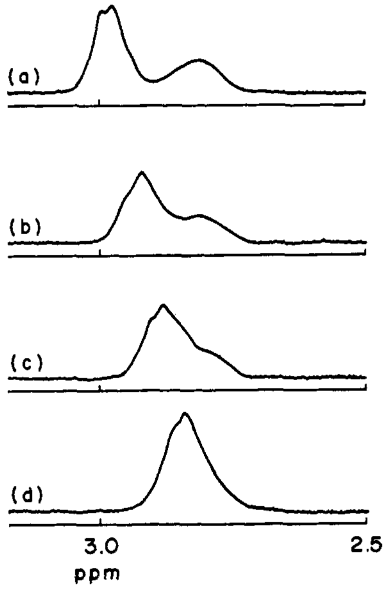

Figure 3. Pmr spectra (220 MHz) of α-CH_2 resonances observed in equilibrium mixture of o^+o^+- and i^+i^+-[10.10.10] bis(trifluoroacetates) in 50% TFA at 23° containing added NaCl: (a) 0.0 equiv; (b) 0.5 equiv; (c) 1.0 equiv; and (d) 2.0 equiv.

Differences in the behavior of the larger i^+i^+-[10.10.10] ion further clarify the encapsulation phenomenon. The $o^+o^+ \rightleftharpoons i^+i^+$ equilibrium of the [10.10.10] amine in 50% TFA favors the i^+i^+ isomer (K_e = 3.3),[1] and the α-CH_2 resonances occur at 2.82 (o^+o^+) and 2.98 ppm (i^+i^+). When 0.5 equiv of chloride ion is added to the mixture at 23°, the i^+i^+ resonance is instantaneously shifted upfield to 2.92 ppm, whereas no change in position or intensity is detected in the o^+o^+ resonance. The addition of 1.0 equiv of chloride to the original mixture shifts the i^+i^+ resonance to 2.87 ppm, and 2.0 equiv to 2.84 ppm, after which no further change is noted on addition of excess chloride (Figure 3). These observations mean that in i^+i^+-[10,10.10] relative to i^+i^+-[9.9.9]: (1) the forward and reverse rate constants for $i^+i^+ + Cl^- \rightleftharpoons i^+Cl^-i^+$ are much larger, so that only a time-average absorption is detected, and (2) the encapsulation equilibrium constant is large, since the upfield shifts of the α-CH_2 are proportional to the amount of added chloride. Both bromide and iodide are encapsulated rapidly by i^+i^+-[10.10.10], and similar time-average spectra were observed. This suggests that the size of the cavity is an important factor in halide katapinosis. The halide radii and cavity diameters, measured on CPK models, are compared in Table I.[4]

Table I. Equilibrium Constants[a] for Halide Encapsulation by *in,in*-1,(k + 2)-Diazabicyclo[$k.k.k$]alkaneammonium Ions

Halide	r_{ionic}, Å	K, M^{-1} [7.7.7]	[8.8.8]	[9.9.9]	[10.10.10]
Cl^-	1.81	0	0	4	>10
Br^-	1.95	0	0	1	>10
I^-	2.16	0	0	0	>10
Cavity diameter, Å[b]		1.6	2.8	3.6	4.5

[a] K for $i^+i^+ + Hal^- \rightleftharpoons i^+Hal^-i^+$. [b] The cavity diameter was measured with CPK models and is defined as the distance between the faces of "hydrogen-bond" protons in the i^+i^+ isomer.

The stability of the katapinate ions must arise in part from the high positive potential of the hole with respect to anions and from hydrogen bonding within the cavity, [$^+N—H\cdots Cl^-\ H—N^+$] or [$^+N—H\cdots Cl^-\cdots H—N^+$]; it is not unlikely that the latter structure with two hydrogen bonds is involved. It is anticipated that polarizability, heat of hydration, and charge of the anion are also important. Furthermore, there is evidence, to be reported soon, that the encapsulated chloride ion exchanges rapidly with external chloride ion and that the chemical activations observed in encapsulation arise from a prior conformational change in the i^+i^+ ion. The diffusion step, however, may require significant activation with larger anions.

(4) Addition of sodium fluoride to equilibrium mixtures of o^+o^+- and i^+i^+ bis(trifluoroacetates) in water caused the free amine to precipitate due to the high basicity of fluoride ion; in acidic media, bifluoride ion formation obscures encapsulation. The high heat of hydration of fluoride ion may also hinder katapinosis.

C. H. Park, H. E. Simmons
Contribution No. 1402, Central Research Department
Experimental Station
E. I. du Pont de Nemours and Company
Wilmington, Delaware, 19898
Received November 13, 1967

Stable Halo Enamines. Possible SN1-Type Solvolysis

Sir:

Enamines have been studied intensively and are widely used in synthesis.[1] However, there are but a few reports on halogenation of enamines.[2] To our knowledge there is no previously reported successful isolation of halo enamines. We have successfully synthesized and isolated 1-bromo-2-(4-morpholino)-1,2-diphenylethene (I) and 1-chloro-2-(4-morpholino)-1,2-diphenylethene (II).[3] These compounds are crystalline and can be kept under nitrogen at room temperature for weeks.

Reactions of the *cis* form of 1-(4-morpholino)-1,2-diphenylethene (III)[4] with N-bromosuccinimide and N-chlorosuccinimide in benzene under nitrogen at room temperature gave I in 79% yield and II in 65% yield, respectively. Both I and II were isolated as mixtures of *cis* and *trans* isomers.

Table I. Nmr Spectra of Enamines[a]

	Chemical shift of morpholino hydrogens 2,6-	3,5-
cis-I	218	181
trans-I	204	150
cis-II	218	182
trans-II	205	150
cis-III	217	167

[a] Recorded for solution in carbon tetrachloride with tetramethylsilane as the internal standard on a Varian A-60 instrument. All chemical shifts are given in cycles per second downfield from TMS. The 2,6-hydrogen and 3,5-hydrogen signals appear as two triplets with a coupling constant of 5 cps.

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(1) For reviews on enamines, see: (a) K. Bla'ha, *Advan. Heterocyclic Chem.*, **6**, 147 (1966); (b) J. Szmuskovicz, *Advan. Org. Chem.*, **4**, 1 (1963).

(2) (a) R. L. Pederson, J. L. Johnson, R. P. Holysz, and A. C. Off, *J. Am. Chem. Soc.*, **79**, 1115 (1957); (b) I. J. Borowitz, as cited by Szmuskovicz in ref 1b.

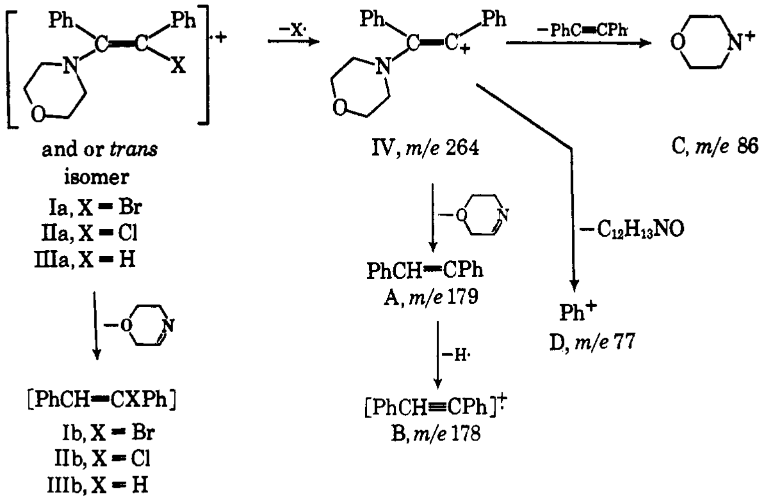
(3) Structures for both compounds are sustained by elemental analyses and mass spectra, as well as by ultraviolet, infrared, and nmr spectra.

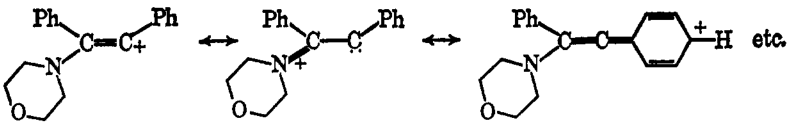
(4) M. E. Munk and Y. K. Kim, *J. Org. Chem.*, **30**, 3705 (1965).

Table II. Mass Spectra of Enamines

Molecular and fragmented ions			Metastable ions	
m/e	Relative intensity, %	Assigned for ion	m/e obsd (calcd)	Assigned for fragmentation
		Bromo Enamine I		
345	44	Ia (^{81}Br)	203.2 (203.2)	Ia (^{79}Br) $\longrightarrow$ IV
343	44	Ia (^{79}Br)	203.1 (202.1)	Ia (^{81}Br) $\longrightarrow$ IV
264	100	IV	177.0 (177.0)	A $\longrightarrow$ B
260	<1	Ib (^{81}Br)	121.4 (121.4)	IV $\longrightarrow$ A
258	<1	Ib (^{79}Br)	28.0 (28.0)	IV $\longrightarrow$ C
179	79	A		
178	64	B		
86	64	C		
77	32	D		
		Chloro Enamine II		
301	25	IIa (^{37}Cl)	233.2 (233.2)	IIa (^{35}Cl) $\longrightarrow$ IV
299	72	IIa (^{35}Cl)	231.6 (231.6)	IIa (^{37}Cl) $\longrightarrow$ IV
264	100	IV	177.0 (177.0)	A $\longrightarrow$ B
216	9	IIb (^{37}Cl)	155.0 (155.0)	IIa (^{37}Cl) $\longrightarrow$ IIb (^{37}Cl)
214	29	IIb (^{35}Cl)	153.2 (153.2)	IIa (^{35}Cl) $\longrightarrow$ IIb (^{35}Cl)
179	72	A	121.4 (121.4)	IV $\longrightarrow$ A
178	63	B	28.0 (28.0)	IV $\longrightarrow$ C
86	37	C		
77	14	D		
		Enamine III		
265	100	IIIa	263.0 (263.0)	IIIa $\longrightarrow$ IV
264	97	IV	177.0 (177.0)	A $\longrightarrow$ B
180	6	IIIb	122.3 (122.3)	IIIa $\longrightarrow$ IIIb
179	23	A	121.4 (121.4)	IV $\longrightarrow$ A
178	48	B	120.9 (120.9)	IIIa $\longrightarrow$ A
86	15	C	119.6 (119.6)	IIIa $\longrightarrow$ B
77	21	D	28.0 (28.0)	IV $\longrightarrow$ C

Attempts to separate the isomers were frustrated as the halo enamines isomerized and hydrolyzed in solution. When the compounds were first isolated, the *cis* forms were present in larger amounts. Equilibrium mixtures were obtained after the halo enamines were heated in aprotic solvents overnight. Munk and Kim reported similar isomerization for enamine III.[4] The nmr signals (see Table I) for morpholino hydrogens have different chemical shifts for the different geometrical isomers. This allowed us to follow the isomerizations and determine the equilibrium mixture compositions. It was found that the equilibrium mixture compositions were: *cis*:*trans* 50:50 for bromo enamine I and 67:33 for chloro enamine II. According to Munk and Kim the equilibrium mixture composition for enamine III is *cis*:*trans* 88:12.[4] Since the nmr spectra of I and II are practically identical, the steric effect seems to be most important in determining the relative stabilities of the geometrical isomers. More work is in progress to confirm this.





IV

The mass spectra of compounds I–III (see Table II) showed very interesting fragmentation patterns.[5] In all cases the most important fragmented ion was the ion IV, *m/e* 264. Most of the other ions were formed by further fragmentation of ion IV, as was confirmed by the presence of corresponding metastable ions. The loss of morpholidine from the molecular ions was observed in the spectra of II and III but not in the spectrum of I, suggesting that a bromine atom was lost more readily than both chlorine and hydrogen atoms. This agreed with the observed order of increasing relative molecular ion intensity: Ia < IIa < IIIa. The higher intensity of ion B, *m/e* 178, than that of ion A, *m/e* 179, and the relative low intensity of ion C, *m/e* 86, in the spectrum of III was a result of loss of morpholine from molecular ion IIIa directly.

The ease of formation of ion IV from halo enamines I and II can be rationalized insofar as ion IV is resonance stabilized. This suggested to us that under proper conditions I and II may undergo SN1-type reactions.[6]

Although enamine III is quite stable and only reacts with water when acid is present, both I and II react with water rapidly in polar solvents. Benzoin, benzil, and morpholine hydrohalides were the major products. Addition of silver nitrate to solutions of I or II in different polar solvents resulted in the formation of silver halides immediately. Silver ion accelerated the solvolysis with water, giving similar product compositions to that of uncatalyzed reactions. These findings agree with a SN1-type solvolysis which is also suggested by a primary kinetic study by nmr techniques. Detailed kinetic data are being collected.

Acknowledgment. We wish to thank in part the support of the University of Connecticut Research Foundation, The Research Corporation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We are in debt to Professor S. R. Smith for some of the mass spectra.

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(5) For mass spectra of some aliphatic enamines, see: H. J. Jakobson, S. O. Lawesson, J. T. B. Marshall, G. Schroll, and D. H. Williams, *J. Chem. Soc.*, 940 (1966).

(6) For reported SN1-type solvolyses of olefinic halides, see: (a) C. A. Grob and G. Cseh, *Helv. Chim. Acta*, **47**, 194 (1964); (b) C. A. Grob, J. Csapilla, and G. Cseh, *ibid.*, **47**, 1590 (1964).

(7) University of Connecticut Predoctoral Fellow, 1966–1968.

Samuel J. Huang, Marie V. Lessard[7]
Department of Chemistry and Institute of Material Science
University of Connecticut, Storrs, Connecticut 06268

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On the Formation of Isotactic α-Methine Configurations at the Growing Ends of Polyacrylate Anions

Sir:

It was reported previously[1] that the growing ends of polyacrylate anions react stereospecifically with H_2O, HCl, or CH_3COOH added to the Grignard-initiated polymerization solution. The present communication is concerned with determination of the position of addition preferred by the proton from H_2O, etc., on the terminal α carbon of the acrylate oligomer.

One of the two addition positions on the terminal α carbon which is to be occupied by the next monomer in an isotactic form is hereafter denoted by α_i, and the other position by α_s (see Figure 1). The steric relations of α_i and α_s to β_g and β_t of the terminal unit are shown in Figure 2 for three rotational isomers in which the terminal ester group (X) and the α carbon of the preceding unit (C_α) are in *trans*, *gauche*, and *gauche′* relations. Here β_g and β_t indicate the positions of a β proton oriented *gauche* and *trans*, respectively, to the vicinal two ester groups for the hypothetical planar zigzag skeletal conformation with the ester groups of the last two units on the same side of the plane (see Figure 1).

The probability that the terminal ester group is oriented *trans* to the α carbon of the preceding unit may be larger than that for orientation on either of the two *gauche* conformations. When this is applied to $Ph(CHDCDX)_2H$, the β_g proton of the last unit has higher or lower probabilities than the β_t proton to be *trans* to the terminal α proton, depending on whether the α proton is at α_i or α_s (see Figure 2). Since the *trans* coupling constant is known to be three to four times larger than the *gauche* coupling constant,[2] the signal separation in the β_g proton doublet is expected to be larger or smaller than the separation in the β_t doublet depending on whether the terminal α proton is at α_i or α_s.

The nmr spectra of $Ph(CHDCDX)_nD$ prepared from isopropyl acrylate-α,β-d_2 with $\gamma = 6$ and $\gamma = {}^1/_6$ are shown in Figures 1A, 1B, and 5 of a preceding paper.[3] Here γ indicates the ratio of β-D *trans* to X to D *cis* in the monomer employed. The following relations were found[3] between the intensity ratio $\kappa'(n)$ of the lower to the higher field β-proton signal[4] of the last unit of $Ph(CHDCDX)_nD$ and the intensity ratio $\kappa(n)$ of the lower to the higher field *meso*-methylene signal (assigned to β_g and β_t, respectively[3]) of the *n*th unit of a higher homolog with isotactic α-methine configurations formed in the same polymerization solution: $\kappa'(2) = \kappa(2)$; $[\kappa'(2) \text{ for } \gamma = {}^1/_6] = 1/[\kappa'(2) \text{ for } \gamma = 6] \approx 0.8$; for $n \geq 3$, $\kappa(n) \approx \gamma$ and $[\kappa'(n) \text{ for } \gamma = 6] \gg 1 \gg [\kappa'(n) \text{ for } \gamma = {}^1/_6]$.[4] From the relations between $\kappa'(n)$ and $\kappa(n)$ for $n \geq 2$, the lower and higher field β-proton signals of the last unit of $Ph(CHDCDX)_2D$ are assigned to the β_g and β_t protons, respectively.

The spectra of the backbone protons of $Ph(CHDCDX)_2H$ prepared from isopropyl acrylate-α,β-d_2 with $\gamma = 6$ using H_2O to terminate the polymerization are shown in Figures 3a and 3b. The signal groups near τ 7.8 and 8.2 were previously[3] assigned to the α and β protons of the second unit, respectively. Four peaks are found in the β signal group. The peaks with a separation of 8.7 cps are assigned to the β_g proton and the peaks with a separation of 7.2 cps to the β_t proton, because only these combinations are compatible with the separation between the two large peaks of the α proton and with the chemical shift of the β_g and β_t signals of

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(1) T. Yoshino, H. Iwanaga, and K. Kuno, *J. Am. Chem. Soc.*, **89**, 6773 (1967).

(2) For example, T. Yoshino, Y. Kikuchi, and J. Komiyama, *J. Phys. Chem.*, **70**, 1059 (1966).

(3) T. Yoshino, J. Komiyama, and H. Iwanaga, *J. Am. Chem. Soc.*, **89**, 6925 (1967).

(4) For $n \geq 3$, only one methylene signal was found for the last unit. The τ value of the signal in benzene solution decreases with increase of γ of the monomer employed, showing that the signal is composed of β_g and β_t signals with a small separation and $[\kappa'(n) \text{ for } \gamma = 6] \gg 1 \gg [\kappa'(n) \text{ for } \gamma = {}^1/_6]$.