peated with 30 ml of 50% aqueous ethanol. The combined aqueous ethanol solutions were cooled to give 2.3 g of **2**. When the oily portion insoluble in aqueous ethanol was allowed to stand at room temperature, 2.9 g of phenyl disulfide, mp 60°, separated. The yield was 90%.

Reaction of *p*-Nitrobenzenethiol with 1.—Five grams (0.029 mole) of **1** was added to a solution of 9 g (0.058 mole) of *p*-nitrobenzenethiol in 100 ml of absolute ethanol. After refluxing for 8 hr, the reaction mixture was allowed to stand at room temperature, and the crystals were separated by filtration and recrystallized from ethanol to give 8 g (90%) of *p*-nitrophenyl disulfide, mp 180–182.5°.

Reaction of *o*-Aminobenzenethiol with 1.—A solution of 2.5 g (0.02 mole) of *o*-aminobenzenethiol and 3.5 g (0.02 mole) of **1** in 50 ml of anhydrous benzene was refluxed for 4 hr. After cooling, the crystals which deposited were separated by filtration and recrystallized from methanol to give 2.3 g (67%) of *o*-aminophenyl disulfide, mp 93°.

Reaction of 2-Naphthalenethiol with 1.—To a solution of 2.3 g (0.014 mole) of 2-naphthalenethiol in 50 ml of anhydrous chloroform was added 2.5 g (0.014 mole) of **1**. After refluxing for 5 hr, the reaction solution was evaporated under reduced pressure to remove the chloroform. The residue was recrystallized from ethanol to give 2 g of 2-naphthyl disulfide, mp 132°. The yield was 88%.

Reaction of 2-Mercaptobenzothiazole with 1.—Five grams (0.029 mole) of **1** was added to a solution of 9.7 g (0.058 mole) of 2-mercaptobenzothiazole in 100 ml of anhydrous benzene (or ethanol), and the mixture was refluxed for 30 min. After cooling, the crystals which separated were filtered and recrystallized from benzene or ethanol give 2,2′-dithiobisbenzothiazole, mp 181°, in quantitative yield.

Registry No.—**1**, 1972-28-7; ethanol, 64-17-5; isopropyl alcohol, 67-63-0; cyclohexanol, 108-93-0; benzyl alcohol, 100-51-6; *p*-nitrobenzyl alcohol, 619-73-8; α-methylbenzyl alcohol, 98-85-1; benzhydrol, 91-01-0; dodecanol, 112-53-8; 1,2-propanediol, 57-55-6; semicarbazone derivative of **1**, 7429-48-3; 2,4-dinitrophenylhydrazone derivative of **1**, 7429-49-4; hydrazobenzene, 122-66-7; *p*-anisidine, 104-94-9; ethanethiol, 75-08-1; 2-propanethiol, 75-33-2; 2-propene-1-thiol, 870-23-5; 1-dodecanethiol, 112-55-0; benzenethiol, 108-98-5; *p*-nitrobenzenethiol, 1849-36-1; *o*-aminobenzenethiol, 137-07-5; 2-naphthalenethiol, 91-60-1; 2-mercaptobenzothiazole, 149-30-4.

Acknowledgment.—We are grateful to Dr. Chikayoshi Nagata for his suggestions, assistance, and guidance during the course of this investigation. We express also our appreciation to Dr. Tomoichiro Akiba, Director of this laboratory, for his encouragement.

Alkylation of Active Hydrogen Compounds by N-Vinylamides

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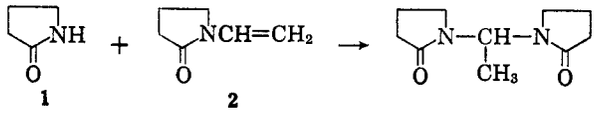
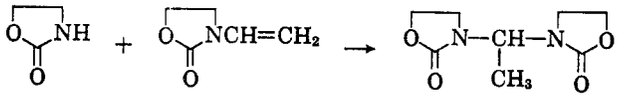
Active hydrogen compounds such as amides, urethans, sulfonamides, thiols, and alcohols are alkylated by N-vinylamides, urethans, or sulfonamides under acidic conditions in high yields.

The acid-catalyzed alkylation of 2-pyrrolidinone (**1**) by N-vinyl-2-pyrrolidinone (**2**) has been reported by Breitenbach.[2,3] More recently a similar reaction has

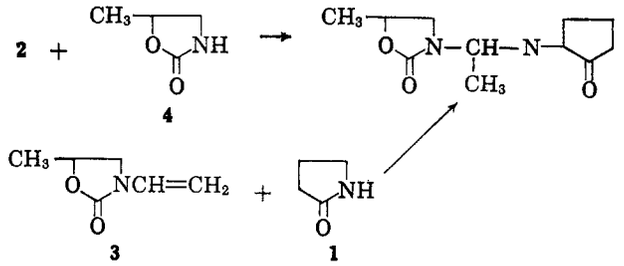


been reported between 2-oxazolidinone and N-vinyl-2-oxazolidinone.[4] As part of a developmental program on derivatives of N-vinyl-5-methyl-2-oxazolidinone[5,6]



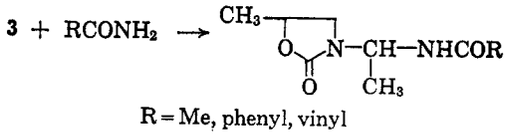
(**3**), we have investigated acid-catalyzed reactions of **3** and related derivatives.

If the original mechanism suggested by Breitenbach is correct, one should obtain the same product from **1** and **3** or from **2** and 5-methyl-2-oxazolidinone (**4**). We found that this is, indeed, the case. Mixture melting points were not completely definitive (the melting point of the product from **1** and **3** was 94–98°; the



product from **2** and **4** had mp 91–95°, mmp 92–96°);[7] however, the identity of the two products was supported by elemental analysis, infrared, and nmr.

Since cyclic amides and carbamates reacted, it seemed reasonable to assume that open-chain amides or urethans would react similarly. Indeed, acetamide, benzamide, or acrylamide were alkylated in excellent yields by either N-vinyl-5-methyl-2-oxazolidinone (**3**) or N-vinyl-2-pyrrolidinone (**2**). The double bond



R = Me, phenyl, vinyl

of acrylamide is retained producing an N-substituted acrylamide. The new monomers polymerized readily with typical radical catalysts, but all efforts produced

(1) Lakeside Laboratories, Milwaukee Wis.

(2) J. W. Breitenbach, F. Galinovsky, H. Nesvabda, and E. Wolf, *Monatsh.*, **87**, 580 (1956).

(3) J. W. Breitenbach, *J. Polymer Sci.*, **23**, 949 (1957).

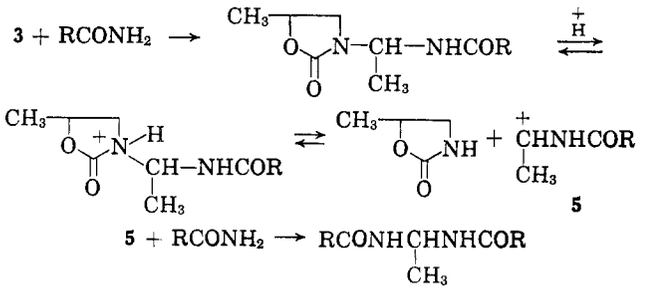
(4) A. Kutner, *J. Org. Chem.*, **26**, 3495 (1961).

(5) W. E. Walles, W. F. Tousignant, and T. Houtman, Jr., U. S. Patent 2,891,058 (1959).

(6) W. W. Bakke, U. S. Patent 2,905,690 (1959).

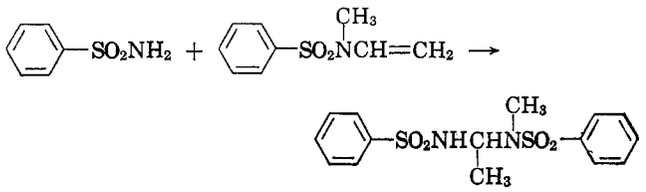
(7) Since the product contains two asymmetric centers, it will consist of a pair of diastereoisomers. Selective loss of small amounts of one isomer could readily account for the differences.

only insoluble gels. The gellation of the polymers is likely due to trace amounts of N,N′-ethylidinediacrylamide. The formation of this could be due to traces of acetaldehyde present in the N-vinyl compound, since it was found that all samples of **3** contained acetaldehyde at levels up to several hundred parts per million. Alternately this could be explained on the basis of a "transalkylation" reaction. Studies presented later



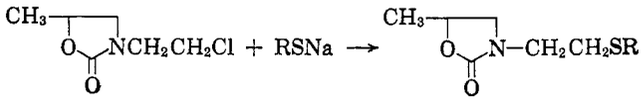
in this work indicate that transalkylation is apparently not a serious side reaction. However, we can not discount the possible formation of trace amounts of the ethylidine compound by this route. Frequently less than 1–2% of cross-linking agent is sufficient to cause gellation in polymers.

The behavior of sulfonamides in this reaction was investigated next because of their formal resemblance to amides. All sulfonamides investigated gave the expected products in yields over 90%. The high yields with sulfonamides was probably due to a combination of high reactivity and low solubility of the products in the reaction medium. The high reactivity of the sulfonamides was also demonstrated by the ready reaction of benzenesulfonamide with the relatively hindered N-vinyl-N-methylbenzenesulfonamide.



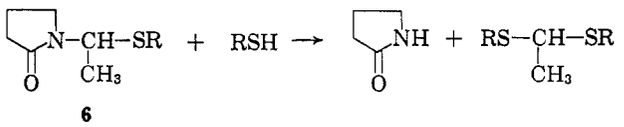
In view of the reactivity of amides and sulfonamides it was anticipated that imides would behave similarly. However, we were unsuccessful in affecting reaction between succinimide or phthalimide and **3**.

Mercaptans are another class of compounds possessing an electron pair that should undergo alkylation. We found that mercaptans are probably the most reactive class of compounds studied. Mercaptans may also undergo spontaneous free-radical addition to olefins; however, free-radical addition would occur at the terminal carbon atom.[8,9] Attachment of the alkylthio group to the same carbon as the nitrogen was proved by hydrolysis of the adduct with aqueous acid in the presence of 2,4-dinitrophenylhydrazine to give acetaldehyde (isolated as the 2,4-dinitrophenylhydrazone), thus indicating the ionic nature of the reaction. Infrared analysis also indicated that under acid conditions attachment of the alkylthio group always occurred at the nonterminal carbon. The acid-catalyzed products from N-vinyl-2-oxazolidinones all showed a strong, sharp bond at 8.05 μ while 3-(2-alkylthioethyl)-2-oxazolidinones prepared from the 3-(2-chloroethyl)-2-oxazolidinones and sodium mercaptides[9,10] all had a strong sharp band at 7.95 μ which was absent in the acid-catalyzed products. Comparison of the free-radical adduct from **2** and 1-octanethiol



by glpc also indicated the absence of any significant amounts of free-radical product in the acid-catalyzed reaction.[11]

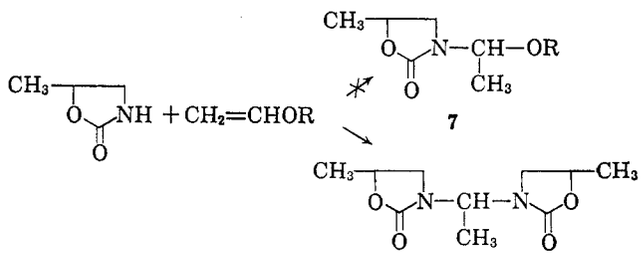
In order to test our previous hypothesis regarding the transalkylation reaction, N-vinyl-2-pyrrolidinone was treated with a molar excess of 1-octane- or 1-pentanethiol. No 2-pyrrolidinone or dithio acetal was detected by glpc. The resistance of dithio acetals to



hydrolysis[12] in contrast to the relative ease of hydrolysis of the 1-[(1-alkylthio)ethyl]-2-pyrrolidinones suggests that if transalkylation is a significant factor in these reactions, it should be particularly favorable in the thiol case. However, when **6** was treated with concentrated hydrochloric acid, the dithio acetal was isolated in 43%. The presence of 2-pyrrolidinone was shown by glpc.

N-Vinylsuccinimide was found to be unreactive toward thiols, in accord with our observations of the nonreactivity of imides in this system (see above). N-Vinyl-N-methylbenzenesulfonamide reacted readily with the thiols as would be predicted by the reactivity of sulfonamides with the N-vinylamides studied.

It occurred to us that vinyl ethers might alkylate amides in the same manner as the vinylamides; however, the only product isolated was the corresponding ethylidine bis compound.[13] Apparently **7** undergoes



protonation as it is formed to produce the same intermediate which is obtained by protonating the N-vinyl derivative. This intermediate may then react further

(8) F. W. Stacey and J. F. Harris, Jr., *Org. Reactions*, **13**, 164 (1963).

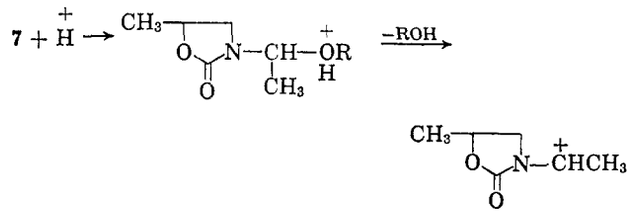
(9) M. F. Shostakovskii, F. P. Sidel'kovskoya, and F. S. Kolodkin, *Bull. Acad. Science USSR*, 155 (1962).

(10) R. A. Hickner, U. S. Patent 3,188,317 (1965).

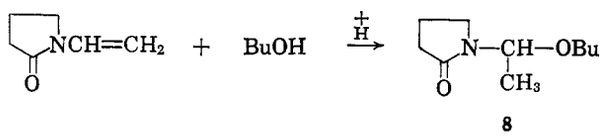
(11) The apparently purposeless switch from the oxazolidinone to pyrrolidinone series in several places in this paper was dictated by physical properties of the products. The former series was used where lower solubility and higher melting points was desired while the latter series was studied when higher volatility was desired.

(12) (a) A. Schoenberg and W. Asker, *J. Chem. Soc.*, 604 (1946); (b) E. Campaigne, "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press Inc., New York, N. Y., 1961, pp 134–145.

(13) R. A. Hickner, W. W. Bakke, and C. I. Judd, U. S. Patent 3,072,652 (1963).

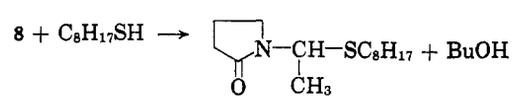


with 5-methyl-2-oxazolidinone. To test this hypothesis, N-vinyl-2-pyrrolidinone was treated with 1-butanol in the presence of anhydrous hydrogen chloride. That



8

the expected reaction had occurred was indicated by the disappearance of the infrared absorption at 2.9 and 6.15 μ for the hydroxyl and double bond, respectively, and appearance of a strong ether band at 9.1 μ. However, attempts to distil **8** resulted in disproportionation to a complex mixture of butanol, dibutyl acetal, and other unidentified products.[14] When crude **8** was treated with 1-octanethiol, 1-[(octylthio)ethyl]-2-pyrrolidinone was produced as evidenced by glpc comparison with the product from N-vinyl-2-pyrrolidinone and 1-octanethiol.



In summary, we can conclude that (1) under acidic conditions the reactions of N-vinylamides, N-vinylsulfonamides, vinyl ethers, and N-(1-alkoxyalkyl)-amides differ in degree rather than kind, and (2) most compounds containing an NH adjacent to a single carbonyl or sulfonyl group or containing an SH should undergo acid-catalyzed alkylation by N-vinyl compounds in which the nitrogen is adjacent to a single carbonyl or sulfonyl group.

Experimental Section

Equipment.—All melting points were determined on a Fisher-Johns block. An F & M Model 500 gas–liquid partition chromatograph was used with a 2 ft × 0.25 in. SE 30 on Chromosorb W column, and a helium flow rate of 80 cc/min. The gas–liquid partition chromatograph was programmed at 15°/min from an initial temperature of 100°.

Materials.—The thiols, amides, imides, and sulfonamides were purchased from Eastman. 2-Pyrrolidinone and N-vinyl-2-pyrrolidinone from General Aniline and Film Co., were redistilled through an 8-in. Vigreux column. N-Vinylsuccinimide was purchased from Monomer-Polymer Laboratories and *n*-butyl ether was obtained from Union Carbide Corp. 5-Methyl-2-oxazolidinone was prepared by the method of Close,[15] bp 121–124° (2 mm), n^{25}D 1.4595. The N-vinyl-2-oxazolidinones were prepared by direct vinylation:[6] N-vinyl-5-methyl-2-oxazolidinone bp 88–89° (1.5 mm), n^{25}D 1.4752; N-vinyl-5-ethyl-2-oxazolidinone, bp 84–86° (0.8 mm), n^{25}D 1.4762. N-Vinyl-N-methylbenzenesulfonamide was prepared by the method of Cairns and Sauer,[16] bp 139–140° (4 mm), n^{25}D 1.5464 (lit.[16] n^{25}D 1.5468).

General Procedure for Addition Reactions.—One mole of the N-vinyl compound and 1 mole of the active hydrogen compound were dissolved or suspended in benzene. Anhydrous hydrogen chloride was bubbled in until the temperature began to rise. External cooling was applied if necessary to prevent the temperature from rising above 50°. Most products precipitated readily from benzene with the exception of the thiol adducts. The solid products were collected by vacuum filtration and in some cases recrystallized from ethanol. The thiol adducts were distilled through a flash still. The products prepared, physical properties, and analyses are listed in Tables I and II. All products, except the thiol adducts, developed the odor of acetaldehyde when left exposed in air.

Reaction of N-Vinyl-2-pyrrolidinone (2) with 5-Methyl-2-oxazolidinone (4).—A solution of 20.2 g (0.2 mole) of **4** in 50 ml of benzene was acidified to pH 1 with anhydrous HCl and 22.2 g (0.2 mole) of **2** was added dropwise while maintaining the temperature below 40. Stirring was continued an additional 0.5 hr. The precipitate was dissolved in methylene chloride and the solution was neutralized with anhydrous ammonia, and filtered to remove the salt. The solvent was removed at reduced pressure. The solid collected by vacuum filtration and washed with ether–benzene (5:1). The solid weighed 35.5 g (84.1%). After a second washing as described above the product melted at 87.5–91°.

Anal. Calcd for $C_{10}H_{16}N_2O_3$: C, 56.35; H, 8.00; N, 13.1. Found: C, 56.60; H, 7.68; N, 13.07.

A small sample of the above product recrystallized from 2B absolute ethanol melted at 91–95°.

Reaction of N-Vinyl-5-methyl-2-oxazolidinone (3) with 2-Pyrrolidinone (1).—A solution of 16.8 g (0.2 mole) of **1** in 50 ml of benzene was treated with 25.4 g (0.2 mole) of **3** as in the above example. The crude product was dissolved in methylene chloride, neutralized with anhydrous ammonia, and filtered. The crude product was triturated with ether–benzene (5:1) and dried to give 31 g (74%) of product melting at 93–96°.

Anal. Calcd for $C_{10}H_{16}N_2O_3$: C, 56.35; H, 8.00; N, 13.1. Found: C, 56.65; H, 7.72; N, 13.35.

The above crude product after retrituration with ether–benzene melted at 94–98°. A mixture melting point of this product with that from **2** and **4** was 91.5–96°. The infrared spectra of the two products were essentially identical in solution in CCl_4 or CS_2 or as mulls. The nmr spectra showed no sensible differences.

Polymerization of Products from Acrylamide and N-Vinyl-2-pyrrolidinone or N-Vinyl-5-methyl-2-oxazolidinone. A.—A solution of 15 g of freshly prepared product from N-vinyl-5-methyl-2-oxazolidinone, 15 g of **3**, and 0.35 g of α,α'-azobisisobutyronitrile was heated at reflux for 2.5 hr. The reaction mixture at this point was a gel which could not be stirred.

B.—A solution of 30 g of product from N-vinyl-2-pyrrolidinone and 300 mg of azobisisobutyronitrile in 70 ml of 50% aqueous methanol was heated at reflux for 10 min at which time an insoluble gel had formed. The product was also insoluble in water, 95% ethanol, acetone, or chlorobenzene.

C.—A solution of 20 g of product from N-vinyl-5-methyl-2-oxazolidinone, 1 g of concentrated ammonium hydroxide, and 0.1 g of 30% aqueous hydrogen peroxide was heated to 70° under a nitrogen atmosphere. After a few minutes an insoluble gel had formed.

Attempted Reaction of N-Vinyl-5-methyl-2-oxazolidinone (3) and Phthalimide.—A suspension of 73.6 g (0.5 mole) of phthalimide in 63.5 g (0.5 mole) of **3** and 200 ml of benzene was treated with anhydrous hydrogen chloride. No temperature rise occurred. After stirring for 1 hr, the mixture was filtered to give 71 g (96.5%) of material which did not depress the melting point of phthalimide.

Attempted Reaction of N-Vinyl-5-methyl-2-oxazolidinone and Succinimide.—Succinimide (49.5 g, 0.5 mole) suspended in a solution of 63.5 g (0.5 mole) of **3** and 200 ml of benzene was acidified with anhydrous hydrogen chloride. A small temperature rise occurred, apparently owing to heat of solution. After stirring for 1 hr the solid (45 g) was collected by filtration. A mixture melting point with succinimide was undepressed.

Ultraviolet-Catalyzed Addition of 1-Octanethiol to N-Vinyl-2-pyrrolidinone (2).—A 600-ml beaker was placed in a water bath through which cold water was circulated. The bath was placed on a magnetic stirrer and a stirring bar was used to stir the contents of the beaker. The beaker was charged with 43.8 g (0.3 mole) of 1-octanethiol and 33.3 g (0.3 mole) of **2** was added dropwise while irradiating with a G.E. UA-2 lamp. After irradiating for 6 hr the crude product was charged to a flash still. After

(14) M. F. Shostakovskii, F. P. Sidel'kovskaya, and M. G. Zelenskaya, *Bull. Acad. Sci. USSR*, 488 (1959).

(15) W. J. Close, *J. Am. Chem. Soc.*, **73**, 95 (1951).

(16) T. L. Cairns and J. C. Sauer, *J. Org. Chem.*, **20**, 627 (1955).

TABLE I

ALKYLATION OF AMIDE-TYPE COMPOUNDS

N-Vinyl compd	Active H compd	Mp, °C[a]	Yield, %	Formula	—Calcd, %— C	H	—Found, %— C	H
N-Vinyl-2-pyrrolidinone	Acrylamide	*b*	90	$C_9H_{14}N_2O_2$	59.38	7.70	59.37	7.58
N-Vinyl-2-pyrrolidinone	Benzenesulfonamide	143–145	95	$C_{12}H_{16}N_2O_3S$	53.72	5.97	54.16	6.34
N-Vinyl-2-pyrrolidinone	5-Methyl-2-oxazolidinone	91–95[c]	84	$C_{10}H_{16}N_2O_3$	56.35	8.00	56.60	7.68
N-Vinyl-5-methyl-2-oxazolidinone	Acetamide	145–148	50	$C_8H_{14}N_2O_3$	51.48	8.28	51.57	7.58
N-Vinyl-5-methyl-2-oxazolidinone	Acrylamide	*b*	53	$C_9H_{14}N_2O_3$	54.55	7.06	55.23	7.32
N-Vinyl-5-methyl-2-oxazolidinone	*p*-Toluenesulfonamide	143–146	91	$C_{13}H_{18}N_2O_4S$	52.38	6.04	52.76	5.98
N-Vinyl-5-methyl-2-oxazolidinone	Benzamide	156–159	93	$C_{13}H_{16}N_2O_3$	62.90	6.45	62.84	6.43
N-Vinyl-5-methyl-2-oxazolidinone	2-Pyrrolidinone	94–98	74	$C_{10}H_{16}N_2O_3$	56.35	8.00	56.63	7.72
N-Vinyl-5-methyl-2-oxazolidinone	Benzenesulfonamide	145–148	93	$C_{12}H_{16}N_2O_4S$	50.70	5.63	50.38	5.55
N-Vinyl-N-methylbenzenesulfonamide	Benzenesulfonamide	133–136	58	$C_{15}H_{18}N_2O_4S_2$	50.83	5.08	50.92	5.01

[a] Many of these compounds are mixtures of two diasteriomers so that recrystallization can concentrate isomers and result in different melting points. [b] Polymerizes. [c] See discussion regarding these products.

TABLE II

ALKYLATION OF THIOLS

N-Vinyl compd	Thiol	Bp, °C (mm)	$n^{25}D$	Yield, %	Formula	—Calcd, %— C	H	—Found, %— C	H
N-Vinyl-2-pyrrolidinone	*n*-Dodecyl	155–165 (0.2)	1.4844	88	$C_{18}H_{35}NOS$	68.95	11.17	69.10	11.23
N-Vinyl-2-pyrrolidinone	*n*-Octyl-	144 (0.5)	1.4896	87	$C_{14}H_{27}NOS$	65.35	10.48	65.02	10.59
N-Vinyl-5-methyl-2-oxazolidinone	*n*-Dodecyl-	>160 (0.5)	1.4752	87	$C_{18}H_{35}NO_2S$	65.70	10.70	65.93	10.97
N-Vinyl-5-methyl-2-oxazolidinone	Benzene-	*a*	1.5570	75	$C_{12}H_{15}NO_2S$	60.72	6.36	60.46	6.43
N-Vinyl-5-methyl-2-oxazolidinone	*n*-Octyl-	*a*	1.4778	87	$C_{14}H_{27}NO_2S$	65.30	10.57	64.90	10.15
N-Vinyl-N-methylbenzenesulfonamide	*n*-Dodecyl-	*a*	1.5090	84	$C_{21}H_{37}NO_2S_2$	63.42	9.38	63.73	9.33
N-Vinyl-N-methylbenzenesulfonamide	*p*-Chlorobenzyl-	*a*	1.5870	98	$C_{16}H_{18}NO_2S_2Cl$	54.02	5.06	54.16	4.90
N-Vinyl-5-ethyl-2-oxazolidinone	3-Methylbutyl-	130–140 (0.15)	1.4804	30	$C_{12}H_{23}NO_2S$	58.73	9.45	58.84	9.20

[a] Not distilled.

removing 3.6 g of lights boiling up to 148° (0.1 mm), two product cuts were collected: cut A, bp 147–150° (0.3–0.5 mm), $n^{25}D$ 1.4958; cut B, bp 147° (0.3 mm), $n^{25}D$ 1.4963.

Anal. Calcd for $C_{14}H_{27}NOS$ (cut B): C, 65.30; H, 10.57. Found: C, 64.90; H, 10.30.

The nmr of a 20% $CDCl_3$ solution supported the structure.

The retention time on glpc (T_i = 100°, 15°/min) was 12.9 min while the acid-catalyzed adduct (see below) had a retention time of 12.6 min. A glpc of the mixed products resolved the two components readily.

Structure Proof of Adduct from N-Vinyl-2-pyrrolidinone and 1-Dodecanethiol.—A solution of 3.13 g (0.01 mole) of the title product, 1.98 g (0.01 mole) of 2,4-dinitrophenylhydrazine, 15 ml of water, 50 ml of 2B absolute ethanol, and 5 ml of sulfuric acid was heated at reflux for 30 min. On cooling 1.30 g (65%) of the product crystallized out, which melted at 146–147° after trituration with ethanol. A mixture melting point with acetaldehyde–2,4-dinitrophenylhydrazone was undepressed.

Structure Proof of Adduct from N-Vinyl-5-methyl-2-oxazolidinone and 1-Dodecanethiol.—A solution of 3.27 g (0.01 mole) of adduct was reacted as above to give 1.30 g (65%) of 2,4-dinitrophenylhydrazone which did not depress the melting point of an authentic sample.

Preparation of 1,1-Bis(octylthio)ethane (Dioctyl Thial of Acetaldehyde).—1-Octanethiol (29.2 g, 0.2 mole) was acidified with anhydrous HCl and 10.0 g (0.1 mole) of butyl vinyl ether was added dropwise. Occasional cooling was applied to keep the temperature below 50°. Stirring was continued for an additional 0.5 hr and the crude product was transferred to a flash still. A forecut (7.0 g) was taken up to a head temperature of 135° (0.21 mm) followed by 28.5 g (89.5%) of product, bp 135–142° (0.2–0.4 mm), $n^{25}D$ 1.4814.

Anal. Calcd for $C_{18}H_{38}S_2$: C, 67.90; H, 12.03; S, 20.13. Found: C, 67.92; H, 11.69; S, 20.00.

Acid-Catalyzed Addition of 1-Octanethiol to 2.—A solution of 58.4 g (0.4 mole) of 1-octanethiol in 25 ml of methylene chloride was acidified to pH 1 with anhydrous hydrogen chloride and 44.4 g (0.4 mole) of 2 added dropwise with cooling to keep the temperature below 48°. A 20-ml sample was neutralized with anhydrous ammonia and filtered, and the solvent was removed. This product eluted faster on the glpc than the radical product (see above).

Another 20-ml sample was pipetted out (pH still 1) and 5 ml of 1-octanethiol was added. Samples were taken at intervals over a several-hour period and submitted to glpc analysis. No dithio acetal was detected. [The above experiment was repeated using 1-pentanethiol. The single product was eluted in 8.0 min (T_i = 100°, 15°/min)].

A 13-g sample of the adduct was treated slowly with 25 ml of concentrated HCl. Initially the reaction was clear, but became cloudy within a few minutes. After standing for 10 min, the two-phase system was extracted with chloroform and the solution was dried with drierite, and evaporated. The crude product (3.6 g, 43%) was shown by glpc to be identical with the dithio acetal, $n^{25}D$ 1.4808.

Anal. Calcd for $C_{18}H_{38}S_2$: C, 67.90; H, 12.03; S, 20.13. Found: C, 68.40; H, 11.55; S, 19.65.

Glpc analysis of the aqueous phase showed the presence of 2-pyrrolidinone.

Reaction of 1-Butanol with N-Vinyl-2-pyrrolidinone.—A solution was prepared of 111 g (1.0 mole) of N-vinyl-2-pyrrolidinone and 74 g (1.0 mole) of 1-butanol. The infrared spectrum had a strong band at 6.15 μ for the double bond and a strong hydroxyl band. The flask was cooled to 12° with an ice bath and anhydrous HCl was sparged in gently until the temperature began to rise. The temperature rose rapidly to 45°. The cooling bath was removed and stirring was continued for 1 additional hr. The mixture was then stirred for 0.5 hr with anhydrous sodium carbonate. The infrared spectrum indicated nearly complete absence of double bond and hydroxyl. Distillation through an 8-in. Vigreux column gave a liquid fraction of 110 ml which boiled at 63–98° (3.0 mm) (most boiling at 96–98°). Infrared showed a moderate hydroxyl band at 2.9, a moderate C=C band at 6.18, and a broad ether band at 9.1 μ. The presence of dibutyl acetal was supported by comparison with an authentic sample. A solid residue weighing 43 g remained in the pot.

***In Situ* Reaction of 1-(1-Butoxyethyl)-2-pyrrolidinone with 1-Octanethiol.**—1-Butanol (29.6 g, 0.4 mole) was acidified with anhydrous hydrogen chloride and 44.4 g (0.4 mole) of N-vinyl-2-pyrrolidinone was added dropwise over a 10-min period. The temperature rose to 45°. Upon cooling to room temperature, the infrared spectrum showed no double-bond absorption at 6.1 μ and only a slight hydroxyl absorption.

1-Octanethiol (58.4 g, 0.4 mole) was added dropwise during 6 min to the above product which was still acid whereupon the temperature rose to 43°. After stirring for 1 hr, anhydrous sodium carbonate and a dropperful of concentrated NH_4OH were added. The vapor phase chromatograph indicated the product to be a mixture of 1-butanol and 1-[(1-octylthio)ethyl]-2-pyrrolidinone. Distillation of a 65-g sample through a flash still gave a forecut of butanol and 46.7 g (91%) of the octylthio compound, bp 144–146° (0.5 mm), $n^{25}D$ 1.4892.

Anal. Calcd for $C_{14}H_{27}NOS$: C, 65.30; H, 10.48. Found: C, 64.95; H, 10.15.

The retention time on the glpc was identical with that of the acid-catalyzed product of 1-octanethiol to **2**.

Attempted Reaction of N-Vinyl uccinimide with 1-Dodecanethiol.—A solution of 10.9 g (0.1 mole) N-vinylsuccinimide and 20.2 g (0.1 mole) of 1-dodecanethiol in 50 ml of methylene chloride at 21° was treated with 5 drops of concentrated sulfuric acid. After several minutes when no apparent reaction had occurred, and additional 5 drops of sulfuric acid was added. After standing for an additional 45 min the infrared spectrum of the solution was identical with the starting solution.

Registry No.—$C_9H_{14}N_2O_2$, 7594-58-3; $C_{12}H_{16}N_2O_3S$, 7594-59-4; $C_8H_{14}N_2O_3$, 7594-61-8; $C_9H_{14}N_2O_3$, 7594-62-9; $C_{13}H_{18}N_2O_4S$, 7594-63-0; $C_{13}H_{16}N_2O_3$, 7594-64-1; $C_{10}H_{16}N_2O_3$, 7594-60-7; $C_{12}H_{16}N_2O_4S$, 7594-66-3; $C_{15}H_{18}N_2O_4S_2$, 7594-67-4; $C_{18}H_{35}NOS$, 5681-84-5; $C_{14}H_{27}NOS$, 7594-69-6; $C_{18}H_{35}NO_2S$, 5681-87-8; $C_{12}H_{15}NO_2S$, 5681-86-7; $C_{14}H_{27}NO_2S$, 7594-72-1; $C_{21}H_{37}NO_2S$, 7594-73-2; $C_{16}H_{18}NO_2S_2Cl$, 7594-74-3; $C_{12}H_{23}NO_2S$, 5681-85-6; $C_{18}H_{38}S_2$, 7594-76-5.

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Acridizinium Ion Chemistry. VI.[1] Reaction with Bases. II[2]

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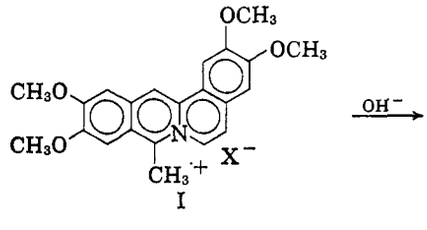
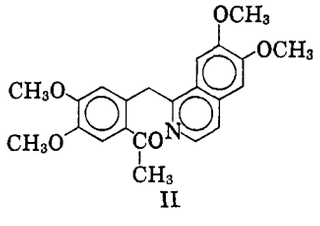
In basic solution the acridizinium ion under goes ring opening and can give base-catalyzed condensation of the type to be expected if 2-(2-formylbenzyl)pyridine were present. The easily prepared oxime of 2-(2-formylbenzyl)pyridine has been converted to 2-(2-cyanobenzyl)pyridine which proved to be a convenient starting material for the preparation of acridizinium and benzo[*b*]quinolizin-6-one derivatives.

In what was apparently the first paper to describe a quinolizinium derivative, Schneider and Schroeter[3] showed that coralyn (8-methyl-2,3,10,11-tetramethoxybenz[*a*]acridizinium, I) cation, in the presence of a base, underwent ring opening to afford a methyl ketone (II). By analogy it would be expected that addition of base to the acridizinium ion (III) might yield 2-(2-formylbenzyl)pyridine (V), probably *via* the pseudo-base (IV). Frost and Saylor[4] have invoked this equilibrium to explain the change in mode of polarographic reduction and the nature of the ultraviolet absorption spectrum in this system with increasing pH. It was reported earlier[5,6] that addition of base to an aqueous solution of acridizinium ion (III) leads to the precipitation of a red or brown powder. Although this powder has not yet been purified, evidence has been adduced (Experimental Section) which suggests that the material is a mixture of the aldehyde (V) and the pseudo-base (IV).



I



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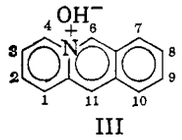

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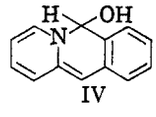
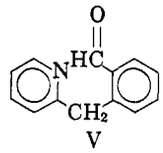


IV



V

Evidence for the existence of the aldehyde (V) in basic alcohol solution was afforded by sodium borohydride reduction to afford the corresponding benzyl alcohol, 2-(2-hydroxymethylbenzyl)pyridine, which was isolated as the methoperchlorate. Proton magnetic resonance measurements support the assigned structure.

The most convincing chemical evidence for the presence of the formylbenzylpyridine (V) in an acridizinium solution that has been made basic was afforded by the formation of an oxime (VIIIa, 87%) or a semicarbazone (VIIId, 76%). The proton magnetic resonance spectra of the oximes (VIa–c) made it quite clear that the ring had opened in the indicated manner. On

(1) For the preceding communication of this series, see C. K. Bradsher and J. D. Turner, *J. Org. Chem.*, **31**, 565 (1966).

(2) This investigation was supported by Public Health Service Research Grant No. CA-05509 of the National Cancer Institute.

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(4) J. G. Frost and J. H. Saylor, *Rec. Trav. Chim.*, **82**, 828 (1963).

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(6) C. K. Bradsher and J. H. Jones, *J. Am. Chem. Soc.*, **81**, 1938 (1959).