The Benzidine Rearrangement. V.[1]

First-order Acid Dependence with 4,4′-Divinylhydrazobenzene

H. J. SHINE AND J. T. CHAMNESS

Department of Chemistry, Texas Technological College, Lubbock, Texas

Received September 4, 1962

4,4′-Divinylhydrazobenzene (I) has been prepared. The rates of the acid-catalyzed rearrangement of I in 95% ethanol at 0° and 25°, and in 75% *t*-butyl alcohol at 25° were determined. The rearrangement was followed by both the Bindschedler's Green titration method and spectrophotometrically. In each case the rearrangement was first-order in acid, over the range of acid concentrations 0.001 to 0.05 *M*. The rate of rearrangement of I is faster than that of hydrazobenzene. The product of rearrangement is neither the semidine nor the bis-*p*-aminophenylbutadiene. The product decomposes slowly with charring above 300°, is insoluble in ethanol, and has no unsaturation. The rearrangement is not accompanied by extensive disproportionation as is observed in the rearrangement of other di-*p*-substituted hydrazobenzenes. It is proposed that the product is a polymer that accompanies the *o*-benzidine type of rearrangement.

We have observed, with the rearrangement of 2,2′-hydrazonaphthalene, the connection between acid order and acid concentration which Banthorpe, Hughes, and Ingold[2] discovered in the rearrangement of 1-phenyl-2-β-naphthylhydrazine; that is, that the trend is from second-order at higher to first-order at lower acid concentrations.

The importance of rate data in interpreting the mechanism of the acid-catalyzed rearrangement of hydrazo compounds has been evident in the last few years. The rearrangement of hydrazobenzene was shown to be second order with respect to acid by Hammond and Shine.[3] Confirmation of second-order acid catalysis was provided by Carlin, Nelb, and Odioso[4] and by Croce and Gettler.[5]

In more recent years cases of rearrangement of substituted hydrazobenzenes have been disclosed in which a non-integral order of acid dependence was observed. These are *o*-hydrazotoluene,[6] 4-methyl-4′-chlorohydrazobenzene,[7] and 4-*t*-butyl-4′-chlorohydrazobenzene.[7] Since the variation in acid order with change in hydrazo structure must be capable of incorporation in a general mechanistic scheme for the benzidine rearrangement, and since, in one case,[7] the non-integral orders (1.58 and 1.51) were attributed to steric effects in the hydrazo compound, we were interested in investigating the kinetics of rearrangement of a number of pertinent hydrazo compounds.

Because of our prior interest in hydrazonaphthalenes[1] we chose to work with 2,2′-hydrazonaphthalene; while, because of the proposals concerning steric effects[7] we chose to work with some *p,p*′-disubstituted hydrazobenzenes.

The cases of 2,2′-hydrazonaphthalene and its isomers have now been reported by Banthorpe, Hughes, and Ingold,[2] in whose publications there are established cases of first-order and mixed-order acid dependence.

We have also worked with 2,2′-hydrazonaphthalene,[8] and have found that in acetone containing 25% water by volume, the rearrangement has an acid dependence that varies with acid concentration. The order in acid is close to 2 at acid concentrations of 0.01 to 0.02 *M* and approaches 1 in the region of 0.005 *M*, the ionic strength being 0.02 in all cases. Banthorpe, Hughes, and Ingold have observed an acid dependence of 1.15 with this case. The results with 2,2′-hydrazonaphthalene in our solvent and acid range, the details of which are available,[8] but which we shall omit in view of the prior publication,[2] confirm the observation, made by Banthorpe, Hughes, and Ingold with 1-phenyl-2-β-naphthylhydrazine, that it is at lower, rather than higher, acid concentrations that the trend to first-order acid dependence occurs.

We wish to report now our investigation of the acid-catalyzed rearrangement of 4,4′-divinylhydrazobenzene, I. This compound undergoes a transformation in acid solution by a process clearly first-order in acid.

Kinetic Results

The rate of rearrangement of I was measured by the Bindschedler's Green technique[9] and also spectroscopically. The rate data from the titration method are given in Table I, while those from the spectroscopic method are given in Table II.

TABLE I

RATE CONSTANTS[a,b] FOR THE REARRANGEMENT OF 4,4′-DIVINYLHYDRAZOBENZENE IN 95% ETHANOL AT 0°

[Hydrazo] = 2.5×10^{-3} *M*; ionic strength = 0.05.

Run	$[H^+] \times 10^2$	10^2k, min.$^{-1}$
1	5.30	16.7
2[c]	4.03	11.9
3[c]	3.00	9.93
4[c]	2.20	6.45
5	3.80	11.9
6	3.03	8.82
7	2.00	6.29
8	2.07	6.05
9	1.00	3.11
10	5.01	14.0
11	1.04	2.67

[a] Calculated by the method of least squares; H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Co., Inc., Princeton, N. J., 6th printing, 1946, p. 502. [b] Bindschedler's Green method. [c] Lithium perchlorate used for maintaining ionic strength; in all other runs lithium chloride was used.

---

(1) For Part IV, see H. J. Shine, F.-T. Huang, and R. L. Snell, *J. Org. Chem.*, **26**, 380 (1961).

(2) D. V. Banthorpe, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2386–2444 (1962).

(3) G. S. Hammond and H. J. Shine, *J. Am. Chem. Soc.*, **72**, 220 (1950).

(4) R. B. Carlin, R. G. Nelb, and R. C. Odioso, *ibid.*, **73**, 1002 (1951).

(5) L. J. Croce and J. D. Gettler, *ibid.*, **75**, 874 (1953).

(6) R. B. Carlin and R. C. Odioso, *ibid.*, **76**, 100 (1954).

(7) M. J. S. Dewar and H. McNicholl, *Tetrahedron Letters*, **5**, 22 (1959).

(8) Unpublished work described in the M.S. degree thesis of S. J. Burdick, Texas Technological College, August, 1961.

(9) (a) M. J. S. Dewar, *J. Chem. Soc.*, 777 (1946); (b) H. J. Shine, R. L. Snell, and J. C. Trisler, *Anal. Chem.*, **30**, 383 (1958).

Table II

Rate Constants[a,b] for the Rearrangement of 4,4'-Divinylhydrazobenzene at 25°

[Hydrazo] = 5×10^{-5} *M*; ionic strength = 0.05.

Solvent	$[H^+] \times 10^3$	10^2k, min.$^{-1}$	$[H^+] \times 10^3$	10^2k, min.$^{-1}$
95% ethanol	1.0	4.60	6.0	30.2
	1.0	4.54	6.0	30.4
	2.0	8.91	7.0	36.2
	2.0	9.03	7.0	34.1
	3.0	13.3	8.0	36.6
	3.0	13.8	8.0	39.6
	4.0	18.4	9.0	46.3
	4.0	18.8	9.0	45.8
	5.0	21.1	10.0	48.6
	5.0	22.8	10.0	48.8
75% *t*-butyl alcohol	1.0	5.41	5.0	26.5
	1.0	5.55	5.0	26.2
	2.0	10.6	6.0	28.9
	2.0	10.6	6.0	30.4
	3.0	16.1	7.0	34.8
	3.0	16.0	7.0	34.3
	4.0	21.2	8.0	37.8
	4.0	21.5	8.0	38.9

[a] Calculated by the method of least squares. [b] Spectroscopic method.

The rate of rearrangement of I is faster than that of hydrazobenzene. Comparison can be made with the data reported by Carlin[4] for hydrazobenzene in 95% ethanol. At 0.15° and in 0.102 *M* acid the rate constant for hydrazobenzene is 0.015 min.$^{-1}$, while the rate constant obtained by us for the rearrangement of I at 0° in 95% ethanol, which was only 0.053 *M* in acid, was eleven times larger, that is 0.167 min.$^{-1}$

Because of the rapid rate of rearrangement of I it was not possible to go to ratios of acid to substrate concentration higher than those in Table I and use the Bindschedler's Green method. We found that the disappearance of I can be followed directly in the spectrophotometer, so that, from runs with high acid to substrate ratios, rates with half-lives of about one minute could be followed easily. Fig. 1 shows a series of traces obtained at time intervals with I dissolved in acidic ethanol. The gradual disappearance of I is seen at 287 mμ, the λ_{max} of this hydrazo compound.

The logarithms of the rate constants given in Tables I and II were plotted against those of the acid concentrations. The data from ethanol solutions are plotted in Fig. 2. The slopes of these plots were calculated by the method of least squares and were: titration method of following rates, 1.04; spectroscopic method (ethanol), 1.09; (*t*-butyl alcohol), 0.94.

Rate constants determined in conditions in which only the initial hydrazo concentration was varied did not differ sensibly from one and another.

Product Analysis

The product was isolated from rearrangements in both 95% ethanol and in wet ether. The product was a pale yellow solid which did not melt below 300°. Above this temperature blackening and decomposition occurred slowly. It was not appreciably soluble in ethanol and other common organic solvents. Elemental analysis agreed with the empirical formula of I.

The ultraviolet and infrared spectra of the product were compared with those of known materials. Fig. 1 shows that rearrangement in ethanol leads to a very simple spectrum. The ultraviolet spectrum of the isolated product taken in acidic ethanol had a maximum at 240 mμ and a broad shoulder at 290 mμ. Neutralization of a rearrangement solution with sodium hydroxide gave a spectrum with increased absorption in the 240-mμ region and a weak absorption at 287 mμ. The spectrum indicating this is labeled N in Fig. 1.

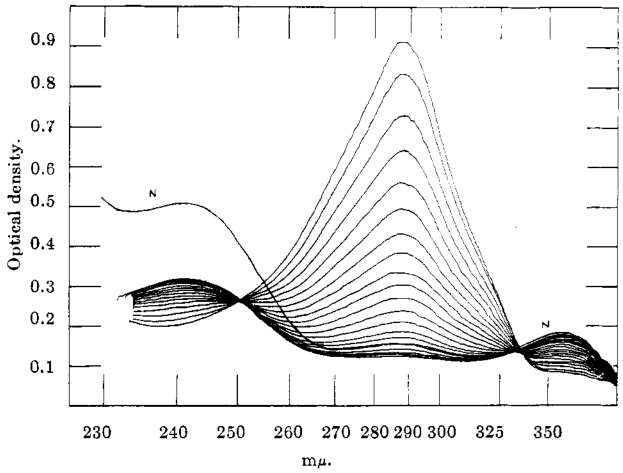


Fig. 1.—The change in the ultraviolet spectrum of 4,4'-divinylhydrazobenzene in weakly acidic 95% ethanol. The traces showing the decrease in absorption at 287 mμ were recorded at 5-min. intervals. The trace N was made after neutralizing the acid.

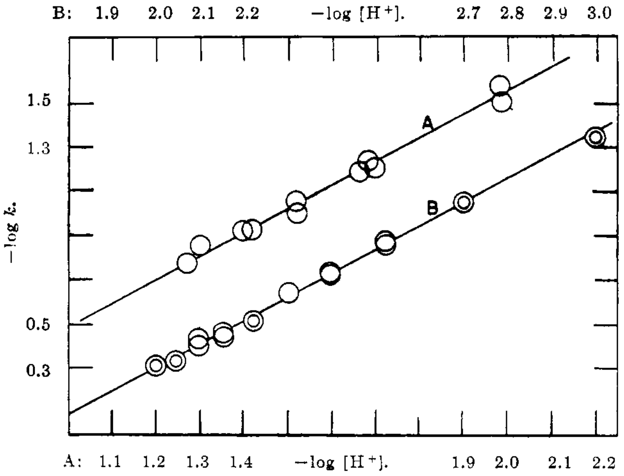


Fig. 2.—Plots relating rate constants for the rearrangement of 4,4'-divinylhydrazobenzene in 95% ethanol to acid concentration. A, titration method; B, spectroscopic method.

The infrared spectrum varied very little from preparation to preparation even though some times the product had a greenish tinge and had become hard and resinous in appearance. The bands of the vinyl group and substituted vinyl group bands near 900 and 1000 cm.$^{-1}$ were absent. *p*-Vinylaniline has two sharp bands at 900 and 995 cm.$^{-1}$. Several 1,4-diphenylbutadienes were examined and had sharp bands in the region 990–995 cm.$^{-1}$. In the product the aromatic region was very simply represented by one large band centering at 825 cm.$^{-1}$, indicative of 1,4 or 1,2,4-substitution. In the shorter wave length region, the aromatic triplet between 2850 and 3000 cm.$^{-1}$ was clearly observed while between 2900 and 3500 cm.$^{-1}$ the aromatic primary amine was shown strongly. These characteristics are shown in Fig. 3, in which the spectrum of polyvinylaniline is included. The polyvinylaniline was made by

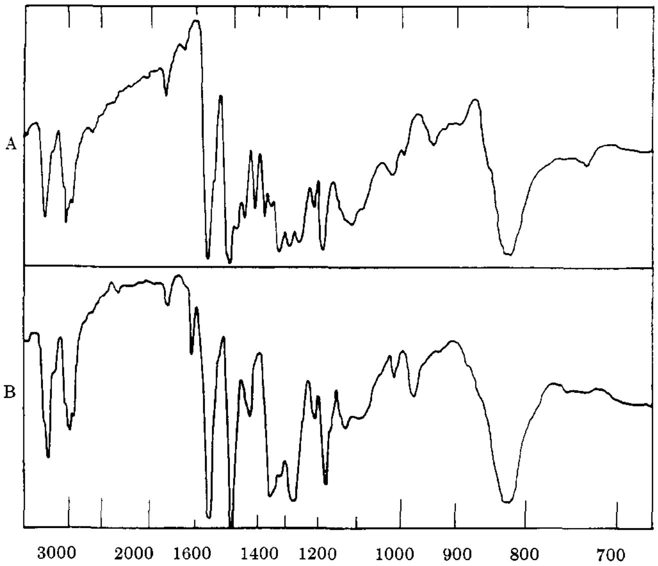


Fig. 3.—Infrared spectra: A, polyvinylaniline; B, the product of rearrangement of 4,4′-divinylhydrazobenzene.

the thermal polymerization of *p*-vinylaniline. Further analysis in the region 1100 to 1600 cm.$^{-1}$ is complicated by the overlapping of the aromatic and amino absorptions.

Discussion

The coincidence of the kinetic orders in acid determined by the Bindschedler's Green and spectroscopic methods leaves us with no doubt that in each case we have measured the rate of disappearance of the hydrazo group. Since the amount of azostyrene present at the end of reaction was always very small the dis appearance of the hydrazo group could not have resulted from either oxidation or disproportionation. The possibility of reduction[10] of the hydrazo compound to *p*-vinylaniline is also eliminated by our having carried out the reaction in wet ether and aqueous *t*-butyl alcohol and also failing to detect acetaldehyde in the ethanolic reaction medium. Thus, we conclude that the kinetics we have recorded are those of a true rearrangement, first-order in both hydrazo compound and in acid.

It is evident that I rearranges more rapidly than hydrazobenzene. We would anticipate that I is a weaker base than hydrazobenzene, and that the rate of attack of a second proton on the monoprotonated ion, which would lead to second-order acid kinetics, would be slower in the case of I than in that of hydrazobenzene. Thus, using the interpretation of rearrangement by two independent routes recently given,[7] we have followed in I the rate of rearrangement by a first-order process dominant because of the now less facile, compared with hydrazobenzene, attack of a second proton on the monoprotonated ion.

At the onset of this work we had anticipated that the product of rearrangement would be either the semidine or, less likely, 1,4-di(*p*-aminophenyl)-1,3-butadiene. It is our opinion now that neither of these is the product.

The melting point and solubility characteristics of the product make it evident that it is not simply the semidine.[11] Further, it does not seem that the product has the semidine unit in it. The ultraviolet spectra of semidines are characterized by three well defined maxima, as shown by Carlin for the dimethyl case and as we have found in the diethyl and dichloro cases.[12] These maxima are in the regions 240, 280, and 300 mμ. In acid solution the dimethylsemidine[13] absorbs strongly at 279 mμ and only moderately at 235 mμ. In the last region absorption is not characterized by a maximum. This is clearly different from our product in acid solution.

The product, furthermore, is not a 1,4-diphenylbutadiene, a decision based on the absence of unsaturation bands in the infrared and the absence of the characteristic close trio of bands between 340–380 mμ in the ultraviolet spectrum of the product.

The product is, indeed, very much like polyvinylaniline, as seen in the infrared spectra, Fig. 3. *p*-Vinylaniline is consumed only very slowly in mildly acidic ethanol. The characteristic band at 275 mμ slowly disappears and after a week or more the spectrum is very much like that obtained by rearrangement of I. That is, the acidic solution of *p*-vinylaniline after two weeks has two broad bands at 345 and 242 mμ. Addition of sodium hydroxide no longer gives the strong band at 275 mμ, as happens when a fresh, acidic solution of the amine is treated this way, but gives a spectrum very similar to the one labeled N in Fig. 1; that is, a strong band at 238 mμ, a weaker one at 287 mμ, and lastly a very weak broad band at 345 mμ. Unfortunately, we were able to retrieve only a gummy product from allowing *p*-vinylaniline to stand in acid for several weeks. The fact that the amine changes so slowly in this solution also stresses that *p*-vinylaniline is not the initial product in the rearrangement of I.

It is our proposal that the product is a polymer whose formation is initiated by the rearrangement that occurs intramolecularly. The rearrangement we choose is not the customary semidine type but the *o*-benzidine. We have noted earlier[1] that 1-phenyl-2-β-naphthylhydrazine forms the *o*-benzidine product both by thermal and acid-catalyzed rearrangement. The thermal rearrangements of this and other hydrazonaphthalenes may be Claisen type rearrangements, but the acid-catalyzed rearrangements are true benzidine rearrangements. Some of these, which lead to the *o*-benzidine products, rearrange by the first-order acid process.[2] It is our view in the present case that the process, which is first order in acid, leads to the *o*-benzidine product intermediate and that this intermediate is involved[1] in a way so far unknown, in initiating further reaction with available vinyl groups. Since *p*-vinylaniline is consumed only slowly in acidic ethanol solution, there is no reason to believe that either the semidine or the *o*-benzidine would be consumed at an appreciably dif-

---

(10) R. B. Carlin and G. S. Wich, *J. Am. Chem. Soc.*, **80**, 4023 (1958).

(11) It is interesting to compare the properties of our product with those of 2,2′-divinylbenzidine reported by R. H. Wiley and N. R. Smith, *ibid.*, **70**, 2295 (1948), from the rearrangement of 3,3′-divinylhydrazobenzene. That is, the 2,2′-divinylbenzidine had m.p. 123°. Heating it to 135° gave an infusible insoluble polymer. Attempts to prepare 3,3′-divinylhydrazobenzene by reduction of *m*-nitrostyrene with zinc and hydrochloric acid gave a polymer. G. Komppa, Inaugural dissertation, Helsingfors, 1893 (we wish to thank the Librarian, University of Helsinki for a gift of a copy of this dissertation), reports the 2,2′-divinylbenzidine as being readily soluble in ether, benzene, and hot alcohol; and fairly soluble in cold alcohol.

(12) Unpublished work of J. T. Chamness.

(13) We wish to thank Professor Carlin for so kindly sending us this compound.

ferent rate from *p*-vinylaniline if they were dissolved in weakly acidic ethanol. Similarly we think that I itself would not undergo a fast reaction at its vinyl groups in weakly acidic ethanol unless its hydrazo group was first involved in a rearrangement scission.

Experimental[14]

Materials.—Ethanol was stock 95% and used without further treatment. The *t*-butyl alcohol was Eastman (White Label) and was allowed to crystallize, the supernatant liquid being discarded; this was done three times.

p-Nitrostyrene was made according to the method of Strassburg, Gregg, and Walling.[15]

4,4'-Divinylazobenzene.—A mixture of 90 ml. of ethanol, 15 ml. of 12 *N* sodium hydroxide, and 7 g. of *p*-nitrostyrene was heated to boiling in a 250-ml., two-neck flask equipped with a reflux condenser. Zinc dust (25 g.) was added in small portions. Boiling was continued for 30 min. after the addition was complete, and the hot solution was filtered into a large volume of cold water. The precipitated red, gummy solid was filtered, dried, and sublimed at 120° and 2 mm. The sublimed solid was recrystallized several times from 95% ethanol to give 0.95 g. (17% yield), m.p. 138–138.5°.

Anal. Calcd. for $C_{16}H_{14}N_2$: C, 82.03; H, 6.02; N, 11.95. Found: C, 81.84; H, 6.18; N, 12.22.

The infrared spectrum showed a strong band at 997 cm.$^{-1}$ and a strong doublet at 906, 915 cm.$^{-1}$.

4,4'-Divinylhydrazobenzene (I).—The azo compound was reduced in acetone solution with zinc dust and aqueous ammonium chloride. The colorless acetone solution was filtered through sintered glass into a large volume of dilute aqueous ammonium hydroxide that had been de-gassed by stirring under a water aspirator vacuum for 30 min. The colorless I was filtered quickly, washed with water and dried in a vacuum desiccator. In all of the kinetic and product work the I used was prepared not more than 18 hr. prior to use. The product had a capillary melting point of 115°, determined by plunging into the melting point bath at various temperatures.

Anal. Calcd. for $C_{16}H_{16}N_2$: C, 81.32; H, 6.83; N, 11.85. Found: C, 81.01; H, 6.84; N, 11.99.

1,4-Bis(*p*-nitrophenyl)-1,3-butadiene.—This compound was unknown when first made in our laboratory. Subsequently, it was reported by Buckles and Franklin,[16] *via* the decarboxylation of the corresponding pentadienoic acid. We used the simpler preparation *via* the Wittig reaction. To a solution of 11.6 g. of *p*-nitrophenyl triphenylphosphonium bromide (m.p. 275°)[17] and 5.0 g. of *p*-nitrocinnamaldehyde[18] (m.p. 139–140°, 2,4-dinitrophenylhydrazone m.p., 278–279°) in 137 ml. of absolute ethanol was added in small portions a solution of 0.2 g. of lithium metal in 103 ml. of absolute ethanol. After standing overnight at room temperature the solution was diluted with 100 ml. of water. The precipitate formed was filtered, washed with water, and dried. Recrystallization twice from *p*-xylene gave yellow-brown needles, m.p. 268–269°. Two more crystallizations from dimethylformamide gave m.p. 270–270.5° (lit.,[16] for the *trans–trans* isomer, 257.5–259°). Yield: 3.7 g. (44.3%).

Anal. Calcd. for $C_{16}H_{12}N_2O_4$: C, 64.86; H, 4.08; N, 9.46. Found: C, 64.77, 64.92; H, 4.25, 4.09; N, 9.26, 9.71.

1,4-Bis(*p*-acetamidophenyl)-1,3-butadiene.—One gram of the dinitro compound and 14 g. of zinc dust were boiled for 12 hr. with 120 ml. of acetic acid and 10 ml. of water. After cooling, the solution was decanted into 300 ml. of concentrated ammonium hydroxide. The light yellow solid was filtered, washed with ethanol, and dried giving 0.97 g. (90% yield). Crystallization from a mixture of dimethylformamide and methanol gave a colorless product, m.p. 356–357°.[19]

Anal. Calcd. for $C_{20}H_{20}N_2O_2$: C, 74.98; H, 6.29; N, 8.75. Found: C, 75.03; H, 6.23; N, 8.72.

The ultraviolet spectrum of a chloroform solution showed a triplet of peaks at 341, 358, and 380 mμ, and a small absorption at 278 mμ.

The following 1,4-substituted butadienes were donated[20]: 1,4-diphenyl-, 1-*p*-nitrophenyl-4-phenyl-, and 1-*p*-acetamidophenyl-4-phenyl-1,3-butadiene.

***p*-Vinylaniline.**—This was prepared by the aluminum amalgam reduction of *p*-nitrostyrene[21] in moist ether solution. Boiling of the reaction mixture was continued until a test sample was completely soluble in dilute hydrochloric acid. The amine was obtained by removing the ether under reduced pressure after filtering. The amine was not distilled and was stored at −10°. N-acetyl derivative, m.p. 139.5–140°; lit.,[21] 135–136°.

Rate Work.—Bindschedler's Green was prepared as earlier.[9b] Solutions containing approximately 3.2 g./l. were used. Commercial 20% aqueous titanium trichloride was diluted (7 ml./l.) and standardized with solutions of recrystallized potassium dichromate. Lithium chloride and lithium perchlorate were dried by heating and were stored in a desiccator. Alcoholic solutions of hydrogen chloride were made by bubbling the gas into 95% ethanol. The solutions were standardized prior to use. Rates of rearrangement were measured as described elsewhere.[3]

The spectroscopic procedure is illustrated with the following example. A solution of 8.8 mg. of I in 50 ml. of ethanol was diluted tenfold to 7.5×10^{-5} *M*. Two ml. of this solution was pipetted into a ground-glass stoppered cell (Pyrocell Manufacturing Co., Westwood, N. J.). To this was added 1 ml. of an ethanol solution containing hydrogen chloride and lithium chloride. The stoppered cell was shaken while in the cell holder, inserted in the spectrophotometer previously set to read in transmission at 287 mμ. Readings were taken at time intervals, converted to optical density and the logarithms were plotted against time. As an example, the acidic solution added last was made by diluting 3 ml. of 0.1 *M* ethanolic hydrogen chloride to 50 ml. with ethanol and adding 0.3054 g. of lithium chloride. By using 1 ml. of this solution and 2 ml. of the I solution and assuming the volumes to be additive, the solution in the cell was 2×10^{-3} *M* in acid, 5×10^{-5} *M* in I and had an ionic strength of 0.05. In this case the rate data following were obtained.

Time (min.):	0	1	2	3	4	5	6	7	8
% Trans.:	10.7	12.5	14.8	17.5	20.2	23.5	26.4	29.4	31.8

A plot of log optical density against time gave a straight line whose calculated slope (ref. *a*, Table I) was -3.87×10^{-2}, giving a rate constant of 8.91×10^{-2} min.$^{-1}$.

The temperature of the cell compartment was maintained at 25° by pumping water from a temperature controlled bath through the coils of the cell compartment. The solutions used were brought to bath temperature prior to pipetting. A Beckman DK-2 instrument and a Beckman controlled-temperature cell compartment were used.

Product Isolation.—The following is one of the several preparations carried out. The I, 0.206 g., was dissolved in 100 ml. of 95% ethanol and 2 ml. of 1 *N* ethanolic hydrogen chloride was added. Evaporation of the solvent with a jet of nitrogen was started 15 min. later. The solid residue obtained was dissolved in 1 *N* hydrochloric acid and the solution was extracted several times with ether. The acid solution was poured onto 2 g. of sodium hydroxide pellets. A light yellow solid precipitated and this was filtered, washed with water, and dried, giving 0.200 g. (96.5%). Reprecipitation from dimethylformamide and drying 24 hr. at 70° and 1 mm. gave a light yellow solid.

Anal. Calcd. for: $C_{16}H_{16}N_2$: C, 81.32; H, 6.83; N, 11.85. Found: C, 80.96; H, 7.12; N, 11.77.

This solid was not soluble in ethanol, chloroform, benzene, diethylene glycol dimethyl ether, and water. It was soluble in dimethylformamide, dilute aqueous acid and dimethylsulfoxide.

A similar result was obtained when the rearrangement solution was not evaporated but was neutralized with ammonium hy-

---

[14] Analyses by Schwarzkopf Microanalytical Laboratories, Woodside 77, N. Y.

[15] R. W. Strassburg, R. A. Gregg, and C. Walling, *J. Am. Chem. Soc.*, **69**, 2141 (1947).

[16] W. E. Franklin, Ph.D. dissertation, State University of Iowa, February, 1960. University Microfilms, Inc., Ann Arbor, Mich.

[17] R. N. McDonald and T. W. Campbell, *J. Org. Chem.*, **24**, 1969 (1959).

[18] T. Nishimura, *J. Japan. Chem. Soc.*, **25**, 54 (1952).

[19] L. Katz, *et al.*, U. S. Patent 2,852,556 (September 16, 1958), list this compound but do not give a melting point.

[20] We wish to thank Dr. Tod W. Campbell, E. I. du Pont de Nemours and Co., Wilmington, Del., for these compounds.

[21] J. H. Boyer and H. Alul, *J. Am. Chem. Soc.*, **81**, 2136 (1950).

droxide solution. Filtration of the flocculent precipitate was very tedious.

In two cases the azostyrene in the product was found to be 1.7% and 1.2% of the I used.

Infrared spectra were obtained with a Perkin–Elmer "Infracord," Model 137. All solids were run in potassium bromide pellets. *p*-Vinylaniline was run neat between sodium chloride plates.

Acknowledgment.—This work is part of a program of research that has been supported by the Robert A. Welch Foundation, the National Science Foundation (grant no. G-14551), and Texas Technological College (grant no. 1654). We wish to thank these donors for their support.

Organic Sulfur Compounds. I. Synthesis of *sec*-Mercaptoalkylamine Hydrochlorides[1a,b]

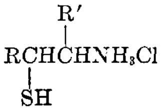
F. I. CARROLL, J. D. WHITE, AND MONROE E. WALL

The Natural Products Laboratory, Research Triangle Institute, Durham, North Carolina

Received September 28, 1962

Methods for the preparation of *sec*-mercaptoalkylamine hydrochlorides are presented. The scheme used for the preparation of these compounds involves the preparation of *sec*-benzylthionitroalkanes, followed by reduction of the nitro group with lithium aluminum hydride and reductive debenzylation with sodium in liquid ammonia to free the mercaptan. Several procedures for preparing the requisite *sec*-benzylthionitroalkanes involving isolation of nitroölefins followed by the addition of benzyl mercaptan or reaction of the latter with nitroölefins formed *in situ* are discussed.

The synthesis of mercaptoalkylamines is a subject of current interest because of the antiradiation activity of some of these compounds.[2,3] Although there are numerous reports of the synthesis of compounds in which the mercapto group is attached to a primary carbon atom, there is a paucity of data concerning the synthesis of mercaptoalkylamines bearing sulfur on secondary or tertiary carbon atoms. This paper describes the preparation of a group of new *sec*-mercaptoalkylamine hydrochlorides of type I or II shown below. In addition, improved procedures for preparing nitroolefins and *sec*-benzylthionitroalkane precursors are described.



$$\mathrm{RCH(SH)CH(R')NH_3Cl}$$

I. R = alkyl, R′ = H
II. R = alkyl, R′ = CH_3 or C_2H_5

We initially planned to use the reaction scheme outlined in Chart A for the preparation of the *sec*-mercaptoalkylamine hydrochlorides.

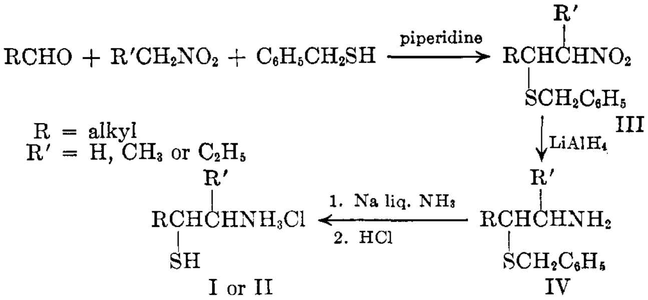


CHART A

Parham and Ramp[4] reported that nitromethane, propionaldehyde and benzyl mercaptan mixed in the absence of solvent and a catalytic amount of piperidine added, reacted exothermically to give 2-benzylthio-1-nitrobutane in nearly quantitative yield. These authors suggested that the 2-benzylthio-1-nitrobutane was apparently formed by the addition of benzyl mercaptan to 1-nitrobutene formed *in situ*. Our initial attempts to extend this method to longer chain aldehydes were unsatisfactory. The reaction products were impure and because of decomposition could not be distilled without undue losses. Therefore, we turned our attention to the route shown in Chart B.

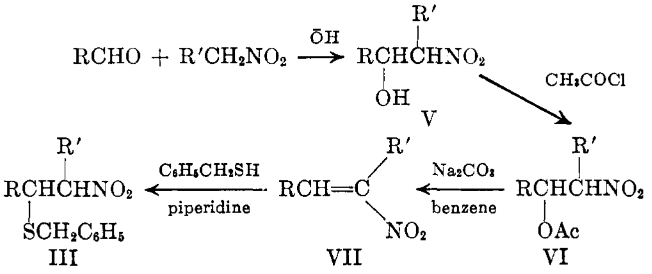


CHART B

Each of the four steps in Chart B is reported to occur in good yield. The major disadvantage was that several distillations were required. We overcame this difficulty, however, by preparing the desired nitroölefin from the appropriate aldehyde and nitroalkane without purification of either the nitro alcohol or the nitro acetate. The nitro alcohol was prepared by allowing the aldehyde and the nitroalkane to condense in the presence of aqueous alcoholic sodium hydroxide according to the method of Sprang and Degering.[5] The progress of the reaction was followed by the disappearance of the carbonyl band of the aldehyde and the appearance of a strong hydroxyl absorption at 3560–3600 cm.$^{-1}$. The nitro acetates could be obtained directly from the crude nitro alcohols. The simplest procedure was to add acetyl chloride directly to the

---

(1) (a) This investigation was supported by the Department of the Army and the U. S. Army Medical Research and Development Command, contract no. DA-49-193-MD-2164; (b) part of this material was presented at the 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962.

(2) Proposed Anti-Radiation Drug Program, Part 2 and 3, Department of Radiobiology, Walter Reed Army Institute of Research, Walter Reed Army Medical Center.

(3) T. P. Johnston and A. Gallagher *J. Org. Chem.*, **26**, 3780 (1961).

(4) W. E. Parham and F. L. Ramp, *J. Am. Chem. Soc.*, **73**, 1293 (1951).

(5) C. A. Sprang and E. F. Degering, *ibid.*, **64**, 1063 (1942).