R value of 0.14. The structural work was ended at this stage; the molecule in the solid state has the *E* configuration.

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Registry No. **1**, 588-72-7; **2**, 87373-88-4; **3**, 15436-06-3; **4**, 71338-94-8; **5**, 15436-11-0; **6**, 588-73-8; **7**, 80806-45-7; **8**, 35822-50-5; **9**, 87373-89-5; **10**, 37630-43-6; **11**, 156-60-5; **12**, 40588-88-3; **13**, 764-45-4; **14**, 87373-90-8; **15**, 49651-56-1; **16**, 57295-88-2; **17**, 42848-09-9; **18**, 87373-91-9; **19**, 87373-92-0; **20**, 156-59-2; **21**, 40588-74-7; **22**, 764-44-3; **23**, 87373-93-1; **24**, 53715-35-8; **26**, 66566-71-0; **27**, 40920-18-1; **28**, 39137-72-9; **29**, 13046-50-9; **31**, 20890-80-6; **31** sulfone, 18723-83-6; **32**, 20890-79-3; **34**, 87373-94-2; **34** disulfone, 87373-97-5; **35**, 87373-95-3; **35** disulfone, 33998-47-9; **37**, 87373-96-4; **39**, 77159-30-9; Me_2CHSNa, 20607-43-6; MeSNa, 5188-07-8; trichloroethylene, 79-01-6; tetrachloroethylene, 127-18-4.

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Structure Resonance Theory and Electrophilic Reactivity of Helicenes. Theoretical Correlations

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The partial rate factors of protodetritiation of four helicenes containing 26 different reaction sites are correlated with various reactivity indices, i.e., the Herndon structure count ratios, Dewar's reactivity numbers, and π cation localization energies. The results show that that Herndon structure count ratio is superior to the other two parameters in this application. Also, the data indicate that differences in positional reactivities in helicenes are influenced by both steric requirements and resonance energy differences between the π hydrocarbon and the respective intermediate. In addition, the observed correlations suggest that the regular increase in reactivity with ring size at a given site, except for the C(1) position, seems to be due to the effect of differences in resonance energies and not to the increased distortion of the aromatic rings as previously suggested.

Studies of protodetritiation of trihelicene (phenanthrene),[1] tetrahelicene,[2] pentahelicene,[3] and hexahelicene[4] in trifluoroacetic acid provided rate data for many positions of these compounds covering a reactivity range of about seven orders of magnitude (Chart I). These data are ideal to test the applicability of the simple parameterized molecular orbital and valence bond theories. In earlier applications the reactivities of many benzenoid hydrocarbons were successfully correlated with the algorithm ln SC(ratio), where SC(ratio) is the ratio of the principal resonance structures of a reaction intermediate (SC_I) to that of the reactant (SC_R). For example, the

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