spectra indicated about 4.5% incorporation of deuterium at the tertiary carbon.

Registry No.—**1**, 696-30-0; **2**, 644-98-4; **3**, 25128-23-8; **3** dipicrate, 25128-24-9; **4**, 25128-42-8; **4** dipicrate, 37387-92-1; **5**, 37387-93-2; **5** dipicrate, 37387-94-3; **6**, 37387-95-4; **6** picrate, 37387-96-5; **7**, 6304-18-3; **8**, 37387-98-7; **8** picrate, 37387-99-8; **9**, 37387-00-4; **9** dipicrate, 37388-01-5; **10**, 37388-02-6; **12**, 17755-30-5; **13**, 15031-78-4.

Acknowledgment.—We thank the Office of Naval Research and the Commercial Solvents Corporation for generous support. We are indebted to our colleague Professor Nathan Kornblum for helpful discussions.

Heteronuclear Stabilized Carbonium Ions. II. *N*-Aroyl- and Aryl-2-oxazolinium Cations. Intermediates in a New Class of Neighboring Group Reactions[1]

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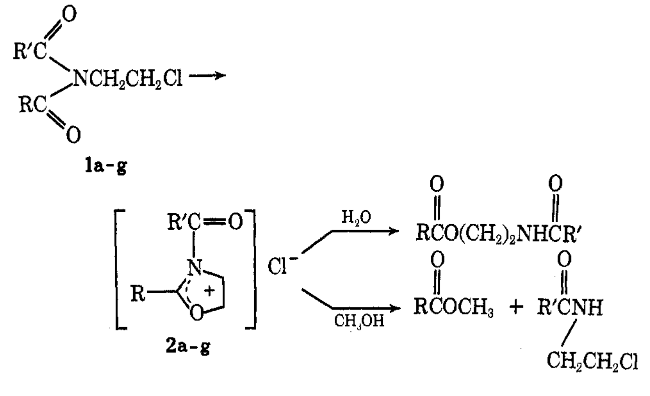
N-(2-Chloroethyl)-*N*-acyl/aroyl benzamides/acetamides were solvolyzed under several conditions: (a) in refluxing aqueous acetonitrile; (b) in aqueous acetonitrile with equimolar amounts of $AgNO_3$ (25°); and (c) in refluxing methanol. Hydrolyses produced the corresponding amido esters while methanolyses produced equimolar amounts of methyl esters and *N*-2-chloroethylamides. These solvolyses represent a new class of neighboring group reactions involving imide moiety participation, presumably *via* *N*-aroyl/acyl-2-oxazolinium cations. Several such cations were synthesized, isolated, and characterized. Evidence for the intervention of these cations in the solvolyses is presented. The preferred preparative route for the cations involved cyclization of appropriate *N*-(2-chloroethyl)imides with $AgBF_4$ or $AgSbF_6$. Selective participation of the better carbonium ion stabilizing carbonyl function was observed when cyclizing unsymmetrical imides. The ambident character of these cations was noted in that chloride ion attack occurred at the 5 position to produce *N*-(2-chloroethyl)imides; hydrolyses and methanolyses involved nucleophilic attack at the 2 position, producing, respectively, amido esters and equimolar amounts of methyl esters as well as 2-substituted 2-oxazolinium salts. Proposed solvolyses mechanisms are discussed.

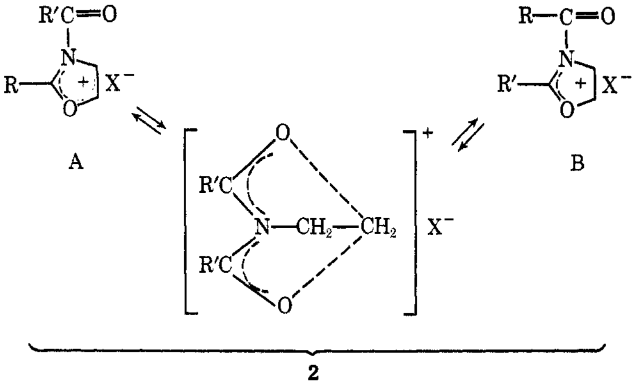
Participation of amide groups *via* 2-oxazolinium salts to produce various solvolysis products is well known. These reactions have been studied extensively by Winstein,[2] Heine,[3] and others.[4,5] In some instances these 2-oxazolinium salts[2,6] have actually been isolated and characterized. Although this area has received considerable attention, to our knowledge no report of imide group participation has yet appeared in the literature.

Recently, we noted that certain imides [*i.e.*, *N*-(2-chloroethyl)-*N*-acyl/aroyl benzamides/acetamides, **1a–g**], underwent facile solvolysis reactions in aqueous acetonitrile or in methanol as shown below.



These transformations represent a new class of neighboring group reactions in which *N*-aroyl/acyl-2-oxazolinium cations, **2a–g**, are postulated as transient intermediates.

Fry[7] first proposed these cations as intermediates in the ring opening of 2-oxazolines with acid chlorides. More recently, Nehring and Seeliger[8] proposed these cations as intermediates in the thermal equilibration of *N*-(2-chloroethyl)-*N*-benzoyl acetamide to mixtures of the symmetrical *N*-(2-chloroethyl)-*N*-(aroyl/acyl) benzamide and acetamide.



2

The unique structure of these cations offers the possibility of assessing various carbonyl participation aptitudes under equilibrating conditions as well as an opportunity to determine the effect of electronic and resonance properties of various R and R′ substituents on charge distribution in the oxazoline ring. As shown for the related 1,3-dioxolenium system,[9–11] the

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[1] Presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.

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

[3] H. Heine, *ibid.*, **78**, 3708 (1956).

[4] B. Capon, *Quart. Rev., Chem. Soc.*, **18**, 45 (1964).

[5] S. Hünig, *Angew. Chem., Int. Ed. Engl.*, **3**, 548 (1964).

[6] M. E. Kreling and A. G. McKay, *Can. J. Chem.*, **37**, 504 (1959).

[7] E. M. Fry, *J. Org. Chem.*, **15**, 802 (1950).

[8] R. Nehring and W. Seeliger, *Justus Liebigs Ann. Chem.*, **709**, 113 (1967).

[9] H. Hart and D. A. Tomalia, *Tetrahedron Lett.*, **No. 29**, 3383 (1966).

[10] D. A. Tomalia and H. Hart, *ibid.*, **No. 29**, 3389 (1966).

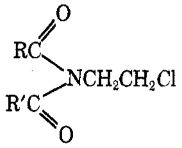
[11] H. Hart and D. A. Tomalia, *ibid.*, 1347 (1967).

heterocyclic ring protons should serve as suitable electron density probes for assessing such charge delocalization by nmr spectroscopy.

The possibility of observing these phenomena in 3-acyl or aroyl-2-substituted 2-oxazolinium systems, as well as the need for demonstrating the intermediacy of these cations in *N*-(2-chloroethyl)imide solvolysis reactions, prompted the synthesis and an investigation of these cations.

Results and Discussion

Solvolysis Reactions of the Imides.—Seven imides, **1a–g**, were examined under three different solvolysis conditions: (A) in refluxing H_2O-CH_3CN (20:80, v/v); (B) in H_2O-CH_3CN (20:80) with equimolar $AgNO_3$ (25°); and (C) in refluxing methanol. Under conditions A and C a dramatic reduction in pH accompanied by the liberation of substantial amounts of chloride ion was observed upon heating. In the case of condition B a drop in pH with the concurrent formation of AgCl was noted.

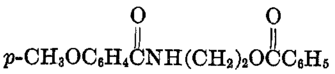


1a–g

	R	R′
1a	C_6H_5	C_6H_5
1b	p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$
1c	CH_3	CH_3
1d	p-$NO_2C_6H_4$	p-$NO_2C_6H_4$
1e	p-$CH_3OC_6H_4$	C_6H_5
1f	C_6H_5	p-$NO_2C_6H_4$
1g	C_6H_5	CH_3

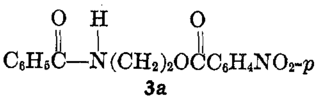
Essentially quantitative conversion to the corresponding amido esters was observed in refluxing aqueous acetonitrile (reaction times 2–27 hr) for the imides **1a**, **b**, and **d**. Imide **1c** appeared to hydrolyze anomalously to a mixture of acetic acid and 2-hydroxyethylamine·HCl rather than to *N*-(2-acetamido)ethyl acetate. However, further work showed that this expected amido ester hydrolyzes very rapidly to these products under condition A.

In the case of unsymmetrical imide **1e**, characteristic infrared absorption bands in the fingerprint region allowed an assessment of the relative amounts of the two possible amido esters that would be expected from this reaction. A predominance of 2-(*p*-anisamido)ethyl benzoate (**3**), accompanied by smaller amounts of 2-(benzamido)ethyl *p*-anisate was observed. Hydrolysis of **1f** gave a mixture of the two possible esters, 2-(benzamido)ethyl *p*-nitrobenzoate (**3a**) and 2-(*p*-nitrobenzamido)ethyl benzoate (**3b**). The predominating ester was not distinguishable by usual spectroscopic techniques. These reactions were also monitored by nmr spectroscopy. For example, imide **1a** exhibited an nmr spectrum (CD_3CN) which consisted of a complex multiplet at δ 7.66–7.05 ppm and two finely split triplets centered at δ 4.38 and 4.00 ppm (A_2B_2 type pattern). These protons were present in a ratio of 5:1:1, respectively. Hydrolysis was followed by observing the disappearance of the two upfield triplets accompanied by concurrent formation of two new multiplets centered at δ 4.46 and 3.76 ppm. Similarly, a new multiplet developed in the aromatic region at δ 8.25–7.67 ppm in addition to another multiplet at δ 7.67–7.08 ppm. The proton integration ratio was consistent with the proposed structure for the hydrolysis product.



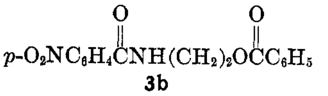
$$p\text{-}CH_3OC_6H_4\overset{O}{\overset{\|}{C}}NH(CH_2)_2O\overset{O}{\overset{\|}{C}}C_6H_5$$

3



$$C_6H_5\overset{O}{\overset{\|}{C}}\text{—}\overset{H}{\overset{|}{N}}(CH_2)_2O\overset{O}{\overset{\|}{C}}C_6H_4NO_2\text{-}p$$

3a



$$p\text{-}O_2NC_6H_4\overset{O}{\overset{\|}{C}}NH(CH_2)_2O\overset{O}{\overset{\|}{C}}C_6H_5$$

3b

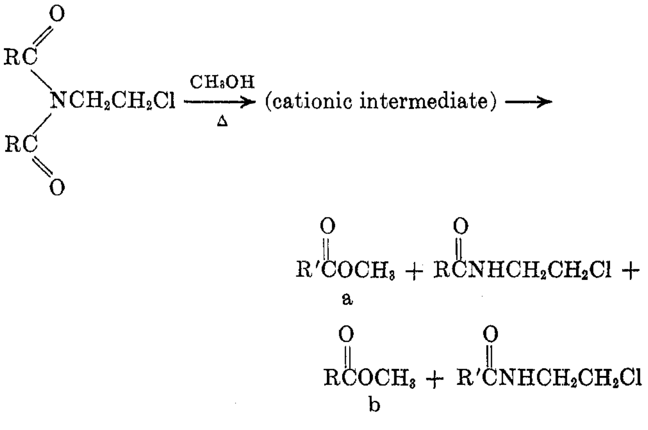
Attempts to hydrolyze analogous cyclic imides [*e.g.*, *N*-(2-chloroethyl)succinimide and *N*-(2-chloroethyl)phthalimide] were unsuccessful. Even after reflux periods of 30–90 hr, complete recovery of starting materials was observed.

Treatment of imides **1a–d** under conditions B (*i.e.*, aqueous acetonitrile–$AgNO_3$) produced the same products as described above. Yields and products are described in the Experimental Section. In one instance, unsymmetrical imide **1e** was found by infrared analysis to have hydrolyzed under these conditions to a predominance of 2-(benzamido)ethyl *p*-anisate accompanied by 2-(*p*-anisamido)ethyl benzoate (**3**) as a minor product. This product distribution is the reverse of that obtained in the absence of the silver reagent (*cf.* condition A). Further comment on this aspect will be made later.

Methanolysis of **1a–d** under conditions C produced the corresponding methyl esters and *N*-(2-chloroethyl)amides in fair to excellent yield. Unsymmetrical imides **1e–g** gave in each instance a four-component mixture of the corresponding methyl esters and *N*-(2-chloroethyl)amides as shown in Table I. According to glc analysis of the methyl esters, imides **1e** and **1f** solvolyzed in a nonselective manner, whereas **1g** led to

TABLE I

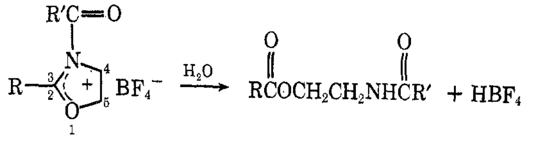
PRODUCT DISTRIBUTION FROM METHANOLYSIS OF UNSYMMETRICAL IMIDES



Imide	Mol % a	Mol % b
1e, R = C_6H_5; R′ = p-$CH_3OC_6H_4$	50	50
1f, R = C_6H_5; R′ = p-$NO_2C_6H_4$	57	43
1g, R = C_6H_5; R′ = CH_3	90	10

a predominance of methyl acetate accompanied by a minor amount of methyl benzoate.

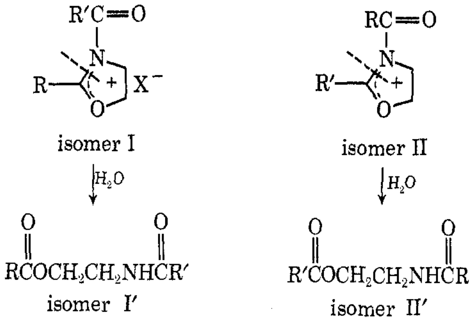
In order to test the intermediacy of oxazolinium cations 2 in these solvolyses, a number of these salts were synthesized, isolated, and solvolyzed as described later. When R = R′ (*i.e.*, **2a–c**), the same amido esters were obtained as were isolated from the hydrolysis of imides **1a–c**.



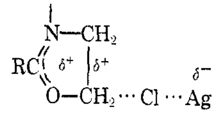
2a-c, e-g

	R	R′
2a	C_6H_5	C_6H_5
2b	p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$
2c	CH_3	CH_3
2e	p-$CH_3OC_6H_4$	C_6H_5
2f	C_6H_5	p-$NO_2C_6H_4$
2g	CH_3	C_6H_5

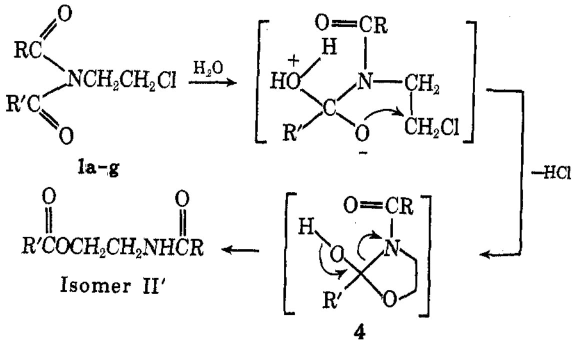
This provides compelling evidence for the intermediacy of these salts. These products presumably arise *via* a selective cleavage between the 2 and 3 positions of the oxazolinium ring.[7,12,13] Because of the asymmetry of imides **1e–g**, isomeric cations I or II are possible intermediates depending on which amide carbonyl group participates in the displacement of the chloride ion. Based on work with authentic cations, hydrolysis of these cations would be expected to lead to the respective amido esters I′ and II′. Under condition A, imide **1e** hydrolyzed preferentially to amido ester (isomer II′) according to infrared analysis. Hence it appears that cation **2e** (isomer II), where R′ = C_6H_5, R = p-$CH_3OC_6H_4$, is the primary cationic intermediate in this hydrolyis and presumably arose by participation of the benzamido group. Under condition B (*i.e.*, in the presence of $AgNO_3$), the predominance of amido ester I′ was noted, thus suggesting that participation of the p-anisamido group *via* cation **2e** (isomer I) prevailed under those conditions.



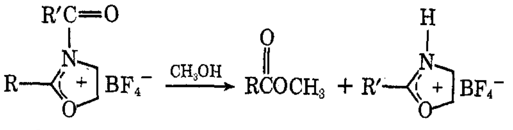
The latter selectivity can be readily rationalized in terms of the more nucleophilic carbonyl group (*i.e.*, R = p-anisamido) participating in the stabilization of the incipient carbonium ion generated by the silver reagent as shown below.



In the absence of a silver reagent, the preferential participation of the less nucleophilic carbonyl group (*i.e.*, R′ = benzamido) is more difficult to explain, unless one invokes a mechanism as shown below. In this case the solvent attacks the more electron-deficient carbonyl group to produce the intermediate **4**. It should be noted that this intermediate is the same as that obtained in the first stage of the hydrolysis of cation **2e** (isomer II).



Additional evidence for the intermediacy of cations 2 was gained from methanolysis experiments. As described later, the cations solvolyzed very selectively to a stoichiometric mixture of the corresponding methyl benzoates and 2-oxazolinium salts. Although the methanolysis experiments with **1a–g** produced the corresponding methyl benzoates and N-(2-chloroethyl)-amides rather than the oxazolinium salt, it is well known that 2-substituted 2-oxazolinium hydrochlorides collapse readily to N-(2-chloroethyl)amides under the solvolysis conditions used.[14] In view of the fact that methanolysis of **1e**, **1f**, and **1g** yielded four-component mixtures of the corresponding methyl esters and N-(2-chloroethyl)amides (Table I) it seems apparent that both isomeric cations in each case (*i.e.*, isomers I and II) are intervening in these solvolysis reactions. Again the lack of selectivity observed for imides **1e** and **1f** may be explained by means of the proposed mechanism involving initial attack of the solvent on the carbonyl function followed by explusion of chloride ion. This mechanism, however, does not explain the selectivity observed in the methanolysis of **1g**, which is not well understood at this time.



2a-c, e-g

Synthesis and Characterization of N-Aroyl- and N-Acyl-2-oxazolinium Cations.—Several approaches to the synthesis of these cations were attempted. They may be divided into two general methods. The first was to generate an oxocarbonium ion in the presence of an oxazoline with the expectation that carbonium ion capture would lead to formation of the desired 3-(aroyl or acyl)-2-(aryl or alkyl)-2-oxazolinium salts (see route A.) The second method was to cyclize appropriate N-(2-chloroethyl)-N-aroyl or -acyl benzamides with silver tetrafluoroborate or silver hexafluoroantimonate (route B).

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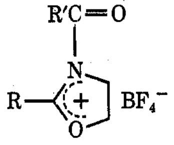
[12] Control experiments involving submission of these authentic amido esters, p-$CH_3OC_6H_4CONH(CH_2)_2OCOC_6H_5$, $C_6H_5CONH(CH_2)_2OCOC_6H_4$-$NO_2$-$p$, and p-$NO_2C_6H_4CONH(CH_2)_2$, to hydrolysis conditions showed no tendency to isomerization to the isomeric amido esters.

[13] P. Allen, Jr., and J. Ginos, *J. Org. Chem.*, **28**, 2759 (1963).

[14] A. A. Goldberg and W. Kelly, *J. Chem. Soc.*, 1919 (1948).

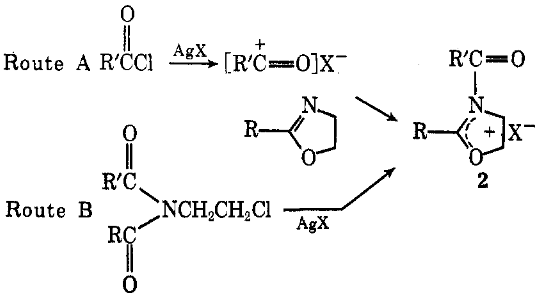
Table II

3-(Aroyl/acyl)-2-(aryl/alkyl)-2-oxazolinium Salts

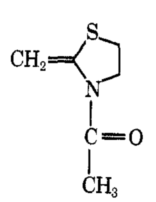


Cation	R′	R	Mp, °C	Route	Yield,[a] %	Analysis[h]		
						C	H	N
2a	C_6H_5	C_6H_5	98–100[e]	B	91	56.7	4.16	4.13
						56.6	4.32	4.30
2a′	C_6H_5	C_6H_5	125–127[c]	A[b]	100	39.5	2.87	2.87
						39.7	2.78	2.90
2b	*p*-$CH_3OC_6H_4$	*p*-$CH_3OC_6H_4$	128.5–130[e]	B	75	54.2	4.51	3.51
						52.6	4.54	3.47
2c	CH_3	CH_3	88.5–90[c]	B	60	33.6	4.67	6.55
						33.7	4.95	6.62
2e	C_6H_5	*p*-$CH_3OC_6H_4$	140–144[f]	B	77	55.4	4.35	3.81
						55.1	4.44	3.85
2f	*p*-$O_2NC_6H_4$	C_6H_5	163–166[g]	B	60	50.0	3.39	7.30
						50.2	3.43	7.40
2g	C_6H_5	CH_3	140–142[d]	B	100	47.8	4.25	4.90
						47.7	4.35	4.90

[a] Crude yields. [b] Hexafluoroantimonate salt. [c] CH_2Cl_2–CH_3CN. [d] CH_3CN. [e] CH_2Cl_2. [f] CH_2Cl_2–Et_2O. [g] CH_3CN–Et_2O. [h] Top row, calculated; bottom row, found.



Successful syntheses of cations **2** by route A were dependent upon the nature of the R′ and R substituents of the acid chloride and oxazoline, respectively. Both substituents R′ and R had to be aryl in order to obtain **2** as the predominant product. Complex product mixtures resulted when the oxazoline substituent R was alkyl and the acid chloride substituent R′ was aryl. Perhaps the complexity of this reaction is related to the reaction of 2-methyl-2-thiazoline with acetyl chloride, wherein at least three products have been identified. The ketene *N*,*S*-acetal, **5**, was postulated as a key intermediate in this acetylation.[15] Earlier work by Sheehan and coworkers[16] has also implicated such an intermediate in the reaction of 2-methyl-2-thiazoline with phthaloylglycyl chloride.



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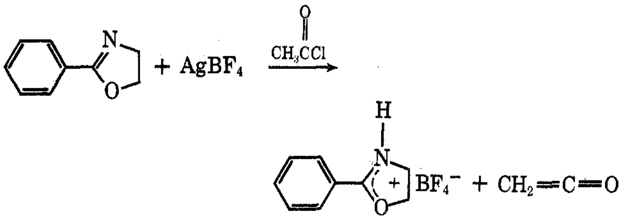
When the acid chloride substituent was alkyl (*i.e.*, R′ = CH_3) and the oxazoline substituent was aryl (*i.e.*, R = phenyl), route A produced ketene and the corresponding 2-aryl-2-oxazolinium salt. For example, when acetyl chloride was added to a mixture of 2-phenyl-2-oxazoline and silver tetrafluoroborate, nearly a quantitative yield of ketene and 2-phenyl-2-oxazolinium tetrafluoroborate was produced.



Adding aroyl chloride to a stoichiometric amount of 2-aryl-2-oxazoline and silver hexafluoroantimonate produced the desired 3-aroyl-2-aryl-2-oxazolinium salts **2** as the major products. The same reaction with silver tetrafluoroborate was not so clean. It is quite possible that the complexity of this reaction results from the known disproportionation of oxocarbonium tetrafluoroborates to acid fluorides and boron trifluoride.[17]

Route B proved to be the preferred method for preparing cations **2**. Both symmetrical and unsymmetrical *N*-2-chloroethyl precursors were prepared according to a modified method of Nehring and Seeliger.[8] Cyclizations of these imides proceeded readily with either silver tetrafluoroborate or hexafluoroantimonate.

The cations **2a–c**, **e–g**, were isolated as white, crystalline products which were extremely reactive toward moisture and other nucleophiles (see Table II). Nuclear magnetic resonance, infrared, and elemental analyses were in agreement with the proposed cation structures. Characteristic reactions which also support the structure of these cations will be described

Cation	R	R′
2e	C_6H_5	*p*-$CH_3OC_6H_4$
2f	*p*-$NO_2C_6H_4$	C_6H_5
2g	C_6H_5	CH_3

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(15) L. V. Grobvosky, *Diss. Abstr.*, **28**, 3993B (1967).

(16) J. C. Sheehan, C. W. Beck, K. R. Henery-Logan, and J. J. Ryan, *J. Amer. Chem. Soc.*, **78**, 4478 (1956).

(17) G. E. Olah, S. J. Kuhn, W. S. Tolgysei, and E. B. Baker, *ibid.*, **84**, 2733 (1962).

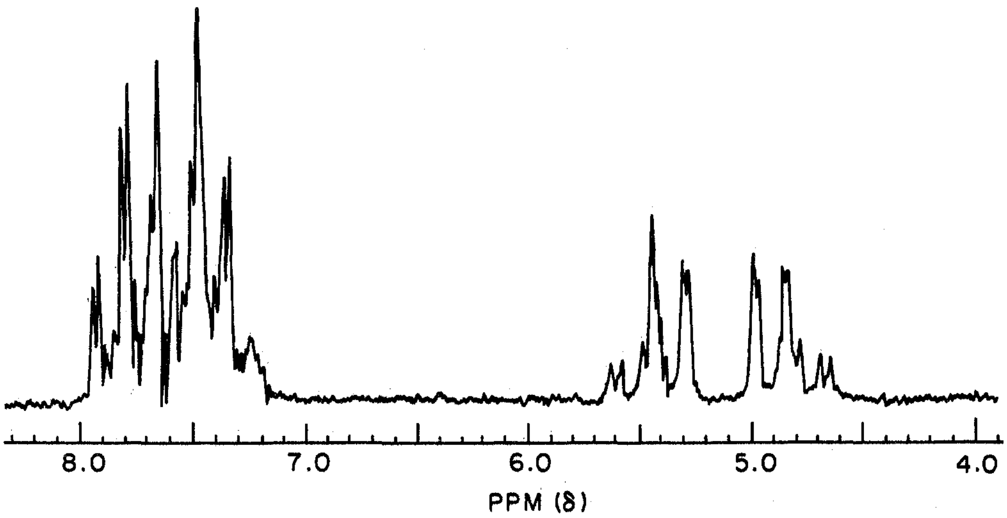


Figure 1.—Nuclear magnetic resonance spectrum of 3-benzoyl-2-phenyl-2-oxazolinium tetrafluoroborate (CD_3CN).

later. Infrared spectra of the cations **2** contained fairly intense absorption bands at 1725–1750 cm^{-1} for the carbonyl function and a similar type absorption at 1655–1710 cm^{-1} for the moiety

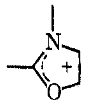
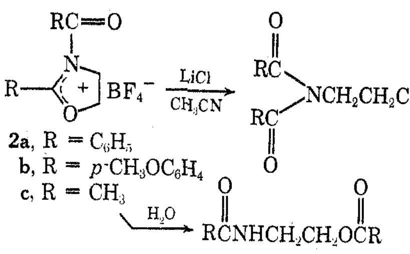


Figure 1 illustrates a typical nmr spectrum of one of these cations. A distinguishing feature of the nmr spectra was the deshielding of the oxazoline ring protons in the cations compared to the unquaternized oxazolines. Table III describes these data.

3-Acylated or aroylated oxazoline[7,18,19] and thiazoline salts[15] have been postulated as intermediates in the reactions of these heterocyclic rings with acid chlorides or acid anhydrides.

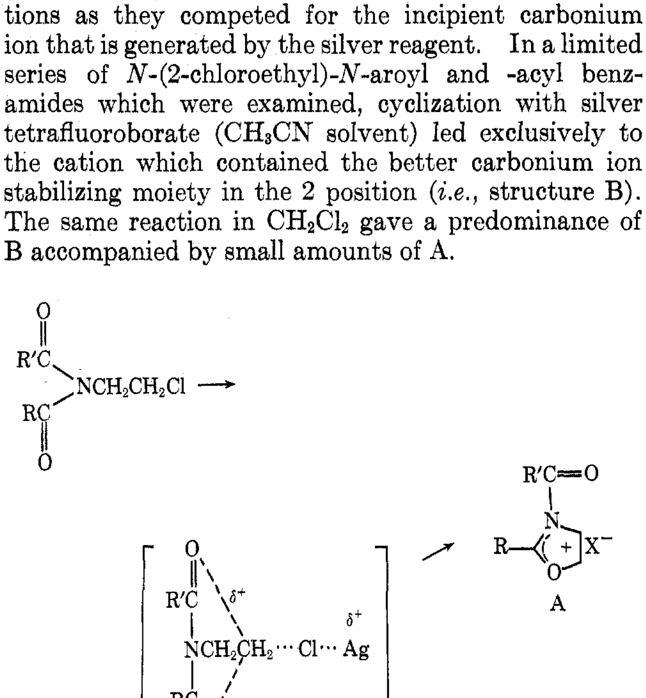
Fry[7] has shown that under anhydrous conditions 2-phenyl-2-oxazoline reacts with *p*-nitrobenzoyl chloride to yield *N*-(2-chloroethyl)-*N*-benzoyl-*p*-nitrobenzamide, whereas 2-(*p*-nitrobenzamido)ethyl benzoate is produced in the presence of water. Although no attempts to isolate these oxazoline salts have been reported thus far, an extensive but unsuccessful effort to trap the *N*-acetyl-2-methyl-2-thiazolinium salt has been described.[15]

The intermediacy of these salts in the reaction of acid chlorides with 2-oxazolines both under anhydrous conditions and in the presence of water is now well established. For example, 3-benzoyl-2-phenyl-2-oxazolinium tetrafluoroborate underwent immediate ring opening with LiCl in anhydrous acetonitrile to produce *N*-(2-chloroethyl)-*N*-(benzoyl)benzamide. Likewise, the reaction of this cation with water resulted in a rapid, high-yield conversion to *N*-(2-benzamido)ethyl benzoate.



2a, R = C_6H_5
b, R = p-$CH_3OC_6H_4$
c, R = CH_3

It was felt that the cyclizations of unsymmetrical *N*-(2-chloroethyl)-*N*-aroyl or -acyl benzamides would present a unique opportunity to determine neighboring group participation aptitudes of various carbonyl functions as they competed for the incipient carbonium ion that is generated by the silver reagent. In a limited series of *N*-(2-chloroethyl)-*N*-aroyl and -acyl benzamides which were examined, cyclization with silver tetrafluoroborate (CH_3CN solvent) led exclusively to the cation which contained the better carbonium ion stabilizing moiety in the 2 position (*i.e.*, structure B). The same reaction in CH_2Cl_2 gave a predominance of B accompanied by small amounts of A.



A

B

Evidence for the assignment of structure B to cations **2e** and **2f** was obtained by hydrolysis experiments. Fry[7] previously reported that the reaction of 2-phenyl-2-oxazoline with *p*-nitrobenzoyl chloride in the presence of water gave 2-(*p*-nitrobenzamido)ethyl benzoate. It was concluded that this compound resulted from

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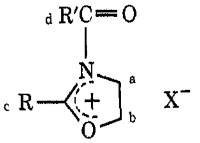
[18] P. G. Tryon, U. S. Patent 2,410,318 (1947).

[19] 3-Acylated 2-oxazolinium salts have been postulated as intermediates in the reaction of 2-(1-aziridinyl)-2-oxazolines with various acid chlorides [D. A. Tomalia, N. D. Ojha, and B. P. Thill, *J. Org. Chem.*, **34**, 1400 (1969)].

Table III

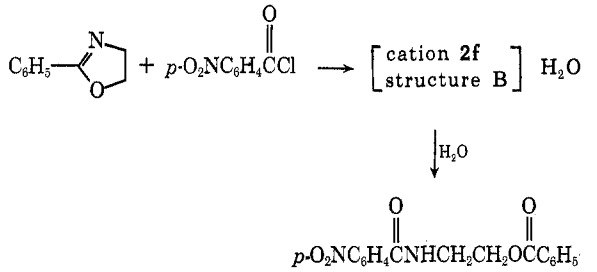
Nmr Chemical Shifts (δ)[a] of 3-(Aroyl/acyl)-2-(aryl/alkyl)-2-oxazolinium Salts



Cation	a	$\Delta\delta_a$[b]	b	$\Delta\delta_b$[b]	c	d
2a	4.83 (t)	0.85	5.46 (t)	1.07	7.21–7.99 (m)	
2b	4.71 (t)	0.75	5.28 (t)	0.90	6.97 (d), 7.76 (d), 7.91 (d) *p*-CH_3O, 3.86 (s)	
2c	4.49 (t)	0.28	5.14 (t)	0.79	2.48 (s)	2.76 (s)
2e	4.74 (t)	0.76	5.30 (t)	0.91	6.94 (d), 7.77 (d) (*p*-CH_3O), 3.87 (s) 7.33–8.09 (m)	
2f	4.88 (t)	0.91	5.51 (t)	1.12	7.38–8.20 (m)	
2g	4.51 (t)	0.53	5.21 (t)	0.82	2.56 (s)	7.58–8.03 (m)

[a] Chemical shifts were measured in CD_3CN with TMS as an internal standard: s = singlet, d = doublet, t = triplet, m = complex multiplet. [b] Difference in chemical shift between the cation and unquaternized 2-substituted 2-oxazolines (CD_3CN).

cleavage between the 2 and 3 position of the oxazoline ring. Fry postulated that cation **2f** with structure B

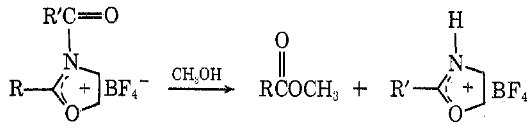


was the transient intermediate in this reaction. Adding our cation **2f** to water led to an immediate and quantitative conversion to 2-(*p*-nitrobenzamido)ethyl benzoate, which was shown by a mixture melting point to be identical with the product obtained by Fry. Assuming that our cation hydrolyzes by cleavage between the 2 and 3 position of the oxazoline ring, this demonstrates that cation **2f** has structure B. Hydrolysis of **2e** produced 2-(benzamido)ethyl *p*-anisate exclusively, thus leading to our assignment of structure B to this cation.

The structural assignment for cation **2g** is more tenuous in that the hydrolysis of this material does not lead to an amido ester as observed for all of the other cations, **2a**,**b**,**c**,**e**,**f**. However, based on analogy to the cations **2e** and **2f** wherein the better electron-donating substituent resided in the 2 position, we favor the assignment of structure B to cation **2g**. This assignment is supported by nmr in that the methyl signal in **2g** (2.56 ppm) is nearly the same ($\Delta\delta$ 0.08 ppm) as that for the 2-methyl substituent in cation **2c** (2.48 ppm). Comparing the methyl signal of cation **2g** to that of the 3-methyl substituent in **2c** (2.76 ppm), one finds a difference in chemical shift of 0.20 ppm (see Table IV).

Whereas amido esters were produced when R and R′ were both aryl or alkyl, cation **2g** hydrolyzed inexplicably to a mixture of acetic acid and the corresponding *N*-(2-hydroxyethyl)benzamide. An authentic sample of the anticipated amido ester [*i.e.*, *N*-(2-benzamido)ethyl acetate] was treated under the same conditions (*i.e.*, HBF_4) without any apparent hydrolysis, thus indicating that it is not the source of the products.

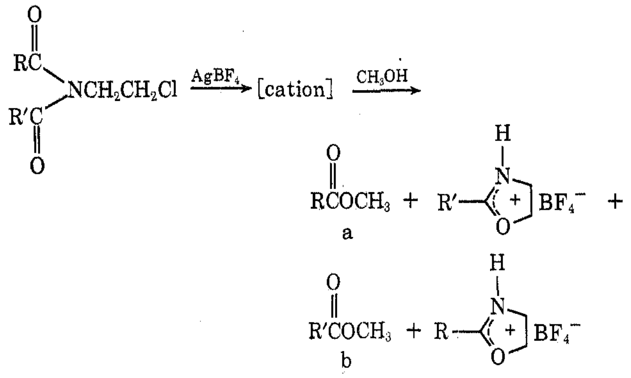
Allowing the cations to react with methanol resulted in a quantitative conversion to a mixture of the corresponding methyl ester and 2-substituted 2-oxazolinium salt. For example, cation **2a** (R = R′ = C_6H_5)



underwent methanolysis to a mixture of methyl benzoate and 2-phenyl-2-oxazolinium tetrafluoroborate. In the case of those cations resulting from unsymmetrical imide precursors (*i.e.*, **2e**, **2f**, and **2g**) both crude cations and purified cations were solvolyzed. Characterization of these products allowed us to determine the extent of selectivity of the cyclization process as well as the methanolysis. The purified cations were found to solvolyze selectively to methyl esters with the acyl or aroyl portion (R) being derived from the 2 substituent of the cation and oxazolinium salt substituent (R′) coming from the 3 substituent of the cation. Examination of the crude cations showed that selectivity still persisted, thus further corroborating the selectivity of the cyclization of the imides to the cations. Table IV shows the ratio of methyl esters arising from

Table IV

Product Distribution from Methanolysis of Crude Cations Derived from Unsymmetrical Imides

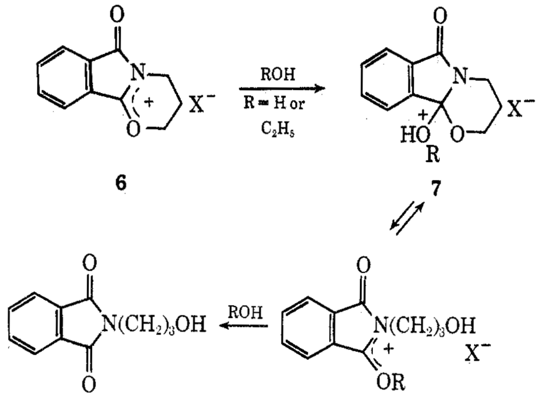


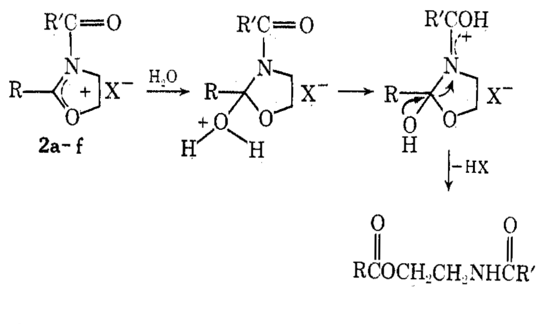
Imide	Mol % a	Mol % b
2e, R′ = C_6H_5; R = *p*-$CH_3OC_6H_4$	100	0
f, R′ = *p*-$NO_2C_6H_4$; R = C_6H_5	97	3
g, R′ = C_6H_5; R = CH_3	90	10

the methanolysis of unpurified cations as determined by glc analyses.

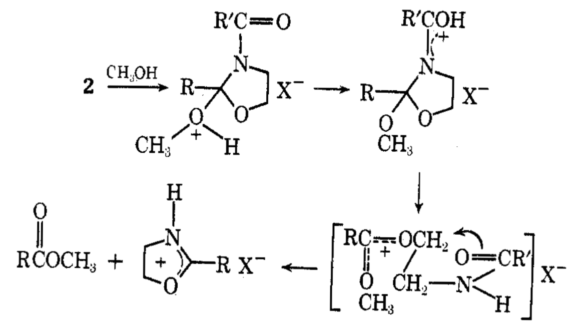
3-(Aroyl/acyl)-2-(aryl/alkyl)-2-oxazolinium salts are unquestionably ambident cations as defined by Hünig.[5] Depending upon the nature of the nucleophile, these cations are susceptible to attack at both the 2 and 5 positions. It is of interest to compare the reactivity of these cations to that of the structurally related *N,O*-trimethylenephthalimidium cation **6** reported recently by Hünig.[5]

Our cations appear to be very similar to Hünig's cation **6** in regard to preferred nucleophilic attack at either the 2 or 5 position. Halide ion reactions are completely analogous in each series. Differences do arise in the prototropy in the incipient cations that form as a result of water or alcohol attack at the 2 position. For example, Hünig found that the incipient cation **7** resulting from the attack of water or ethanol at the 2 position of cation **6** cleaved between the 2 and 6 position to produce γ-hydroxypropylphthalimide in each case. Fry's work as well as this present investigation have shown that cations **2a–f** undergo hydrolyses which result from cleavage between the 2 and 3 positions to produce amido esters. This mode of hydrolysis is analogous to the hydrolysis of 3-alkyl 2-substituted 2-oxazolinium salts, which has been described in detail by Allen and Ginos.[13] Cation **2g** is the only member of this series that hydrolyzes anomalously. The data are too meager to speculate on the mode of this transformation at this time.



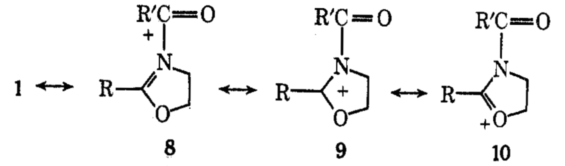


Methanolysis of **2** also appears to involve initial attack at the 2 position. Products arising from these reactions can be best rationalized in terms of a prototropy and cleavage between the 2 and 3 position as shown in eq 1.



(1)

All of the above reactions can be rationalized in terms of formal charge delocalization to various sites. Contributing structures to the resonance hybrid **1** can be represented by ammonium ion (**8**), carbonium ion (**9**), or oxonium ion (**10**) type species. Reaction of



these cations with chloride ion can be visualized as a result of the oxonium ion character due to species **10**. Initial stages of the hydrolysis and methanolysis reactions presumably occur *via* the carbonium ion species **9**.

Experimental Section

General.—The *N*-acyl/aroyl-*N*-(2-chloroethyl)benzamides/acetamides were prepared according to the method of Nehring and Seeliger.[8] Special care had to be exercised in purifying these materials by distillation. Prolonged heating of the unsymmetrical intermediate resulted in scrambling of the acyl and aroyl groups.

In the solvolysis reactions of the imides, aqueous acetonitrile (20:80 v/v) was used for the hydrolyses while anhydrous methanol was used for the methanolyses.

Silver tetrafluoroborate and hexafluoroantimonate were obtained from Alfa Inorganic.

For preparation of the cations, it was essential to carefully dry all reagents to at least 10 ppm of water or less. All operations with the cations were performed under anhydrous conditions in a drybox.

Nuclear magnetic resonance (nmr) spectra were recorded on a Varian A-60 spectrometer. Chemical shifts are reported as parts per million relative to tetramethylsilane. Samples for infrared spectra were prepared as KBr pellets and scanned on a Perkin-Elmer 337 spectrometer. Melting points were determined in a capillary and are uncorrected unless otherwise noted. Vapor phase chromatography work was conducted on an F & M Model 500 unit.

Solvolysis Reactions of Imides. *N*-(2-Chloroethyl)-*N*-(benzoyl)benzamide (1a). Condition A.—A 2-g (0.007 mol) sample of **1a** was dissolved in 20 ml of aqueous acetonitrile. Upon warming, the homogeneous solution became very acidic within minutes (*i.e.*, pH <2). After refluxing for 21 hr and removing solvent, a sticky white solid residue was obtained, 1.4 g. Recrystallization from ethanol–water yielded a white powder which melted at 83–87° (lit.[14] mp 88–89°). Infrared and nmr spectra of this product were identical with those of genuine 2-(benzamido)-ethyl benzoate prepared according to Fry.[7] A mixture melting point with authentic **1a** was undepressed.

Condition B.—A mixture of **1a** (2.87 g, 0.01 mol) and silver nitrate (1.69 g, 0.01 mol) in 20 ml of aqueous acetonitrile was stirred for 28 hr at room temperature (25°). Silver chloride was filtered, 0.8 g (56%). Removal of solvent from the filtrate gave 1.9 g (70%) of an off-white solid which was identified as 2-(benzamido)ethyl benzoate by ir, nmr, and mixture melting point.

Condition C.—A 2.5-g sample of **1a** was dissolved in 30 ml of anhydrous methanol. Under anhydrous conditions this reaction mixture was refluxed for 14 hr. Nmr analysis of the crude reaction mixture at this point indicated that methanolysis was 54% complete. Removal of solvent gave a gummy white solid which had the odor of methyl benzoate. The presence of this

TABLE V
SOLVOLYSES OF IMIDES

Imide	Condition A R′CONHCH$_2$CH$_2$OCOR	Condition B R′CONHCH$_2$CH$_2$OCOR	Condition C
1b	R = R′ = *p*-MeOC$_6$H$_4$ Mp 120–122° (EtOH–H$_2$O) [lit.[g] mp 127° (EtOH–Et$_2$O)]	R = R′ = *p*-MeOC$_6$H$_4$ Mp 118–112°	*p*-MeOC$_6$H$_4$COOMe + *p*-MeOC$_6$H$_4$CONH(CH$_2$)$_2$Cl[a]
1c	HOCH$_2$CH$_2$NH$_2$·HCl contaminated with CH$_3$COOH and CH$_3$CONHCH$_2$CH$_2$OCOCH$_3$	R = R′ = CH$_3$ (dark orange oil)	CH$_3$COOMe[b] + CH$_3$CONHCH$_2$CH$_2$Cl (dark orange oil)
1d	R = R′ = *p*-NO$_2$C$_6$H$_4$ Mp 182–187° (CH$_3$COOH) (lit.[h] mp 188–189°)	Same as A	*p*-O$_2$NC$_6$H$_4$COOMe + *p*-O$_2$NC$_6$H$_4$CONH(CH$_2$)$_2$Cl
1e	Mixture of two possible esters[c] (see text)	Mixture of two possible esters[c] (see text)	*p*-CH$_3$OC$_6$H$_4$COOMe, C$_6$H$_5$COOMe, *p*-CH$_3$OC$_6$H$_4$CONH(CH$_2$)$_2$Cl, C$_6$H$_5$CONH(CH$_2$)$_2$Cl[d]
1f	Mixture of two possible esters	Same as A	C$_6$H$_5$COOMe, C$_6$H$_5$CONH(CH$_2$)$_2$Cl, *p*-O$_2$NC$_6$H$_4$COOMe, *p*-O$_2$NC$_6$H$_4$CONH(CH$_2$)$_2$Cl[e]
1g	Complex mixture	Same as A	CH$_3$COOMe, CH$_3$CONHCH$_2$CH$_2$Cl, C$_6$H$_5$COOMe, C$_6$H$_5$CONH(CH$_2$)$_2$Cl[f]

[a] Recrystallization from CCl$_4$ gives two components. Amide was identical with an authentic sample obtained from reaction of *p*-MeOC$_6$H$_4$COCl + aziridine. [b] Glc analysis: 10 ft silicone gum (410), He flow 50 ml/min; isothermal at 75° for 7 min and then 8°/min; 2.8 min = CH$_3$COOMe; 12–21 min = amide. [c] Each of the pure esters (prepared independently) was treated under these same hydrolysis conditions (20:80 aqueous acetonitrile at reflux). No interconversion was observed. [d] Presence of all four verified by glc analysis. See footnote *b*. Conditions: isothermal at 100° for 13 min followed by heating at 4°/min. [e] Glc analysis. See footnote *b*. Conditions: isothermal at 200°. [f] Glc analysis. See footnote *b*. Conditions: isothermal at 75° for 7 min followed by heating at 8°/min. [g] E. Bergman, *Recl. Trav. Chim. Pays-Bas*, **71,** 168 (1952). [h] S. Franket and M. Cornelius, *Ber.*, **51,** 1654 (1918).

ester was confirmed by ir and nmr spectral comparisons with authentic methyl benzoate. The white solid was identified as a mixture of *N*-2-chloroethyl benzamide and starting material. Recrystallization of this mixture from CCl$_4$ gave pure *N*-2-chloroethyl benzamide, which was identical in every respect with an authentic sample which had been prepared by the reaction of benzoyl chloride with aziridine.[20]

The solvolyses of the other imides are summarized in Table V.

Preparation of Authentic Amido Esters.—Authentic amido esters were either prepared according to the method of Fry[7] (*i.e.*, reaction of appropriate 2-substituted 2-oxazolines with carboxylic acids) or according to the references cited herein. The preparation of two new amido esters is described below.

***N*-(2-Benzamidoethyl) *p*-Anisate.**—A mixture of *p*-anisic acid (1.52 g, 0.01 mol) and 2-phenyl-2-oxazoline (1.37 g, 0.0093 mol) was heated at 130° for 30 min. Upon cooling, the reaction mixture crystallized. This solid was ground up, washed with 10% sodium bicarbonate, and recrystallized from acetone. An analytical sample was obtained as a white powder, mp 126–129°.

Anal. Calcd for C$_{17}$H$_{17}$NO$_4$: C, 67.7; H, 5.63; N, 4.67. Found: C, 67.7; H, 5.72; N, 4.70.

***N*-(2-*p*-Anisamidoethyl) Benzoate.**—A mixture of benzoic acid (0.405 g, 0.0033 mol) and 2-(*p*-methoxyphenyl)-2-oxazoline (0.55 g, 0.0031 mol) was heated for 45 min at 100°. The solid product obtained upon cooling to room temperature was ground and washed with 10% sodium bicarbonate. Recrystallization from ethanol gave a white powder, mp 108–112°.

Anal. Calcd for C$_{17}$H$_{17}$NO$_4$: C, 67.7; H, 5.63; N, 4.67. Found: C, 67.9; H, 5.71; N, 4.73.

Preparation of Cations. Route A. Reaction of 2-Phenyl-2-oxazoline and AgSbF$_6$ with Benzoyl Chloride.—To a stirred solution of dry 2-phenyl-2-oxazoline (3.55 g, 0.0242 mol) and silver hexafluoroantimonate (8.3 g, 0.0242 mol) in 60 ml of anhydrous nitromethane was added 3.42 g (0.0242 mol) of freshly distilled benzoyl chloride. The addition was made in four increments over a period of 1 hr. After the brown reaction mixture was allowed to stir for 23 hr, silver chloride was filtered and found to weigh 3.48 g (100% of theory). Removal of solvent from the filtrate gave a sticky, dark red residue which exhibited an nmr spectrum which was essentially identical with that obtained for cation **1a**. (See Table III for nmr data.) This crude product was purified by dissolving in equal volumes of methylene chloride and acetonitrile, cooling with Dry Ice, and then adding just enough diethyl ether to cause precipitation. The product was obtained as a white powder, mp 125–127°.

B. Reaction of 2-Phenyl-2-oxazoline and AgBF$_4$ with Acetyl Chloride.—A slurry of 2-phenyl-2-oxazoline (3.0 g, 0.021 mol) and silver tetrafluoroborate (4.0 g, 0.021 mol) in 20 ml of methylene chloride was stirred as acetyl chloride (1.61 g, 0.021 mol) was added dropwise. The mixture turned a milky white color and was accompanied by gas evolution. Bubbling the gas through methanol produced methyl acetate. The gas was identified as ketene. After the reaction mixture was stirred for 4 hr at room temperature, silver chloride was filtered and found to weigh 2.65 g (92% of theory). Removal of solvent from the filtrate yielded 4.33 g of a beige-colored powder which was identified as 2-phenyl-2-oxazolinium tetrafluoroborate, mp 116–118°.

Route B. Cyclization of *N*-Aroyl/Acyl-*N*-2-chloroethyl Benzamide or Acetamide with Silver Reagents.—Under anhydrous conditions, 0.02 mol of the appropriate *N*-aroyl/acyl-*N*-2-chloroethyl benzamide or acetamide in 40 ml of dry methylene chloride or acetonitrile was stirred as silver tetrafluoroborate or hexafluoroantimonate (0.02 mol) was added in one portion. The reaction mixture was stirred overnight, during which time a substantial amount of blue-gray precipitate was formed. Solvent was removed under vacuum, leaving essentially a quantitative yield of solid residue consisting of cation plus silver chloride. Product distribution between cation A and B was assessed by extracting this residue with acetonitrile and analyzing by nmr spectroscopy. Complete conversion to cation B always resulted when acetonitrile was used as the reaction solvent. When methylene chloride was used as the solvent for the preparation of cations **2g** or **2e**, cation B was the major product accompanied by small amounts of cation A. In one instance the crude reaction product, **2g**, was quenched in an excess of anhydrous methanol. The methanolysis products were analyzed by both nmr spectroscopy and glc. Methyl acetate was the major product accompanied by small amounts of methyl benzoate.

The cations were generally obtained in crude yields of 60–100%. Analytical samples of the cations were obtained by recrystallization from acetonitrile, CH$_2$Cl$_2$, or a combination of these solvents with diethyl ether (Dry Ice cooling). These data and physical properties of the cations are listed in Table II.

Hydrolysis of 3-Acetyl-2-methyl-2-oxazolinium Tetrafluoroborate (2c).—A sample of cation **2c** (220 mg) was added to 1 ml of D$_2$O, giving a homogeneous acidic solution. After standing overnight, the reaction mixture was scanned by nmr. The spectrum consisted of two singlets at 2.06 and 2.10 ppm, as well as two triplets centered at 3.36 and 3.70 ppm. These signals were identical with those recorded for authentic *N*-(2-acetamido)-ethyl acetate in D$_2$O.

Hydrolysis of 3-Benzoyl-2-methyl-2-oxazolinium Tetrafluoroborate (2g).—A sample of cation **2g** (0.35 g) was added to 2.5 ml of D$_2$O and allowed to stand overnight at room temperature. The reaction mixture was found to contain an equimolar amount of acetic acid and 2-hydroxyethyl benzamide by nmr analysis.

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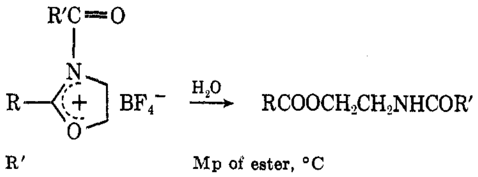
(20) H. Bestian, *Justus Liebigs Ann. Chem.*, **566,** 210 (1950).

Table VI



Cation	R	R′	Mp of ester, °C	Structure proof
2a	C_6H_5	C_6H_5	85–87	Identical with authentic ester (ir and nmr) (mp 88–89°)[a]
2b	p-$CH_3OC_6H_4$	p-$CH_3OC_2H_4$	121–122.5 (EtOH–H_2O)	Identical with authentic ester (ir + nmr); undepressed mixture melting point
2e	p-$CH_3OC_6H_4$	C_6H_5	127–129 (acetone)	Identical with authentic ester (ir and nmr) (mp 126–129°)[b]
2f	C_6H_5	p-$O_2NC_6H_4$	140–144 (abs EtOH)	Identical with authentic ester (ir and nmr);[b] undepressed mixture melting point

[a] Reference 14. [b] Reference 7.

Acetic acid exhibited a singlet at 2.15 ppm, whereas the amide displayed two triplets at 3.57 and 3.85 ppm as well as a complex multiplet at 7.46–7.90 ppm. The above signals were identical with those observed for authentic samples in each case. Authentic 2-hydroxyethyl benzamide was prepared by azeotropic (toluene) removal of water from a mixture of benzoic acid and 2-aminoethanol. Hydrolysis reactions of the other cations are shown in Table VI.

Methanolysis of 3-Acetyl-2-methyl-2-oxazolinium Tetrafluoroborate (2c).—Anhydrous methanol was added to a sample of cation **2c** in CD_3CN. The nmr spectrum of this mixture now contained two singlets at 3.62 and 2.00 ppm for methyl acetate. 2-Methyl-2-oxazolinium tetrafluoroborate was identified as the other component. The nmr of this material consisted of a slightly split singlet at 2.40 ppm and two triplets centered at 4.06 and 5.01 ppm. Removal of the solvent and other volatile material gave the crystalline oxazoline salt, mp 40–42°.

Methanolysis of 3-Benzoyl-2-methyl-2-oxazolinium Tetrafluoroborate (2g).—A sample of *N*-acetyl-*N*-(2-chloroethyl)-benzamide (3.1 g, 0.014 mol) in 50 ml of dry methylene chloride was treated with silver tetrafluoroborate (2.68 g, 0.014 mol) and then allowed to stir at room temperature for 24 hr. Solvent was removed under vacuum followed by the addition of anhydrous methanol (10 ml). The liquid phase was decanted and analyzed by glc. The major volatile product was methyl acetate (90 mol %) accompanied by small amounts (10 mol %) of methyl benzoate. The major nonvolatile component was identified by nmr as 2-phenyl-2-oxazolinium tetrafluoroborate.

When the cation **2g** was prepared in acetonitrile and then treated with methanol in the same manner, only methyl acetate was observed as the volatile component.

Methanolysis of 3-Benzoyl-2-(*p*-methoxyphenyl)-2-oxazolinium Tetrafluoroborate (2e).—To a purified sample of cation **2e** in CD_3CN was added anhydrous methanol. A slightly exothermic reaction was noted. The nmr spectrum of this mixture now contained a singlet at 3.83 ppm which was enhanced by the addition of methyl *p*-anisoate. In addition, two triplets at 4.26 and 5.18 ppm as well as a complex multiplet at 8.14 to 7.54 ppm were noted and are identical with those observed for authentic 2-phenyl-2-oxazolinium tetrafluoroborate.

A sample of the crude reaction product obtained by cyclization of *N*-benzoyl-*N*-(2-chloroethyl)-*p*-anisamide in CH_2Cl_2 was quenched in methanol. Analysis of the resulting solution by glc (silicone gum rubber, 410, 10-ft column) revealed the presence of only methyl *p*-anisoate.

Methanolysis of 3-(*p*-Nitrobenzoyl)-2-phenyl-2-oxazolinium Tetrafluoroborate (2f).—Anhydrous methanol was added to a purified sample of cation **2f** in CD_3CN. After several hours at room temperature, the sample was analyzed by nmr and found to contain methyl benzoate and 2-(*p*-nitrophenyl)-2-oxazolinium tetrafluoroborate in equimolar amounts. The salt was isolated as a tan, crystalline solid by removing all of the volatile components under vacuum. Recrystallization from methylene chloride and ether gave a tan powder melting at 143–146.5°. The nmr spectrum consisted of a quartet centered at 8.35 ppm and two triplets centered at 5.26 and 4.36 ppm (CD_3CN).

Anal. Calcd for $C_8H_8N_2O_3BF_4$: C, 38.6; H, 3.22; N, 9.95. Found: C, 38.5; H, 3.18; N, 10.1.

A sample of crude cation, **2f**, was treated in a similar manner with anhydrous methanol. Analysis of the reaction mixture by glc showed the presence of methyl benzoate and methyl *p*-nitrobenzoate in a ratio of 97:3 mol %, respectively.

Preparation of 2-Aryl- and Alkyl-2-oxazolinium Tetrafluoroborates.—While a solution of *N*-(2-chloroethyl)acetamide or benzamide[20] (0.0265 mol) in 40 ml of anhydrous acetonitrile was stirred, silver tetrafluoroborate (5.15 g, 0.0265 mol) was added in one portion. A white precipitate formed immediately. After the reaction mixture was stirred at room temperature for ~16 hr, silver chloride was removed by filtration. Evaporation of the solvent gave the corresponding oxazolinium tetrafluoroborate salts. Crude yields of the salts varied between 90 and 100%. Physical constants and recrystallization solvents are as described below.

2-Methyl-2-oxazolinium tetrafluoroborate was a white, hygroscopic solid, mp 40–42° from methylene chloride.

Anal. Calcd for $C_4H_8NOBF_4$: C, 27.9; H, 4.65; N, 8.15. Found: C, 27.8; H, 4.45; N, 7.90.

2-Phenyl-2-oxazolinium tetrafluoroborate was a white, crystalline material, mp 119.5–121° from methylene chloride.

Anal. Calcd for $C_9H_{10}NOBF_4$: N, 6.23. Found: N, 5.80.

2-(*p*-Methoxyphenyl)-2-oxazolinium tetrafluoroborate was a white solid, mp 178–180° from a mixture of acetonitrile and diethyl ether.

Anal. Calcd for $C_{10}H_{12}NO_2BF_4$: C, 45.3; H, 4.53; N, 5.28. Found: C, 45.3; H, 4.53; N, 5.30.

2-(*p*-Nitrophenyl)-2-oxazolinium tetrafluoroborate was a tan solid, mp 143–146.5° from methylene chloride–ether.

Anal. Calcd for $C_9H_9N_2O_3BF_4$: C, 38.6; H, 3.22; N, 9.95. Found: C, 38.5; H, 3.18; N, 10.1.

Reaction of Cation 2c with LiCl.—Anhydrous LiCl (0.09 g, 2.1 mmol) was added to a solution of **1c** (0.597 g, 2.1 mmol) in 40 ml of dry acetonitrile. An nmr spectrum of this reaction mixture was recorded within 5 min after combination of the reagents and found to be identical with the spectrum obtained for an authentic sample of *N*-2-chloroethyl-*N*-benzoyl benzamide prepared by the method of Nehring and Seeliger.[8]

Registry No.—**1a**, 17209-17-5; **1b**, 37056-12-5; **1c**, 17101-83-6; **1d**, 37056-14-7; **1e**, 37056-15-8; **1f**, 37056-16-9; **1g**, 17101-84-7; **2a**, 36994-88-4; **2a′**, 36994-89-5; **2b**, 36994-90-8; **2c**, 36994-91-9; **2e**, 36994-92-0; **2f**, 36994-93-1; **2g**, 36994-94-2; *N*-(2-benzamidoethyl) *p*-anisate, 37056-18-1; *N*-(2-*p*-anisamidoethyl) benzoate, 37056-19-2; *N*-(2-*p*-anisamidoethyl) *p*-anisate, 37056-20-5; 2-methyl-2-oxazolinium tetrafluoroborate, 37047-99-7; 2-phenyl-2-oxazolinium tetrafluoroborate, 37048-00-3; 2-(*p*-methoxyphenyl)-2-oxazolinium tetrafluoroborate, 37017-01-9; 2-(*p*-nitrophenyl)-2-oxazolinium tetrafluoroborate, 37048-01-4.

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