$$ClCH_2CH_2Cl + CN^- \longrightarrow ClCH_2CH_2CN + Cl^-$$

$$ClCH_2CH_2CN + CN^- \longrightarrow CH_2{=}CH{-}CN + HCN + Cl^-$$

$$CH_2{=}CHCN + HCN \longrightarrow NCCH_2CH_2CN$$

Cyanoethylation of hydrogen cyanide was found to be considerably slower than formation of acrylonitrile from 3-chloropropionitrile and cyanide ion. If separation of acrylonitrile from the reaction mixture at a rate greater than cyanoethylation of hydrogen cyanide could be accomplished, it should be possible to use this reaction as a preparative method for acrylonitrile.

Friedman and Shechter[3] have recently shown that the use of dimethyl sulfoxide as solvent greatly enhances the rate of cyanide ion reactions with alkyl halides. Ethylene dichloride, ethylene dibromide, and 1-bromo-2-chloroethane reacted with sodium cyanide in dimethyl sulfoxide in a system placed under vacuum which allowed the acrylonitrile to be flashed from the mixture as it was formed. The following results were obtained.

Ethylene dihalide	% Yield acrylonitrile
$ClCH_2CH_2Cl$	6.4
$ClCH_2CH_2Br$	45.0
$BrCH_2CH_2Br$	82.4

The pressure which could be placed on the system was dependent on the boiling point of the ethylene dihalide. With ethylene dibromide a much lower pressure was possible, resulting in faster rate of removal of acrylonitrile from the reaction mixture and thus higher yield.

Experimental

Rate of Reaction of Sodium Cyanide with Ethylene Dichloride in Anhydrous Methanol.—Sodium cyanide was dissolved in anhydrous methanol at room temperature to prepare an approximately saturated solution. The solution was filtered and added to 0.0500 mole of ethylene dichloride in a 100.0-ml. volumetric flask. Aliquots (10.0 ml.) of this solution were pipetted into separate flasks and these were placed into a constant temperature bath held at 50 ± 1°. At various time intervals a sample was removed and the cyanide ion concentration determined by titration with standard silver nitrate solution in the presence of ammonia and potassium iodide.[4] The following data were obtained.

Time, hr.	$[CN^-]$ mole/l.
0	1.088
28.5	1.009
48.0	0.940
148.0	.724
192.5	.652

From these data the approximate second-order rate constant was evaluated as 3.0×10^{-4} l. mole^{-1} hr.$^{-1}$.

Reaction of Sodium Cyanide with 3-Chloropropionitrile.—A saturated solution of sodium cyanide in methanol was prepared and added to 0.0500 mole of 3-chloropropionitrile in a 100.0-ml. volumetric flask at room temperature. The concentration of sodium cyanide was approximately 1.0 *M*. Immediately a precipitate began to form and after 5 min. the precipitation appeared to be complete. An aliquot of the liquid portion of the reaction mixture was analyzed for cyanide ion and the solution was found to be 0.946 *M* in cyanide ion. The mixture was filtered and the precipitate was found to be practically pure sodium chloride. Analysis of the liquid portion of the reaction mixture by vapor phase chromatography revealed that the solution contained no 3-chloropropionitrile but contained 0.0425 mole of acrylonitrile.

Preparation of Acrylonitrile from Ethylene Dibromide and Sodium Cyanide.—A flask was fitted with a stirrer, an inlet through which solid could be added in small portions, and a reflux condenser with the exit leading through a Dry Ice trap to a vacuum pump. In the flask were placed 500 ml. of dimethyl sulfoxide and 187.8 g. (1.00 mole) of ethylene dibromide. The mixture was heated to 100° and the pressure lowered until refluxing in the reflux condenser was vigorous (74 mm.). Solid sodium cyanide (25.8 g., purity 95%, 0.500 mole) was added in small portions during a period of 32 min. After addition was complete, the pressure was lowered and heating continued until there was nothing passing into the Dry Ice trap. From the Dry Ice trap was obtained 121.1 g. of liquid. By vapor phase chromatographic analysis of this liquid, it was found to be a solution of 10.9 g. (0.206 mole) of acrylonitrile in ethylene dibromide. This corresponds to 82.4% yield to acrylonitrile based on consumed sodium cyanide.

The same procedure carried out on 1-bromo-2-chloroethane and ethylene dichloride gave, respectively, 45.0 and 6.4% yield of acrylonitrile.

The column used for vapor phase chromatographic analysis was an 8 ft. × $^3/_{16}$ in., stainless steel tube packed with a composition of Celite and tricresyl phosphate which was 30% tricresyl phosphate. The area under the acrylonitrile peak in the chromatograms was measured with a planimeter and compared to a calibration curve.

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[3] L. Friedman and H. Shechter, *J. Org. Chem.*, **25**, 877 (1960).

[4] H. H. Willard and N. H. Furman, "Elementary Quantitative Analysis," D. Van Nostrand Co., Inc., Princeton, N. J., 1940, p. 186.

The Base-catalyzed Isomerization of Allyl to Propenyl Sulfides

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The fact that allyl sulfides will isomerize to their propenyl analogs under the influence of base has been shown previously by Tarbell and co-workers.[1,2] In view of recent investigation on the base-catalyzed isomerizations of allyl to propenyl ethers,[3–5] 1- to 2-olefins,[6] and allyl- to propenylamines,[7] it was of interest to extend the investigation on the allyl sulfide isomerizations. In particular, it was

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[1] D. S. Tarbell and M. A. McCall, *J. Am. Chem. Soc.*, **74**, 48 (1952).

[2] D. S. Tarbell and W. E. Lovett, *ibid.*, **78**, 2259 (1956).

[3] C. C. Price and W. H. Snyder, *ibid.*, **83**, 1773 (1961).

[4] T. J. Prosser, *ibid.*, **83**, 1701 (1961).

[5] D. M. Simons and J. J. Verbanc, *J. Polymer Sci.*, **44**, 303 (1960).

[6] A. Shriesheim, J. H. Hofmann, and C. A. Rowe, Jr., *J. Am. Chem. Soc.*, **83**, 3731 (1961).

[7] C. C. Price and W. H. Snyder, *Tetrahedron Letters*, **2**, 69 (1962).

TABLE I

THE BASE-CATALYZED ISOMERIZATION OF ALLYL TO PROPENYL SULFIDES

Sulfide	Base[a]	Equiv. base, moles C=C	Temp., °C.	t,[c] hr.	%[d] Yield	%[e] Isomerized	% *cis* Isomer
Allyl *n*-hexyl	KOH(86%)	2.8	80	4 days	..	>99	[g]
Allyl *n*-hexyl	KO*t*-Bu	0.93	80	28	..	>99	66 ± 14[f]
Allyl *n*-hexyl	NaO*t*-Bu	1.0	60	21	69.2	>99	59 ± 17[f]
Allyl *n*-hexyl	$Me_4\overset{+}{N}\overset{-}{O}H\cdot 5H_2O$	2.3	80	21	..	>95	[g]
Allyl *n*-hexyl	*n*-$Bu_4\overset{+}{P}\overset{-}{O}$*t*-Bu[b]	1.2	R.T.	24	..	>90	[g]
Allyl *t*-butyl	KO*t*-Bu	1.0	R.T.	24	..	>99	[h]
Allyl *t*-butyl	NaO*t*-Bu	1.0	R.T.	11 days	47.8	>99	[h]
Allyl *t*-butyl	KOH(86%)	1.2	80	4 days	..	>99	[h]
Diallyl	KO*t*-Bu	0.34	R.T.	1 month	37.1	>99	64.1[i]
Diallyl	KO*t*-Bu	.49	R.T.	22	45.5	>99	63.0[i]
Diallyl	KOH(86%)	.5	80	3 months	33.6	89.5	62.5[i]
Diallyl	NaO*t*-Bu	.51	R.T.	22	57.5	>99	60.1[i]

[a] The isomerizations generally were carried out in the absence of solvent or in some cases in 1,2-dimethoxyethane. Work-up of reaction mixtures generally was accomplished by addition of excess water followed by ether extraction of the organic product. The product then was recovered by distillation. [b] Prepared by mixing dimethoxyethane solutions of potassium *t*-butoxide and tetra *n*-butyl phosphonium iodide. The clear supernatant layer was used. [c] This was the total reaction time used and has no kinetic significance as such. [d] Includes recovered allyl and propenyl derivatives. [e] Calculated from the recovered allyl and propenyl derivatives. The allyl content was determined either by infrared (10.1-μ band) or by gas chromatography. [f] By gas chromatography (25% THEED on Chromosorb, column temperature = 130°). The large uncertainty was caused by the close proximity and assymmetric shape of the peaks. [g] The infrared spectra of these products were virtually superimposable on that of propenyl *n*-hexyl sulfide produced by isomerization with sodium *t*-butoxide suggesting that the *cis* contents were about the same as those produced by this base. [h] The *cis* content of the propenyl *t*-butyl sulfides was judged to be similar to that of the propenyl *n*-hexyl sulfides based on comparison of the intensities of the C—H out-of-plane bending vibrations at 15.15 μ (*cis*) and 10.64 μ (*trans*) with those in the *n*-hexyl derivative. [i] Calculated from the percentages of the three geometric isomers (*cis, cis; cis, trans;* and *trans, trans*) obtained in each isomerization as determined by gas chromatography.

TABLE II

PHYSICAL CONSTANTS OF ALLYL AND PROPENYL SULFIDES[a]

Sulfide	B.p. °C.	P, mm.	$n^{20}D$	d^{20}_4	MR (calcd.)	MR (obsd.)
Allyl *n*-hexyl[b]	98–99	21	1.4689	0.855	51.27	51.55
Propenyl *n*-hexyl	88	10	1.4772	.857	51.27	52.21
Allyl *t*-butyl[c]	143	Atm.	1.4633	.842	42.03	42.62
Propenyl *t*-butyl	143–145	Atm.	1.4706	.844	42.03	43.10
Diallyl	69.5–69.8	76	1.4909	.894	36.93	36.95
Dipropenyl	60–61	28	1.5112	.897	36.93	38.12
cis,cis-Dipropenyl	...	..	1.5095[d]	...		
cis,trans-Dipropenyl	...	..	1.5112[d]	...		
trans,trans-Dipropenyl	...	..	1.5075[d]	...		

[a] See ref. 2 for comparison. [b] Prepared by the procedure described in ref. 2. [c] Prepared by displacement of sodium *t*-butyl mercaptide on allyl bromide. The sodium *t*-butyl mercaptide was prepared by cleavage of di-*t*-butyl disulfide with sodium metal in 1,2-dimethoxyethane solvent. [d] Determined at 25°.

TABLE III

INFRARED AND ULTRAVIOLET ABSORPTION OF PROPENYL SULFIDES

	Infrared absorption (μ)			Ultraviolet absorption[c]	
	C=C stretching	C—H out-of-plane		λ_{max},	ϵ_{max},
Sulfide		*cis*	*trans*	(mμ)	(l./mole-cm.)
Propenyl *n*-hexyl	6.19 (w)[a]			225, 249	5800, 3120
cis-Propenyl *n*-hexyl		15.15 broad			
trans-Propenyl *n*-hexyl			10.71		
Propenyl *t*-butyl	6.20 (w)[a]	15.15 broad	10.64	222, 248	4470, 3240
Dipropenyl	6.15 sh, 6.20 (w–m)[a]			240, 253 sh	10360, 8520
cis,cis-Dipropenyl	6.22 (w–m)[b]	15.12, 10.72[d]		239, 257 sh	10160, 8600
cis,trans-Dipropenyl	6.17, 6.23 (m–s)[b]	15.17	10.72, 13.32[d]	237, 250 sh	12920, 10360
trans,trans-Dipropenyl	6.17 (w)[b]		10.73	243, 260 sh	9110, 7600
Divinyl				240, 259	8150, 7130[e]

[a] 1,2-Dimethoxyethane solvent. [b] Carbon disulfide solvent. [c] In absolute ethanol. [d] The 13.32-μ band appears to be characteristic of the *cis–trans* isomer, whereas the 10.72-μ band is associated with all three geometric isomers. [e] C. E. Scott and C. C. Price, *J. Am. Chem. Soc.*, **81**, 2627 (1959), report values for ϵ_{max} five times the true values. The values reported in Table III have been reproduced many times on gas chromatographically pure divinyl sulfide samples and are in agreement with values reported by K. K. Georgieff and A. Dupre, *Can. J. Chem.*, **37**, 1104 (1959). We are indebted to Dr. Eugene Chang for preparing samples of divinyl sulfide. sh = shoulder; w = weak; s = strong; m = medium.

desired to determine the amounts of *cis* and *trans* isomers produced in these isomerizations. A mechanism proposed previously[3] for the high *cis* specificity in base-catalyzed isomerization of allyl to propenyl ethers would predict that considerably less stereospecificity might be expected in the isomerization of the corresponding sulfides to their propenyl isomers. This would also be in accord with the carbanion mechanism for allyl sulfide rearrangement proposed earlier.[2]

$$\mathrm{CH_2{=}CH{-}CH_2{-}S{-}R \xrightarrow{\text{Base}} CH_3{-}CH{=}CH{-}S{-}R}$$
$$\mathrm{R} = n\text{-hexyl},\ t\text{-butyl, allyl}$$

The three sulfides investigated were found to be isomerized readily by various basic catalysts which included 86% powdered potassium hydroxide, tetramethylammonium hydroxide, and sodium and potassium *t*-butoxides. The *t*-butoxides appeared to be greatly superior to 3.7 molar sodium ethoxide in ethanol at reflux which Tarbell and Lovett[2] had used. For example, diallyl sulfide reacted exothermically (the temperature of the reaction mixture rose from 25 to 60–70° almost immediately upon mixing) with 1 equivalent of potassium *t*-butoxide in 1,2-dimethoxyethane solvent to produce dipropenyl sulfide, b.p. 59–61° (27 mm.), in 45.5% yield after standing overnight at room temperature. Sodium *t*-butoxide did not react to produce any appreciable exotherm under the same conditions, but still afforded complete rearrangement upon standing overnight (dipropenyl sulfide was isolated in 57.7% yield).

Undoubtedly, some of the sulfides were lost by evaporation into the slow stream of nitrogen under which the reactions were carried out. To check this point a few rearrangements were carried out in sealed ampoules and the amounts of propenyl sulfides formed were determined by infrared examination of the double bond absorption intensity. In all cases, the propenyl sulfide content corresponded to yields of better than 90% when referred to the extinction coefficients of known pure samples of the given propenyl sulfide.

Of more immediate interest are the observed *cis* and *trans* contents of the rearranged sulfides. These results are presented in Table I. It can be seen that in all cases examined considerable amounts of *trans* isomers are formed.

It was of interest to determine whether the constant 60–65% *trans* content was the equilibrium *cis–trans* ratio for the propenyl sulfides studied. Samples of propenyl *n*-hexyl and propenyl *t*-butyl sulfides were heated with mercuric acetate or concentrated hydrochloric acid, but no change in *cis* content (as judged by infrared absorption at 15.15 μ *vs.* the *trans* 10.71-μ band) was noted. Mercuric acetate was previously noted as being a particularly effective catalyst for equilibrium *cis–trans* interconversion with the corresponding propenyl ethers.[8] Either these catalysts were ineffective for the sulfides or the *cis–trans* mixture subjected to treatment was already at the equilibrium *cis–trans* ratio.

Separation of the three geometric isomers of dipropenyl sulfide was accomplished in large scale [30-ft. column packed with 25% poly(ethylene oxide) E-9000 on Chromosorb, column temperature = 140°] so that refractive indices and infrared and ultraviolet spectra could be obtained (Tables II and III). Separation of the *cis* and *trans* isomers of propenyl *t*-butyl sulfide could not be made with 6-ft. columns packed with a variety of packing materials at 100° column temperature.

Physical constants and infrared and ultraviolet absorption data agree with those reported previously.[2] In the isomerization of diallyl sulfide under our conditions, no 3-mercapto-1,5-hexadiene was ever isolated in appreciable quantities from the basic extracts obtained in the work up of the isomerization mixtures. This material had been obtained by Tarbell and Lovett[2] in an isomerization carried out with sodium ethoxide in ethanol.

[8] W. H. Snyder, Ph.D. thesis, University of Pennsylvania, 1961.

The Nature of the Reaction of 2-Methylpyridine with Aniline and N-Methylaniline

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Recently it was necessary to prepare mixtures of aniline in 2-methylpyridine. The observation that there was a considerable amount of heat produced on mixing these amines raised a point of curiosity regarding the nature of the molecular interaction.

There is evidence from infrared studies that aniline does not hydrogen bond to itself.[1] However, 2-methylpyridine is about one hundred times as strong a base as aniline and might serve as an acceptor base for the aniline amine hydrogens. Further possibilities for interactions also exist. While 2-methylpyridine does not have any hydrogens bonded to nitrogen, the hydrogens of the methyl groups are sufficiently acidic for the compound to take part in aldol-like condensations. Thus, the possibility of interactions of these methyl hydrogens with the aniline can not be ruled out. Finally, the possibilities also exist that charge transfer complexes or simple dipole–dipole inter-

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[1] L. J. Bellamy and R. L. Williams, *Spectrochim. Acta*, **9**, 341 (1957).