

crystallized when the oil was dissolved in ethanol. Removal of alcohol and chromatography of the residue afforded two solid fractions. The first, after recrystallization from alcohol, afforded 0.25 g. (50.8%) of benzyl thiocyanate, m.p. 39–41°. The second fraction, upon recrystallization from alcohol, gave an additional 0.19 g. (15.4%) of the thiocarbamate ester derivative.

**Methyl 6-Phenyl-4,5-dithiahexanoate (XIV).**—When 1.0 g. (4.13 mmoles) of XIV was cleaved under the usual conditions 0.31 g. (33.8%) of N,N-diphenylcarbamylnitrile, m.p. 124–125°, was obtained. The nitrile was obtained in 91.5% yield when N,N-diphenylcarbanyl chloride and sodium cyanide were allowed to react under the cleavage conditions. Removal of ether afforded 1.57 g. of an oil consisting of 13.4% methyl  $\beta$ -thiocyanopropionate and 12.2% benzyl thiocyanate (ethyl phenylacetate; 140°; 235 cc./min.; 49 and 96 sec.).

The remaining oil was chromatographed on alumina and afforded four solid fractions. The first, recrystallized from petroleum ether (30–60°), yielded 0.35 g. (69.4%) of dibenzyl disulfide. The second, recrystallized from ethanol, gave 0.2 g. (21.8%) of N,N-diphenylcarbamylnitrile. Recrystallization of the third and fourth fractions from eth-

anol afforded 0.11 g. (8.3%) of the thiocarbamate derivative of benzyl mercaptan, m.p. 120–123°, and 0.14 g. (10.7%) of the derivative of methyl  $\beta$ -mercaptoacetate, m.p. 95–96°. Mixture melting points with authentic samples<sup>10</sup> were not depressed.

**Preparation of Methyl  $\beta$ -Thiocyanopropionate.**—The ester used for the calibration curve in the preceding experiment was prepared in 82.1% yield from methyl  $\alpha$ -bromopropionate and potassium thiocyanate; b.p. 98° at 3 mm.,  $n_D^{25}$  1.4770,  $d_4^{25}$  1.1913.

*Anal.* Calcd. for  $C_6H_7NO_2S$ : C, 41.36; H, 4.86; N, 9.65; S, 22.09. Found: C, 41.55; H, 4.97; N, 9.67; S, 22.16.

**Methyl 5,5-Dimethyl-3,4-dithiahexanoate (XV).**—Trituration of the oil, resulting from the cleavage of 1.0 g. (5.15 mmoles) of XV with ether, afforded 0.80 g. (70.2%) of N,N-diphenylcarbamylnitrile. Analysis of the residue in the vapor fractometer indicated only unchanged disulfide was present (140°; 235 cc./min.; 43 sec.). Distillation of the residue yielded 0.79 g. (79%) of XV,  $n_D^{25}$  1.4987; reported<sup>1</sup>  $n_D^{25}$  1.4985. The residue from the distillation was recrystallized from ethanol and afforded an additional 0.20 g. (17.5%) of the carbamylnitrile.

[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORY, THE UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, N. C.]

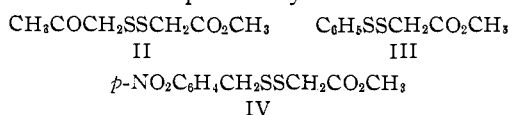
## The Chemistry of Aliphatic Disulfides. III.<sup>1</sup> Formation of Sulfides During Cleavage by Cyanide Ion<sup>2</sup>

BY RICHARD G. HISKEY AND F. I. CARROLL<sup>3,4</sup>

RECEIVED MAY 17, 1961

Cyanide ion cleavage of three unsymmetrical disulfides yield unsymmetrical sulfides as the major product and, in addition, small amounts of thiocyanates and trapped mercaptans. The more stable mercaptide is preferentially produced. Formation of sulfide occurs as the result of a secondary reaction between mercaptide and thiocyanate formed in the initial cleavage. Evidence is presented for the equilibrium nature of the reaction. Possible mechanisms are discussed.

The direction of cyanide ion cleavage of several unsymmetrical aliphatic disulfides has been found<sup>1</sup> to be related to the stability of the mercaptide ion produced: the mercaptide of greater anionic stability and the corresponding alkyl thiocyanate predominate. In order to provide a more thorough test of this proposal,<sup>5,6</sup> substrates containing a potential mercaptide of stability equal to or greater than the previously used sodium carboxymethyl mercaptide (I) were desirable. Thus methyl 6-keto-3,4-dithiaheptanoate (II), " $\Delta pK_a$ " 0.06,<sup>7</sup> methyl 4-phenyl-3,4-dithiabutanoate (III), " $\Delta pK_a$ " 1.28, and methyl 5-(4-nitrophenyl)-3,4-dithiapentanoate (IV) were cleaved using the general conditions previously described.<sup>1</sup> The re-



sults, reported in Table I, were obtained from ex-

(1) Part II, R. G. Hiskey and F. I. Carroll, *J. Am. Chem. Soc.*, **83**, 4644 (1961).

(2) Supported in part by a Fredrick Gardner Cottrell Grant from the Research Corporation.

(3) Abstracted from the Ph.D. dissertation of Mr. F. I. Carroll, June, 1961.

(4) Tennessee Eastman Corp. Fellow, 1959–1960; National Science Foundation Coöperative Fellow, 1960–1961.

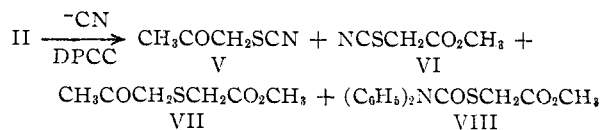
(5) O. Foss, *Acta Chem. Scand.*, **4**, 401 (1950).

(6) (a) A. J. Parker and N. Kharasch, *J. Am. Chem. Soc.*, **82**, 3071 (1960); (b) A. J. Parker and N. Kharasch, *Chem. Revs.*, **59**, 583 (1959).

(7) The  $pK_a$ 's of the various mercaptans are recorded in ref. 1, Table II.

periments involving small amounts of the disulfides or mercaptides and thiocyanates. The yields reported undoubtedly represent minimum values and must be considered qualitative. Additional products may well be formed.

Treatment of II with cyanide ion (Table I, a) afforded approximately equal amounts of thio-cyanoacetone (V) and methyl thiocanoacetate (VI) as would be expected from a consideration of the  $\Delta pK_a$  value. The major product of reaction was, however, methyl 5-keto-3-thiahexanoate (VII) obtained in 39.7% yield together with a similar amount of sodium thiocyanate and unreacted N,N-diphenylcarbanyl chloride (DPCC). A 16.1% yield of the N,N-diphenylthiocarbamate derivative of methyl mercaptoacetate (VIII) was isolated although no derivative of mercaptoacetone was obtained, presumably due to oxidation or dimerization.



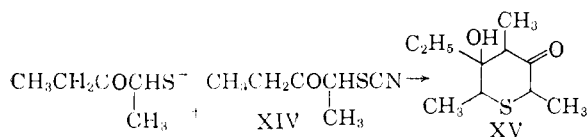
The cleavage of IV (Table I, e) provided 40.5% of sodium thiocyanate and 35.3% of recovered trapping agent. Although no pure sulfide was obtained, a liquid fraction with an infrared spectrum virtually identical to authentic sulfide was isolated by elution chromatography. The absence of VI was indicated by the vapor fractogram of the reaction mixture. The di-*p*-nitrobenzyl disulfide pro-

TABLE I  
 PRODUCTS OBTAINED FROM CYANIDE CLEAVAGE OF DISULFIDES AND THE REACTION OF MERCAPTIDES WITH ALKYL THIOCYANATES

Reaction	$\frac{\%}{(\text{C}_6\text{H}_5)_2\text{NCOSR}}$	$\frac{\%}{(\text{C}_6\text{H}_5)_2\text{NCOSR}'}$	$\frac{\%}{\text{RSCN}}$	$\frac{\%}{\text{R}'\text{SCN}}$	$\frac{\%}{\text{NaSCN}}$	$\frac{\%}{\text{RSR}'}$	$\frac{\%}{(\text{C}_6\text{H}_5)_2\text{NCOCl}}$	$\frac{\%}{\text{RSSR}}$
(a) II + $-\text{CN}$ R = $\text{CH}_3\text{COCH}_2-$ R' = $\text{CH}_3\text{O}_2\text{CCH}_2-$		16.1	7.4	14.2	42	39.7	26.8	
(b) III + $-\text{CN}$ R = $\text{C}_6\text{H}_5-$ R' = $\text{CH}_3\text{O}_2\text{CCH}_2-$	29.2	11.4	12.5	22.4	39.9	39.5	38	19.7
(c) RS $^-$ + RSCN X VI	11.6	7.8	7.1	31.7	47.9	31.2	37.9	4.0
(d) RSCN + R'S $^-$ XIII I	17.5	7.1	11.5	15.7	47.9	33.4	8.3	19.8
(e) IV + CN R = $p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2-$ R' = $\text{CH}_3\text{O}_2\text{CCH}_2-$		23.6		0.0	40.5		35.3	48.7
(f) RSCN + R'S $^-$ IX I		4.5			33.8		35.3	32.5

duced (48.7%) presumably resulted from the instability of the *p*-nitrobenzyl thiocyanate (IX) formed in the reaction. The formation of IX as the predominant thiocyanate is in agreement with the fact that no VI could be detected and that only VIII (23.6%) was obtained. Although the  $pK_a$  of *p*-nitrobenzyl mercaptan is not known, cleavage<sup>1</sup> of the same substrate without a nitro group, methyl 5-phenyl-3,4-dithiapentanoate, produced only 4.15% VI and thus the possibility that cleavage occurred in a single direction in the case of IV is not unreasonable.

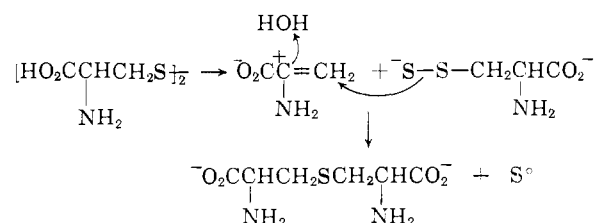
Fission of III with cyanide ion (Table I, b) also produced the more stable anion, sodium phenyl mercaptide (X) (Fig. 1). The *N,N*-diphenylthiocarbamate derivative of thiophenol (XII) and VIII were obtained in a ratio of 2:1 and the yields of phenylthiocyanate (XIII) and VI were also in accord with this ratio. The unsymmetrical sulfide, methyl 3-phenyl-3-thiopropanoate (XI), was again the predominant product in 39.5% yield. Thus despite the fact that the formation of the more stable mercaptide and corresponding thiocyanate is the favored possibility, the ultimate course of the reaction is apparently governed by nature of the primary cleavage products. Sulfide formation was observed only when an alkyl thiocyanate containing a labile  $\alpha$ -carbon atom (V, IX) or a highly nucleophilic mercaptide ion (X) was produced. In agreement with this, the cyanide ion cleavage of several symmetrical aliphatic  $\alpha$ -keto disulfides, has been shown<sup>8</sup> to result in sulfide formation. Also when 2-thiocyano-3-pentanone (XIV) was treated with the corresponding mercaptide, the cyclic sulfide XV and thiocyanate ion were obtained.<sup>8</sup>



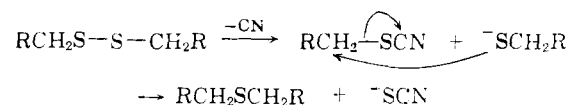
The only other example of this transformation is the conversion of free or combined cystine to lan-

(8) F. Asinger, M. Thiel and W. Schafer, *Ann.*, **637**, 146 (1960).

thionine<sup>9</sup> by cyanide ion in aqueous solution or dilute alkali. It has been suggested that the reaction occurs by either: (a)  $\beta$ -elimination of an alkylthiolsulfenate anion<sup>10</sup> followed by loss of sulfur and



recombination of the olefin and cysteine mercaptide; or (b) by a secondary bimolecular displacement reaction between the equilibrium mixture of primary products formed by the nucleophile.<sup>6b</sup> The present data are in accord with the latter proposal.



The lability of the  $\beta$ -carbon atom in cystine presumably is increased by anchimeric assistance of the nitrogen atom. As previously mentioned, however, the formation of lanthionine from the alkali cleavage of cystine probably follows a different course.<sup>11</sup>

Since XI was cleanly produced from III and a reasonable material balance could be obtained, this reaction was investigated in more detail. Consideration of the proposed mechanism for nucleophilic cleavage of the sulfur-sulfur bond<sup>5,6</sup> suggested that a reaction between VI and X in the presence of *N,N*-diphenylcarbonyl chloride should afford the same products obtained from cleavage of III; however, a similar experiment involving I and XIII should give mainly VIII and unreacted

(9) M. J. Horn, D. B. Jones and S. J. Ringel, *J. Biol. Chem.*, **138**, 141 (1941).

(10) D. S. Tarbell and D. P. Harnish, *Chem. Revs.*, **49**, 1 (1951); J. M. Swan, *Angew. Chem.*, **68**, 215 (1956); *Nature*, **179**, 965 (1957).

(11) J. P. Danehy and J. A. Kreuz, *J. Am. Chem. Soc.*, **83**, 1109 (1961).

XIII. As anticipated, the reaction products obtained from treatment of VI with X were identical to those obtained from III (Table I, c). The lower amount of products in the experiments involving added mercaptides may arise from the addition of insufficient mercaptide since the limiting reagent in all cases was the mercaptide ion. However, when XIII and I (Table I, d) were allowed to react in the presence of trapping agent *the same products in comparable yields were isolated*. This unexpected result indicated that the products from the previous cleavage reactions<sup>1</sup> probably resulted from thermodynamic control of the reaction. Therefore, the cleavage reactions studied involve a mercaptide reaction which is *faster than the reaction of mercaptide with N,N-diphenylcarbonyl chloride*. The fact that the same amount of the 2,4-dinitrophenylthioether of I was obtained when methyl 5-phenyl-3,4-dithiapentanoate was cleaved in the presence of 2,4-dinitrochlorobenzene<sup>1</sup> suggests that this reagent may also react relatively slowly with the displaced mercaptide. When *p*-nitrobenzyl thiocyanate was treated with I under the same conditions a similar result was obtained (Table I, f).

These observations are consistent with at least two mechanisms: (a) The one previously suggested,<sup>5,6</sup> providing the reactions ( $k_1$  and  $k_2$ ) between the primary products to regenerate III are very fast (Fig. 1); or (b) a process involving initial

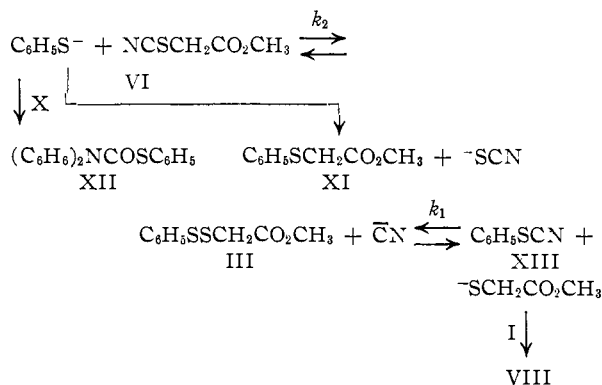


Fig. 1.

cleavage *in a direction as yet undetermined*, followed by rapid reversible recombination of the primary products to form the intermediate XVI. The intermediate would then exist in rapid equilibria with the primary cleavage products (Fig. 2). Path a would lead to the observed equilibrium mixture of primary products *via* III while these products could be generated in path b through XVI. The present data do not allow a decision between the two possibilities. Experiments designed to clarify this point are in progress.

#### Experimental<sup>12</sup>

**Methyl 6-keto-3,4-dithiaheptanoate (II)** was prepared by the sulfenyl-thiocyanate method<sup>13</sup> in 34% yield, b.p. 99.5° at 0.2 mm.,  $n_D^{25}$  1.5218,  $d_4^{25}$  1.2575; *MR* calcd. 46.80, found 47.11.

*Anal.* Calcd. for  $\text{C}_6\text{H}_{10}\text{O}_3\text{S}_2$ : C, 37.10; H, 5.19; S, 33.01. Found: C, 37.13; H, 5.14; S, 32.98.

(12) Boiling points and melting points are uncorrected. Elemental analysis by Micro Tech Laboratories, Skokie, Ill.

(13) R. G. Hiskey, F. I. Carroll, R. M. Babb, J. O. Bledsoe, R. T. Puckett and B. W. Roberts, *J. Org. Chem.*, **26**, 1152 (1961).

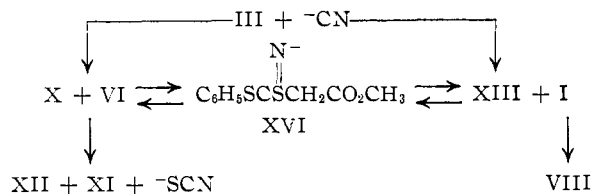


Fig. 2.

**Methyl 6-phenyl-3-carbomethoxy-4,5-dithiahexanoate** was obtained in 96% yield by treatment of 6-phenyl-3-carboxy-4,5-dithiahexanoic acid<sup>13</sup> with diazomethane; b.p. 82° at 0.005 mm.,  $n_D^{25}$  1.1716, m.p. 38–39°.

*Anal.* Calcd. for  $\text{C}_{13}\text{H}_{16}\text{O}_4\text{S}_2$ : C, 52.03; H, 5.33; S, 21.36. Found: C, 52.26; H, 5.57; S, 21.34.

**Methyl 4-Phenyl-3,4-dithiabutanoate (III)** was obtained in 46.4% yield,<sup>13</sup> b.p. 125° at 0.5 mm.,  $n_D^{25}$  1.5892,  $d_4^{25}$  1.2367; *MR* calcd. 58.04, found 58.42.

*Anal.* Calcd. for  $\text{C}_9\text{H}_{10}\text{O}_2\text{S}_2$ : C, 50.44; H, 4.70; S, 29.92. Found: C, 50.58; H, 4.58; S, 30.04.

**Cyanide Cleavage of Methyl 6-Keto-3,4-dithiaheptanoate (II).**—The cleavage of II was conducted in the manner previously described<sup>1</sup> using 1.0 g. (5.15 mmoles) of disulfide and 1.19 g. (5.15 mmoles) of *N,N*-diphenylcarbonyl chloride. Removal of acetonitrile afforded an oil which gave 0.175 g. (42%) of sodium thiocyanate when treated with ether. The residue (2.00 g.) obtained from the filtrate consisted of 14.2% of VI and 47.1% of VII (ethyl phenylacetate; 252 cc./min.; 49 sec. and 132 sec.). The sulfide and thiocyanacetone exhibited the same retention times under the vapor phase chromatography conditions. The percentage of the two components was determined by quantitative infrared analysis using the 2150  $\text{cm}^{-1}$  thiocyanate absorption peak to distinguish the two compounds. The analysis indicated 7.4% of V was present and thus the actual yield of VII was 39.7 ± 3%. Authentic VI<sup>14a</sup> and VII,<sup>14b</sup> used to obtain the calibration curves, were prepared as described. Chromatography of the filtrate on alumina gave 0.32 g. (26.8%) of *N,N*-diphenylcarbonyl chloride, m.p. 83–84°, and 0.25 g. (16.1%) of VIII, m.p. 106–110°.

**Cyanide Cleavage of Methyl 4-Phenyl-3,4-dithiabutanoate (III).**—Cleavage of 1.0 g. (4.65 mmoles) of III afforded 0.15 g. (39.9%) of sodium thiocyanate. The vapor fractogram of the remaining residue (2.00 g.) indicated the presence of 39.5% XI (ethyl phenylacetate; 140°; 235 cc./min.; 106 sec.), 12.5% of XIII<sup>15</sup> and 22.4% of VI (ethyl benzoate; 110°; 265 cc./min.; 83 sec. and 127 sec.).

Chromatography of the residue afforded four fractions which were recrystallized and identified by mixture melting point with authentic samples as: 0.10 g. (19.7%) of diphenyl disulfide, m.p. 60–61°; 0.41 g. (38%) of *N,N*-diphenylcarbonyl chloride; 0.40 g. (29.2%) of XII<sup>16</sup>; and 0.16 g. (11.4%) of VIII.

**Methyl 3-Phenyl-3-thiopropionate (XI).**—The sulfide, used for the calibration curve in the previous experiment, was obtained in 75.4% yield from sodium phenyl mercaptide and methyl bromoacetate; b.p. 87–90° at 0.3 mm.,  $n_D^{25}$  1.5570; reported<sup>17</sup> 262–263° at 760 mm.,  $n_D^{25}$  1.5569.

**Reaction of VI with X.**—The mercaptide was prepared in the following manner. To 1 ml. of methanol containing 4.65 mmoles of sodium methoxide was added 0.512 g. (4.65 mmoles) of thiophenol. The mercaptide, precipitated with 20 ml. of dry ether, was washed several times by decantation with ether and dissolved in 25 ml. of acetonitrile. The mercaptide solution was added to 1.08 g. (4.65 mmole) of *N,N*-diphenylcarbonyl chloride and 0.61 g. (4.65 mmole) of VI in 75 ml. of acetonitrile. The stirred reaction mixture was kept at 45–50° for 10 hr. under a nitrogen atmosphere.

Repetition of the isolation procedure used in the cleavage reaction of III afforded 0.18 g. (47.9%) of sodium thiocyanate and 1.80 g. of residue. The vapor fractogram

(14) (a) J. Tcherniac, *J. Chem. Soc.*, **115**, 1071 (1919); (b) E. A. Fehnel and A. P. Paul, *J. Am. Chem. Soc.*, **77**, 4241 (1955).

(15) The phenyl thiocyanate used for the calibration curve was prepared in 23% yield by the method of L. Gattermann and W. Haussknecht, *Ber.*, **23**, 738 (1890), b.p. 232–233°.

(16) R. G. Hiskey, F. I. Carroll, R. L. Smith and R. T. Corbett, *J. Org. Chem.*, **26**, in press (1961).

(17) Y. Uyeda, *J. Chem. Soc. Japan*, **52**, 410 (1931).

of the residue indicated the presence of 23.7% XI, 7.1% XIII and 31.7% of VI.

The remaining residue afforded 0.41 g. (37.9%) of N,N-diphenylcarbonyl chloride when treated with alcohol. Alumina chromatography of the residue gave 0.02 g. (3.96%) of diphenyl disulfide, 0.08 g. (7.4%) of N,N-diphenylcarbonyl chloride, 0.16 g. (11.6%) of XII and 0.11 g. (7.78%) of VIII.

**Reaction of XIII with I.**—To 1.08 g. (4.65 mmoles) of N,N-diphenylcarbonyl chloride and 0.628 g. (4.65 mmoles) of XIII in 75 ml. of acetonitrile was added 4.65 mmoles of I in 25 ml. of acetonitrile. After 10 hours at 45–50°, 0.18 g. (47.9%) of sodium thiocyanate was obtained. Analysis of the residue (2.00 g.) indicated the presence of 33.4% XI, 11.5% of XIII and 15.7% of VI.

Chromatography of the remaining liquid gave 0.1 g. (19.8%) of diphenyl disulfide, 0.09 g. (8.3%) of N,N-diphenylcarbonyl chloride, 0.24 g. (17.5%) of XII and 0.19 g. (7.15%) of VIII.

**Cyanide Cleavage of Methyl 5-(4-Nitrophenyl)-3,4-dithiapentanoate (IV).**—Cleavage of 1.0 g. (3.66 mmoles) of IV in the usual manner with the exception that a nitrogen atmosphere was used afforded a green oil when the acetonitrile was removed. Addition of ether gave 0.12 g. (40.5%) of sodium thiocyanate. The vapor fractogram of the remaining oil (1.64 g.) indicated no volatile compo-

nents were present (30/60 mesh Celite columns containing 2% and 4% Carbowax were used over a temperature range of 90–140°). Authentic 4-(5-nitrophenyl)-3-thiabutanate was not eluted under these conditions.

The oil was chromatographed on alumina and afforded three solid fractions which were recrystallized and identified as: 0.30 g. (35.3%) of N,N-diphenylcarbonyl chloride; 0.30 g. (48.7%) of *p*-nitrobenzyl disulfide, m.p. 122–124°; 0.26 g. (23.6%) of VIII. A fourth fraction, 0.005 g., m.p. 58–67°, was not identified. Although no pure sulfide could be obtained, the infrared spectrum of one of the liquid fractions was virtually identical to a spectrum of the authentic sulfide.

**Reaction of IX with I.**—A solution of 3.66 mmoles of I in 25 ml. of acetonitrile was added to 0.85 g. (3.66 mmoles) of N,N-diphenylcarbonyl chloride and 0.71 g. (3.66 mmoles) of IX<sup>18</sup> in 75 ml. of acetonitrile. Isolation of the products in the manner described gave 0.10 g. (33.8%) of sodium thiocyanate and a green oil, shown to contain no volatile products. Chromatography of the oil gave 0.30 g. (35.3%) of carbonyl chloride, 0.20 g. (32.5%) of *p*-nitrobenzyl disulfide and 0.05 g. (4.5%) of VIII. A liquid fraction exhibited an infrared spectrum essentially identical to authentic methyl 4-(4-nitrophenyl)-3-thiabutanate, but no pure sulfide could be isolated.

(18) E. E. Reid, *J. Am. Chem. Soc.*, **39**, 124 (1917).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA 4, PENNA.]

## N,N-Divinylaniline and Its Polymerization

By EUGENE Y. C. CHANG<sup>1</sup> AND CHARLES C. PRICE

RECEIVED MAY 20, 1961

N,N-Divinylaniline has been prepared by the pyrolysis of N,N-bis-(2-trimethylammonioethyl)-aniline dihydroxide. Radical polymerization and copolymerization of this monomer in dilute solutions gave soluble polymers with low residual double bond content. A cyclization polymerization mechanism is proposed. The copolymerization parameters for N,N-divinylaniline, divinyl sulfone and divinyl ether have been determined. The *Q*- and *e*-values for divinylaniline were found to be 0.15 and -1.6, respectively; those for divinyl sulfone were 0.14 and 1.4; and those for divinyl ether were 0.04 and -1.3. The higher *Q*-values of these divinyl monomers compared with those of the corresponding monovinyl monomers indicated enhanced reactivity due to direct interaction of neighboring double bonds. The stronger ultraviolet absorption of N,N-divinylaniline compared to that of N-phenylpyrrole also suggested the existence of resonance interaction between the two vinyl groups and the aromatic ring chromophore in N,N-divinylaniline. N,N-Divinylaniline showed a chain transfer constant of *C* = 0.034 in methyl methacrylate polymerization and *C* = 0.013 in styrene polymerization.

The similarity of the valence shell structures of nitrogen and oxygen suggests that N-vinyl compounds should have polymerization characteristics close to those of O-vinyl compounds and that a monomer such as N,N-divinylaniline should undergo a cyclization polymerization in the presence of a second monovinyl monomer similar to that of divinyl ether reported by Butler.<sup>2</sup>

The object of this work was therefore to prepare N,N-divinylaniline and to study its polymerization by radical catalysis. The copolymerization parameters of divinyl sulfone and divinyl ether were also determined for comparison.

### Results and Discussion

**Monomer Synthesis.**—A process analogous to that for the preparation of N-methyl-N-vinylaniline<sup>3</sup> was adopted. N,N-Bis-(2-hydroxyethyl)-aniline was converted to N,N-bis-(2-bromoethyl)-aniline by treatment with phosphorus tribromide. The dibromide was treated with excess anhydrous trimethylamine in ethanol at room temperature to

give N,N-bis-(2-trimethylammonioethyl)-aniline dibromide. This quaternary ammonium bromide was then converted to the corresponding dihydroxide by silver oxide. N,N-Divinylaniline was obtained by pyrolysis of the diquaternary ammonium hydroxide at 150° under a nitrogen atmosphere. The compound absorbed two moles of hydrogen upon catalytic hydrogenation and the hydrogenated product was identical with N,N-diethylaniline.

Figure 1 illustrates the ultraviolet spectrum of N,N-divinylaniline together with those of several other reference compounds. The larger area covered by the bands of N,N-divinylaniline compared to N-phenylpyrrole indicates that there could be additional interaction arising in the divinylaniline molecule due to the freedom of rotation of the two vinyl groups to assume extra conjugating forms. The two "vinyl" groups in N-phenylpyrrole have restricted positions in a ring. Two possible conformations for the direct interaction between the two vinyl groups in divinylaniline are postulated as shown by formulas I and II.

In form I one vinyl group lies toward the back of the aniline plane and the other vinyl group lies toward the front. In form II the two vinyl groups lie toward the same side of the aniline plane. Simi-

(1) American Viscose Corp. Fellow, 1959–1960.

(2) G. B. Butler, Abstract of April, 1958, A.C.S. Meeting, San Francisco, Calif., p. 6-R. G. B. Butler, Abstract of Sept., 1958, A.C.S. Meeting, Chicago, Ill., p. 32-T.

(3) J. von Braun and G. Kirschbaum, *Ber.*, **52**, 2261 (1919).