panied by substantial decomposition, but indicated strong *m/e* 186 peaks. In addition, ^{13}C and off-resonance proton decoupled ^{13}C NMR results were quite consistent.

(20) T. J. Katz, M. Yoshida, and L. C. Siew, *J. Am. Chem. Soc.*, **87**, 4516 (1965).

(21) Both the relatively sharp melting point and NMR spectrum suggest that we have produced a single isomer. Inspection of the models with regard to steric preferences for the first methyl group incorporated together with maximum overlap of the monocarbanion suggests that this is probably the trans isomer.

Halocyclization of *N*-Allylbenzamide Derivatives. Effects of Halogenating Agent, Alkene Substitution, and Medium

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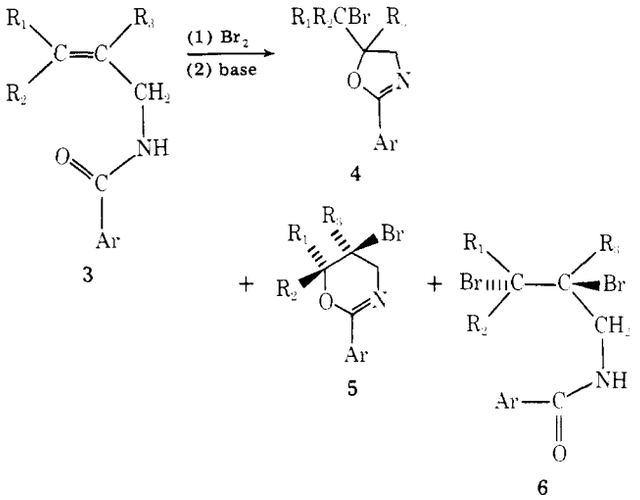
Halogenation of *N*-allylamide derivatives produces ring-closure products and addition products in varying amounts depending on the halogenating agent, the alkene structure, and the solvent. Concerted addition–cyclization does not occur in these systems when the alkene is activated by attached groups which aid in the delocalization of transition state charge. Instead, the results from the studies of these systems are best explained by invoking carbocation intermediates or carbocation-like product-forming steps. Equilibria between halonium ions and haloalkyl carbocations are probably not established in these reactions owing to the high reactivity of the carbocations in the presence of good nucleophiles. There remains the possibility that **3c–e,** like **3a** and **3b,** are brominated via a bromonium ion intermediate as the product-forming species. If this mechanism is operative, these reactions provide a rare example of fused mode cyclization in such circumstances.

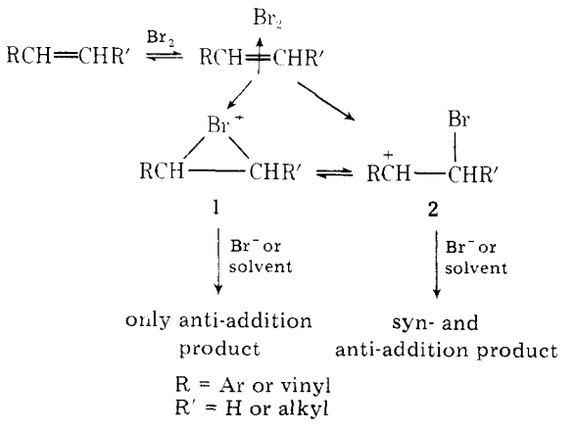
Since first postulated by Roberts and Kimball,[1] cyclic bromonium ions have been considered important intermediates in the electrophilic bromination of most alkenes.[2] Evidence for ethylenebromonium ion intermediates and bromination mechanisms incorporating them seems well justified when the alkene is nonconjugated.[3-10] Conjugated alkenes such as styrene derivatives[3,11] and dienes[12] often behave differently.[13,14] The mechanistic change, which is revealed by the study of product stereochemistry and the application of linear free-energy relationships, arises because the resonance stabilized substituted β-bromoethyl cation **2** has an energy similar to that of its isomeric bromonium ion, Scheme I.

We began the present work with the goal of ascertaining whether or not ions **1** and **2** were both important product-forming intermediates. We chose to compare results of halogenation studies of the series of amides **3a–e** because of the neighboring amide group which should participate in these reactions thus aiding in assigning a structure to the intermediates. At the outset we assumed that there is a strong tendency of ring opening–ring closures of substances like bromonium ions to strongly prefer the spiro mode over fused mode cyclizations,[15-19] eq 1. Thus, one predicts that five-membered ring bromocylization products would arise from



3–10a, $R_1 = R_2 = R_3 = H$; Ar = phenyl
b, $R_1 = R_2 = H$; $R_3 = Me$; Ar = phenyl
c, $R_1 = Me$; $R_2 = R_3 = H$; Ar = *p*-nitrophenyl
d, $R_1 = R_2 = Me$; $R_3 = H$; Ar = *p*-nitrophenyl
e, $R_1 = Ph$; $R_2 = R_3 = H$; Ar = *p*-nitrophenyl

Scheme I



3a–e when the substrates react via amide attack on the bromonium ion, e.g., structure **7**, eq 2. However, the favored carbocation intermediates from **3d** and **3e** should be the tertiary cation **8d** and the benzylic cation **8e,** respectively, and these would cyclize only to the six-membered rings **5d** and **5e,** respectively, eq 3.[20] We have also investigated the effect of the medium on these addition–cyclization reactions.

Results and Discussion

The *p*-nitrobenzamides **3c–e** (Ar = *p*-nitrophenyl) were prepared and brominated in acetic acid and in carbon tetrachloride giving bromocyclization products and dibromides.[21] In each case, these products were isolated and their structures determined by the use of elemental analysis, IR, NMR, and mass spectroscopy. The stereochemistry of the dibromides isolated from the bromination of **3c** and **3e** was consistent with

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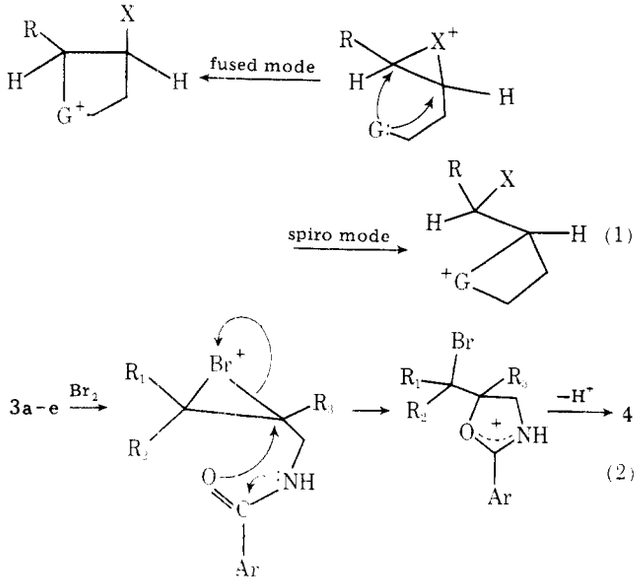
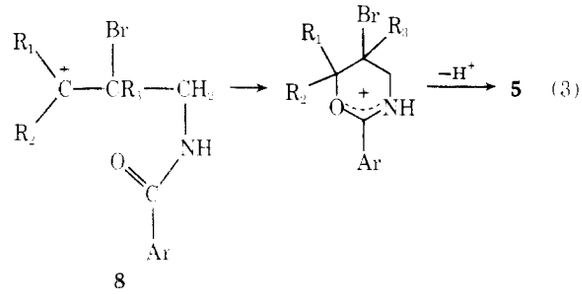
Table I. Halogenation of N-Allylbenzamide Derivatives

alkene	halogenation agent	solvent	react temp, °C	% yield[a] of halocyclization products(s)	cyclization ratio O-5:O-5	% yield[a] of dihalide	ratio of cyclization to addition
CH_2=$CHCH_2NHCOPh$ (**3a**)	Br_2[b]	$CHCl_3$	0	42	100:0	55	43:57
	Br_2[b]	AcOH	15	45	100:0	49	48:52
CH_2=$C(CH_3)CH_2NHCOPh$ (**3b**)	Br_2[c]	MeOH	−78	63	100:0	*d*	*d*
	Cl_2[c]	MeOH	−78	47	100:0	*d*	*d*
	F_2[c]	MeOH	−78	21	100:0	*d*	*d*
t-CH_3CH=$CHCH_2NHCO$-*p*-$NO_2C_6H_4$ (**3c**)	Br_2	CCl_4	25–30	36	48:52[e]	58	36:64
	Br_2	AcOH	16–18	61	21:79[e]	30	67:33
	NRS	AcOH	26	71	34:66[e]	*f*	*f*
	Cl_2	AcOH	25–28	30[e]	40:50[e]	23	57:43
$(CH_3)_2C$=$CHCH_2NHCO$-*p*-$NO_2C_6H_4$ (**3d**)	Br_2	CCl_4	16–18	61[e]	0:100	22[e]	73:27
	Br_2	AcOH	16	82[e]	0:100	16[e]	84:16
	Br_2[g]	AcOH	16	95	0:100	5[e]	95:5
t-$PhCH$=$CHCH_2NHCO$-*p*-$NO_2C_6H_4$ (**3e**)	Br_2	CCl_4	25	36	0:100	64	36:64
	Br_2	AcOH	18	76	0:100	22	77:23

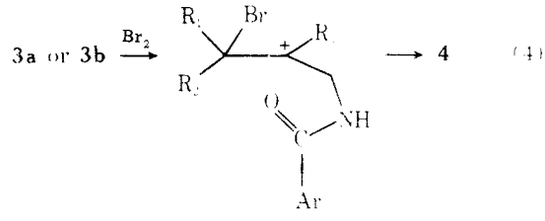
[a] Isolated yields unless otherwise stated; balance in some cases is unreacted amide, see Experimental Section. [b] Reference 22. [c] Reference 23. [d] NMR analysis indicated the presence of dihalides and halo ether products; however, these products were not isolated; reference 22. [e] Determined by gas chromatography. [g] Dihalide cannot form and acetoxy halide was not sought. [g] A molar excess of Br_2 was used in this run.

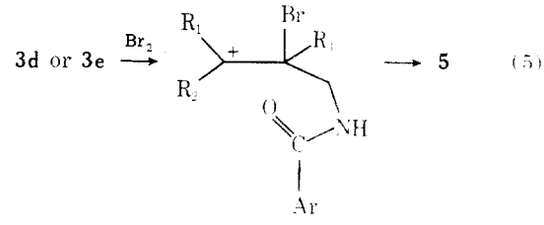




anti addition of bromine. Likewise, the dihydrooxazine derivatives obtained from bromocyclization of **3c** and **3e** were found to contain the ring bromine and methyl (from **3c**) or phenyl (from **3e**) in a trans arrangement. In one case, **3c**, chlorination in acetic acid was also carried out. The products, their relative ratios, and yields are given in Table I along with some comparative data of other reactions. Through control experiments **6d** was found to be solvolytically unstable; the product data shown have thus been confirmed by gas chromatography in questionable cases.

Cyclization Mode. Significantly, we observed a change in the mode of cyclization as the hydrogens about the vinyl system are replaced with a methyl or phenyl group. Goodman and Winstein[22] and Merritt[23] have studied halocyclization of the terminally unsubstituted N-allylamides **3a** and **3b**. The five-membered ring (an oxazoline), and not the six-membered ring (a dihydrooxazine), is the only cyclic product. This is consistent with cyclization via intermediate **9** or Markovnikov-like cyclization of intermediate **7**. The amides **3d** and **3e** would give a similar bromonium ion (**7**) as **3a** or **3b** but would give the respective tertiary or benzylic carbocations **10d** or **10e** and not the secondary cations **9d** or **9e**. According to our assumption that the spiro cyclization mode would preferentially occur, intermediates **7d** and **7e** would yield oxazoline derivatives **4** while **9d** and **9e** could only give the dihydrooxazine derivatives **5d** and **5e**, respectively. Since only the latter form in this instance either carbocations are involved or fused mode cyclization is occurring.[24]





The more symmetrically substituted amide **3c** provides an interesting contrast to what appears as limiting behavior of the other amides under all conditions; a mixture of the five- and six-membered ring products was formed. Formation of a six-membered ring product by amide group attack on the bromonium ion from **3c** would require fused mode cyclization

(spiro route highly favored); alternatively, these results are accommodated by amide group attack on the open secondary carbocation **10c**.

Either of the explanations above are unsatisfying based on the conventional view of fused vs. spiro cyclizations[15] or of simple disubstituted alkene brominations.[2,5] The stereochemical studies of Rolston and Yates,[3] for example, showed considerable differences between the behavior of the isomeric 2-butenes when compared to isomeric 1-phenypropenes. While >99% anti addition was observed for the butenes under a variety of conditions, significant amounts of syn addition were noted for the 1-phenylpropenes. A reasonable conclusion was that the benzyl-like carbocation in the latter case allowed for a different mechanism.[5] It is of course possible to extend the carbocation mechanism to trisubstituted alkenes where tertiary alkyl carbocations form (e.g., **3d**), but secondary carbocations in these processes have not been strongly indicated by other evidence. Since the possibility of fused mode cyclization, albeit unfavorable, has not been shown to be impossible, this alternative seems the better choice until more proof exists to favor the secondary carbocations.

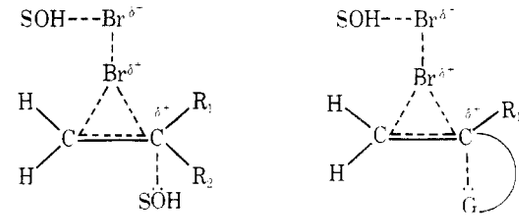
Halogenation Agent. Although the halonium ion mechanism is advocated for chlorination as well as for bromination of alkyl substituted alkenes,[2] it is well known that, relative to their open carbocation isomers, chloronium ions do not enjoy the stability of bromonium ions.[10,25] Thus, when analyzing the results of halocyclization studies, this stability trend should be evident if the stability–selectivity principle[26] is followed. We believe such a trend is indeed evident from the results compiled in Table I. Merritt[23] found a steady decrease in the halocyclization fraction as the halogen was varied from bromine to fluorine in the halogenation of **3b** in methanol. We found a smaller amount of cyclic product when **3c** was chlorinated than when it was brominated in acetic acid.

There is probably little or no bridging in fluorination reactions.[2b,25] Therefore, if all of the halogenations of **3b** occurred at equal rates (which, of course, they do not) ca. 20% cyclization product could be expected. That is, the neighboring amide group will capture a rather constant percentage of the carbocationic intermediates because the energy of that process regardless of the halogen is nearly a constant. Likewise halide ion and solvent trapped product should be nearly a constant.

Now let us consider halonium ion intermediates. Despite its attractiveness, the cyclization trend is not explained by invoking the intermediacy of a greater amount of halonium ion as the size of the halogen is increased. The problem with that rationale can be seen by considering the stability–selectivity relationships of the various halonium ion–halide systems. Assuming the halonium ion stability order bromonium > chloronium > fluoronium, the nucleophilicity order Br^- > Cl^- > F^- > amide group, and operation of the stability–selectivity principle, one would predict that the bromonium ion is more likely to react with the bromide ion rather than the amide group while the less stable (less selective) chloronium ion would react relatively better with amide group as compared to the chloride ion. Thus the wrong cyclization trend is predicted.

A plausible explanation comes from the consideration of the different halogenation mechanisms, their rates, i.e., F_2–alkene > Cl_2–alkene > Br_2–alkene, and the Hammond postulate.[27] The charge developed in the transition state upon halogenation increases in the order: fluorination < chlorination < bromination. The charge at carbon upon bromination could be large enough to allow for nucleophilic solvation of the transition state.[28–32] The solvent or a nucleophilic neighboring group, e.g., the amide group, could fulfill this role by solvation of the backside of the carbon as shown in Scheme II. It follows from established principles that the later the transition state

Scheme II



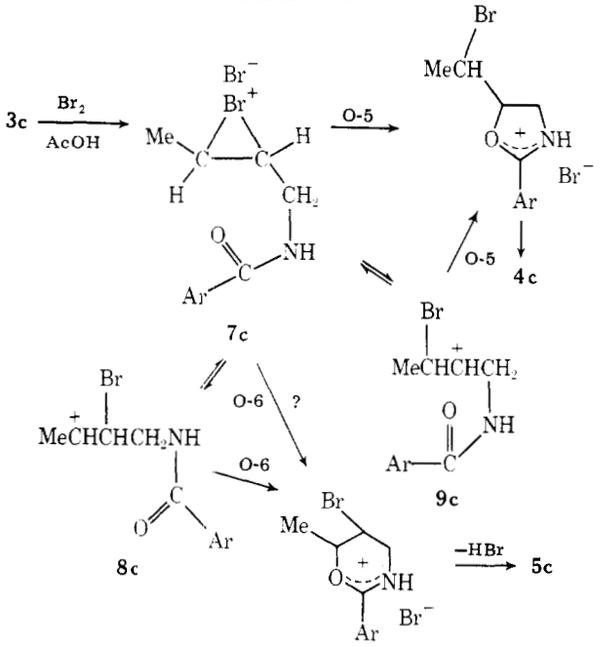
the more important structures like those in Scheme II become. Obviously, the halogen, solvent, and neighboring group can affect the importance of them.[33] Because of the entropy loss involved in ordering a neighboring group-solvated transition state, bromination and, to a lesser extent, chlorination may give such highly structured transition states with the extent depending on alkene structure and solvent.[34] *N*-Bromosuccinimide (NBS), which in some solvents reacts by rate-limiting nucleophilic attack on a bromonium-like species,[35] may best illustrate the concepts proposed to explain the effect of the halogenation agent, Table I. Using the reagent with **3c**, the amount of cyclization product increased (as compared to Br_2) and the five-membered ring product (O-5 cyclization) increased relative to the six-membered ring product (O-6 cyclization).

Solvent Effects. While we have considered some general solvent effects above, it is interesting to consider solvent effects on product composition,[36] Table I. Acetic acid, which is more polar and nucleophilic than carbon tetrachloride, allows for a larger fraction of cyclization than carbon tetrachloride or chloroform. This trend is consistent with the proposal above, Scheme II, as the charge developed in the transition state would be greater in the more polar solvent despite the higher rate.[34] This trend is also consistent with what one would expect if the competitive attack on a bromonium ion by bromide and the neighboring group is considered. As the charge developed at carbon is less, the better nucleophile, bromide ion, should fare better. This alone does not account for all of our observations, however, since the six-membered ring products, even from **3c**, may be formed from amide attack on a carbocation and not a bromonium ion.

If we examine the data from bromination of **3c** in acetic acid and in carbon tetrachloride the trend expected from the intermediacy of the carbocation **8c** and the bromonium ion **7c** is present.[37–39] Of the two carbocations, substituent effects favor **8c** over **9c**, Scheme III. Carbocation **9c** may also be a product-forming intermediate, but the data do not allow for a decision as to whether it or the bromonium ion **7c** leads to the five-membered ring product. In carbon tetrachloride there is more product formation via the bromonium ion **7c** and hence the greater proportion of cyclic product is the O-5 cyclization product. Also, there is a significant amount of dibromide (only anti addition) consistent with the theory that the better nucleophile reacts faster with the bromonium ion. In the better ionizing solvent, acetic acid, the amount of dibromide decreased and the O-6 cyclization fraction increased. The actual amount of O-5 cyclic product remained nearly constant.

Reaction Stereochemistry. The observation that only anti addition products are formed is generally consistent with bromonium ion intermediates.[2] Thus, since the dihydrooxazine formed from **3c** and **3e** is the one with the bromine and methyl or phenyl group trans, it is consistent with stereospecific ring closure and not with the intermediacy of carbocations. The reasons for this need to be discussed. A possible stereospecific pathway to the dihydrooxazines has been mentioned and eliminated.[24] While it is possible that the trans isomer forms from the carbocation because it is the more stable one,[40] it is highly probable that the carbocations are

Scheme III

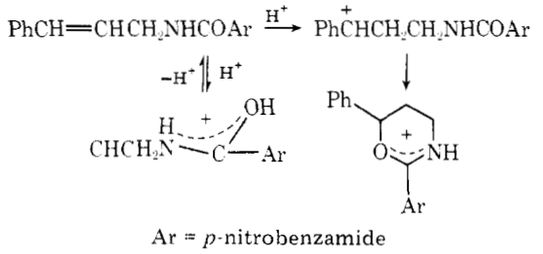


captured by bromide ion or the neighboring group before a significant amount of rotation can occur. In fact, it is entirely possible for there to be a merger of mechanisms as the solvent stabilization of the intermediates and cation stabilities vary. For example, cation **8** is not expected to be very stable in carbon tetrachloride; therefore it is probable that under these conditions **8** is never fully formed. Instead partially formed **8** is intercepted along the reaction coordinate to **8** to give product. A number of investigations lend support to this nonlimiting view of the mechanism.[41]

Comparison with Other Studies. McManus et al.[42] have reported the acid-catalyzed cyclization of N-allylamides and similar compounds. The results of these studies, which were carried out in 50–96% aqueous sulfuric acid, were consistent with cyclization via carbocation formation. For example, N-allyl-*p*-nitrobenzamide gave only oxazolinium product by an O-5 route while *N*-cinnamyl-*p*-nitrobenzamide gave exclusively the O-6 product via the more stable benzylic carbocation, Scheme IV. Nakai et al.[43,44] have observed similar protonation results with dithiocarbamates and have also studied the cyclization of the dithiocarbamate **11** which can undergo competitive O-5 and O-6 cyclization, Scheme V. Both O-5 and O-6 cyclization products were obtained with the relative ratios of five- and six-membered ring cations varying with the acid catalyst.[45] That these results parallel our bromination results is taken as strong evidence for the carbocationic nature of the product-forming intermediates in our bromination studies.

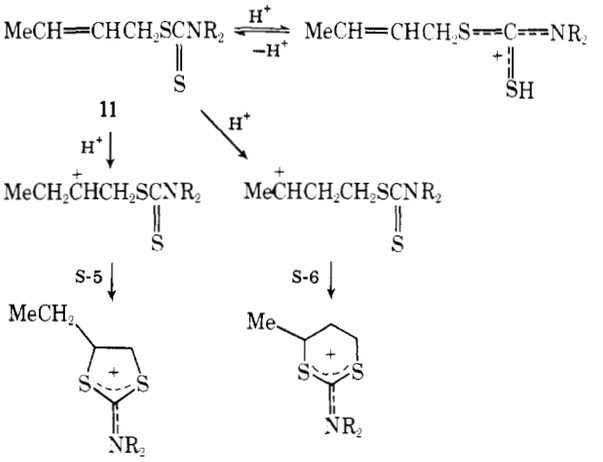
In stark contrast to our studies, Nakai et al.[44] have found that, regardless of the substitution pattern, bromination (in carbon tetrachloride) of N-allyl dithiocarbanate derivatives (i.e., **12 a–e**) leads only to five-membered ring products of

Scheme IV



Ar = *p*-nitrobenzamide

Scheme V

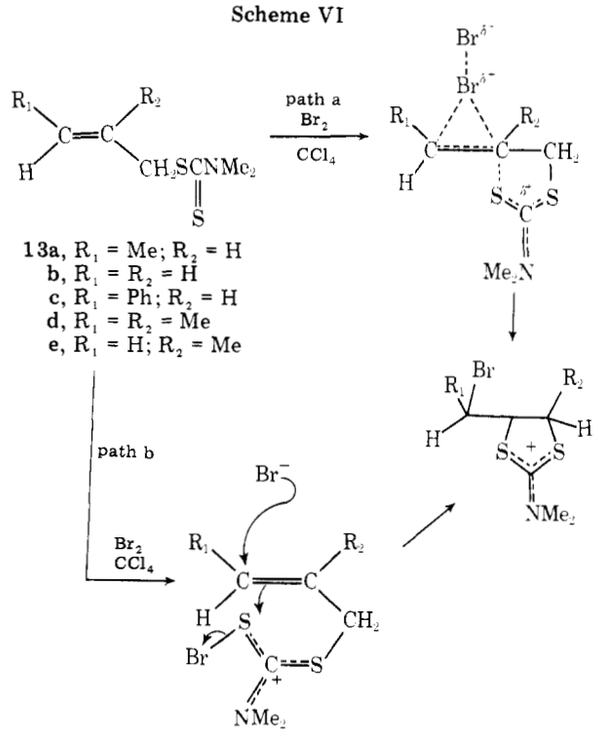


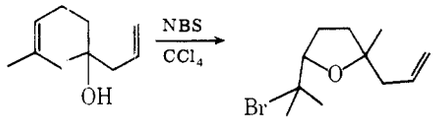
bromocyclization. There are two reasonable rationales for the differences between our results and those of Nakai et al., the reactions could proceed solely by an anchimerically assisted route (path a, Scheme VI), or electrophilic attack could initially occur at sulfur with subsequent bromide ion (or tribromide ion) attack at carbon to give the observed cyclic product (path b). The latter mechanism (path b) is attractive because of the high nucleophilicity of the sulfur and the similarity with brominations thought to proceed by initial electrophilic attack other than at carbon.[14] Nevertheless, because the cyclic salts are said to immediately precipitate from solution,[44] path a is assumed to be preferred.

Our bromocyclization results are also different from those of Klein et al.[46] who report exclusive O-5 ring closure upon NBS treatment of linalool, eq 6. This reaction is obviously anchimerically assisted since the expected product (cf. eq 2) from that route and not from the route involving carbocations is formed.

Conclusions. Numerous factors are shown to affect the amount of halocyclization and dihalide fractions upon halogenation of alkenes bearing a proximate nucleophilic neighboring group. Because of the way the product fractions are

Scheme VI





(6)

varied we conclude that nucleophilic solvent or neighboring group assistance may be important in the rate-determining and product-determining step. In anchimerically assisted addition–cyclizations, the neighboring group fulfills the role solvent may otherwise fulfill and the rate-determining and product-determining steps are the same. When polar solvents are employed or when carbocation stabilizing substituents are attached to the alkene carbons, there is a tendency to form carbocations and halonium ion intermediates. Because of the difference in reactivity of these intermediates, the products in such cases can largely be accounted for by excluding significant participation of the halonium ion as an important product-forming intermediate. The product stereochemistry, however, suggests that the carbocationic intermediates are most often trapped before significant rotation can occur, hence the halonium ion ring opening tends to merge with nucleophilic attack on carbocation to give a spectrum of product-forming reactions from S_N1-like on the one end to S_N2-like on the other.

Experimental Section

General. Melting points were taken in capillaries with a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were recorded of films or KBr disks with a Beckman Acculab I, a Beckman IR-5A, or Beckman IR-10 spectrometer. Proton nuclear magnetic resonance spectra were obtained with a Bruker HFX-10 90 MHz spectrometer equipped with a spin decoupler or with a Varian EM-360 60-MHz spectrometer. Unless otherwise stated, internal tetramethylsilane (Me_4Si) was used as an internal reference standard ($\delta = 0$). The mass spectra were recorded with a CEC 21-110 mass spectrometer. Elemental analyses were determined by Gailbraith Laboratories, Inc., Knoxville, Tenn. Gas chromatographic analyses were obtained using a Hewlett-Packard Series 5750 gas chromatograph equipped with a flame ionization detector and a Model 3370A electronic integrator and printout. Owing to decomposition of the halogenated compound by metal columns, glass columns with on column injection were used throughout. Analysis of the halogenation mixtures was performed using a 6-ft glass column packed with 6% OV-210 on Gas Chromosorb Q (80–100 mesh). Freshly opened reagent grade solvents and reagents were used as obtained. Other solvents and reagents were purified by recrystallization or distillation and drying. *N*-Cinnamylamine was prepared in best yields by use of the Delepine reaction[47] and was converted to its *p*-nitrobenzamide as previously described.[43] The other amines were prepared from commercially available purified chlorides or bromides using a modification of the Gabriel synthesis[48] described for the crotyl derivative by Roberts and Mazur.[49]

***N*-Crotyl-*p*-nitrobenzamide (*N*-(*trans*-2-buten-1-yl)-*p*-nitrobenzamide) (3c).** Freshly distilled crotyl chloride (bp 83–84 °C) (45.5 g, 0.5 mol) and potassium phthalimide (93.0 g, 0.5 mol) were dissolved in 500 mL of dimethyl sulfoxide in a 1000-mL round-bottom flask fitted with a reflux condenser and the resulting solution was heated to mild reflux (190 °C) for 2 h. The solution was cooled and poured into 500 mL of an ice and water mixture. The phthalimide, which precipitated, was vacuum filtered, washed with water while on the funnel, and dried in air at room temperature to yield 87.0 g (86.6%) of crude *N*-crotylphthalimide. This material was used without purification or characterization in the next step.

The crude *N*-crotylphthalimide (87.0 g, 0.43 mol) was added to 400 mL of ethylene glycol in a 100-mL round-bottom flask fitted with a reflux condenser. Hydrazine hydrate (19.0 g of 64% solution, 0.38 mol) was added and the solution was heated to reflux for 2 h. A distillation head and condenser were then fitted to the reaction flask, and the solution was distilled to a head temperature of 190 °C at atmospheric pressure. The residue, consisting of ethylene glycol and phthalhydrazide, was discarded. The distillate containing water and *N*-crotylamine was added to 5.0 g of potassium hydroxide, which resulted in two liquid phases. The water-miscible bottom phase was discarded. The top phase, consisting of *N*-crotylamine, residual water, and ethylene glycol, was fractionally distilled yielding 16.3 g (46.6%) of *N*-crotylamine, bp 82–86% (lit.[49] bp 81–82 °).

N-Crotylamine (15.9 g, 0.22 mol) was dissolved in 100 mL of ether in a 250-mL round-bottom flask. Pyridine (45 mL) and freshly recrystallized *p*-nitrobenzoyl chloride (35.0 g, 0.19 mol) were added to the flask and the contents were swirled for several minutes. Removal of volatile material in vacuo resulted in a light yellow solid which was extracted with 150 mL of methanol. The methanol insoluble material had a melting point in excess of 160 °C. Methanol was removed in vacuo from the dissolved solids to give a light yellow solid. Recrystallization from methanol yielded 12.1 g (29%) of *N*-crotyl-*p*-nitrobenzamide (**3c**): mp 108–110 °C; IR (KBr) 3340 (s), 1650 (s), 1500 (s), 1550 (s), 1530 (s), 1490 (m), 1350 (s), 1240 (m), 1110 (m), 970 (m), 870 (m), 720 (m), 680 cm^{-1} (m); NMR (Me_4Si, $CDCl_3$) δ 1.67 (d, 3 H, J = 6 Hz, CH_3), 3.98 (t, 2 H, J = 5 Hz, CH_2), 5.60 (m, 2 H, nonequivalent vinyl protons), 7.19 (5, br, 1 H, NH), 7.97 (d, 2 H, J = 9 Hz, equivalent aryl protons), 8.22 (d, 2 H, J = 9 Hz, equivalent aryl protons).

Anal. Calcd for $C_{11}H_{12}N_2O_3$: C, 59.99; H, 5.49. Found: C, 59.81; H, 5.35.

***N*-(3-Methyl-2-buten-1-yl)-*p*-nitrobenzamide (3d).** Following the procedure for the preparation of **3c**, freshly distilled 1-chloro-3-methyl-2-butene was converted to **3d** in 16% overall yield; after recrystallization from methanol: mp 106–108 °C; IR (KBr) 3300 (s), 1650 (s), 1560 (s), 1530 (s), 1350 (s), 1200 (m), 1120 (m), 975 (m), 850 (m), 700 cm^{-1} (m); NMR (Me_4Si, $CDCl_3$) δ 1.69 (s, 6 H, CH_3), 4.01 (t, 2 H, J = 5 Hz, CH_2), 5.26 (t, 1 H, J = 5 Hz, CH), 8.17 (d, 2 H, J = 9 Hz, equivalent aryl protons).

Anal. Calcd for $C_{12}H_{14}N_2O_3$: C, 61.54; H, 5.98. Found: C, 61.75, H, 5.96.

Bromination of 3c, 3d, and 3e. General Procedure in Acetic Acid. Bromine in acetic acid (ca. 0.5–1 mmol/mL) was slowly added by glass syringe to a well-stirred solution of the allylic amide in acetic acid (ca. 0.05–2 mmol/mL). Precipitation of the bromocyclic salt(s) occurred over the course of the addition. Diethyl ether was added to double the volume and precipitate the remaining dissolved bromocyclic salt(s). The salt(s) were filtered, washed with ether, dried, and treated with an excess of anhydrous triethylamine. The resulting solution was diluted with ether (*ca.* 20-fold excess) and extracted twice with water. The ethereal solution was then dried (Na_2SO_4) and evaporated in vacuo to give the free base (oxazoline or oxazine or mixture). The filtrate from the salt filtration contained the dibromide.

Bromination of 3c in Acetic Acid. Following the general procedure above, **3c** (1.0 g., 4.5 mmol) reacted with bromine (0.73 g, 4.5 mmol) to give 1.06 g (61%) of a mixture of *trans*-2-*p*-nitrophenyl-5-bromo-6-methyl-5,6-dihydro-4*H*-oxazinium bromide (**5c·HBr**) and 2-*p*-nitrophenyl-5-(1-bromoethyl)oxazolinium bromide (**4c·HBr**): IR (KBr) 3200–2400 (s), 1730 (m), 1675 (s), 1600 (m), 1525 (s), 1480 (m), 1350 (s), 1270 (s), 1150 (m), 1010 (m), 850 (s), 700 cm^{-1} (s). After treatment with triethylamine, the residue from the ether solution was 0.82 g (60% overall) of a mixture of *trans*-2-*p*-nitrophenyl-5-bromo-6-methyl-5,6-dihydro-4*H*-oxazine (**5c**) and 2-*p*-nitrophenyl-5-(1-bromoethyl)-2-oxazoline (**4c**) (mp 89–105 °C): IR (KBr) 1650 (s), 1600 (s), 1520 (s), 1340 (s), 1260 (s), 1100 (s), 1070 (m), 860 (m), 840 (m), 790 cm^{-1} (s); NMR (Me_4Si, $CHCl_3$) 1.62 (d, 3 H, J = 6 Hz, CH_3), 1.78 (d, 3 H, J = 6 Hz, CH_3), 3.78–4.89 (m, CH and CH_2), 7.78–8.84 (m, aryl protons). The ratio of methyl protons by NMR integration of δ 1.62 vs. those at δ 1.78 was 79:21. Gas chromatographic analysis gave an 80:20 ratio.

Anal. Calcd for $C_{11}H_{11}N_2O_3Br$: C, 44.17; H, 3.71. Found: C, 44.24; H, 3.75.

The oxazine and oxazoline mixture (0.78 g) was dissolved in 20 mL of benzene and poured onto a column (2.4 × 20.0 cm) of Flurosil (80 g) prepared in benzene. Elution with benzene/ether (75/25 v/v) gave 0.15 g of pure **5c** free of its isomer which came off with the remainder of the oxazine: NMR (Me_4Si, $CDCl_3$) δ 1.62 (d, 3 H, J = 6 Hz, CH_3), 3.98 (m, 3 H, CHBr and CH_2), 4.43 (m, 1 H, $HC-CH_3$), 8.04 (d, 2 H, J = 9 Hz, equivalent aryl protons), 8.10 (d, 2 H, J = 9 Hz, equivalent aryl protons); mass spectrum (70 eV) *m/e* (rel intensity) 300, 298 (3, M^+), 219 (5, $M^+ - Br$), 191 (10, $ArC(O^+)=NCH=CH_2$), 179 (15, $HO^+CArN=CH_2$), 150 (30, $ArC\equiv O^+$), 41 (100, $N^+CH=CH_2$).

The filtrate from filtering the bromocyclic salt mixture yielded an oily reddish brown residue when dried. The residue was triturated with water (100 mL) to yield 0.52 g (30%) of N-(*erythro*-2,3-dibromobutyl)-*p*-nitrobenzamide (**6c**), mp 128–133 °C, from the trans addition of bromine. Recrystallization from methanol gave the pure amide: mp 135–138 °C; IR (KBr) 3300 (s), 1640 (s), 1590 (m), 1530 (s), 1510 (s), 1340 (s), 1320 (s), 1300 (s), 1240 (m), 1150 (m), 950 (m), 860 (m) 810 (m), 700 (m), 670 (m), 650 cm^{-1} (m); NMR (Me_4Si, $CDCl_3$) δ 1.96 (d, 3 H, (J = 6 Hz, CH_3), 3.67–4.89 (m, 4 H, NCH_2 and CHBr), 5.67 (br s, NH), 8.13 (d, 2 H, J = 8 Hz, aryl protons), 8.35 (d, 2 H, J = 8 Hz, aryl protons).

Anal. Calcd for $C_{11}H_{12}N_2O_3Br_2$: C, 34.76: H, 3.18. Found C, 34.84; H, 3.14.

In a separate experiment, *N*-bromosuccinimide (0.41 g, 2.3 mmol) was added with stirring over a 5-min period to **3c** (0.50 g, 2.3 mmol) in 25 mL of acetic acid. Precipitation of the oxazinum and oxazolinium salts (acetates) did not occur either in the reaction sequence or with the addition of ether (50 mL) to the solution. After the solvents were removed in vacuo, ether (50 mL) and pyridine (6 g) were added to the resulting air-dried precipitate. the **5c/6c** ratio in the resulting solution was determined by GLC analysis to be 34:66. This solution, neglecting the solvent, contained *N*-crotyl-*p*-nitrobenzamide (**3c**) (11%), the oxazine **5c** (47%), the oxazoline **4c** (24%), and an unidentified product (18%) that may be the result of elimination (pyridine present) or it may be the bromo acetate addition product.

Bromination of 3d in Acetic Acid. Following the general procedure given above, bromine (0.68 g, 4.3 mmol) was reacted with **3d** (1.0 g, 4.3 mmol) to yield 1.25 g (75%) of 2-*p*-nitrophenyl-5-bromo-6,6-dimethyl-5,6-dihydro-4*H*-oxazinium bromide (**5d·HBr**): IR (KBr) 3200–2400 (s), 1730 (m), 1675 (s), 1600 (m), 1525 (s), 1480 (m), 1370 (m), 1350 (s), 1300 (m), 1150 (m), 1110 (s), 1010 (m), 850 (s), 775 (m), 700 cm^{-1} (s). This salt subsequently gave 0.97 g (72%) of 2-*p*-nitrophenyl-5-bromo-6,6-dimethyl-5,6-dihydro-4*H*-oxazine (**5d**): mp 112–113 °C (from methanol); IR (KBr) 1650 (s), 1600 (s), 1520 (s), 1430 (m), 1340 (s), 1280 (s), 1180 (m), 1090 (s), 1070 (m), 850 (s), 690 cm^{-1} (m); NMR (Me_4Si, $CHCl_3$) δ 1.56 (s, 3 H, CH_3), 1.63 (s, 3 H, CH_3), 3.98 (m, 3 H, CHBr and CH_2), 8.08 (d, 2 H, J = 9 Hz, equivalent aryl protons), 8.12 (d, 2 H, J = 9 Hz, equivalent aryl protons).

Anal. Calcd for $C_{12}H_{13}N_2O_3Br$: C, 46.02; H, 4.19. Found: C, 46.00, H, 4.13.

The filtrate from filtration of the oxazinium salt yielded only a brown tar when evaporated on a rotary evaporator at 21 °C. The tar was not characterized but was assumed to arise, at least in part, from decomposition of the dibromide addition product **6d.** Since isolation of the dibromide from this reaction mixture proved unlikely, a reaction mixture was prepared in the same molar ratios given above. The solution, which contained a white precipitate of the oxazinium salt, was treated with sufficient anhydrous triethylamine to neutralize the acetic acid and liberate **5d.** Excess triethylamine in the reaction mixture produced a two-phase liquid system which was reduced to a single liquid phase with the addition of an equal volume of acetone. A GLC analysis of the resulting solution revealed 82% **5d,** 16% *N*-(2,3-dibromo-3-methylbutyl)-*p*-nitrobenzamide (**6d**), and 2% of the starting amide **3d.** Based on mass response factors from GLC analysis of known amounts of the pure components, a complete mass balance was achieved.

In a reaction sequence similar to that above, a 100% molar excess of bromine was used. A GLC analysis of the reaction products indicated a 95% yield of **5d** and 5% **6d.**

Bromination of 3e in Acetic Acid. Following the general procedure given above, bromine (0.52 g, 3.3 mmol) was reacted with **3e** (0.93 g, 3.3 mmol) to give 1.10 g (76%) of *trans*-2-*p*-nitrophenyl-5-bromo-6-phenyl-5,6-dihydro-4*H*-oxazinium bromide (**5e·HBr**): mp 182.5–183.5 °C (from acetone/ether); IR (KBr) 3050–2850 (s), 1725 (s), 1600 (m), 1525 (s), 1490 (m), 1340 (m), 1315 (m), 1265 (s), 1110 (m), 1080 (s), 1005 (m), 705 (s), 690 cm^{-1} (m); NMR (Me_4Si, CF_3CO_2H) δ 8.56 (s, 4, *p*-nitrophenyl protons); 7.57 (s, 5, phenyl protons), 5.40 (m, 1, CHPh), 4.46 (m, 2, CH_2), 3.82 (m, 1, CHBr). After treatment with triethylamine, the oxazinium salt (1.0 g, 2.3 mmol) gave 0.66 g (81%) of *trans*-2-*p*-nitrophenyl-5-bromo-6-phenyl-5,6-dihydro-4*H*-oxazine (**5e**): mp 141–143 °C (from ethyl acetate); IR (KBr) 1660 (s), 1605 (s), 1520 (s), 1340 (s), 1260 (s), 1100 (s), 1020 (m), 865 (m), 855 (s), 770 (m), 750 (m), 695 cm^{-1} (s); NMR ($CDCl_3$) 3.88 (m, 2, CH_2), 4.23 (m, 1, CHBr), 5.34 (d, 1, J = 7.2 Hz, CHPh), 7.27 (s, 5, phenyl ring protons), 8.00 (m, 4, *p*-nitrophenyl ring protons).

Anal. Calcd for $C_{16}H_{13}N_2O_3Br$: C, 53.21; H, 3.60. Found: C, 53.10; H, 3.58.

Upon standing, the filtrate from the oxazinium salt filtration yielded 0.23 g of precipitate (mp 171–172 °C). Evaporation of this filtrate and recrystallization from ethanol yielded an additional 0.09 g for a total of 0.32 g (22%) of *erythro*-2,3-dibromo-3-phenylpropyl-*p*-nitrobenzamide (**6e**) resulting from trans addition of bromine: IR (KBr) 3350 (s), 1650 (s), 1605 (s), 1555 (s), 1525 (s), 1455 (m), 1425 (m), 1350 (s), 1325 (s), 1315 (s), 1050 (m), 965 (m), 870 (s), 765 (m), 720 (m), 710 (m), 645 (s), 690 (m), 650 cm^{-1} (m); NMR (Me_4Si, CF_3CO_2H) δ 8.21 (d, 2, J = 8.2 Hz, *p*-nitrophenyl ring protons), 7.90 (d, 2, J = 8.2 Hz, *p*-nitrophenyl ring protons), 7.18 (s, 5, phenyl ring protons), 4.95 (d, 1, J = 9.5 Hz, PhCHBr), 4.34 (m, 1, CHBr), 3.90 (m, 2, CH_2).

Anal. Calcd for $C_{16}H_{14}N_2O_3Br_2$: C, 43.66; H, 3.16. Found: C, 43.49; H, 3.28.

General Procedure in Carbon Tetrachloride. Owing to the relative insolubility of the amides in carbon tetrachloride the solvent volume was greater than for similar reactions in acetic acid. Thus, bromine in carbon tetrachloride (ca. 0.5–1 mmol/mL) was added by syringe to the amide in carbon tetrachloride (ca. 1 mmol/100 mL). The Br_2/CCl_4 solution was added over a 0.25–1-h period to an Al-foil-wrapped flask containing the alkene solution. The precipitate of the oxazinium/oxazolinum salts was filtered and the precipitate was washed with anhydrous diethyl ether and air dried. The free bases were generated from the salts by the same procedure given above for the acetic acid reactions. The ether and carbon tetrachloride filtrates from the salt filtration and washings were concentrated in vacuo to yield the dibromide addition products.

Bromination of 3c in Carbon Tetrachloride. Following the general procedure above, bromine (0.36 g, 2.3 mmol) was reacted with **3c** (0.5 g, 2.3 mmol) yielding 0.31 g (36%) of a mixture of the bromocyclic salts which in turn gave 0.22 g (33% overall) of a mixture of the bromooxazoline **4c** and the bromooxazine **5c** in a ratio of 48:52, respectively (by NMR integration of the methyl peaks at δ 1.62 and 1.78). The ether and carbon tetrachloride filtrates yielded 0.59 g (58%) of the dibromide **6c,** mp 135–138 °C. All products proved to be identical with those from the acetic acid run by NMR, IR, mmp, and GLC analysis.

Bromination of 3d in Carbon Tetrachloride. Bromine (0.775 g 4.72 mmol) was reacted with **3d** (1.10 g, 4.70 mmol) to give an immediate reddish precipitate. Owing to the lability of dibromide **6d** and its low solubility in carbon tetrachloride, the solvent was evaporated with a nitrogen jet, and the residue was extracted (soxhlet) with hexane to separate **6d** from **5d·HBr.** The hexane was evaporated with a nitrogen jet to yield 0.41 g of a mixture of unreacted starting material (**3d**) and the dibromide **6d.** Recrystallization from benzene/hexane (25/75) gave 0.04 g (2% overall) of pure *N*-(2,3-dibromo-3-methylbutyl)-*p*-nitrobenzamide (**6d**) (mp 122–123 °C): (KBr) 3300 (s), 1665 (m), 1650 (s), 1610 (m), 1560 (s), 1530 (s), 1370 (m), 1350 (s), 1330 (m), 1300 (m), 1190 (m), 1100 (m), 870 (m), 710 (m), 690 (m); NMR (Me_4Si, $CDCl_3$) 1.90 (s, 3 H, CH_3), 2.02 (s, 3 H, CH_3), 3.67 (m, 1 H, CHBr), 4.56 (m, 2 H, NCH_2), 6.87 (br, s, 7 H, NH), 8.00 (d, 2 H, J = 8 Hz, aryl protons), 8.33 (d, 2 H, J = 8 Hz, aryl protons).

Anal. Calcd for $C_{12}H_{14}N_2O_3Br_2$: C, 36.57; H, 3.56: N, 7.11. Found: C, 36.73; H, 3.48, N. 7.34.

The bromocyclic salt **5d** remaining in the extraction thimble was shown to be identical with that from the acetic acid run by IR. The product ratios, however, were determined by GLC from a separate reaction mixture analyzed immediately after reaction and with triethylamine. Analysis by GLC revealed a composition of 61% of the oxazine **5d,** 22% of the dibromide **6d,** and 15% unreacted amide **3d.**

Bromination of 3e in Carbon Tetrachloride. Following the general procedure, bromine (0.18 g, 1.1 mmol) was reacted with **3e** (0.30 g, 1.1 mmol) giving a quantitative precipitate of the oxazinium salt **5e·HBr** along with the dibromide **6e.** Quantitative IR analysis (empirical ratio method) of the solid mixture revealed the composition to be 36% **5e·**HBr and 64% **6e.** Recrystallization from acetone/ether gave material identified by IR and NMR comparisons as the bromooxazinium salt **5e·**HBr. Recrystallation of the residue from ethanol/water gave the dibromide **6e,** mp 165 °C, which had an IR identical with that from bromination of **3e** in acetic acid.

Chlorination of 3c in Acetic Acid. *N*-Crotyl-*p*-nitrobenzamide (**3c**) (1.0 g, 4.6 mmol) was added over a 5-min period with stirring to a solution of chlorine (0.32 g, 4.6 mmol) in acetic acid (22 mL) in a 100-mL round-bottom flask at a temperature of 25–28 °C. The solution changed from a moderate to a light yellow color with addition. An additional 33 mL of acetic acid was added to the solution. Triethylamine (7.2 g, 71 mmol) was added to 10 mL of this solution without the formation of a precipitate, and the solution was analyzed by GLC. The elution pattern obtained was identical to that of the bromination products. Analysis by GLC allowed the following assignments: chlorooxazoline (12%), chlorooxazine (18%), chlorine addition product (23%), and unreacted starting amide **3c** (47%).

Product Stability Studies. Stability of 6e. A sample of **6e** was dissolved in trifluoroacetic acid (TFA) in an NMR tube. The ^1H NMR of the solution was recorded immediately and at intervals of approximately 1 h for several hours and then after standing overnight. The initial spectrum was that of the amide **6e** (or its N-protonated form). The spectra obtained subsequently had chemical shifts and multiplicities similar to those from **5e.** It was therefore assumed that in protic solvents **6e** cyclizes to **5e** or its cis isomer with a half-life of several hours at room temperature. In CCl_4 **6e** was sparingly soluble but indefinitely stable.

Stability of 6c. The stability of **6c** in acetic acid and CCl_4 was confirmed by dissolution of samples of **6c** in these solvents and recovering them after 2 h or more. Like **6e, 6c** showed some tendency

to slowly solvolyze probably by cyclization to **4c** or **5c** (or its cis isomer).

Stability of 6d. The absence of **6d** as a product from the bromination of **3d** suggests that **6d** may be solvolytically unstable rapidly forming **5d.** This was confirmed by demonstrating that **6d** was formed as a product in the bromination reaction (GLC analysis, see above) and by showing that **6d** rapidly deteriorates upon dissolution in acetic acid.

Stability of 4c·HX and 5c·HX. The composition of a particular mixture of **4c** and **5c,** isolated from a bromination reaction of **3c,** was determined by integration of the methyl protons in its ^1H NMR ($CDCl_3$) to be 47/53 **4c/5c,** respectively. A separate sample of this mixture dissolved in TFA and held at room temperature for 2 h contained the same composition as determined by NMR.

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Registry No.—**3c,** 67393-51-5; **3d,** 55289-73-1; **3e,** 34562-10-2; **4c,** 67393-52-6; **4c·HBr,** 55289-78-6; **5c,** 67393-53-7; **5c·HBr,** 67393-54-8; **5d,** 67393-55-9; **5d·HBr,** 67393-56-0; **5e,** 51979-14-7; **5e·HBr,** 52246-91-0; **6c,** 67393-57-1; **6d,** 55289-77-5; **6e,** 51979-15-8; crotyl chloride, 4894-61-5; potassium phthalimide, 1074-82-4; *N*-crotylphthalimide, 67393-58-2; *N*-crotylamine, 56930-04-2; *p*-nitrobenzoyl chloride, 122-04-3; 1-chloro-3-methyl-2-butene, 503-60-6.

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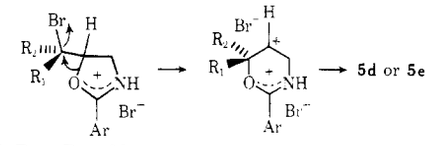

i, $R_1 = R_2 = Me$
ii, $R_1 = Ph$; $R_2 = H$

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(36) Solvent effects on rates have been thoroughly treated in recent articles, cf. ref. 29 and 31.
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