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# REACTIONS OF HALOGENATED ACRYLONITRILE DERIVATIVES WITH ARYLSULFINATE SALTS

## A NOVEL CHAIN SHORTENING REACTION[1]

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**Abstract**—Reaction of α,β-dichloroacrylonitrile with arylsulfinate salts in refluxing ethanol gave high yields of arylsulfonylacetonitriles. A proposed intermediate, α-chloro-β-*p*-tolylsulfonylacrylonitrile can be isolated and can be converted to *p*-tolylsulfonylacetonitrile under the conditions of the reaction. β,β-Dichloroacrylontrile similarly gives acetonitrile derivatives on reaction with sulfinate salts.

NUCLEOPHILIC displacement of halide ions from the β-positions of α,β-unsaturated ketones and esters is greatly aided by the electron-accepting abilities of the CO groups.[2] Scotti and Frazza have recently reported that β-halocrylonitriles similarly are quite susceptible to nucleophilic attack. Reaction of β-chloroacrylonitrile with sodium *p*-tolylsulfinate was found to give β-*p*-tolylsulfonylacrylonitrile in high yield.[2b]

We recently reacted α,β-dichloroacrylonitrile with several arylsulfinate salts, expecting to obtain the α-chloro-β-arylsulfonylacrylonitriles. To our surprise, however, the reactions often resulted in shortening the acrylonitrile to give acetonitrile derivatives. Further investigation showed that other types of substituted acrylonitriles also gave acetonitrile, rather than acrylonitrile, derivatives on reaction with nucleophilic agents.

This paper reports several reactions of this type, and some observations about their mechanisms.

### *Reactions of sulfinate salts with α,β-dichloroacrylonitrile*

α,β-Dichloroacrylonitrile (I) was prepared by dehydrochlorination of α,β,β-trichloropropionitrile with quinoline.[3] The NMR spectrum of the product (in $CDCl_3$) suggested that both *cis* and *trans* isomers were produced, as had previously been concluded from polarographic studies.[3] Two different vinyl proton absorptions at τ 2·73 and τ 2·95, in the intensity ratio 4:1, were present in the spectrum. Comparison with the spectra of the *cis* and *trans* isomers of β-chloroacrylonitrile and β-*p*-tolylsulfonylacrylonitrile (Table I) led to the assignment of the lower field absorption to the isomer in which the nitrile group and β-hydrogen atom were *cis* to each other.[4] No

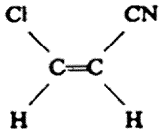
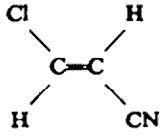
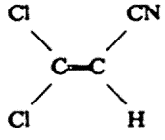
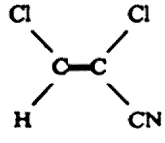
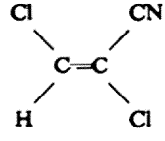
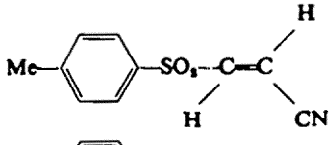
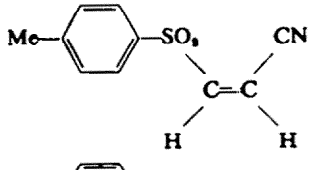
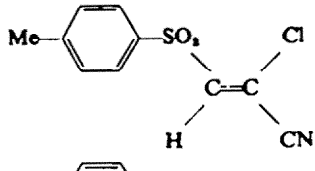
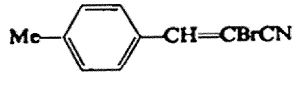
[1] Part of this work has been published as a preliminary communication: M. V. Kalnins and B. Miller, *Chem. & Ind.* 555 (1966).

[2a] N. K. Kotschetkov, *Chem. Tech.* 7, 518 (1955). Also, see Refs. in: [b] F. Scotti and F. J. Frazza, *J. Org. Chem.* 29, 1800 (1964).

[3] W. H. Jura and R. J. Gaul, *J. Am. Chem. Soc.* 80, 5402 (1958).

[4] H. Hogeveen, G. Maccagnani and F. Taddei, [*Rec. Trav. Chim.* 83, 937 (1964)] have shown that in β-arylsulfonylacrylic acids the CO group has a greater deshielding effect on a β-hydrogen *cis* to it than on one *trans* to it.

TABLE 1. VINYL PROTON NMR SPECTRA FOR SUBSTITUTED ACRYLONITRILES (IN $CDCl_3$)

| Compound | β α (—C=C—CN) Chemical shift, τ (ppm) α | β | J, (c/s) |
|---|---|---|---|
|  | 4·15 | 3·00 | 7·5 |
|  | 4·20 | 2·88 | 14·0 |
|  | 4·07 | — | |
|  | — | 2·73 | — |
|  | — | 2·95 | — |
|  | 3·47 | 2·69 | 15·8 |
|  | 3·97 | 2·93 | 11·5 |
|  | — | 2·66 (trans at 2·77?) | — |
|  | — | 2·63 | — |

attempt was made to separate the two isomers, since further work indicated that both isomers gave similar reactions with nucleophilic reagents.

Addition of I to one molar equivalent of sodium *p*-tolylsulfinate dihydrate (II) in refluxing ethanol gave, after 1 hr, 33–44% yields of *p*-tolylsulfonylacetonitrile (III). Compound III was identical with the reaction product of II with chloroacetonitrile.[5] The apparently low yields of III could be increased by raising the molar ratio of II to I. When I was added to 2 equivalents of II, III was obtained in 99% yield. III must, therefore, be obtained from both the *cis* and *trans* isomers of I.

The increase in the yield of III when more than one molar equivalent of II is used is presumably due to liberation of hydrogen chloride during the reaction, which converts one equivalent of sulfinate anion to the acid, as is shown in equation 1:

$$\underset{\text{I}}{\text{CHCl=CClCN}} + 2\,\underset{\text{II}}{\text{C}_7\text{H}_7\text{SO}_2\text{Na}} + \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} \longrightarrow \underset{\text{III}}{\text{C}_7\text{H}_7\text{SO}_2\text{CH}_2\text{CN}} + \text{C}_7\text{H}_7\text{SO}_2\text{H} + \text{C}_2\text{H}_5\text{OCH(=O)} + 2\,\text{NaCl} \quad (1)$$

Ethyl formate, the other organic product of the reaction, could be isolated from the reaction mixture by VPC.

Reaction of I with one molar equivalent of sodium benzenesulfinate, sodium *p*-chlorobenzenesulfinate, or sodium *p*-nitrobenzenesulfinate similarly gave the corresponding arylsulfonylacetonitriles in yields of 39–47%.

Several possible mechanisms can be conceived for formation of arylsulfonylacetonitriles from I. Perhaps the simplest path, formally, would be displacement of a chloride ion from the α-carbon of I, followed by reaction of the resulting sulfone with water or alcohol (Eq. 2). However, the evidence for the very high reactivity of

$$\text{I} + \text{RSO}_2^{\ominus} \longrightarrow \begin{matrix} \text{H} \\ \text{Cl} \end{matrix}\!\!>\!\text{C}=\text{C}\!<\!\begin{matrix} \text{SO}_2\text{R} \\ \text{CN} \end{matrix} \xrightarrow{\text{H}_2\text{O}} \text{HC}(=\text{O})\text{—CH}(\text{SO}_2\text{R})\text{CN} \xrightarrow{\text{EtOH}} \text{III} + (\text{C}_2\text{H}_5\text{OCH(=O)}) \quad (2)$$

β-haloacrylonitriles, as compared to vinyl halides lacking a strong electron-withdrawing group in the β-position,[2] is so strong that this mechanism should only be resorted to if all other paths have been ruled out.

Alternatively, I might react with solvent, rather than a sulfinate ion, to give chloroacetonitrile (Eq. 3), which then would react with sulfinate salts to give sulfonylacetonitriles. This path, however, can readily be shown to be incorrect. Compound

$$\text{I} + \text{H}_2\text{O} \xrightarrow{?} \text{HC}(=\text{O})\text{—CHCl—CN} \xrightarrow{\text{EtOH}} \text{ClCH}_2\text{CN} + \text{C}_2\text{H}_5\text{OCH(=O)} \quad (3)$$

I was recovered unchanged after one hour in refluxing aqueous ethanol. Addition of carboxylate salts to raise the pH of the solution above that of a solution of sulfinate salts had no effect. The initial reaction, therefore, must involve both I and II.

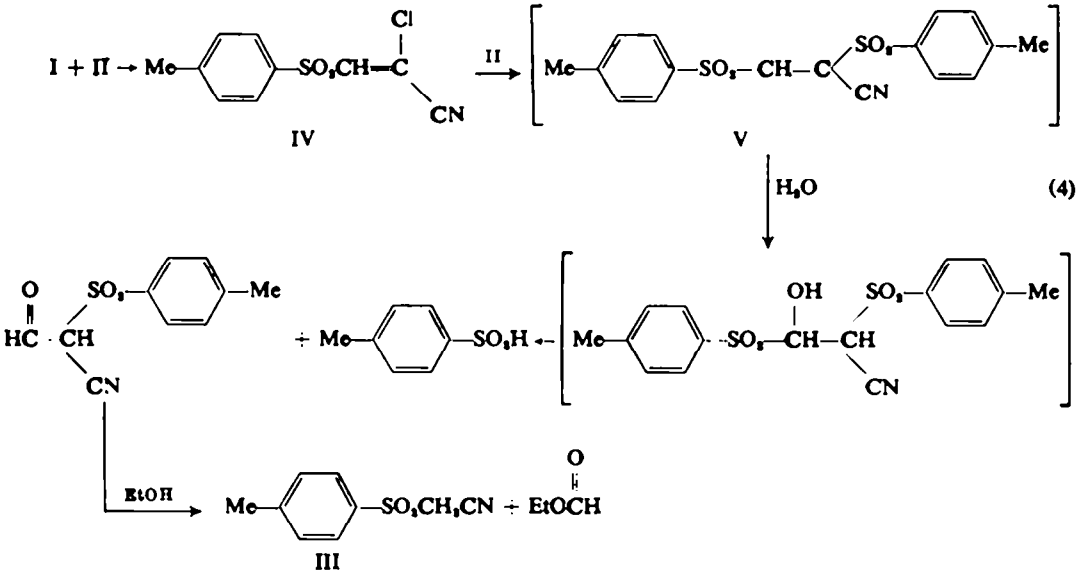
[5] J. Troeger and W. Hille, *J. Prakt. Chim.* 71, 226 (1905).

*Formation and reactions of α-chloro-β-p-tolylsulfonylacrylonitrile*

Since other paths seem quite improbable, the expected displacement of a chloride ion from the β-position of I to give α-chloro-β-p-tolylsulfonylacrylonitrile (IV) seems a necessary first step in formation of III. That this is, in fact, the case was demonstrated by isolation of a 44% yield of IV, together with a small amount of III, by slow addition of one equivalent of II to a solution of I in ethanol at 0°. Somewhat higher yields (61%) of IV could be obtained by addition of II to a solution of I in DMF.

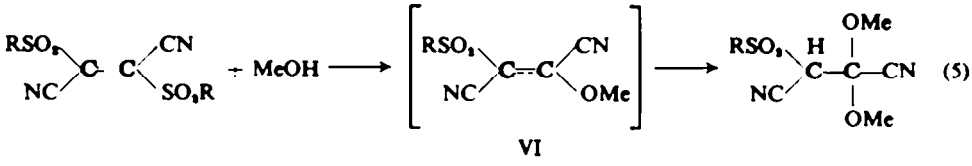
The geometry of IV is not certain. The crude product has a vinyl proton absorption at τ 2·66, and a smaller (ca. 10% of the intensity) peak at τ 2·77. The minor peak is eliminated on recrystallization. We are tentatively assuming the minor peak represents the geometrical isomer of IV, and are therefore assigning the *cis* H and CN geometry to IV, on the basis of the arguments used to assign structures to the dichloroacrylonitriles.

Reaction of IV with one molar equivalent of II in refluxing ethanol for ½ hr gave an 86% yield of III. Prolonged refluxing in aqueous ethanol in the absence of added II also resulted in the partial conversion of IV to III. The "uncatalyzed" reaction is presumably aided by *p*-toluenesulfinic acid produced as the reaction progresses.




The susceptibility of IV to nucleophilic attack is presumably due to the presence of the electron accepting sulfone group β- to the chlorine atom. The disulfonylcyanoethylene (V), which would be formed by replacement of chloride by II, should be readily attacked by alcohols or water. Martin has reported that sulfonyl groups in 1,2-dicyano-1,2-disulfonylethylenes are rapidly displaced by alcohols to give α,α-dialkoxy-β-sulfonylsuccinonitriles.[6] The monoalkoxy ethylene VI, which is most probably an intermediate in that reaction,[6] seems likely to be less reactive than V to nucleophiles, since the alkoxy group should increase the electron density at the double bond.

[6] E. L. Martin, *J. Am. Chem. Soc.* **85**, 2449 (1963).

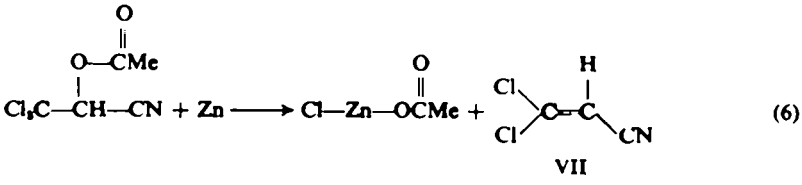


VI

*Preparation and reactions of β,β-dichloroacrylonitrile*

In view of the unexpected results obtained with α,β-dichloroacrylonitrile, it seemed of interest to study the reactions of II with β,β-dichloroacrylonitrile (VII). Compound VII was prepared by reduction of α-acetoxy-β,β,β-trichloropropionitrile with zinc. Reaction of VII with one molar equivalent of II in refluxing ethanol again gave III in 42% yield, comparable to the yield from reaction of II with I.

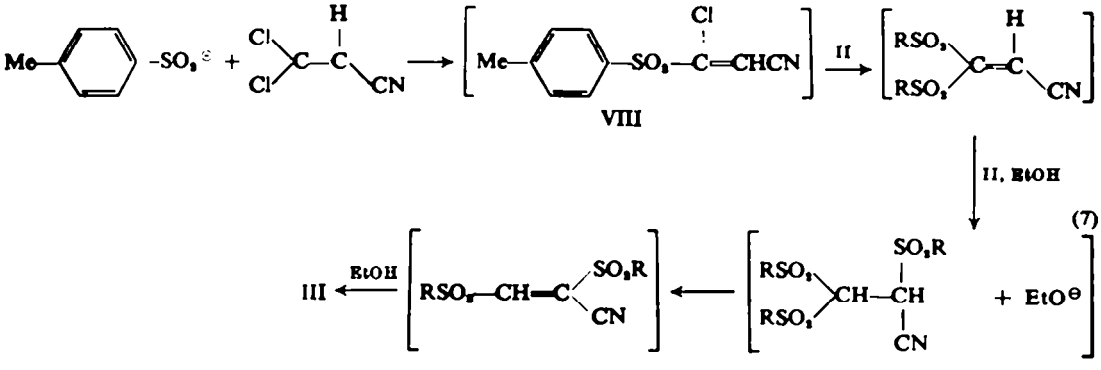
One possible mechanism for formation of III from VII is shown in Eq. 7. The presumed intermediate VIII could not be isolated from reaction of II and VII in ethanol. When II was added slowly to a solution of VII in DMF at 0°, however, an oily



VII

(6)

product was obtained which had a conjugated nitrile band at 4·5 μ in its IR spectrum. VPC analysis showed the product to be essentially free of VII, and to contain only about 10% of III. Refluxing the oily product with II in aqueous ethanol converted it completely to III. It seems probable, therefore, that VIII was a major constituent of that material.



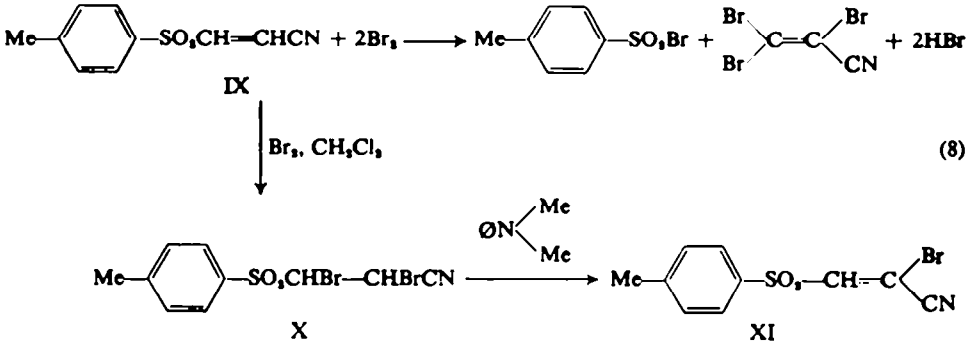
VIII

(7)

To confirm this hypothesis, we attempted to synthesize VIII by addition of chlorine to *trans*-β-*p*-tolylsulfonylacrylonitrile, (IX) followed by dehydrochlorination of the product. Despite several attempts in sealed tubes and in solvents, however, only starting material could be recovered. Addition of bromine to IX did occur, although the reaction was very slow. In one attempt to increase the rate of addition, IX was heated in excess bromine for 1 hr. The products of the reaction were *p*-tolylsulfonyl bromide and tribromoacrylonitrile. The desired dibromide X could be prepared by

allowing IX to stand in methylene chloride with one equivalent of bromine for 24 hr. The same dibromide (m.p. 89–91°) was obtained under the same conditions from *cis*-*p*-tolylsulfonylacrylonitrile. The *cis* IX was presumably isomerized to *trans* IX under the reaction conditions, possibly by addition of bromine atoms to the double bond.

Dehydrohalogenation of X with potassium t-butoxide in t-butanol or dimethylaniline in chloroform gave a monobromide with a vinyl proton peak at $\tau$ 2·63 in its NMR




spectrum. It was therefore considered to be the α-bromo-α-cyanoethylene XI, rather than the desired β-bromo isomer. Reaction of XI with II in refluxing ethanol again gave III in 43% yield, presumably by a path similar to Eq. 4.

## EXPERIMENTAL[1]

*Reaction of α,β-dichloroacrylonitrile with sodium p-tolylsulfinate*

(a) 1:1 *Molar ratio.* To a refluxing soln of sodium *p*-tolylsulfinate dihydrate (23·8 g, 0·10 mole) in 125 ml anhyd EtOH was added α,β-dichloroacrylonitrile (12·2 g, 0·10 mole). The reaction mixture was stirred under reflux for 1 hr and filtered while hot to remove NaCl. Evaporation of the solvent under vacuum left 6·93 g (35·5%) *p*-tolylsulfonylacetonitrile, m.p. 140–143°. Recrystallization from benzene gave colorless needles, m.p. 149·5–150·5°, undepressed by admixture with an authentic sample.[8]

Similar reactions with the appropriate sodium arylsulfinates gave *phenylsulfonylacetonitrile*,[8] m.p. 113–115 (39% yield); p-*chlorophenylsulfonylacetonitrile*,[8] m.p. 173–175° (41% yield); and p-*nitrophenylsulfonylacetonitrile*, m.p. (from EtOH) 171–173°, (42·5% yield). (Found: C, 42·8; H, 2·79; N, 12·2; S, 14·45. Calc. for $C_9H_6N_2SO_4$: C, 42·5; H, 2·67; N, 12·4; S, 14·2%.)

(b) 1:2 *Molar ratio.* The reaction between α,β-dichloroacrylonitrile and sodium *p*-tolylsulfinate dihydrate was carried out as in method A, except that 2 molar equivs of the salt were used to one of the nitrile. When worked up as in method A, the reaction gave a 99% yield of crude *p*-tolylsulfonyl acetonitrile, m.p. 145–147°.

*Preparation of α-chloro-β-p-tolylsulfonylacrylonitrile*

A soln of α,β-dichloroacrylonitrile (12·2 g, 0·10 mole) in 50 ml DMF was cooled to 0° and stirred. Sodium *p*-tolylsulfinate dihydrate (21·4 g, 0·10 mole) was added in small portions over a period of 20 min, while the temp was maintained below 1°. The reaction mixture was stirred for an additional 10 min, and then poured into 1 l. ice-water. The pale yellow ppt was filtered, washed with cold water, and dried under vacuum to give 14·8 g (61·2%) of solid, m.p. 88–90°. Two recrystallizations from pentane gave colorless crystals, m.p. 94–95°. (Found: C, 49·95; H, 3·35; Cl, 14·75; N, 5·97; S, 13·0. Calc. for $C_{10}H_8ClNO_2S$: C, 49·7; H, 3·31; Cl, 14·7; N, 5·80; S, 13·25%.)

A small portion (0·8 g) of the product was insoluble in pentane. It was identified as *p*-tolylsulfonylacetonitrile by comparison of IR spectra and mixed m.p.

[1] All m.p.s are corrected. NMR spectra were taken on a Varian A-60 spectrometer in $CDCl_3$ soln. Microanalyses by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

*Conversion of α-chloro-β-p-tolylsulfonylacrylonitrile to p-tolylsulfonylacetonitrile*

To a refluxing soln of α-chloro-β-*p*-tolylsulfonylacrylonitrile (2·0 g, 0·0083 mole) in 15 ml 95% EtOH was added sodium *p*-tolylsulfinate dihydrate (1·8 g, 0·084 mole). After ½ hr, the reaction mixture was cooled in ice and the solid product (1·4 g, 86%) m.p. 149–150°, was filtered and dried in air. It was identified as *p*-tolylsulfonylacetonitrile by its m.p. and IR spectrum.

*Preparation of β,β-dichloroacrylonitrile*

A soln of α-acetoxy-β,β,β-trichloropropionitrile[8] (25·0 g, 0·115 mole) in 100 ml THF was refluxed on a steam bath, and Zn dust (7·50 g, 0·115 mole) which had previously been washed with HCl was added in small portions through the top of the condenser. Vigorous ebullition followed each addition of Zn. The total addition time was 1·5 hr. Most of the solvent was then evaporated under vacuum and the residue quickly distilled at 2 mm press and a bath temp of 170° to give 37·0 g colorless fluid. This was redistilled at atm press to give 8·5 g (0·070 mole, 61%) of β,β-dichloroacrylonitrile, b.p. 139–142°. (Found: C, 29·5; H, 1·55; N, 11·7; Cl, 58·5. Calc. for $C_3HCl_2N$: C, 29·5; H, 0·83; N, 11·5; Cl, 58·2%.)

*Reaction of β,β-dichloroacrylonitrile with sodium p-tolylsulfinate dihydrate*

(a) *In ethanol.* β,β-Dichloroacrylonitrile (3·66 g, 0·030 mole) was added drop by drop to a soln of sodium *p*-tolylsulfinate dihydrate (6·43 g, 0·030 mole) in 30 ml refluxing abs EtOH. After refluxing for 1 hr, the hot reaction mixture was filtered to remove NaCl. The filtrate was cooled in ice. The resulting ppt was filtered off and dried in air to give 2·43 g (41·6%) *p*-tolylsulfonylacetonitrile, m.p. 148°.

(b) *In DMF.* Sodium *p*-tolylsulfinate dihydrate (2·65 g, 0·0125 mole) was added over a ½ hr period to a stirred soln of β,β-dichloroacrylonitrile (1·50 g; 0·0123 mole) in 20 ml DMF at 0°. The mixture was stirred for 15 min after the end of the addition. It was then poured into ice-water and extracted with $CH_2Cl_2$. The $CH_2Cl_2$ soln was washed twice with water, dried and evaporated to give 1·90 g yellow oil, which could not be crystallized. Its IR spectrum had a peak at 4·5 μ. VPC analysis on a 6 ft, 2% silicone oil column showed the product to contain less than 1% of 3,3-dichloroacrylonitrile, and about 10% of *p*-tolylsulfonylacetonitrile. The crude product was dissolved in 20 ml EtOH, sodium *p*-tolylsulfinate dihydrate (2·0 g) added, and the mixture refluxed for 1 hr. The hot soln was filtered to remove salt and cooled in ice. The pptd solid, m.p. 146–148°, weighed 1·70 g (71%) and was identified as *p*-tolylsulfonylacetonitrile by its IR spectrum.

*Preparation of α,β-dibromo-β-p-tolylsulfonylpropionitrile*

(a) *From* trans-p-*tolylsulfonylacrylonitrile. Trans-p*-tolylsulfonylacrylonitrile (5·0 g, 0·0242 mole) was suspended in 50 ml $CH_2Cl_2$. A soln of Br (4·10 g, 0·0256 mole) in 10 ml $CH_2Cl_2$ was added. The mixture was allowed to stand at room temp for 24 hr, by which time the color had faded to a light orange. Evaporation of the solvent left 8·90 g orange oil, which crystallized on scratching. Two recrystallizations from benzene–hexane gave 6·0 g (0·0164 mole, 68%) white crystals, m.p. 132–134°. (Found: C, 32·6; H, 2·49; N, 3·57; Br, 43·9. Calc. for $C_{10}H_9Br_2NO_2S$: C, 32·7; H, 2·45; N, 3·71; Br, 43·7%.)

(b) *From* cis-p-*tolylsulfonylacrylonitrile. cis-p*-Tolylsulfonylacrylonitrile was prepared by the method of Scotti and Frazza.[2b] Recrystallization from benzene–pentane gave the pure *cis*-sulfone as white needles, m.p. 87–88° (reported, m.p. 73–85°[2b]). Reaction of 10·0 g of the sulfone (0·0483 mole) with 8·0 g Br (0·050 mole) in 30 ml $CH_2Cl_2$ at room temp for 70 hr gave 11·5 g dibromide, m.p. 131–134° (from hexane), identical with the product obtained from the *trans*-sulfone.

*Reaction of* trans-p-*tolylsulfonylacrylonitrile with excess bromine*

A mixture of Br (9·5 g, 0·059 mole) and *trans-p*-tolylsulfonylacrylonitrile (2·0 g, 0·0097 mole) was refluxed on a steam bath for 2 hr. Evaporation of the excess Br left a brownish, evil-smelling, partly crystalline residue which was twice recrystallized from benzene to give 1·0 g (0·00425 mole, 44%) *p*-tolylsulfonyl bromide, m.p. 94–95° (reported,[9] m.p. 96°). Reaction of the bromide with

[8] A. Pinner and F. Fuchs, *Chem. Ber.* **10**, 1058 (1877).
[9] R. Otto and O. v. Gruber, *Liebigs Ann.* **142**, 98 (1867).

EtONa in EtOH gave ethyl *p*-tolylsulfonate, identical in IR spectrum and VPC retention times with an authentic sample.

The residual material from the recrystallization was chromatographed on Woelm neutral alumina, eluting with pentane–$CH_2Cl_2$. Evaporation of the solvent gave 0·70 g brown solid, which was recrystallized from benzene–hexane to give 0·6 g α,β,β-tribromoacrylonitrile (0·00207 mole, 21%) as pale yellow needles, m.p. 97–99°. (Found: C, 12·6; N, 4·64; Br, 82·1. Calc. for $C_3Br_2N$: C, 12·4; N, 4·84; Br, 82·3%.)

*Preparation of α-bromo-β-p-tolylsulfonylacrylonitrile*

(a) Dimethylaniline (1·0 g, 0·00828 mole) was added to a suspension of 3·0 g α,β-dibromo-β-*p*-tolylsulfonylpropionitrile (0·0082 mole) in 50 ml chf. The mixture became homogeneous after 10 min. It was refluxed for 2 hr, cooled, washed with dil HCl and dried over $MgSO_4$. Evaporation of the solvent left 2·0 g yellow oil, which was chromatographed through a short (1 inch) column of neutral alumina and eluted with $CH_2Cl_2$. Evaporation of the solvent gave a colorless oil which crystallized on scratching. Recrystallization from benzene gave 1·2 g (0·0042 mole, 51%) α-bromo-β-*p*-tolylsulfonylacrylonitrile, m.p. 89–91°. (Found: C, 41·8; H, 2·91; S, 11·2; Br, 27·8. Calc. for $C_{10}H_8NSO_2Br$: C, 42·1; H, 2·81; S, 11·2; Br, 28·0%.)

(b) A suspension of α,β-dibromo-β-*p*-tolylsulfonylpropionitrile (6·0 g, 0·0174 mole) in 50 ml t-butyl alcohol was cooled in ice and stirred while a soln of potassium t-butoxide (2·3 g, 0·0177 mole) in 50 ml t-butyl alcohol was slowly added. The mixture turned a deep brown at the start of the addition. At the end of the reaction, the mixture was dissolved in $CH_2Cl_2$, washed several times with water, dried and evaporated to give 0·78 g gummy solid. The product was quickly chromatographed through a thin pad of alumina and eluted with $CH_2Cl_2$ to give 0·4 g while solid. Recrystallization from hexane gave 0·20 g (0·00070 mole, 4%) solid, m.p. 87–89°. The IR spectrum and mixture m.p. showed the product to be identical with that from method A.

*Reaction of α-bromo-β-p-tolylsulfonylacrylonitrile with sodium p-tolylsulfinate dihydrate*

A mixture of sodium *p*-tolylsulfinate (0·75 g, 0·0035 mole) and α-bromo-β-*p*-tolylsulfonylacrylonitrile (1·0 g, 0·0035 mole) in 10 ml 95% EtOH was refluxed for 1 hr. The hot soln was filtered and the filtrate cooled in ice. The ppt (0·29 g, 43%) m.p. 143–145°, was identified as *p*-tolylsulfonylacetonitrile by its IR spectrum.