ning-band column gave pure 4-acetamido-N,4-dimethyl-2-pentanone, b.p. 47° (4 mm.).

Anal. Calcd. for $C_9H_{17}NO_2$: C, 63.12; H, 10.00; N, 8.18. Found: C, 63.03; H, 10.24; N, 8.00.

Silver Nitrate Catalyzed Reaction. A. In Dimethylformamide.—To a well-stirred solution of 10 g. of the acetylenic amide in 30 ml. of dimethylformamide there was added a solution of 2 g. of silver nitrate in 3 ml. of dimethylformamide. The mixture became warm and, after it had returned to room temperature, it was poured with stirring into a mixture of ether, salt, ice, and water. The mixture was stirred vigorously and the layers were separated; the ether layer was dried, filtered, and concentrated. The oxazoline was then distilled. See Table II.

B. In Aqueous Methanol.—To a well-stirred solution of 10 g. of the acetylenic amide in 20 ml. of methanol there was added a solution of 2 g. of silver nitrate in 2–3 ml. of water. The temperature of the mixture usually rose to 50–60°. After the reaction mixture had returned to room temperature, a solution of sodium chloride was added followed by 100 ml. of chloroform. The mixture was filtered and the layers were separated. The organic layer was dried and concentrated. The product was purified either by distillation or by recrystallization. Mixtures were obtained in most cases where R and R^1 of VIII were larger than methyl. See Table III for the ketoamides and Table II for the oxazolines.

Use of Other Catalysts.—Silver nitrate, ferric chloride, and cupric acetate gave better than 90% conversions. The reactions were run in aqueous methanol as above and the residues from the concentration of the chloroform solution were analyzed by vapor phase chromatography. The yields of the products were not calculated, but the per cents of conversion were approximated.

Hydration Using Cupric Acetate as Catalyst.—To a stirred solution containing 15 g. of N-acetyl-N,1,1-trimethyl-2-propynylamine, 50 ml. of methanol, and 15 ml. of water was added a slurry of 2.0 g. of cupric acetate in 5 ml. of water. The temperature at the time of addition of the catalyst was 20°. After 5 min. the temperature had risen to a maximum of 60° and after 20 min. was 25°. At this time a mixture of 10 g. of NaOH in 50 ml. of cold water and 200 ml. of ether was added. The layers were separated and the organic layer was dried over $MgSO_4$; the per cent of ketoamide was determined by v.p.c. (100% conversion). Distillation of the product yielded 11.0 g. (66%) of the ketoamide IXa.

Acknowledgment.—The microanalyses were performed by Messrs. William Brown, Howard Hunter, George Maciak, and Alfred Brown. Many of the starting materials were prepared by Dr. Dwight Morrison and Mr. Lawrence White. The infrared spectra were obtained by Mrs. Doris Stephens and Miss Martha Hofmann and the n.m.r. spectra by Mr. John Klemmn. The authors wish to thank especially Dr. Harold Boaz and Messrs. Paul Landis and Donald Woolf, Jr., for their invaluable services in interpreting and compiling the infrared and n.m.r. data.

Potential Antiradiation Agents.[1] Preparation and Polymerization of S-Vinyl-N-vinylthiocarbamates[2,3]

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Three S-vinyl-N-vinylthiocarbamates (IV) have been prepared by dehydrochlorination of the respective S-2-chloroethyl-N-2-chloroethylalkylthiocarbamates (III). The monomers were polymerized under a variety of conditions in an attempt to prepare linear, high molecular weight polymers containing a predominant amount of the tetrahydro-1,3-thiazin-2-one moiety along the backbone of the polymer chain. Free-radical-initiated polymerization was found to favor the formation of poly-S-vinyl recurring units, while cationic initiation favored the formation of repeating poly-N-vinyl units. Cyclopolymerization was favored by high dilution and decreasing size of the alkyl substituent. Attempts to isolate polymeric α-amino γ-thiols (VIII) formed on hydrolysis of the resultant "terpolymers" (VII) proved unsuccessful.

The investigation of various compounds as protective agents against ionizing radiation has been considerable since the discovery by Patt,[6] *et al.*, in 1950 that mice could be protected by cysteine from otherwise lethal doses of radiation by X-rays. The most promising agents to date appear to be 2-aminoethanethiol and 2-aminopropanethiol and several of the S-substituted derivatives.[7,8] None of the radiobiological protectants now known, however, satisfy the criterion of being highly active over a period of long duration. We have therefore undertaken the preparation of compounds with possible latent effects,[9] *i.e.*, low activity and toxicity during transport of the drugs to the tissues where the formation of more active agents may take place, as well as polymeric analogs of 2-mercaptoethylamine[10] and 3-mercaptopropylamine (reported herein). In the case of the latter two, the assumption is made that their relatively high molecular weights would make of them long-lasting radioprotective agents.

It has recently been established that nonconjugated di- and triolefinic monomers can be polymerized to yield linear, high molecular weight polymers containing carbocyclic rings along the backbone of the polymer chain.[11] The method of cyclopolymerization has, in fact, been recently employed in this laboratory to prepare polymers with recurring dithiolcarbonate[12,13] and

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(2) Presented at the 141st National Meeting of the American Chemical Society, Washington, D. C., March 1962.

(3) This is the Xth in a series of papers concerned with the preparation and properties of new monomers and polymers.

(4) Postdoctoral Fellow, Polytechnic Institute of Brooklyn, 1960–1962.

(5) This article is taken from the dissertation of B. A. submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Chemistry).

(6) H. M. Patt, D. E. Smith, E. B. Tyree, and R. L. Straube, *Proc. Soc. Expll. Biol. Med.*, **73**, 18 (1950).

(7) A. Pihl and L. Eldjarn, *Pharmacol. Rev.*, **10**, 437 (1958), and references cited therein.

(8) D. R. Kalkwarf, *Nucleonics*, **18**, 76 (1960), and references cited therein.

(9) C. G. Overberger, H. Ringsdorf, and B. Avchen, *J. Med. Chem.*, in press.

(10) C. G. Overberger, H. Ringsdorf, and B. Avchen, *ibid.*, **30**, 232 (1965).

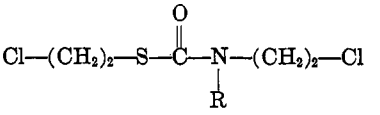
(11) C. S. Marvel, *J. Polymer Sci.*, **48**, 101 (1960), and references cited therein.

(12) H. Ringsdorf and C. G. Overberger, *Makromol. Chem.*, **44/46**, 418 (1961).

(13) C. G. Overberger and W. H. Daly, *J. Org. Chem.*, **29**, 757 (1964).

TABLE I

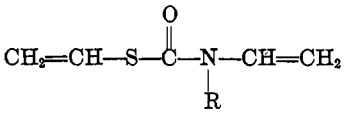
S-2-CHLOROETHYL-N-2-CHLOROETHYLALKYLTHIOCARBAMATES



R	Yield, %	B.p., °C. (mm.)	n_D (°C.)	Formula	Calcd., % C	H	Cl	N	S	Found, % C	H	Cl	N	S
CH_3	86	107 (0.5)	1.5268 (25)	$C_6H_{11}Cl_2NOS$	33.34	5.13	32.81	6.48	14.84	33.90	5.25	32.94	6.92	14.88
C_2H_5	80.3	112 (0.7)	1.5185 (27.5)	$C_7H_{13}Cl_2NOS$	36.53	5.69	30.81	6.09	13.93	36.99	5.77	30.20	6.23	14.19
n-C_4H_9	83	123 (0.5)	1.5121 (25)	$C_9H_{17}Cl_2NOS$	41.86	6.64	27.46	5.42	12.42	42.18	6.69	27.12	5.93	12.65

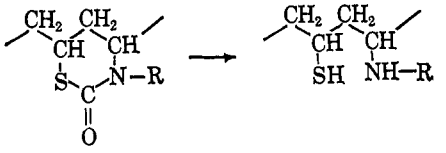
TABLE II

S-VINYL-N-VINYLTHIOCARBAMATES

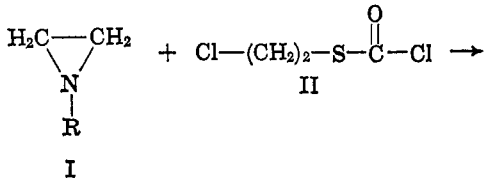


R	Yield, %	B.p., °C. (mm.)	n_D (°C.)	Formula	Calcd., % C	H	N	S	Found, % C	H	N	S
CH_3	35.7	54 (1.7)	1.5514 (25)	C_6H_9NOS	50.32	6.33	9.78	22.39	50.36	6.52	9.37	22.24
C_2H_5	38	60 (1.7)	1.5328 (24)	$C_7H_{11}NOS$	53.47	7.05	8.99	20.39	53.65	7.12	8.97	19.83
n-C_4H_9	45	68 (0.6)	1.5139 (25)	$C_9H_{15}NOS$	58.34	8.16	7.56	17.31	58.39	8.40	7.47	17.42

dithiolformal[14] units. It was therefore felt that polymers with the recurring tetrahydro-1,3-thiazin-2-one moiety along the backbone of the polymer chain might serve as precursors to polymeric mercaptoamines in which the sulfhydryl and amine functions were both covalently bound to the main chain and were in a γ position to each other, *i.e.*, an alternating copolymer composed of the "vinyl mercaptan" and "vinylamine" units (eq. 1). This paper describes the preparation and polymerization of S-vinyl-N-vinylthiocarbamates (IV).



(1)



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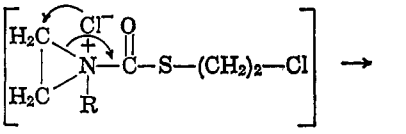
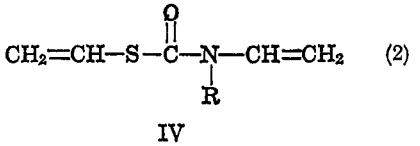


III



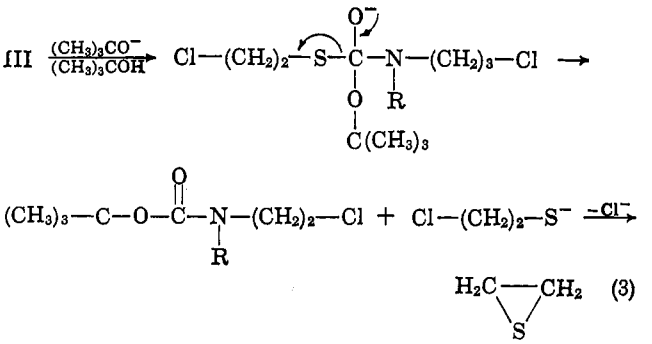
IV

(2)

a, R = CH_3
b, R = C_2H_5
c, R = n-C_4H_9

The reaction scheme employed for the preparation of the divinyl monomers is outlined in eq. 2. The intermediates, S-2-chloroethyl-N-2-chloroethylalkylthiocarbamates (III), were prepared by the reaction of N-alkylaziridines (I) with S-β-chloroethyl chlorothiolformate[12] (II) in etheral solution at ice-bath temperatures. The yields exceed 80% (Table I).

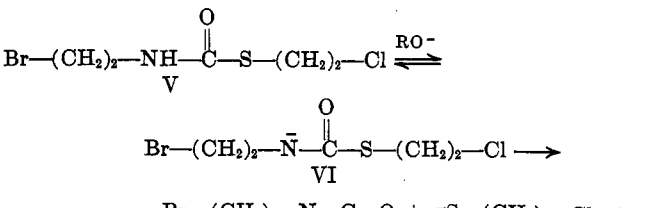
The S-2-chloroethyl-N-2-chloroethylalkylthiocarbamates were dehydrochlorinated with 2 equiv. of potassium t-butoxide in absolute t-butyl alcohol at 50–70° (Table II). The major side products obtained were the O-t-butyl carbamates resulting from transesterification with concurrent formation of ethylene sulfide (eq. 3). The highest yield of monomer was



(3)

found in that case where R was n-butyl. This is obviously due to the greater bulk of this group which hinders attack of the t-butoxide anion at the carbonyl group of III.

A similar attempt to prepare S-vinyl-N-vinylthiocar bamate (IV, R = H) by dehydrohalogenation of S-2-chloroethyl-N-2-bromoethylthiocarbamate[12] (V) proved unsuccessful. On treatment of V with 2 equiv. of



(4)

(14) H. Ringsdorf and C. G. Overberger, *J. Polymer Sci.*, **61**, S11 (1962).

TABLE III
POLYMERIZATION OF S-VINYL-N-METHYLVINYLTHIOCARBAMATE (IVa)

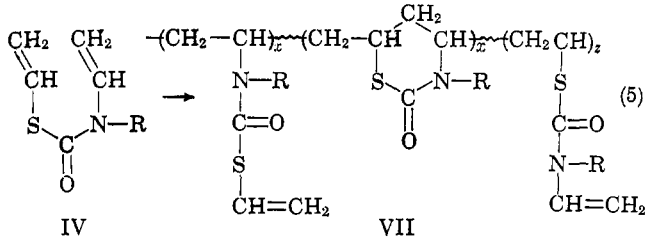
Expt.	Monomer, mg.	Benzene, ml.	M_0, M	ABIN, mg.	Time, hr.	Conversion mg.	Conversion %	Sol. part, mg.	Insol. part mg.	Pendent double bond, mole % Infrared method	Pendent double bond, mole % Bromine addn.	$[\eta]^a$
1	102	10	0.07	1.2	12	11	10.8	21	...	49.0	...	...
2	498	10	0.35	3.5	12	271	54.4	271	Trace	61.5	63.0	...
3	978	10	0.68	5.1	12	774	79.1	493	281	65.0	...	0.21
4	1021	5	1.42	5.0	2	693	68.0	355	338	83.5	84.0	0.19
5	1079	2	3.75	4.9	2	639	59.3	Trace	639	...	...	...

[a] Determined in benzene at 29.2°.

potassium *t*-butoxide in *t*-butyl alcohol or in dimethyl sulfoxide, decomposition of V may proceed as outlined in eq. 3 or, perhaps, by initial proton abstraction followed by decomposition of VI into a mercaptide anion and an isocyanate,[15] or by both eq. 3 and 4 simultaneously.

Results and Discussions

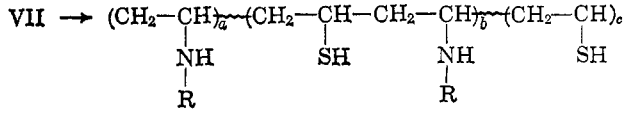
Polymerization of nonconjugated diolefins in which the double bonds are not equivalent, and thus the reactivity ratios of the two bonds are different, have been reported to give some cyclopolymer.[16-19] Most of the polymerization tends to take place through only one (the more reactive) double bond. Polymerization of the S-vinyl-N-vinylthiocarbamates, then, may be expected to yield "terpolymers" composed of the tetrahydro-1,3-thiazin-2-one moiety as well as poly-S-vinyl and poly-N-vinyl units (eq. 5). This was indeed found to be the case. It should perhaps be pointed out that the lack of pure "y" homopolymer does not *a*



(5)

IV VII

priori preclude the stated purpose of this work—*i.e.*, the preparation of polymeric α-amino γ-thiols—for hydrolysis of VII would, in theory, give VIII.



VIII

Polymerizations of the S-vinyl-N-vinylthiocarbamates were carried out in the presence of α,α'-azobisisobutyronitrile (ABIN) as initiator in benzene solution.

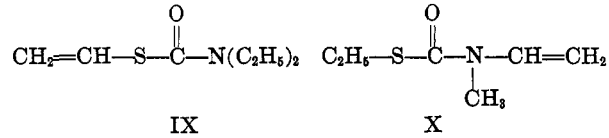
Residual unsaturation in the soluble polymer obtained was determined by infrared spectrum analysis and by bromination in carbon tetrachloride.

The infrared spectrum of the monomeric S-vinyl-N-vinylthiocarbamates are characterized by two distinct vinyl absorption bands. S-Vinyl absorption is of medium intensity and occurs at approximately 1605 cm.$^{-1}$; N-vinyl absorption is of strong intensity and the band occurs at approximately 1640 cm.$^{-1}$. Infrared spectrum analysis was thus accomplished by comparing absorption intensities of the two double bonds of the polymer with that of the divinyl monomer as the standard substance.

Quantitative bromine addition was carried out according to the procedure of Aso, Nawata, and Kamao.[20]

The results of the polymerization of S-vinyl-N-methylvinylthiocarbamate (IVa) are summarized in Table III. Soluble polymers were obtained as fine white powders. They were found to be soluble in such organic solvents as benzene, toluene, chloroform, carbon tetrachloride, and dimethylformamide. The intrinsic viscosities of their benzene solutions were low.

Gelation during polymerization was retarded by dilution of the system. For example, the degree of conversion reached 54.4% without gelation in a solution polymerization after 12 hr. with $M_0 = 0.35$ M (expt. 2). At the same time, however, there is a marked effect upon the degree of conversion (compare expt. 1 and 2). Further examination of Table III indicates that in the polymerization of IVa the intermolecular propagation step is favored over intramolecular ring closure. This is in accord with the fact that S-vinyl-N-diethylthiocarbamate (IX) has been shown[21] to be considerably more reactive than S-ethyl-N-methylvinylthiocarbamate (X) in copolymerization studies. The fact that the S-vinyl monomer IX is more reactive



IX X

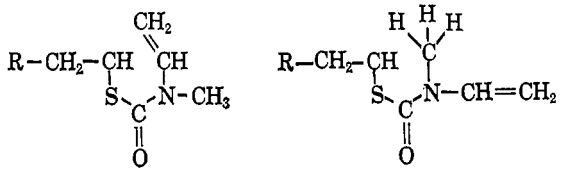
finds its explanation in its relatively high Q value (0.33 as compared to 0.18 for the N-vinyl monomer X), indicating considerable resonance stabilization of the adduct radical. This resonance stabilization, which entails expansion of the sulfur octet, has been invoked by Price and co-workers to explain the relatively high Q values of methyl vinyl sulfide[22] and divinyl sulfide.[23] The infrared spectra of the soluble polymers obtained in the free-radical polymerization of IVa were therefore devoid of S-vinyl absorption. This is true even when $M_0 = 0.07$ M.

(15) See, for example, T. Mukaiyama and M. Iwanami, *J. Am. Chem. Soc.*, **79**, 73 (1957).
(16) E. N. Rostovskii and A. M. Barinova, *Vysokomolekul. Soedin.*, **1**, 1707 (1959).
(17) M. D. Barnett, A. Crawshaw, and G. B. Butler, *J. Am. Chem. Soc.*, **81**, 5946 (1959).
(18) M. D. Barnett and G. B. Butler, *J. Org. Chem.*, **25**, 309 (1960).
(19) R. C. Schulze, M. Marx, and H. Hartmann, *Makromol. Chem.*, **44/46**, 281 (1961).
(20) C. Aso, T. Nawata, and H. Kamao, *ibid.*, **68**, 1 (1963).
(21) H. Ringsdorf, N. Weinshenker, and C. G. Overberger, *ibid.*, **64**, 126 (1963).
(22) C. C. Price and J. Zomlefer, *J. Am. Chem. Soc.*, **72**, 14 (1950).
(23) C. E. Scott and C. C. Price, *ibid.*, **81**, 2672 (1959).

TABLE IV
POLYMERIZATION OF IVa–c UNDER IDENTICAL CONDITIONS

	Monomer, mg.	Benzene, ml.	M_0, M	ABIN, mg.	Time, hr.	Conversion— mg.	Conversion— %	Sol. part, mg.	Insol. part, mg.	Pendent double bond, mole % (infrared method)
N-CH_3	498	10	0.35	3.5	12	271	54.4	271	Trace	61.5
N-C_2H_5	553	10	0.35	3.8	12	273	49.5	244	29	71.5
N-C_4H_9	648	10	0.35	4.0	12	227	35.0	193	34	78.0

Molecular models indicate some crowding in the transition state for the intramolecular ring closure step, wherein the hydrogen atoms of the N-methyl group, which are six atoms removed from the radical site, may exhibit a penultimate effect.[24] Steric inhibition would thus dictate against ring closure and favor the formation of linear polymer. A comparison of the results of the polymerization of monomers IVa–c, under identical polymerization conditions, illustrates this point (Table IV). As can be seen, as the bulk of



the alkyl substituent on nitrogen increases in size, the degree of conversion decreases, the per cent of insoluble polymer increases, and the per cent of pendent vinyl groups rises.

The Effect of Initiator.—In an attempt to overcome the greater reactivity exhibited by the S-vinyl double bond toward free-radical initiation a cationic initiator was employed. Polymerization of IVa in benzene solution (10% by weight) in the presence of a catalytic amount of boron trifluoride etherate resulted in an 85.7% conversion to polymer without gel formation after 3 hr. Infrared spectrum analysis indicated the presence of 42% residual double bond, attributable in its entirety to pendent S-vinyl moieties. The indicated greater reactivity of the N-vinyl group toward cationic initiation is obviously due to its greater negative polarity.

Polymerization of IVb and IVc under these conditions resulted in tacky polymers with low conversion.

Hydrolysis Studies.—The possibility of hydrolyzing the polymeric thiocarbamates was studied in some detail. Treatment of a solution of poly(S-vinyl-N-methylvinylthiocarbamate) in dimethylformamide with a concentrated sodium hydroxide solution at room temperature under a nitrogen atmosphere resulted in the precipitation of a gel-like polymer. This material proved to be fusible, was slightly soluble in 10% aqueous sodium hydroxide, and gave a positive nitroprusside test. Examination of the infrared spectrum of this material showed the presence of a weak peak at 2550 cm.$^{-1}$, indicative of free sulfhydryl.[25] Elemental analysis could not be obtained since the product could not be readily purified owing to its insolubility and sensitivity to air.

Treatment of a finely divided sample of poly(S-vinyl-N-methylvinylthiocarbamate) with a saturated solution of hydrogen bromide in glacial acetic acid failed to evolve carbon dioxide. The material did not dissolve and no visible change was observed. Upon isolating the polymer, however, it was found to be insoluble, indicating that cross linking had occurred. On treatment with constant-boiling hydrochloric acid, on the other hand, there was considerable carbon dioxide evolution with the resultant formation of a dark brown solution which gave a strong nitroprusside test. Attempts to precipitate the polymer by addition to large excess of various water-miscible organic solvents were unsuccessful. Lyophilization of this solution resulted in a tacky polymer which could not be further purified but which showed sulfhydryl absorption in the infrared and almost complete disappearance of the carbonyl band.

It is perhaps worthy of note that after this research was begun a paper appeared[26] wherein it was stated that treatment of vinylphthalimide copolymers with hydrazine hydrate led to polymers containing SH and NH_2 groups which could not be isolated owing to the rapidity with which they underwent oxidation.

Experimental[27]

Materials.—The N-alkylaziridines (I) were purchased from the Borden Chemical Corp., Philadelphia 24, Pa. S-β-Chloroethyl chlorothiolformate (II) and S-2-chloroethyl-N-2-bromoethylthiocarbamate (V) were prepared according to the procedure of Ringsdorf and Overberger.[12]

S-2-Chloroethyl-2-chloroethylmethylthiocarbamate (IIIa).—To a solution of 31.8 g. (0.20 mole) of S-β-chloroethyl chlorothiolformate (II) in 100 ml. of ether and cooled to 0°, there was added dropwise a solution of 11.4 g. (0.20 mole) of N-methylaziridine in 100 ml. of ether. After stirring the reaction mixture overnight, the solvent was removed *in vacuo* and the residue was distilled under reduced pressure. The same procedure was employed for the preparation of IIIb and IIIc. See Table I.

S-Vinyl-N-methylvinylthiocarbamate (IVa).—To a solution of 101.6 g. (0.47 mole) of IIIa dissolved in 150 ml. of absolute *t*-butyl alcohol and heated to gentle reflux, there was added over a 2.5-hr. period a previously prepared solution of 33.2 g. (0.85 g.-atom) of potassium in 637 ml. of *t*-butyl alcohol. The reaction mixture was heated at 35–40° overnight, was neutralized with glacial acetic acid, and was filtered. The filter cake was washed with additional solvent and the combined filtrates were concentrated *in vacuo*. The residue was distilled under reduced pressure in the presence of a small amount of hydroquinone. The same procedure was employed for the preparation of IVb and IVc. See Table II.

Polymerization of the S-Vinyl-N-vinylthiocarbamates.—A thick-walled Pyrex tube containing the monomer, α,α′-azobisisobutyronitrile, and benzene (dried over, and distilled from, calcium hydride) was sealed under reduced pressure after evacua-

(24) For a discussion of the penultimate effect, see M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 206.

(25) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 350.

(26) G. Hardy, J. Varga, K. Nyitrai, I. Czajlik, and L. Zubonyai, *Vysokomolekul. Soedin.*, **6**, 758 (1964).

(27) All melting points are uncorrected; analyses by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., and by Alfred Bernhardt, Mikroanalytisches Laboratorium in Max Planck Institut fur Kohlenforschung, Mulheim (Ruhr), West Germany.

tion of air and the following replacement with dry nitrogen was repeated several times while keeping the tube immersed in an acetone–Dry Ice mixture. The tube was then maintained at polymerization temperature (65°). After the lapse of a given period of time, the contents of the tube were poured into pentane (10:1 excess) containing a trace of phenyl-β-naphthylamine as an inhibitor against oxidation or further polymerization. The precipitated polymer was washed thoroughly with pentane and dried *in vacuo*. In such case that gelation occurred during polymerization, the insoluble gel was separated by centrifugation.

Acknowledgment.—The authors gratefully acknowledge support of this work from the Office of the Surgeon General of the United States Army under Contract No. DA-49-193-MD-2032.

Reductions with Metal Hydrides. XVII. Reduction of 1,3-Thiazanes[1a]

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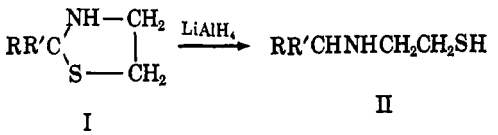
Received March 26, 1965

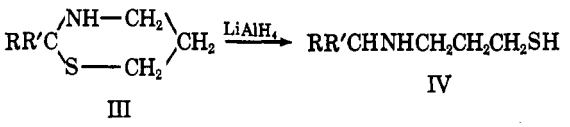
Reduction of 2-substituted 1,3-thiazanes (1-thia-3-azacyclohexanes) with lithium aluminum hydride gives N-substituted 3-aminopropyl mercaptans, $RNHCH_2CH_2CH_2SH$. Contrary to earlier implications, even 2-aryl-substituted thiazanes appear to exist largely as such rather than as the tautomeric Schiff bases.

In a previous publication[1] we described the reduction of thiazolidines (I) to β-alkylaminoethyl mercaptans (II) by means of lithium aluminum hydride.



I II

The present paper reports the extension of the reduction reaction to 1,3-thiazanes (III) which are reduced to γ-alkylaminopropyl mercaptans (IV). Apart from



III IV

the intrinsic interest of ascertaining whether the six-membered heterocyclic rings were hydrogenolyzed as easily as the five-membered ones, the present study serves to answer two questions which had arisen in connection with earlier work. One refers to the structure of the thiazanes (III) which had been suggested[2] to exist in tautomeric equilibrium with substantial portions of the Schiff bases, $RR'C{=}NCH_2CH_2CH_2SH$, in cases where R = phenyl. The other point has to do with the overreduction of the β-alkylaminoethyl mercaptans (II), with excess hydride, to ethylamines $RR'CHNHCH_2CH_3$.[1] In connection with ascertaining possible mechanisms of this hydrogenolysis, it was of interest whether the next higher homologs (IV) would be similarly hydrogenolyzed.

Thiazanes (III) were readily obtained from aldehydes or ketones by treatment with the previously described[3] 3-amino-1-propanethiol. The compounds synthesized and their properties are listed in Table I.

Since it had been previously suggested[2] on the basis of the appearance of a strong infrared absorption band at 1650 cm.$^{-1}$ that the condensation product of benzaldehyde and 3-mercaptopropylamine existed principally in the Schiff base rather than the thiazane form, the infrared, ultraviolet, and n.m.r. spectra of this compound were recorded. The infrared spectrum showed no band at 1650 cm.$^{-1}$, but only weak absorption at 1600 cm.$^{-1}$ (probably a phenyl band) in either a KBr pellet or chloroform solution. The ultraviolet spectrum in absolute ethanol was structureless, as reported previously.[2] As Schiff bases ArC(R)=NR are known[4] to have a strong absorption band ($\epsilon \sim 17{,}000$) at 2470 Å. the Schiff base structure would seem to be excluded.[5] The n.m.r. spectrum corroborates the thiazane structure: singlet (1) at τ 8.63 (NH), quintet (2) at 8.36 (central methylene), broad multiplet (4) at 7.10–6.83 (methylenes next to N and S), singlet (1) at 4.95 (benzylic hydrogen), and multiplet (5) at 2.75 (phenyl). The signal position for the benzylic hydrogen is close to that in 2-phenylthiazolidine (τ 4.54) and remote from that of the PhCH=N— proton in the Schiff base structure (τ 3.2[6]). Of course, the n.m.r. spectrum does not entirely exclude a rapidly equilibrating mixture of thiazane and Schiff base with the equilibrium shifted toward the former structure, but if such an equilibrium does exist, the infrared and ultraviolet spectra indicate that it must lie very far on the side of the thiazane.

The characteristic C=N absorption in the infrared was also missing in the spectra of 2-phenyl-2-methyl-1,3-thiazane (from acetophenone) and of 2-(*p*-chlorophenyl-1,3-thiazane (from *p*-chlorobenzaldehyde). The thiazane derived from cyclohexanone is known[2] not to exist in the Schiff base form.[7]

Reduction of the thiazanes with lithium aluminum hydride proceeded smoothly to give the corresponding amino mercaptans IV, except in the case of the 3-

(1) (a) Paper XVI: E. L. Eliel and R. A. Daignault, *J. Org. Chem.*, **30**, 2450 (1965); (b) E. L. Eliel, E. W. Della, and M. M. Rogić, *ibid.*, **27**, 4712 (1962).

(2) E. D. Bergmann and A. Kaluszyner, *Rec. trav. chim.*, **78**, 327 (1959).

(3) S. D. Turk, R. P. Louthan, R. I. Cobb, and C. R. Bresson, *J. Org. Chem.*, **27**, 2846 (1962).

(4) G. E. McCasland and E. C. Horswill, *J. Am. Chem. Soc.*, **73**, 3923 (1951).

(5) Only in the case of the *o*-chlorobenzaldehyde condensation product with 3-amino-1-propanethiol did we, on one occasion, obtain a product which showed a *small* infrared band at 1650 cm.$^{-1}$ and some ultraviolet absorption. However, in a second preparation, the material did not show these characteristics. Because of this lack of reproducibility of properties, the compound is not reported here.

(6) From the n.m.r. spectrum of $C_6H_5CH{=}NCH_2CH_2OH$ which, on the basis of infrared and ultraviolet spectroscopic evidence, has the previously proposed Schiff base structure: *cf.* E. D. Bergmann, *Chem. Rev.*, **53**, 325 (1953).

(7) Since the condensation product of benzaldehyde and 3-amino-1-propanethiol was reported in ref. 2 to have a structureless ultraviolet spectrum (the spectrum is actually reproduced in the paper), it seems puzzling how the Schiff base structure could have been assigned with any confidence on the basis of the infrared spectrum.