Acid-Catalyzed Cyclization Reactions. IX. The Formation of Oxazolinium and Thiazolinium Cations from *N*-Allyl and Substituted *N*-Allylamides, -urethans, -ureas, and -thioureas[1]

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Received April 10, 1970

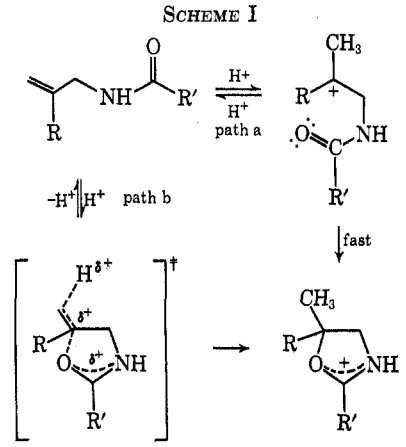
N-Allyl and substituted *N*-allylamides, -urethans, -ureas, and -thioureas have been cyclized in 60–96% sulfuric acid to their corresponding oxazolinium and thiazolinium cations. By drowning certain of these acid solutions into base, a useful synthetic route to 2-oxazolines and 2-thiazolines has been demonstrated. The formation of oxazolinium (**2a–o**) and thiazolinium (**2p–r**) cations was studied by nmr techniques. In general, the simple *N*-allyl derivatives were only protonated at carbonyl oxygen or thiocarbonyl sulfur when introduced into the acid media at room temperature. The cyclic ions (**2**) formed upon heating. The formation of *N*-acylpolyethyleneimines competed with cyclization in some of these examples. *N*-2-Methylallyl and *N*-2-phenylallyl derivatives cyclized immediately at room temperature. The remarkable stability of oxazolinium and thiazolinium cations was indicated by their stability towards heating in acid media and their marked resistance to H–D exchange. Oxazolinium and thiazolinium ions are more resistant to H–D exchange than are oxoniacyclopent-1-enyl and 1,3-dioxoniacyclopent-1-enyl cations. The nmr spectra of these heterocyclic ions are tabulated and discussed. The mechanism of the cyclization process is discussed in light of these findings.

Intramolecular neighboring-group participation by nonbonding and π-bonding electrons in carbonium ion reactions has received considerable attention. Examples include participation by halogen,[4] olefinic bonds,[5] and carbonyl oxygen[6] in solvolytic reactions of trialkyl oxonium ions, halides, and sulfonates. Evidence for participation commonly includes enhanced solvolysis rates in compounds where this participation occurs compared to solvolysis rates of model compounds. In some cases intermediates have been isolated.[6a,7] The ready cyclization of *N*-allylbenzamides to 5-(bromomethyl)-2-phenyl-2-oxazolines upon bromination[8] and to fluorine-containing oxazolines on direct fluorination[9] in polar solvents also represents examples of neighboring-group participation of amide groups.

Heteronuclear stabilized carbonium ions, which are intermediates in the above reactions, have been prepared in many ways[10] and are exceptionally stable if the neighboring heteroatom is oxygen or nitrogen. Few of the reports[10] allow one to judge the relative stability of the ions reported. A recent paper[11] detailing physical studies of triphenylcarbonium ions with multiple neighboring group treats relative stabilities to a limited degree.

In view of the possibility for two discrete pathways for cyclization of allylic amides upon olefinic carbon protonation (see Scheme I), the study of some of these

Scheme I



reactions using nmr techniques to follow the reaction attracted our attention. In addition basic studies of thiazolinium and oxazolinium ions seemed appropriate because of some mention that has been given them with regard to some chemical processes. For example, thiazolinium cations play a role in the reaction mechanism of intramolecular *S*- to *N*-acetyl transfer of *S*-acetylmercaptoethylamine.[12] Oxazolinium cations are intermediate in the preparation of *N*-acyl-substituted polyethylenimines[13] and in the rearrangement of *N*-

(1) (a) For other papers in this series, see S. P. McManus, and J. T. Carroll, *Org. Prep. Proced.*, **2**, 71 (1970), and C. U. Pittman and S. P. McManus, *J. Org. Chem.*, **35**, 1187 (1970). (b) This work was supported in Huntsville in part by the Petroleum Research Fund, administered by the American Chemical Society, and in Tuscaloosa in part by the University of Alabama Research Committee, project 562. (c) A preliminary account of portions of this work was presented: Abstracts, 20th Southeastern Regional Meeting of the American Chemical Society, Tallahassee, Fla., Dec 4, 1968, pp 69–70.

(2) Coprincipal investigator; inquiries should be addressed to S. P. M.

(3) American Chemical Society Petroleum Research Fund Scholar, 1968–1969.

(4) P. E. Peterson and F. J. Slama, *J. Amer. Chem. Soc.*, **90**, 6515 (1968).

(5) For leading references, see (a) T. L. Jacobs and R. S. Macomber, *ibid.*, **91**, 4824 (1969); (b) P. E. Peterson and R. J. Kamat, *ibid.*, **91**, 4521 (1969); and (c) J. W. Wilson, *ibid.*, **91**, 3238 (1969).

(6) (a) H. R. Ward and P. D. Sherman, *ibid.*, **90**, 3812 (1968); (b) S. Oae, *ibid.*, **78**, 4030 (1956); (c) D. J. Pasto and M. P. Serve, *ibid.*, **87**, 1515 (1965); and (d) O. K. J. Kovacs, G. Schneider, L. D. Lang, and J. Apjok, *Tetrahedron Lett.*, 4186 (1967).

(7) S. Winstein, L. Goodman, and R. Boschan, *J. Amer. Chem. Soc.*, **72**, 2311 (1950).

(8) L. Goodman and S. Winstein, *ibid.*, **79**, 4788 (1957).

(9) R. F. Merritt, private communication.

(10) See (a) C. U. Pittman and S. P. McManus, *J. Amer. Chem. Soc.*, **91**, 5915 (1969); (b) G. Olah and P. v R. Schleyer, Ed., "Carbonium Ions," Vol. II and IV, Interscience, New York, N. Y., in press.

(11) R. Breslow, L. Kaplan, and D. LaFollette, *J. Amer. Chem. Soc.*, **90**, 4056 (1968).

(12) R. Barnett and W. P. Jencks, *ibid.*, **90**, 4199 (1968).

(13) (a) W. Seeliger, E. Aufderhaar, W. Diepers, R. Feinauer, R. Nehring, W. Their, and H. Hellmann, *Agnew. Chem. Int. Ed. Engl.*, **5**, 875 (1966); (b) T. G. Basseri, A. Levy, and M. Litt, *J. Polym. Sci., Part B*, **5**, 871 (1967); (c) A. Levy and M. Litt, *ibid., Part A*, **6**, 57, 63 (1968); (d) D. A. Tomalia and D. P. Sheetz, *ibid.*, **4**, 2253 (1966).

TABLE I

NMR SPECTRAL DATA FOR PROTONATED *N*-ALLYLAMIDES, -UREAS, -URETHANS, AND -THIOUREAS (3)[a,b]

Ion	X	CH_2=	=CH-	$-CH_2-$	-NH-	R′
3a	O	5.65–5.91, m	6.22, m	4.59, b	9.5, b	-H, 8.80, s
3b	O	5.71–5.98, m	6.32, m	4.60, t, J = 5	9.16, b	$-CH_3$, 3.00, s
3c	O	5.72–5.97, m	6.34, m	4.74, t, J = 5.3	9.25, t but b	$-C_6H_6$, 6.91–7.39, m
3e	O	5.66–5.90, m	6.22, m	4.67, b	9.20, b	p-$CH_3C_6H_4$, 2.82, s (CH_3), A_2B_2 centered at 7.93
3f	O	5.26–5.55, m	5.86, m	4.35, b	9.10, b	p-FC_6H_4 7.10–7.47, m, 7.70–8.02, m
3g	O	5.60–5.90, m	6.20, m	4.34, d, J = 5–6	Not observed	$-NH_2$, not observed
3h	O	5.65–5.90, m	6.20, m	4.48, d, J = 6	Not observed	$-OCH_3$, 4.64, s
3i	O	5.56–5.82, m	6.26, m	4.27, d, J = 5	Not observed	$-OCH_2CH_3$, 4.72, q, J = 7 1.80, t, J = 7
3p	S	5.70–6.01, m	6.41, m	4.48, b	7.65, b	$-NH_2$, 8.16, b
3q	S	5.64–5.88, m	6.15, m	4.43, b	8.8–9.2, b (area 2)	$-NHC_6H_5$, 7.6–7.98, m

[a] Nmr positions are in ppm downfield from TMS present in internal capillary; the areas of the assigned bands were in the correct ratio with the numbered protons represented by that band in each case. [b] m multiplet, s singlet, d doublet, t triplet, q quartet, b broadened band; resolution of hyperfine splitting not clear; coupling constants (J) given in Hz.

acylaziridines.[14] Thus, we have investigated the acid-catalyzed cyclization of a series of *N*-allyl and substituted *N*-allylamides, -urethans, -ureas, and -thioureas to their corresponding heterocyclic cations and present the results of these studies here.

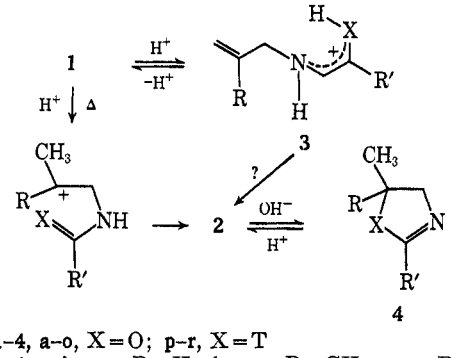
Results and Discussions

Cyclization Studies in H_2SO_4 and Structure Proof of the Heterocyclic Cations.—When allylacetamide (**1b**) is dissolved into 96% H_2SO_4 at room temperature, an nmr spectrum consistent with O protonation of the amide[15] is obtained. Upon heating at 70–85°, the protonated amide (**3b**) undergoes a change as evidenced from the development of a more complex nmr spectrum. The lines assigned to **3b** begin to decrease in intensity as new lines belonging to the 2,5-dimethyloxazolinium cation (**2b**) slowly increase in intensity. After heating for about 10 min, the lines due to protonated amide have disappeared entirely, and the spectrum is consistent with the quantitative formation of the 2,5-dimethyloxazolinium cation (**2b**). During the heating interval, no lines other than those assigned to **2b** and **3b** were observed. The reaction sequence is depicted in Scheme II. All the other *N*-allylamides, -ureas, -thioureas, and -urethans studied were only O or S protonated in 60–90% H_2SO_4 at room temperature. The nmr spectral data of these protonated compounds are summarized in Table I. With the exception of resolution and a charge-induced downfield shift, the spectra are similar in appearance to the amides in CCl_4. All the *N*-allyl derivatives cyclized when heated to 60–100° in the H_2SO_4 solutions.

In a few cases, polymerization of the oxazolinium cations to *N*-acyl-substituted polyethylenimines competes favorably with the initial cyclization. For instance, heating a 96% H_2SO_4 solution of protonated *N*-allylformamide (**3a**) for 3 hr resulted in a very viscous solution of the polymer. By using 82% H_2SO_4 as the solvent, a complex spectrum is obtained on heating which can be attributed to a mixture of the 5-methyloxazolinium cation and protonated polymer.[13] However, only a maximum of a 25% of the cation could be obtained, and further heating led to complete conversion to polymer. Depending on the acidity and the temperature used for the cyclization, polymerization can compete with cyclization during the preparation of **2f** and **2g**.

When *N*-(2-methylallyl)- or *N*-(2-phenylallyl)amides (**1j–o**) were dissolved into 96% H_2SO_4 at 10–15°, their room temperature nmr spectra (determined within 1 min of mixing) indicated the presence of the oxazolinium cations (**2j–o**) without any trace of the protonated amides. Even at −20° in FSO_3H, protonated *N*-(2-methylallyl)acetamide cannot be observed due to quantitative formation of the cyclic ion (**2k**). Apparently, because formation of a tertiary carbonium ion is favorable, these cyclizations compete favorably with O

SCHEME II



1–4, a–o, X = O; p–r, X = T
1–4, a–i, p, q, R = H; j–m, r, R = CH_3; n, o, R = C_6H_5
1–4, for R′, see Table II

(14) H. W. Heine, M. E. Fetter, and E. M. Nicholson, *J. Amer. Chem. Soc.*, **81**, 2202 (1959).

(15) Presence of the characteristic pattern of a monosubstituted vinyl group precludes the formation of the sulfate ester or of the carbonium ion. Protonation of amides at the oxygen function rather than at nitrogen is expected: *cf.* G. A. Olah, J. A. Olah, and R. H. Schlosberg, *J. Org. Chem.*, **35**, 328 (1970).

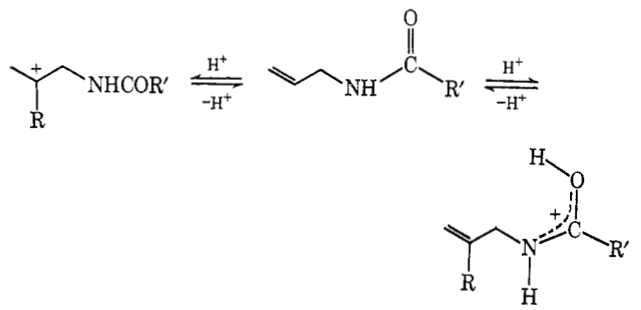
TABLE II

NMR SPECTRA OF OXAZOLINIUM AND THIAZOLINIUM CATIONS IN H_2SO_4

Cation no.	R′	C-4 hydrogens	C-5 hydrogens	C-5 methyl(s)	NH
2a	H, 8.87, s	4.47, m		2.14, d, J = 6	
2b	CH_3, 2.95, s	4.41, m	5.56, m	2.02, d, J = 6.8	9.44, b
2c	C_6H_5, 7.75–8.35, m	4.20, t, J = 10, 4.72, t, J = 10	5.91, m	2.03, d, J = 6	9.98, b
2d	*p*-$NO_2C_6H_4$, A_2B_2 centered at 8.88	4.64, t 5.05, t	6.30, m	2.32, d, J = 6	9.80, b
2e	*p*-$CH_3C_6H_4$, 2.86, s, (CH_3), A_2B_2 centered at 8.04	4.45, b	5.58, m	2.03, d, J = 5.7	9.48, b
2f	*p*-FC_6H_4, 7.08–7.49, m, 7.73–8.20, m	4.50, b	5.61, m	1.79, d, J = 6	9.63
2g	NH_2, not observed	4.19, b	5.50, m	2.07, d, J = 6	Not observed
2h	OCH_3, 4.14, s	3.66, m	4.86, m	1.63, d, J = 5.8	Not observed
2i	OC_2H_5, α 4.30, q, J = 7, β 1.75, t, J = 7	3.64, m	4.79, m	1.84, J = 6.4	Not observed
2j	H, 8.81, s	4.37, s, b		2.17, s	10.22, s (b)
2k	CH_3, 2.90, s	4.34		2.16, s	9.75, s
2l	C_6H_5, 7.75–8.35, m	4.30, s		2.08, s	9.72
2m	*p*-$NO_2C_6H_5$, A_2B_2 pattern, 8.81	4.59, s		2.29, s	10.68, b
2n	CH_3, 3.01, s	4.67, s		2.40, s, 7.83 (C_6H_5)	9.75
2p	NH_2, 8.3, b	4.20,[a] m	5.43,[a] m	2.05, d, J = 6	Not observed
2q	NHC_6H_5, N–H at 9.37, phenyl at 7.6–8.05, m	4.19, b[a] 5.40, b	5.40, b[a]	1.95, d, J = 6	Not observed
2r	NHC_6H_5, N–H at 9.50, 7.47–7.95 m changes to A_2B_2 quartet at 8.33, J_{AB} = 8.2, in 2 weeks	4.17, s		1.98, s	Not observed

[a] Exact assignments of the C-4 and C-5 hydrogens in these compounds is more difficult than in the case of the oxazolines. Studies on the picrate of **2q** indicate the assignment made for that ion; see the Experimental Section for those studies.

protonation. When compared to the necessity of heating in order to generate ions **2a–i**, the ease of formation of oxazolinium ions **2j–o** supports the intermediacy of discrete acyclic carbonium ions as opposed to the direct formation of **2** by neighboring-group participation during C protonation[16] (see Scheme I). One could argue that both paths a and b would be favored by substitution of the vinylic position due to stabilization of the transition state in C protonation. However, the oxazolinium ions possess such remarkable stability that one could not expect any substantial differences in stability in the transition states of the allyl verses methallyl derivatives (due to an extra methyl substituent at the vinyl position) if strong neighboring-group participation is occurring.[17]



(16) S. P. McManus, *Chem. Commun.*, 235 (1969).

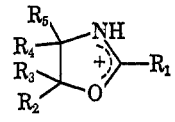
(17) Stated another way: The R group in the transition state shown in path b, Scheme I, would not be expected to contribute much to its stability if neighboring-group participation is well developed in that transition state. The stabilizing effect of the developing oxazolinium ion should swamp out the effect of the methyl group.

This generalization may be extended to the cyclization of thioamides (**1p–r**) to their corresponding 2-amino (or 2-anilino) thiazolinium cations (**2p–r**). The S-protonated *N*-allylthioureas (**1p** and **q**) are only cyclized upon heating several hours at >85°, whereas 1-(2-methylallyl)-3-phenyl-2-thiourea (**1r**) is instantaneously cyclized at 15°.

Definitive identification of the oxazolinium and thiazolinium cations **2a–r** was straightforward. Their formation was accompanied by loss, in the nmr spectra of each ion, of vinylic absorption and the appearance of new bands due to a methyl group(s). In the case of *N*-allyl derivatives **1** (R = H), this new band was a doublet. Whenever R was methyl or phenyl (**1j–o, r**), a new singlet was observed. The nmr spectral data of these ions are summarized in Table II. These particular bands, when combined with the rest of the spectrum, identified the cations. This identification was confirmed in several ways. First, several 2-oxazoline derivatives, which were either commercially available or readily prepared, were treated with cold 96% H_2SO_4 and the nmr spectra of the resulting authentic oxazolinium cations were obtained. These authentic models exhibit nmr spectra which could be compared directly to the spectra of the ions formed by cyclization. Table III summarizes the spectra of these model cations, which to our knowledge have not been previously reported. For proof that these ions were identical with those obtained by cyclization, the 2,5,5-trimethyl-2-oxazolinium cation was prepared by adding an equimolar mixture of methallylacetamide and the parent oxazoline to 96% H_2SO_4; the nmr spectrum revealed a

TABLE III

NMR SPECTRAL DATA OF MODEL OXAZOLINIUM AND THIAZOLINIUM CATIONS IN 90% H_2SO_4. BAND POSITIONS OF THE CATION



Parent compd	Registry no.	R_1	R_2, R_3	R_4, R_5	NH
2-Methyl-2-oxazoline	23704-69-0	2.9, s	5.53, t, J = 9.9	4.62, t, J = 9.9	9.94, b
2-Propyl-2-oxazoline	25898-55-9	α 3.20, t, J = 7 β 1.59, h, J = 7 γ 1.54, t, J = 7	5.56, t, J = 9.8	4.64, t, J = 9.8	9.68, b
2,4,4-Trimethyl-2-oxazoline	25898-56-0	2.90, s	5.17, s	2.03, s	10.01, b
Benzoxazole	25898-57-1	10.16, s	7.9–8.34, m		13.81, b
2,5-Dimethylbenzoxazole	25898-58-2	3.48, s	5-CH_3, 2.86, s, phenyl protons, multiplet centered at 7.69		13.42, s
2-Methylthiazoline	25898-59-3	3.14, s	4.28, t, J = 9.1	4.91, t, J = 9.1	Not observed
2-Methylbenzothiazole	25898-60-6	3.59, s	7.98–8.72, m		4.64, s
Benzothiazole	25898-61-7	10.19, d, J = 5.8	7.81–7.99, m		12.55, b
2,5-Dimethylbenzothiazole	25898-62-8	3.50, s	5-CH_3, 2.79, s, phenyl protons, 7.71–8.18, m		12.49, b
2-Aminothiazoline	25898-63-9	NH_2, not observed	4.17, t, J = 8.0	4.59, t, J = 8.0	Not observed
2-Mercaptothiazoline	25898-64-0	sh, not observed	4.42, t, J = 8	4.93, t, J = 8	9.95

single cation.[18] The nmr spectrum of cation **2k**, which is representative of the spectra obtained for the oxazolinium cations, is recorded in Figure 1.

The identification of the cyclic cations was further strengthened by the isolation of the corresponding oxazolines upon drowning the acid solutions into a well-stirred solution of cold, dilute, excess base with continuous ether extraction. The oxazolines, thus isolated, were identified by ir, nmr, elemental analysis, and studies of their physical properties.[19] Furthermore, when the isolated oxazolines were redissolved into cold 96% H_2SO_4, the same oxazolinium cations (as determined by their nmr spectra) were obtained as had been obtained in the amide cyclizations. As expected, the protonated amides, ureas, and urethans **3** and the cyclic ions **2** exhibited the anticipated downfield nmr chemical shifts relative to their corresponding oxazolines and thiazolines **4**. The magnitude of this charge-induced deshielding is that expected from applying the previous studies of dioxolinium ions[20] and a variety of other protonated compounds.[10b] For similar cations,

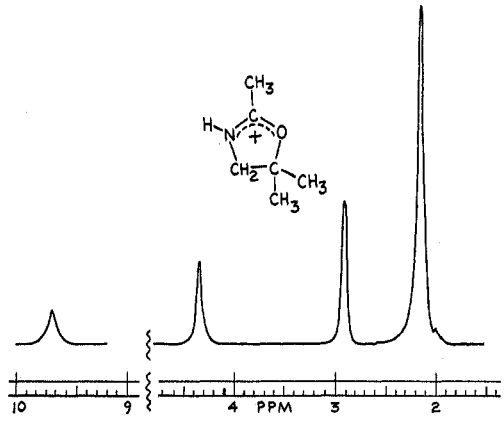


Figure 1.—Nmr spectrum of the 2,5,5-trimethyl-2-oxazolinium cation (**2k**).

Tomalia[21] has correlated $\Delta\delta$ values for different solvents.

The nmr spectra of oxazolines and thiazolines, **4**, where R′ is an alkyl group, exhibit long-range coupling between the α protons or R′ and the C-4 ring protons.[22] The coupling constant generally varies between 1.0 and 2.0 Hz. For instance, in 2-methyloxazoline (**5**) the

(18) The same ion is formed by the rearrangement of 1-acetyl-2,2-dimethylaziridine. In that case, an identified nmr spectrum is obtained; *cf.* Pittman and McManus, ref 1a.

(19) S. P. McManus, J. T. Carroll, P. M. Grohse, and C. U. Pittman, *Org. Prep. Proced.*, **1**, 183, 235 (1969). These references describe a useful and convenient synthetic method for preparing certain substituted oxazolines.

(20) (a) C. U. Pittman, Jr., and S. P. McManus, *Tetrahedron Lett.*, 339 (1969). (b) H. Hart and D. Tomalia, *ibid.*, 3383, 3389 (1966); 1347 (1967).

(21) D. A. Tomalia, N. D. Ojha, and B. P. Thill, *J. Org. Chem.*, **34**, 1400 (1969).

(22) M. A. Weinberger and R. Greenbalgh, *Can. J. Chem.*, **41**, 1038 (1963).

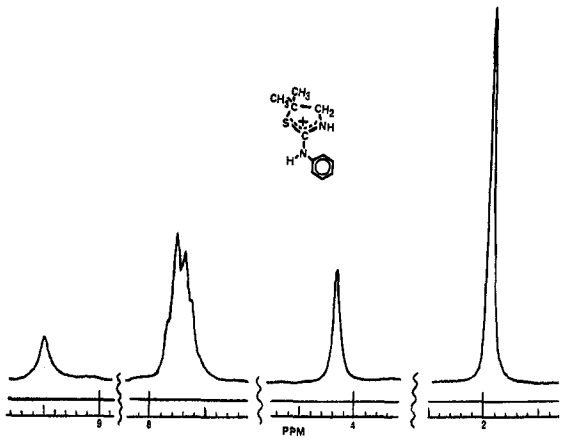
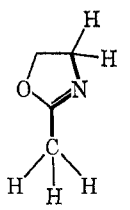


Figure 2.—Nmr spectrum of the 2-anilino-5,5-dimethyl-2-thiazolinium cation (2r).

methyl appears as a triplet (J = 1.4 Hz), while the methyl resonance in the corresponding oxazolinium cation **6** is a singlet. Long-range coupling is also



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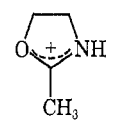

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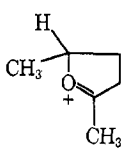
lacking in oxonia- and 1,3-dioxoniacyclopentene cations (**7** and **8**).[10a,20,23] Since each of these ions has a π bond



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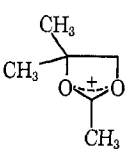

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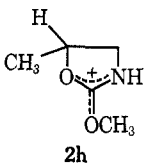
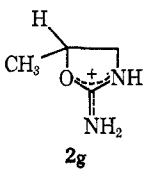
in one resonance structure, the absence of long-range coupling might indicate that σ–π electron interactions, which are thought[24] to be responsible for this type of coupling, are substantially reduced in the ions. An alternate explanation is that the fine structure in the spectra of the ions does not appear because of solvent effects. The latter possibility is currently being investigated.

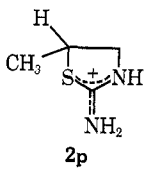
N-Allylurea (**1g**), *N*-carbomethoxyallylamine (**1h**) and its homolog **1i**, *N*-allylthiourea (**1p**), and *N*-allyl-*N'*-phenylthiourea (**1q**) were each protonated in cold 96% H_2SO_4 (see Table I). Heating each acid solution resulted in conversion to the highly resonance stabilized cations **3g–i, p, q**, respectively. The nmr spectra of the



2h



2g



2p

cations (Table II) were straightforward. While conversion of **1h** to cation **2h** was nearly quantitative, attempts to isolate 2-methoxy-5-methyl-2-oxazoline (**4h**) by drowning into excess base in the normal manner[19] failed.

The cyclization of S-protonated allylthiourea (**3p**) in 70–96% H_2SO_4 was much slower than cyclizations of *N*-allylamides, *N*-allylureas, or *N*-allyurethans. About 24 hr at 70° was required to complete the cyclization of **1p** to the 2-amino-5-methyl-2-thiazolinium cation (**2p**) (*vs.* 2 hr for the conversion of **1g** to **2g**). The lack of N–H resonances in the nmr spectra of **2g** and **2o** indicates rapid exchange of these protons in the concentrated acid solution.

1-(2-Methylallyl)-3-phenyl-2-thiourea (**1r**) behaves in a manner analogous to amides **1j–n**. Upon mixing it with 96% H_2SO_4, immediate quantitative conversion to the 2-(anilino)-5,5-dimethyl-2-thiazolinium cation (**2r**) occurs. The nmr spectrum of **2r** is shown in Figure 2. Upon drowning the acid solution of **2r** into a cold dilute base solution, 2-anilino-5,5-dimethyl-2-thiazoline[25] (**4r**) was isolated in 50% yield. Redissolving the isolated thiazoline in 96% H_2SO_4 allowed for quantitative regeneration of cation **2r** as evidenced by the reproduction of an nmr spectrum identical with that in Figure 2.

Cyclization Studies in D_2SO_4 and H–D Exchange Experiments —When allylic amides were cyclized in 96% D_2SO_4, a single deuterium was incorporated in the C-5 methyl group(s) determined by peak intergration. The N–H disappeared, as expected, due to exchange with solvent. *No further* incorporation of deuterium into the ions occurred. The 2-propyl-2-oxazolinium ion, prepared by dissolving the parent oxazoline in acid, showed no H–D exchange, other than N–H, after 14 hr at 120° in 96% D_2SO_4 or after 10 min at 122° in 65% D_2SO_4. Allen and Ginos[26] reported that H–D exchange occurs at the 2-methyl group of 2,3,4,4-trimethyl-2-oxazolinium iodide in 0.005 and 0.1 *M* HI solutions in D_2O. Under their more basic conditions, however, H–D exchange is much more likely than in the present case.

The resistance to H–D exchange is also exhibited by the thiazolinium ions. The 2-methyl-2-thiazolinium cation exhibits no H–D exchange after 1.3 hr at 120° in 96% D_2SO_4 or after 13 min at 122° in 65% D_2SO_4.

When compared to other heteroatom-stabilized cyclic ions, certain trends are evident. Five-membered ring cyclic carbonium ions with a single adjacent heteroatom (O, N, S) incur H–D exchange among both the C-2 methyl hydrogens and the C-3 methylene hydrogens. For example in **7**, the C-2 methyl hydrogens are 34% exchanged during 68 hr at 24° and 65% exchanged during 7 min at 120° in 96% D_2SO_4. The C-3 methylene hydrogens of **7** were 43 and 78% exchanged under those conditions.[23] The C-4 and C-5 hydrogens are not exchanged in 96% D_2SO_4 even after heating overnight at 120°.[10a] Five-membered ring cyclic carbonium ions with two heteroatoms are stabilized sufficiently that H–D exchange does not occur in concentrated acid solutions.[20a]

(23) C. U. Pittman and S. P. McManus, *Chem. Commun.*, 1479 (1968).

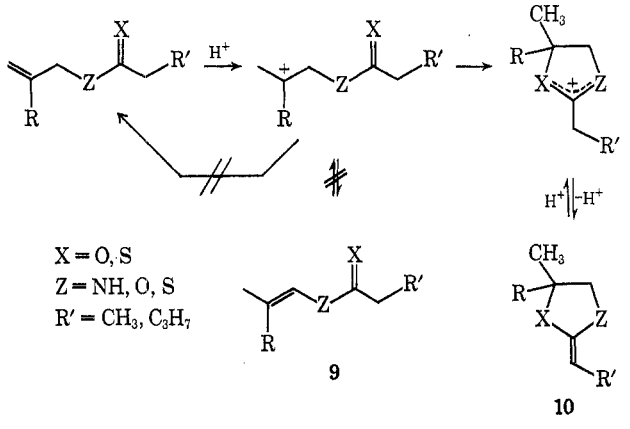
(24) J. W. Emsley, J. Feeney, and L. H. Sutcliff, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, New York, N. Y., pp 176–180.

(25) The endocyclic structure rather than the tautomeric exocyclic structure is assigned in line with the implicit evidence obtained from the study of the analogous 2-anilino-2-oxazoline systems: *cf* J. R. Carson, G. I. Poos, and H. R. Almond, *J. Org. Chem.*, **30**, 2225 (1965).

(26) P. Allen and J. Ginos, *ibid.*, **28**, 2759 (1963).

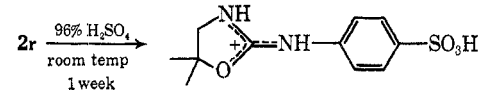
As shown in Scheme III, the intermediate acyclic carbonium ion is not in equilibrium with the starting allyl derivative or vinyl derivative **9**, but must be captured by O (or S) before proton loss occurs. Also, oxazolinium (thiazolinium) cations are not in equilibrium with their *exo*-2-methylene derivatives **10**.

SCHEME III



9 10

Stability of Oxazolinium and Thiazolinium Cations.—Oxazolinium and thiazolinium cations are thermally stable in addition to being relatively resistant to H–D exchange. After 72 hr in 96% H_2SO_4, the 2-phenyl-5-methyl-2-oxazolinium cation remains unchanged. 2,5,-5-Trisubstituted oxazolinium cations were unchanged after several days at 90° in 96% H_2SO_4 or 70% H_2SO_4. The 2-amino-2-thiazolinium cation, **2p**, is unchanged after being heated to 80° in 70% H_2SO_4 for 64 hr. The remarkable ability of the heteroatoms to stabilize a positive charge, within the heterocyclic ring, is illustrated by the para sulfonation of the phenyl ring of the 2-anilino-5,5-dimethyl-2-thiazolinium cation (**2r**) after a week at 22° in 96% H_2SO_4. During this period the nmr spectrum of the phenyl proton changes to an A_2B_2 quartet with an area of 4. Thus, the amino nitrogen is able to support para attack of the phenyl ring in spite of its attachment to the 2 position of a thiazolinium ion!



Oxazolinium and thiazolinium ions do not cleave on heating in strong acid media. This behavior is in contrast to that of the analogous dioxolinium and oxathiolinium cations which readily undergo $A_{AL}1$ cleavage at elevated temperatures.[20a] This suggests that oxazolinium (thiazolinium) ions are more stable (*i.e.*, **2k > 8**).

Characteristics of Cation Nmr Spectra —The chemical shifts of the protons of **2** are shifted downfield with respect to their corresponding 2-oxazolines[21] and 2-thiazolines. The protons at C-5 (adjacent to oxygen) are found more than 0.7 ppm downfield from the protons at C-4 in oxazolinium ions. In thiazolinium ions, the order is reversed and the separation of the C-4 and C-5 protons is more variable.[27] The proton on nitrogen in both sets of ions appears as a broadened singlet due to the nitrogen quadrapole[28] which shortens the spin–lattice relaxation time to a value comparable with the reciprocal of the J_{H-N} coupling constant. This broadening due mainly to asymmetric fields near N, indicates the hybridization at nitrogen is still sp^2 in the cations. When sp^2 hybridized, the electric field symmetry is far lower than in sp^3-hybridized cases such as ammonium ions.[29] It should be noted that the proton at the ring nitrogen is not observed in the spectra of both oxazolinium and thiazolinium ions when amino, anilino, mercapto, or alkoxy substituents are attached at C-2 (*i.e.*, R′). Since these substituents would disperse the charge to a greater degree than with aryl or alkyl substituents (where the proton at nitrogen is observed), the results appear to be contradictory to predictions: at constant acid concentrations, as the basicity of the ring nitrogen increases, the rate of N–H exchange with solvent increases! The expected result occurs in those systems where the N–H is observed: as the acid concentration is decreased, the exchange rate of the N–H with solvent increases. Thus, in 60% H_2SO_4 the nitrogen is not observed in any systems.

The cis and trans vicinal couplings between ring protons at C-4 and C-5 are equal, within experimental error, in the 2-methyl and the 2-propyl oxazolinium ions. This accounts for the clean triplets observed. This is also true of the 2-methyl, the 2-amino, and the 2-mercapto-2-thiazolinium ions. While this is an exception to predictions of the Karplus equation, this phenomenon has been previously observed in dihydrofuran ring systems,[30] five-membered ring oxonium ions[20a,23] as well as being observed in the corresponding oxazolines and thiazolines. The size of these couplings is large, being from 9–10 Hz in 2-alkyl or 2-aryl[1a] oxazolinium and thiazolinium ions. In these cases, the coupling constant increases from 1.0 to 1.5 Hz going from the parent heterocycle to the cation. When a mercapto or amino group is present at the 2 position in the ions, the size of the coupling constant is about 8 Hz and shows no increase when compared with its parent compounds.

Currently, studies are being extended to the formation of six-membered and larger rings in strong acid media. Since the six-membered rings are not expected to be as stable thermodynamically,[31] systems may be designed which will allow an equilibrium between the open-chain carbonium ion and the cyclic ion. Also, the possible similarity between these cyclizations and acid-catalyzed rearrangements of acylaziridines[1a] and acylcyclopropanes[10a] is being studied.

Experimental Section[32]

Materials.—The following were purchased and used without further purification: all compounds in Table II (Aldrich) except 2,4,4-trimethyl-2-oxazoline, which was prepared as previously described,[33] and compounds **1g** and **1p** (Eastman "White Label").

(27) In 2-thiazolines the C-4 protons appear downfield of the C-5 protons rather than the reverse which is true for 2-oxazolines; *cf.* ref 22.

(28) J. D. Roberts, *J. Amer. Chem. Soc.*, **78**, 4495 (1956).

(29) G. V. D. Tiers and F. A. Bovey, *J. Phys. Chem.*, **63**, 302 (1959).

(30) L. M. Jackman, "Applications of NMR Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p 87.

(31) Based on comparison with the isoelectronic carbocyclic derivatives; *cf.* T. S. Sorensen, *J. Amer. Chem. Soc.*, **91**, 6398 (1969).

(32) Unless otherwise noted all nmr spectra were recorded using a Varian HA-100 spectrometer with a variable temperature probe. The chemical shifts are relative to tetramethylsilane as an internal standard (internal capillary in acid solutions). Neutral samples, unless otherwise noted, were run in carbon tetrachloride solutions. Ir spectra were recorded using an IR-10 spectrophotometer. Microanalyses were performed by Gailbraith Laboratories, Inc., Knoxville, Tenn. Melting points (capillary tube) and boiling points are uncorrected.

(33) H. Wenker, *J. Amer. Chem. Soc.*, **57**, 1079 (1935).

TABLE IV

DATA FOR ISOLATED OXAZOLINES AND THIAZOLINES

Compd	Registry no.	Yield, %	Mp °C	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
2,5-Dimethyl-5-phenyl-2-oxazoline	25913-84-2	70	Picrate 152–153			13.86			13.68
2,5-Diphenyl-5-methyl-2-oxazoline	24913-85-3	60	Picrate 153–154			12.01			11.76
2-Anilino-5,5-dimethyl-2-thiazoline	24913-86-4	40	153	64.04	6.84	13.58	63.95	6.76	13.48

Compounds **1l** and **1m** were kindly provided by Dr. R. F. Merritt of the Rohm and Haas Company. The preparation of compounds **1b–f** and **1k** has been described elsewhere.[19]

Allylformamide (1a).—Allylamine (11.4 g, 0.2 mol) was slowly added to 14.8 g (0.2 mol) of ethyl formate in a 50-ml round-bottomed flask equipped with a magnetic stirrer and condenser. After about 5 min heat from the reaction caused the mixture to reflux. The reaction was complete in about 30 min, but stirring was continued overnight. The solution was vacuum distilled to yield 14.0 g (83%) of **1a**, bp 104–107 (14 mm) [lit.[32] 109° (15 mm)], d^{20}_4 1.004 (lit.[34] 1.008).

Methallylformamide (1j).—In the same manner as for the preparation of **1a** above, 10 g (0.141 mol) of methallylamine and 10.8 g (0.141 mol) of ethyl formate produced 10.4 g (70%) of **1j**, bp 78° (1.5 mm), n^{25}_0 1.4641. The nmr spectrum of **1j** contained singlets at δ 148.5 (3 protons) and 337.5 ppm (2 protons), and a multiplet centered at 717 ppm.

Anal. Calcd for C_5H_9NO: N, 14.13. Found: N, 13.89.

***N*-Carbomethoxyallylamine (1h).**—Allyl isocyanate (16.6 g, 0.2 mol, Aldrich) was added dropwise to 50 ml of methanol in a round-bottomed flask fitted with a condenser and magnetic stirrer. Heat produced from the reaction caused gentle refluxing to occur. The mixture was stirred overnight and distilled to yield 17.2 g (75%) of **1h**, bp 92–94° (30 mm) [lit.[35] 179.5–183.5 (748 mm)].

***N*-Carbethoxyallylamine (1i).**—In the same manner as for the preparation of **1h** above, 16.6 g (0.2 mol) of allyl isocyanate reacted with 50 ml of absolute ethanol to yield 20.2 g (78%) of **1i**, bp 92–93° (15 mm) [lit.[36] 92° (15 mm)].

***N*-2-Phenylallylacetamide (1n).**—Potassium phthalimide (10 g, 54 mmol) and 8.2 g (54 mmol) of 2-phenylallyl chloride were added to 100 ml of dimethyl sulfoxide and the resulting solution was heated on a steam bath while being stirred mechanically. After two hr the clear solution was cooled and poured into 300 ml of water containing about 100 g of ice. The phthalimide precipitated and was collected and dried overnight. The crude product weighed 12.9 g (91%) and melted at 116–118°. The phthalimide (10 g) was refluxed for 1 hr with 4.6 ml of hydrazine hydrate in 190 ml of methanol. The solution was cooled, treated with 30 ml of 10 *N* hydrochloric acid, and filtered. The phthalhydrazide was collected triturated with 100 ml of water and filtered, and the combined extracts were evaporated to dryness under reduced pressure. The residue was treated with 30 ml of 20% aqueons potassium hydroxide solution and extracted with three 20-ml portions of ether. The combined extracts were dried (Na_2SO_4) and treated with ketene[18] (about 70 mmol). Removal of the ether under reduced pressure gave 4.1 g (70%) of **1n**, mp 78–79° (from ethanol–water).

Anal. Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.28; H, 7.43; N, 7.80.

The ir spectrum of **1n** was consistant with the assigned structure: 3290 (s), 3080 (m), 2930 (m), 1640 (s), 1533 (s), 1282 (s), 900 (m), and 700 cm^{-1} (m). The nmr spectrum of **1n** confirmed the structure assignment.

***N*-2-Phenylallylbenzamide (1o).**—The amine was prepared in the same manner as for the preparation of **1n** above. In a typical run, the ethereal solution of the amine, prepared from 10 g (33.4 mmol) of the phthalimide, was concentrated at reduced pressure and to the residue was added 20 ml of dry benzene and 5 ml of triethylamine. While maintaining the flask in a bath at 0–5°, 5 g (35.5 mmol) of benzoyl chloride in 20 ml of dry benzene was slowly added with stirring. The solution was allowed to slowly warm to room temperature and after 2 hr the triethylamine hydrochloride salt was filtered and the filtrate was concentrated at reduced pressure. The solid residue was crystallized from ethanol–water to yield 5.3 g (67%) of **1o**, mp 122–123°.

Anal. Calcd for $C_{16}H_{15}NO$: N, 5.90. Found: N, 5.71.

1-(2-Methylallyl)-3-phenyl-2-thiourea (1r).—To a stirred solution of 7.1 g (0.1 mol) methallylamine in 75 ml of absolute ethanol, phenyl isothiocyanate (13.6 g, 0.1 mol) was added with gentle reflux. Ten minutes after the addition was complete, the solution was cooled and to it was added 75 ml of ice water. After standing in the freezer for 0.5 hr, the white crystals were collected, dried, and recrystallized from ethanol–water to yield 21.3 g (81%) of **1r**, mp 79–80° (lit.[37] 80–81°). The ir spectrum of **1r** had major peaks at 3376 (s), 2210 (s), 1596 (m), 1540 (s), 1520 (s), 1315 (m), 1225 (m), 880 (m), and 740 cm^{-1} (m). The nmr spectrum ($CDCl_3$) was consistant with the structure: δ 142 (s, 3 protons), 413 (d, J = 5.5 Hz, 2 protons), 475 (m, 2 protons), 636 (b, 1 proton), 723 (m, 5 protons), and 902 ppm (b, 1 proton).

1-Allyl-3-phenyl-2-thiourea (1q).—This derivative was prepared precisely in the manner described for **1r**, mp 98–99° (lit.[38] 98°).

Isolation of Oxazolines and Thiazolines.—Previously described methods[19] were used to isolate some of the 2-oxazoline and 2-thiazoline derivatives. All isolated compounds were fully characterized. Data on new compounds isolated are compiled in Table IV.

Decoupling Experiments with the Picrate of 1q.—The picrate of **1q**, mp 152–153° (lit.[39] 153°), was prepared from the isolated thiazoline. The nmr spectrum, obtained in acetone-d_6 with a Bruker HFX-90 spectrometer, contained the following: δ 1.58 (d, J = 6 Hz, 3 protons), 3.91 (m, 1 proton), 4.35 (m, 2 protons), 7.47 (s, 5 protons), and 8.81 ppm (s, 2 protons). The N–H protons were not observed. Decoupling experiments between the C-5 methyl group (δ 1.58) and the C-4 and C-5 protons indicated that the C-5 proton is centered at 4.44 ppm. One C-4 proton is then in the multiplet centered at 4.35 ppm and the other is the multiplet at 3.91 ppm.

Registry No.—**1j**, 25913-66-0; **1n**, 25957-50-0; **1o**, 25913-67-1; **1r**, 25913-68-2; **2a**, 25898-39-9; **2b**, 23704-70-3; **2c**, 23704-73-6; **2d**, 25898-42-4; **2e**, 25898-43-5; **2f**, 25898-44-6; **2g**, 25898-45-7; **2h**, 25898-46-8; **2i**, 25898-47-9; **2j**, 25898-48-0; **2k**, 23704-71-4; **2l**, 25898-50-4; **2m**, 25898-51-5; **2n**, 25898-52-6; **2p**, 25898-53-7; **2q**, 25898-54-8; **2r**, 25950-25-8; **3a**, 25913-69-3; **3b**, 25913-70-6; **3c**, 25913-71-7; **3e**, 25913-72-8; **3f**, 25913-73-9; **3g**, 25913-74-0; **3h**, 25913-75-1; **3i**, 25913-76-2; **3p**, 25913-77-3; **3q**, 25913-78-4; 2,5,5-trimethyl-2-oxazolinium cation, 25913-83-1.

Acknowledgments.—The authors acknowledge samples from Dr. R. F. Merritt and discussions with Professors M. T. Emerson and L. D. Kispert.

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(36) M. Bergmann, *Ber.*, **54**, 2147 (1921).

(37) A. Kjaer, K. Rubinstein, and K. A. Jensen, *Acta Chem. Scand.*, **7**, 518 (1953).

(38) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, Wiley, New York, N. Y., 1964, p 326.

(39) F. B. Dains, *J. Amer. Chem. Soc.*, **22**, 181 (1900).