Stereochemistry of Nucleophilic Displacements by Amines on Activated Vinyl Halides

WILLIAM E. TRUCE AND MARTIN L. GORBATY

The Department of Chemistry, Purdue University, Lafayette, Indiana 47907

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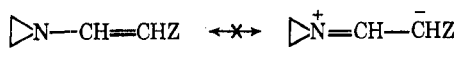
Displacements by ethylenimine on several activated vinylic chlorides (ClC=CZ, where Z = CO_2Et, SO_2Ar, CN, and PhCO) proceed with retention of configuration.

Nucleophilic substitution reactions on vinyl halides activated by electron-withdrawing groups generally proceed readily and with retention of geometric configuration.[1-6] However, like displacements by amines

$$XCH{=}CHZ + N: \longrightarrow NCH{=}CHZ + X:$$

X = halogen; Z = CO_2Et, CN, SO_2Ar, PhCO

were reported to proceed nonstereospecifically, *i.e.*, only one product isomer being obtained from both *cis* and *trans* substrates.[2,5e,6c,d] Recently, it was shown that activated *cis*-enamines readily isomerize to the more thermodynamically stable *trans* structures either by thermal[7a,b] or acid-catalyzed processes.[7c] These isomerizations were precluded by use of ethylenimine (**1**),[7a,8] presumably because the ring strain effect minimized contribution in the product from zwitterionic resonance form 2, which, by lowering the bond order, would have facilitated a thermal isomerization. Also, owing to lower basicity, the adductfro m ethylenimine is less subject to an acid-catalyzed isomerization.



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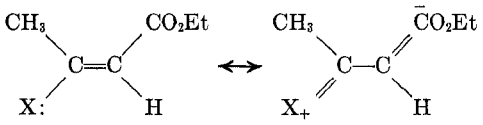
In a brief communication,[8] the preliminary results of the reactions of **1** with β-chloroacrylic esters and analogous sulfones were presented. To establish the generality of stereospecific displacements by **1**, four additional systems were studied, and the results are summarized in Table I. The reactions were carried out in benzene and in absolute ethanol, at 0–25°. The configurational assignments were made on the basis of the α- and β-vinyl proton coupling constants.[9] For the β-substituted crotonate system, where there was no β-vinyl hydrogen, assignments were based on the chemical shift of the β-methyl group, which is known to absorb at lower field when *cis* to the ester group.[10]

When ethyl *cis*-β-chloroacrylate was treated with diethylamine, ethyl *trans*-β-(diethylamino) acrylate was isolated. However, reaction with **1** gave exclusively ethyl *cis*-β-(ethylenimino)acrylate. Treatment of ethyl *trans*-β-chloroacrylate with **1** gave only *trans*-substitution product. Comparison of these data with those obtained from the addition of **1** to ethyl propiolate (Table II) excluded an elimination–addition sequence, and, therefore, a substitution mechanism (involving a dipolar adduct) is proposed for these reactions.

Likewise, ethyl *cis*- and *trans*-β-chlorocrotonates[6a,11] reacted with **1** in a stereospecific manner. Comparison of these data with those in Table II for the addition of **1** to ethyl tetrolate precludes an elimination–addition mechanism.

Incidentally, with the β-aminocrotonates, the *cis* isomer being the more thermodynamically stable[7a,12] accounts for why only *cis*-β-aminocrotonates were isolated from displacement by simple secondary amines on both the *cis* and *trans* substrates[6c,d,12] In fact, other electron-releasing (resonancewise) substituents (*e.g.*, chloro and ethylthio) *trans* to the carbethoxy substituent generally constitute the more stable configuration of the corresponding substituted crotonates.[6a] The greater stability of these *cis* crotonates is accountable by a contribution from form **3**, like resonance interaction being less with the geometrical isomers because of steric inhibition to coplanarity; support for this concept is provided by dipole moment studies.[7c]



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The reactions of *cis*- (**4a**) and *trans*-1-chloro-2-(*p*-tolylsulfonyl)ethene (**4b**) with **1** proceed with complete retention of configuration. An elimination–addition mechanism for **4a** deserves consideration in view of the *trans* stereoselectivity for addition of the amine to the ethynyl sulfone (Table II). However, Modena, *et al.*,[5e] have shown through rate studies that amines react with β-halovinyl sulfones by a direct substitution mechanism, and such characteristics of the elimination–addition

(1) (a) S. Patai and Z. Rappoport, "The Chemistry of Alkenes," Interscience Publishers, Inc., New York, N. Y., 1964, p 525 ff; (b) Z. Rappoport, *Advan. Phys. Org. Chem.*, **7**, 1 (1969).

(2) F. Scotti and E. J. Frazza, *J. Org. Chem.*, **29**, 1800 (1964).

(3) (a) D. Landini and F. Montanari, *Chem. Commun.*, 180 (1967); (b) A. N. Nesmeyanov, M. I. Rybinskaya, and T. G. Kelekhsaeva, *Zh. Org. Khim.*, **4**, 921 (1967); (c) F. Montanari, D. Landini, and B. Cavalchi, *J. Chem., Soc. C*, 1204 (1969).

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(5) (a) L. Maioli and G. Modena, *Gazz. Chim. Ital.*, **89**, 854 (1959); (b) G. Modena and P. E. Todesco, *ibid.*, 866 (1959); (c) G. Modena, P. E. Todesco, and S. Tonti, *ibid.*, **89**, 878 (1959); (d) F. Montanari, *Boll. Sci. Fac. Chim. Ind. Bologna*, **16**, 31 (1958); (e) S. Ghersetti; G. Lugli, G. Melloni, G. Modena, P. E. Todesco, and P. Vivarelli, *J. Chem. Soc.*, 2227 (1965).

(6) (a) D. E. Jones, R. O. Morris, C. A. Vernon, and R. F. M. White, *ibid.*, 2349 (1960); (b) W. E. Truce and J. S. Pizey, *J. Org. Chem.*, **30**, 4355 (1965); (c) R. Vessiere, *Bull. Soc. Chim. Fr.*, 1645 (1959); (d) J. S. Pizey and W. E. Truce, *J. Chem. Soc.*, 865 (1964).

(7) (a) W. E. Truce and D. G. Brady, *J. Org. Chem.*, **31**, 3543 (1966); (b) Y. Shvo and H. Shanan-Atidi, *J. Amer. Chem. Soc.*, **91**, 6683, 6689 (1969); Y. Shvo and I. Belsky, *Tetrahedron*, **25**, 4649 (1969); (c) R. Huisgen, K. Herbig, A. Siegel, and H. Huber, *Chem. Ber.*, **99**, 2526, 2546 (1966).

(8) W. E. Truce, J. E. Parr, and M. L. Gorbaty, *Chem. Ind.* (London), 660 (1967).

(9) L. N. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy to Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, pp 85–87.

(10) (a) R. Morris, C. A. Vernon, and R. F. M. White, *Proc. Chem. Soc. London*, **303** (1958); (b) L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2886 (1960).

(11) *cis* and *trans* refers to the positions of the methyl and carbethoxy groups.

(12) A. Sanchez, M. T. Aldave, and U. Scheidegger, *J. Chem. Soc., C*, 2570 (1968).

TABLE I

STEREOCHEMISTRY OF THE REACTION OF ETHYLENIMINE WITH ClC(R)=CHZ

Substrate			Product		
R	Z	Configuration	% *cis*[a]	% *trans*[a]	Bp (mm) [mp], °C
H	CO_2Et	*cis*	100[b]	0	41 (0.2)
H	CO_2Et	*trans*	0[b]	100	82 (1.0)
CH_3	CO_2Et	*cis*	100	0	86 (6.0)
CH_3	CO_2Et	*trans*	0	100	97–98 (9.0)
H	Ts	*cis* (**4a**)	100[b]	0	[88–89]
H	Ts	*trans* (**4b**)	0[b]	100	[68–70]
H	CN	>97% *cis* (**5a**)	>97	<3	78–79 (11.0)
H	CN	*trans* (**5b**)	0	100	86 (9.0)
H	COPh[c]	*cis* (**6a**)	85 (**8a**)	15 (**8b**)	Oil
H	COPh[c]	*trans* (**6b**)	0	100	Oil
H	*p*-$NO_2C_6H_4$	*cis*	No reaction		
H	*p*-$NO_2C_6H_4$	*trans*	No reaction		

[a] Determined from nmr analysis of crude and purified products. [b] Reference 8. [c] Reactions carried out only in benzene.

TABLE II

ADDITIONS OF ETHYLENIMINE TO ZC≡CR

Substrate			Product[a]	
R	Z	Solvent	% *cis*	% *trans*
H	CO_2Et[b]	Benzene	10	90
		Ethanol	56	44
CH_3	CO_2Et	Benzene	90	10[b,c]
		Ethanol	64	36[b,c]
H	$SO_2C_7H_7$[b]	Benzene	≥95	≤5
		Ethanol	100	0
H	CN	Benzene	93	7
		Ethanol	95	5
H	COPh	Benzene	36	64
		Ethanol	23	77
H	*p*-$NO_2C_6H_4$	Benzene	No reaction	
		Ethanol	No reaction	

[a] Determined by nmr analysis of the crude mixture. [b] Reference 7a. [c] Vessiere, *et al.* [*C. R. Acad. Sci. Paris, Ser. C*, 267, 426 (1968)] report 86% *cis* and 14% *trans* in benzene and 60% *cis* and 40% *trans* in ethanol.

mechanism as were observed in the displacement reactions by amines were claimed to be due to small amounts of alkoxide ion generated by the amine–alcohol equilibrium

$$R_2NH + R'OH \rightleftharpoons R_2\overset{+}{N}H_2 + RO^-$$

It is highly unlikely that **1** could participate in such an equilibrium owing to its low basicity (pK_b = 6.1),[13] and consequently, reaction of **1** with **4a** as well as with **4b** is postulated to proceed by a direct substitution pathway.

Besides carbethoxy and arylsulfonyl, a third activating group employed was cyano as in *cis*- and *trans*-chloroacrylonitriles.[14] The *cis* isomer (**5a**), containing 2-3% *trans* isomer (**5b**) was used as such, while **5b** was obtained pure. The results of the reactions of **1** with **5a** and **5b** are summarized in Table I. Although the *cis* product contained approximately 2-3% *trans* product, there can be no doubt that the reaction is stereospecific, because no more of the *trans* product was found than there was *trans* substrate. The results of the addition of **1** to propiolonitrile are included in Table II. Here again an elimination–addition[15] pathway cannot be excluded for the *cis* isomer based only on these results, but is considered unlikely owing to the basicity of **1**.

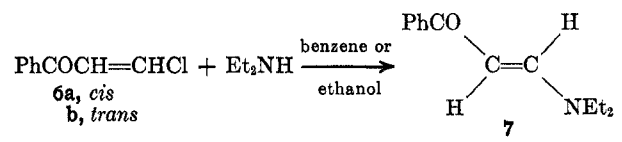
(13) G. J. Buist and H. S. Lucas, *J. Amer. Chem. Soc.*, **79**, 6157 (1957).

(14) A. N. Kurtz, W. E. Billups, R. B. Greenlee, H. F. Hamil, and W. T. Pace, *J. Org. Chem.*, **30**, 3141 (1965).

(15) W. E. Truce and M. M. Boudakian, *J. Amer. Chem. Soc.*, **78**, 2748 (1956).

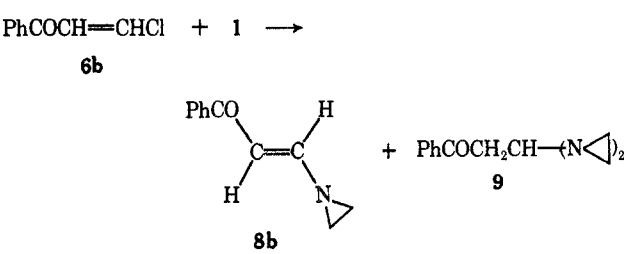
Until recently *cis* isomers of β-halovinyl ketones were unknown.[16] Montanari,[3a,c] and Nesmeyanov[3b] successfully prepared aryl *cis*-β-chlorovinyl ketones, and showed that displacements by thiolate[3a,c] and azide[3b] proceeded with retention of configuration.

When either phenyl *cis*- or *trans*-β-chlorovinyl ketone[3a] was allowed to react with diethylamine, only phenyl *trans*-β-(diethylamino)vinyl ketone (**7**) was



obtained. The results of the reaction of **6a** and **6b** with **1** in benzene are summarized in Table I; those of the additions of **1** to phenyl ethynyl ketone are summarized in Table II. The product of the reaction of **1** with **6b** in absolute ethanol was an amorphous yellow solid, believed to be polymeric material, which was not characterized.

When **6b** was allowed to react with 2 equiv (stoichiometric amount) of **1**, there was obtained an oil of which 95% was phenyl *trans*-β-(ethylenimino)vinyl ketone (**8b**) and 5% β,β-di(ethylenimino)propiophenone



(**9**). The latter no doubt arises from the addition of **1** to **8**, since **9** is also formed when excess **1** is added to phenyl ethynyl ketone. Other cases where **1** adds to activated olefins are the additions to substituted acrylonitriles[17] and to 1,2-bis(*p*-tolylsulfonyl)ethene.[18]

(16) In our attempts to prepare methyl *cis*-β-chlorovinyl ketone, *cis*-β-chloroacrylic acid was treated with 2 equiv of methyllithium according to the procedure of C. Tegner, *Acta Chem. Scand.*, **6**, 782 (1952). However, only starting material could be recovered. Undoubtedly, the lithium salt of *cis*-β-chloroacrylic acid was so insoluble in ether that further reaction with methyllithium was not realized.

(17) L. H. Chance, D. J. Daigele, and G. L. Drake, Jr., *J. Chem. Eng. Data*, **13**, 442 (1968); H. Bestian, *Justus Liebigs Ann. Chem.*, **566**, 210 (1950).

(18) J. S. Meek and J. S. Fowler, *J. Org. Chem.*, **33**, 985 (1968).

TABLE III

CHEMICAL SHIFTS OF THE α PROTONS OF *Trans* YC(R)=CHZ

Registry no.	Z	R	Y	$\delta_{H\alpha}$[a]	Δδ	J_{HH}[b]	Solvent
1883-81-4	CO_2Et	H	▷N	5.25		13.0	$CDCl_3$
13894-28-5			Et_2N	4.43	0.82	13.0	CCl_4
15358-63-1	CO_2Et	CH_3	▷N	5.20			$CDCl_3$
6288-65-9			Et_2N	4.64	0.56		$CDCl_3$
			Piperidino	4.67	0.53		CCl_4
23220-69-1	CN	H	▷N	4.71		14.0	CCl_4
			Piperidino[c]	3.90	0.81	14.0	$CDCl_3$
			Morpholino[d]	3.93	0.78	14.0	$CDCl_3$
			Pyrrolidino[d]	3.64	1.07	13.5	$CDCl_3$
16491-06-8	$SO_2C_7H_7$	H	▷N	5.58		13.0	$CDCl_3$
			Et_2N[e]	4.90	0.68	14.0	$CDCl_3$
			Me_2N[e]	4.90		14.0	$CDCl_3$
	PhCO	H	▷N	6.40		13.0	$CDCl_3$
			Et_2N	5.74	0.66	12.9	$CDCl_3$

[a] δ (parts per million) from tetramethylsilane. [b] Coupling constants are given in cycles per second. [c] Reference 6. [d] T. Sasaki, T. Yoshioka, and K. Shoji, *J. Chem. Soc., C*, 1086 (1969). [e] Reference 7a.

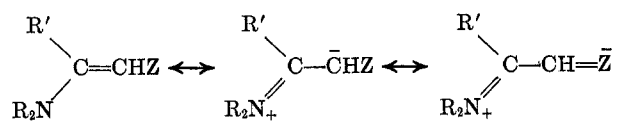
The reaction of 2 equiv of **1** with **6a** in benzene led to an oil which consisted of 71% phenyl *cis*-β-(ethylenimino)vinyl ketone (**8a**) and 14% **8b**, in ratio of 85:15, and 14% **9**. Use of 1 equiv of **1** with **6a** gave a mixture of 57% **8a** and 9.5% **8b** (in a ratio of 85:15) and 22.1% **6a** and 11.4% **6b** (ratio of 66:34).

The reaction of **1** with **6a** appears to be at least largely stereospecific. The fact that some **6b** was observed when a deficiency of amine was used indicated that **6a** was being isomerized, probably through acid catalysis. One equivalent of hydrogen chloride, and thus presumably 1 equiv of amine hydrochloride, was formed for every equivalent of substitution product formed. The conjugate acid of **1** should be acidic enough ($pK_a \cong 8.0$) to provide the acid catalyst. It is known that **6a** is extremely sensitive to acid, and will isomerize in its presence.[3] The data in Table II rule out an elimination–addition sequence.

A final system, which was studied briefly, was the pair, *cis*- and *trans*-*p*-nitro-β-bromostyrene, which failed to react with **1** or diethylamine in either benzene or absolute ethanol, at room temperature or at reflux.

The preceding data have demonstrated the stereospecificity of displacements by **1** on activated vinyl halides and point to the probability that displacements by other amines also proceed with initial retention of configuration, the nonstereospecificity of amine displacements reported by others being due to a facile postisomerization of the initially formed substitution product.

Two mechanisms were proposed for the postisomerization of activated enamines derived from simple amines,[7] the basis of both being a greater contribution to the ground state from a zwitterionic resonance form in enamines derived from simple amines than from those derived from **1**. There is ample evidence to support the concept of the zwitterionic character of the ground states of activated enamines;[19–22,7c] however, no data were available for the ethylenimino derivatives. Hence, it was desirable to determine at least qualitatively, if there is greater zwitterionic character in the ground state of activated enamines from simple amines than in those from **1**. Such contribution would be



expected to produce a pronounced shielding effect on the α proton in the nmr spectrum, causing an upfield shift of the signal.[23] Thus, the chemical shifts of the α protons in a series of β-enamino compounds of the same configuration should offer an estimate of the importance of zwitterionic character in the ground state. It can be seen from the data in Table III that there is a considerable upfield shift of the α protons of enamines derived from simple amines relative to those derived from **1**, supporting the hypothesis of greater zwitterionic character in the ground state of the former. Furthermore, ethyl *cis*-β-(diethylamino)crotonate [λ_{max} 289 mμ (log ε 4.57)] showed a bathochromic shift of 33 mμ relative to ethyl *cis*-β-(ethylenimino)crotonate [λ_{max} 256 mμ (log ε 4.79)].

Experimental Section[24]

Starting Materials.—Ethylenimine was supplied by the Dow Chemical Co., was stored over caustic soda pellets, and was used without further purification. Distilled commercial grade absolute ethanol and spectrophotometric grade benzene were used. Other reagents were obtained through the usual chemical supply companies, and were used without further purification. *cis*- and *trans*-1-chloro-2-(*p*-tolylsulfonyl)ethene,[25,26] phenyl *trans*-

(19) H. W. Duerbeck, *Z. Anal. Chem.*, **235**, 43 (1968).
(20) J. Dabrowski, *Spectrochim. Acta*, **19**, 475 (1963).
(21) A. Shidlovskaya, Y. Syrkin, and N. Kochetkov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 254 (1956).
(22) R. Huisgen and K. Herbig, *Justus Liebigs Ann. Chem.*, **688**, 98 (1965).
(23) N. F. Firrell and P. W. Hickmott, *J. Chem. Soc., B*, 293 (1969); K. Nagarajan and S. Rajappa, *Tetrahedron Lett.*, 2203 (1969).
(24) All microanalyses were carried out by Dr. C. S. Yeh and staff of the Purdue Chemistry Microanalytical Laboratory. All melting points and boiling points are uncorrected. All nmr spectra were run on a Varian A-60 or A-60A with the spectrometer operating at 60 MHz and using tetramethylsilane as an internal standard. Vpc analyses were performed on a Perkin-Elmer Model 154 vapor fractometer at 125–130° on column "O."
(25) L. Maioli and G. Modena, *Boll. Sci. Fac. Chim. Ind. Bologna*, **16**, 86 (1958); *Chem. Abstr.*, **53**, 7080b (1959).
(26) F. Montanari, *Gazz. Chim. Ital.*, **86**, 406 (1956).

β-chlorovinyl ketone,[27] *cis*- and *trans*-*p*-nitro-β-bromostyrene,[4b] phenyl ethynyl ketone,[28] and ethyl tetrolate[29] were prepared by known procedures.

Ethyl *cis*-β-Chloroacrylate.—Esterification of *cis*-β-chloroacrylic acid[14] with ethanol and catalytic sulfuric acid gave a 65% yield of pure product: bp 71–73° (27 mm); nmr (CCl_4) δ 1.30 (t, 3 H, J = 7.0 cps), 4.19 (q, 2 H, J = 7.0 cps), 6.08 (d, 1 H, J = 8.5 cps, α-vinyl proton) 6.62, ppm (d, 1 H, J = 8.5 cps, β-vinyl proton).

Ethyl *trans*-β-Chloroacrylate.—This was prepared in 41% yield as above by esterification of *trans*-β-chloroacrylic acid.[14] The product boiled at 50–51° (22 mm): nmr (CCl_4) δ 1.25 (t, 3 H, J = 7.0 cps), 4.08 (q, 2 H, J = 7.0 cps), 6.09 (d, 1 H, J = 13.0 cps, α-vinyl proton), 7.19 ppm (d, 1 H, J = 13.0 cps, β-vinyl proton).

Ethyl *cis* and *trans*-β-Chlorocrotonate.—These were prepared by the method of Jones, *et al.*[6a] The isomers were separated by fractionation on a spinning-band column to afford vpc pure *cis* ester, bp 48–50° (11.0 mm) [lit.[6a] bp 68–69° (10 mm)], and *trans* ester, bp 62–63° (11.0 mm) [lit.[6a] bp 68–69° (10 mm)], which contained a 10% impurity. The *trans* ester was obtained pure by collection from an Aerograph Autoprep Model A-700, using a 4 ft × 3/8 in. SF 96 column at 128°: nmr (CCl_4) of *cis* ester δ 1.27 (t, 3 H, J = 7.0 cps), 2.56 (d, 3 H, J = 1.5 cps, CH_3C=C), 4.13 (q, 2 H, J = 7.0 cps), 6.00 ppm (m, 1 H, CH_3C=C**H**); nmr (CCl_4) of *trans* ester δ 1.27 (t, 3 H, J = 7.0 cps), 2.24 (d, 3 H, J = 1.5 cps, CH_3C=C), 4.14 (q, 2 H, J = 7.0 cps), 5.93 ppm (m, 1 H, CH_3C=C**H**).

***cis* and *trans*-β-Chloroacrylonitriles.**—These were prepared by pyrolysis of 2,3-dichloropropionitrile according to the method of Kurtz, *et al.*[14] The crude pyrolysate was distilled, bp 28–48° (20 mm), and the distillate was redistilled at atmospheric pressure to give two main cuts, bp 87–139°, which contained α-chloroacrylonitrile and *trans*-β-chloroacrylonitrile, and bp 143–146°, which was 97% pure *cis*-β-chloroacrylonitrile (lit.[2] bp 145°). The first cut was redistilled on a spinning-band column to give pure *trans* isomer: bp 114°; mp 45–46° (lit.[2] bp 118° mp 45°); nmr (CCl_4) of *cis* isomer δ 5.82 (d, 1 H, J = 7.8 cps, α-vinyl proton), 6.95 ppm (d, 1 H, J = 7.8 cps); nmr (CCl_4) of *trans* isomer δ 5.79 (d, 1 H, J = 13.0 cps, α-vinyl proton), 7.15 ppm (d, 1 H, J = 13.0 cps).

Phenyl *cis*-β-Chlorovinyl Ketone.—This was prepared by the method of Montanari.[3a,c] The crude material contained 3–5% starting material, 10–20% *trans* isomer, and product. A portion of this material, 2.3 g, was chromatographed on silica gel (30 cm × 3.5 cm) using a 2:1:1 solution of *n*-hexane–ethyl acetate–petroleum either (bp 30–60) as eluent.[3c] Twenty-milliliter fractions were taken, and fractions 15, 16, and 17, 0.85, g, were combined and shown by nmr to be >98% phenyl *cis*-β-chlorovinyl ketone and <2% starting material: nmr (CCl_4) δ 6.68 (d, 1 H, J = 8.0 cps, α-vinyl proton), 6.98 (d, 1 H, J = 8.0 cps, β-vinyl proton), 7.42 (m, 3 H, aromatic protons), 7.87 (m, 2 H, aromatic protons). *This compound is a lachrymator and vesicant and should be handled with extreme care.*

Propiolonitrile.—A mixture of 3.0 g (0.043 mol) of propiolamide[30] and 10.0 g (0.071 mol) of phosphorus pentoxide were ground and well mixed under a nitrogen stream, and the mixture was transferred to a 100-ml flask equipped with a distillation head. The mixture was heated to 200° and the distillate was collected to give 1.4 g (65%) of propiolonitrile, bp 40–42° (lit.[30] bp 42°).

General Procedure for the Reaction of Ethylenimine with Activated Vinylic Halides.—To a stirred solution of the halide in about half the solvent, in a flame-dried flask under nitrogen at 0° was added dropwise the solution of ethylenimine (two- to threefold excess) in the remaining solvent. The mixture was stirred at 0°, then at room temperature. The reaction mixtures in benzene were filtered and the solvent was removed *in vacuo*. Those in ethanol were worked up by removing the solvent *in vacuo* and treating the residue with ether and water to remove the amine hydrochloride. The crude material was analyzed by nmr and purified by distillation or recrystallization, and the pure product was analyzed by nmr.

Ethyl *cis*-β-(Ethylenimino)acrylate.—The procedure outlined above was used with 1.00 g (0.0075 mol) of ethyl *cis*-β-chloroacrylate, 1.24 g (0.029 mol) of 1, and 50.0 ml of benzene. After stirring for 4 hr at 25° and work-up, the crude material was distilled to give 0.46 g (44%) of product: bp 40–41° (0.2 mm); nmr ($CDCl_3$) δ 1.23 (t, 3 H, J = 7.0 cps), 2.08 (s, 4 H, ethylenimino protons), 4.09 (q, 2 H, J = 7.0 cps), 5.01 (d, 1 H, J = 9.0 cps, α-vinyl proton), 6.54 ppm (d, 1 H, J = 9.0 cps). When absolute ethanol was used, 0.40 g (38%) of the same product was isolated. The spectral data were identical with those reported earlier.[7a]

Ethyl *trans*-β-(Ethylenimino)acrylate.—Ethyl *trans*-β-chloroacrylate (1.00 g, 0.0075 mol) was treated as above with 0.832 g (0.0193 mol) of 1 using 50 ml of benzene. After stirring 4.5 hr and work-up, 0.70 g of liquid, shown to be 47% product (32% yield), was isolated. This was distilled to give pure product: bp 82° (7.0 mm); nmr ($CDCl_3$) δ 1.25 (t, 3 H, J = 7.0 cps), 1.95 (s, 4 H, ethylenimino protons), 4.08 (q, 2 H, J = 7.0 cps), 5.25 (d, 1 H, J = 13.0 cps, α-vinyl proton), 7.40 ppm (d, 1 H, J = 13.0 cps). The reaction in ethanol was stirred at room temperature for 22 hr to give a 75% yield of product. The spectral data were identical with those reported earlier.[7a]

Ethyl *trans*-β-(Diethylamino)acrylate.—This was prepared from 0.75 g (0.0056 mol) of ethyl *cis*-β-chloroacrylate, 1.64 g (0.22 mol) of diethylamine, and 20 ml of absolute ethanol. After stirring for 7 hr, and work-up, 0.75 g (79%) of product was isolated: bp 82° (1.0 mm) [lit.[31] bp 90–91° (0.15 mm)]; nmr (CCl_4) δ 1.20 (overlapping triplets, 9 H), 3.21 (q, 4 H, J = 7.0 cps, CH_3CH_2N), 4.02 (q, 2 H, J = 7.0 cps, CH_3CH_2O), 4.43 (d, 1 H, J = 13.0, α-vinyl proton), 7.30 ppm (d, 1 H, J = 13.0 cps).

Ethyl *cis*-β-(Ethylenimino)crotonate.—The general procedure was followed, using 2.00 g (0.013 mol) of ethyl *cis*-β-chlorocrotonate, 0.295 ml (0.058 mol) of 1, and 20 ml of benzene. The mixture was stirred for 3 days at room temperature. Work-up gave 1.5 g of liquid, 81% of which was product (59% yield). This was distilled to give pure product: bp 86° (6.0 mm); nmr ($CDCl_3$) δ 1.23 (t, 3 H, J = 7.0 cps), 1.96 (s, 4 H, ethylenimino protons), 2.28 (s, 3 H, CH_3C=C), 4.09 (q, 2 H, J = 7.0 cps), 5.20 ppm (s, 1 H, C=C**H**).

Anal. Calcd for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 9.03; mol wt, 155.2. Found: C, 61.67; H, 8.58; N, 8.87; mol wt, 158.

When the reaction was carried out in ethanol, a 71% yield was obtained.

Ethyl *trans*-β-(Ethylenimino)crotonate.—The general procedure was followed using 0.85 g (0.0058 mol) of ethyl *trans*-β-chlorocrotonate and 0.75 ml (0.014 mol) of 1 in 15 ml of benzene. The flask was stoppered and stored at 0–3° for 3 days. The reaction was monitored by vpc which showed only *trans* substrate and *trans* product. Work-up gave 0.70 g (79%) of product: bp 97–98° (9.0 mm); nmr ($CDCl_3$) δ 1.26 (t, 3 H, J = 7.5 cps), 1.93 (s, 3 H, CH_3C=C), 2.15 (s, 4 H, ethylenimino protons), 4.15 (q, 2 H, J = 7.5 cps), 5.15 ppm (s, 1 H, C=C**H**).

Anal. Calcd for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 9.03. Found: C, 61.75; H, 8.40; N, 9.07.

When the reaction was carried out in ethanol, 61% product was obtained.

Ethyl *cis*-β-(Diethylamino)crotonate.—This was prepared from 0.55 g (0.0037 mol) of ethyl *cis*-β-chlorocrotonate and 1.02 g (0.015 mol) of diethylamine in 15 ml of benzene. The flask was stoppered and allowed to stand for 2 weeks at room temperature. Work-up gave 0.40 g of material, 87% of which was product. Distillation gave the pure product: bp 123–124 (6.0 mm) [lit.[32] bp 120–121 (2.5 mm)]; nmr ($CDCl_3$) δ 1.16 (overlapping triplets, 9 H), 2.46 (s, 3 H, CH_3C=C), 3.30 (q, 4 H, CH_3CH_2N), 4.23 (q, 2 H, CH_3CH_2O), 4.64 ppm (s, 1 H, C=C**H**).

***cis*-1-Ethylenimino-2-(*p*-tolylsulfonyl)ethene.**—This was prepared from 1.5 g (0.0070 mol) of **4a**, 2.0 (0.038 mol) of 1, and 50 ml of benzene. After stirring 4 hr at room temperature, the solvent was removed *in vacuo* and the solid was recrystallized from benzene–hexane to give product: mp 88–89° (lit.[7a] mp 88–89°); nmr ($CDCl_3$) δ 2.25 (s, 4 H, ethylenimino protons), 2.50 (s, 3 H, $CH_3C_6H_4$), 5.57 (d, 1 H, J = 9.0 cps, α-vinyl proton), 6.55 (d, 1 H, J = 9.0 cps), 7.30 (s, 2 H, J = 9.0 cps, aromatic protons), 7.90 ppm (d, 2 H, J = 9.0 cps). The same product was obtained in ethanol.

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trans-1-Ethylenimino-2-(*p*-tolylsulfonyl)ethene.—This was prepared, as above, from 1.0 g (0.0046 mol) of **4b**, 2.0 ml (0.038 mol) of 1, and 50 ml of benzene. After 4 hr, the solvent was removed *in vacuo* to give an oil which eventually crystallized, mp 68–70°. A large portion (70%) of starting material was recovered: nmr (CCl_4) δ 1.86 (s, 4 H, ethylenimino protons), 2.50 (s, 3 H, $CH_3C_6H_4$), 5.58 (d, 1 H, J = 13.0 cps, α-vinyl proton), 7.5 ppm (m, 5 H, β-vinyl proton and aromatic protons). The reaction in ethanol gave the same product. The nmr spectrum was completely consistent with the assigned structure.

Anal. Calcd for $C_{11}H_{13}NO_2S$: C, 59.17; H, 5.86; N, 6.27; S, 14.36; mol wt, 223. Found: C, 58.94; H, 5.95; N, 6.17; S, 14.24; mol wt, 225.

cis-β-(Ethylenimino)acrylonitrile.—The general procedure was followed using 0.80 g (0.0092 mol) of **5a**, 1.91 ml (0.037 mol) of 1, and 30 ml of benzene. After stirring at room temperature for 8 hr and work-up, 0.80 g (92%) of crude product was obtained. Distillation gave pure product: bp 78–79° (11.0 mm); nmr (CCl_4) δ 2.12 (s, 4 H, ethylenimino protons), 4.54 (d, 1 H, J = 8.5 cps, α-vinyl proton), 6.75 (d, 1 H, J = 8.5 cps).

Anal. Calcd for $C_5H_6N_2$: C, 63.80; H, 6.42; N, 29.77; mol wt, 94. Found: C, 63.72; H, 6.40; N, 29.98; mol wt, 98.

An 81% yield was obtained in ethanol. This material became an amorphous mass on standing under nitrogen in a sealed ampoule.

trans-β-(Ethylenimino)acrylonitrile.—The above procedure was followed using 0.90 g (0.010 mol) of **5b**, 2.15 ml (0.042 mol) of 1, and 25 ml of benzene. After stirring for 9 hr and work-up, 0.80 g (82%) of crude product was obtained. Distillation afforded pure product: bp 86–86.5° (9.0 mm); nmr (CCl_4) δ 1.98 (s, 4 H, ethylenimino protons), 4.71 (d, 1 H, J = 14.0 cps, α-vinyl proton), 7.10 ppm (d, 1 H, J = 14.0 cps).

Anal. Calcd for $C_5H_6N_2$: C, 63.80; H, 6.42; N, 29.77; mol wt, 94. Found: C, 63.97; H, 6.40; N, 30.00; mol wt, 98.

A 71% yield was obtained in ethanol. This material polymerized on standing under nitrogen in a sealed ampoule.

Phenyl *trans*-β-(Diethylamino)vinyl Ketone.—This was prepared from 1.66 g (0.010 mol) of **6b**, 1.46 g (0.020 mol) of diethylamine, and 30 ml of benzene. Work-up afforded 1.50 g (74%) of crude material which was recrystallized from pentane to give pure product: mp 52–54° (lit.[33] mp 53–54°); nmr ($CDCl_3$) δ 1.15 (t, 6 H, J = 7.5 cps), 3.23 (q, 4 H, J = 7.5 cps), 5.74 (d, 1 H, J = 12.9 cps, α-vinyl proton), 7.32 (m, 3 H, aromatic protons), 7.80 ppm (m, 3 H, aromatic and β-vinyl protons). The same product was obtained in 94% yield in ethanol, and also by addition of diethylamine to phenyl ethynyl ketone in benzene and ethanol.

Reaction of Phenyl *trans*-β-Chlorovinyl Ketone (6b) with Ethylenimine in Benzene.—The general procedure was followed, using 1.66 g (0.010 mol) of **6b**, 1.10 ml (0.021 mol) of 1, and 22 ml of benzene. After 3 hr, the mixture was filtered and the solvent was removed *in vacuo*. The residue was dissolved in ether, washed with water, and dried ($MgSO_4$); the ether was removed *in vacuo* to give 1.40 g (81%) of **8b** contaminated with approximately 5% **9**. Attempted purification by distillation and chromatography of a portion of this material led to decomposition. The remainder became a thick viscous oil which solidified to an amorphous black mass on standing at room temperature over a period of 3 days. A satisfactory analysis could not be obtained: nmr ($CDCl_3$) of **8b** δ 1.97 (s, 4 H, ethylenimino protons), 6.40 (d, 1 H, J = 13.0 cps, α-vinyl proton), 7.40 (m, 3 H, aromatic protons), 7.68 (d, 1 H, J = 13.0 cps), 7.85 ppm (m, 2 H, aromatic protons); nmr ($CDCl_3$) of **9** δ 1.45 (broad singlet, 8 H, ethylenimino protons), 2.38 (t, 1 H, J = 5.9 cps, CH_2CH), 3.32 (d, 2 H, J = 5.9 cps, CH_2CH), 7.3 (m, 3 H, aromatic protons), 7.9 ppm (m, 2 H, aromatic protons).

Reaction of Phenyl *cis*-β-Chlorovinyl Ketone (6a) with Ethylenimine in Benzene. (a) Stoichiometric Amounts.—The procedure above was followed using 0.20 g (0.0012 mol) of **6a**, 0.124 ml (0.0024 mol) of 1, and 20 ml of benzene. After 3.5 hr the mixture was filtered and the solvent was removed *in vacuo* to give 0.15 g of liquid whose nmr spectrum showed it to be a mixture of 72% **8a**, 14% **8b**, in ratio of 82:18, and 14% **9**: nmr (CCl_4) of **8a** δ 2.02 (s, 4 H, ethylenimino protons), 6.09 (d, 1 H, J = 9.0 cps, α-vinyl proton), 6.67 (d, 1 H, J = 9.0 cps), 7.33 (m, 3 H, aromatic protons), 7.84 ppm (m, 2 H, aromatic protons). Further purification was not attempted.

(b) Deficiency of 1.—The general procedure above was followed with 0.22 g (0.0013 mol) of **6a**, 0.0685 ml (0.0013 mol) of 1, and 20 ml of benzene. Work-up as before gave 0.15 g of material whose nmr showed it was a mixture of 57% **8a**, 9.5% **8b** in ratio of 86:14, 22.1% **6a** and 11.4% **6b**, and no **9**.

Reaction of *cis*- and *trans*-*p*-Nitro-β-Bromostyrene with Amines.—The reactions were carried out as above, with diethylamine and 1, in both benzene and ethanol at room temperature and at reflux for 4 hr, but work-up gave starting materials in >95% recovery.

Addition of Ethylenimine to Activated Acetylenes.—The general procedure of Truce and Brady[7a] was followed. The reactions were run in both benzene and ethanol and the results are summarized in Table II.

(a) To Ethyl Tetrolate.—Ethyl tetrolate (0.50 g, 0.0045 mol) was treated with 0.30 ml (0.0058 mol) of 1 in 10 ml of benzene. After standing 200 hr at room temperature, the solvent was removed *in vacuo* to give 62% adducts (Table II). In ethanol, after 80 hr a quantitative yield of adducts was obtained.

(b) To Propiolonitrile.—The above procedure was used with 0.70 g (0.014 mol) of propiolonitrile, 1.07 ml (0.020 mol) of 1, and 25 ml of benzene. After 7 hr 0.85 g (66%) of adducts was obtained. In ethanol, after 2.5 hr, a 77.5% yield of adducts was obtained.

(c) To Phenyl Ethynyl Ketone.—The above procedure was followed with 1.30 g (0.010 mol) of phenyl ethynyl ketone, 0.40 ml (0.0077 mol) of 1, and 10 ml of benzene. After 4 hr the solvent was removed *in vacuo* to give 1.50 g of material, 26% of which was starting material and 74% was a mixture of adducts (Table II). This became a thick dark oil on standing at room temperature. When 0.78 ml (0.015 mol) of 1 was used, 1.60 g of material was obtained which was a mixture of 28% **8a**, 44% **8b**, in a ratio of 38:62, and 28% **9**.

Registry No.—**7**, 23674-58-0; **8b**, 24627-31-4; ethyl *cis*-β-(ethylenimino)crotonate, 24627-32-5; *cis*-β-(ethylenimino)acrylonitrile, 24599-16-4.

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