CHEMISTRY OF ETHYLENEIMINE

XI.* ADDITION OF 2-AMINOMETHYLETHYLENEIMINE

TO AN ACTIVATED CARBON-CARBON DOUBLE BOND

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Products of addition to both primary and secondary amino groups were obtained by reaction of 2-aminomethylethyleneimine with some acrylic acid derivatives. The structures of the compounds obtained were proved by means of their IR and PMR spectra and also by their subsequent chemical transformations.

Continuing our investigation of the chemistry of ethyleneimine [2, 3], we have studied the reactions of 2-aminomethylethyleneimine (I) with compounds containing an activated carbon-carbon double bond. In the present communication we present the results of studies of the reaction of I with acrylic acid derivatives; in future papers we will correlate the reactions of 2-aminomethyl-substituted aziridines with other unsaturated compounds and dienophiles.

The structure of starting aziridine I is characterized by the presence of two nucleophilic amino groups that differ substantially in their reactivities with respect to an activated C=C bond [4, 5]. The reaction of I with acrylic acid derivatives IIa-c via three principal pathways is fundamentally possible:



Quantitative analysis by PMR spectroscopy and gas-liquid chromatography (GLC) of the compositions of the products of cyanoethylation of I or of the reaction of the latter with acrylic acid esters makes it possible to draw a conclusion regarding the preferableness of one of the reaction pathways as a function of the conditions under which the reaction is carried out.

It was found that a mixture of III, IV, and V in various ratios is formed in the reaction of I with IIa-c in aprotic solvents (benzene, toluene, xylene, and chloroform); when the reaction is carried out in benzene, primarily a mixture of III and IV is formed, whereas the chief reaction product is V when higher-boiling solvents are used.

*See [1] for communication X. †Deceased.

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TABLE 1. Parameters of the PMR Spectra of IIIa-c (in 10% CCl_4)



Com- pound	Chemical shifts, * 7, ppm (rel. to tetramethylsilane)										
	H ³ trans	H ³ cis	11:	CH2II	a-CH:	₿-СН:	x	NII			
IIIa IIIb	8,31 d† 8,40 d	8,67d 8,74d	7.95m 7,98 ^m	7.37.7m 7.47.7m	7.11t 7.18t	7.48 t 7.52 t	8.77 (CH ₃) t	8.90 9,02			
Ille	8.41 d	8,76d	7,97m	7.4-7;7m	7,18 ^t	7,52 t	6.20				

*The following spin-spin coupling constants are observed in the three-membered ring: ${}^{2}J_{HH} \sim 0$ Hz, ${}^{3}J_{H^{2}H^{3}cis} = 2.9$ Hz, and ${}^{3}J_{H^{2}H^{3}}trans = 5.5$ Hz.

†Abbreviations: d is doublet, m is multiplet, t is triplet, and q is quartet.



Fig. 1. PMR spectrum of IIIa.



Fig. 2. PMR spectrum of IVa.

The direction of the reaction changes substantially if alcohols are used as the solvent. In this case I adds to IIa-c to give IIIa-c in 90-95% yields.

The structures of the reaction products were proved by IR and PMR spectroscopy.

The PMR spectrum of IIIa (Fig. 1) is characterized by the presence at strong field of a broad singlet of two NH protons with an averaged chemical shift because of rapid proton exchange. The signals of resonance absorption corresponding to three protons of the aziridine ring are seen distinctly. The characteristic spin-spin splitting makes it possible to assign the signals at stronger field (τ 8.67 ppm) to the proton in the cis position relative to the aminomethyl grouping. The signals at weaker field at 8.31 and 7.95 ppm correspond to the trans protons and the ring 2-CH protons. A multiplet of protons of three methylene groups in which a triplet of the AA'BB' type at 7.14 ppm, which is related to the methylene group attached to the exocyclic nitrogen atom, is distinguishable is observed at 7.3-7.8 ppm. The parameters of the PMR spectra of IIIa-c are presented in Table 1.

The formation of a compound of the IV type is observed only in the cyanoethylation of I. Immediate mixing of starting I and II at a temperature no higher than 0° without a solvent is the optimum condition for the preparation of IVa; the yield of IVa in this case is 90%.

The structure of IVa was proved by the results of elementary analysis, gas-liquid chromatography (GLC), and IR and PMR spectroscopy.

An intense band at 1600 cm^{-1} corresponding to the deformation vibrations of a primary amino group is observed in the IR spectrum of IVa in addition to the absorption bands characteristic for structure IV.

The PMR spectrum of IVa (Fig. 2) contains a singlet of the protons of an amino group at 8.5 ppm. The characteristic signals of the protons of the aziridine ring are observed at 8.4-8.8 ppm, and the multiplet at 7.1-7.9 ppm was assigned to the absorption of the protons of an aminomethylene grouping. The decrease in the difference in the chemical shifts between the methylene groups in the NCH₂CH₂CN fragment and the change in the character of the spectrum in the region of resonance absorption of the protons of the aziridine ring as compared with the spectrum of IIIa unambiguously prove structure IVa.

A side reaction in the synthesis of IV is the formation of V, which can be obtained in quantitative yield by immediate mixing of I with 2 moles of II.

In order to confirm the structures of III and IV we obtained derivatives of the latter with several carbonyl compounds:



a $\mathbf{R} = \mathbf{CH}_3$; b $\mathbf{R} = p \cdot \mathbf{CH}_3 \mathbf{C}_6 \mathbf{H}_4$; c $\mathbf{R} = p \cdot \mathbf{CH}_3 \mathbf{OC}_6 \mathbf{H}_4$

Thus, 2-substituted 3-cyanoethyl-1,3-diazobicyclo[3.1.0] hexanes, which are members of the new heterocyclic system that we previously described in [1], were obtained by reaction of IIIa with anisaldehyde or acetaldehyde. The structures of these compounds were proved by the complete similarity between their PMR spectra and the PMR spectra of the previously obtained representative of this class of substances and by the presence of additional singlets at 5.3-5.4 ppm for VIc and of multiplets at 6.7 ppm for VIa. Addition products of the IV type react with aldehydes to give Schiff bases. The IR spectra of VIIa, b contain intense absorption bands of a C = N bond at 1650 cm⁻¹. In addition, the PMR spectra of VIIa, b contain the signal of the absorption of the CH = N fragment at weak field at 1.98 ppm and a multiplet of the AA'BB' type of the protons of the phenyl ring at 2.52 and 2.98 ppm for VIIb.

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EXPERIMENTAL

The IR spectra of Nujol suspensions of the compounds were recorded with a UR-20 spectrometer (with NaCl, NaBr, and LiF prisms). The PMR spectra at 20° were recorded with a Perkin-Elmer R-12A spectrometer (60 MHz) at 20° with tetramethylsilane as the internal standard. The compositions of the reaction products were analyzed with an AGK-6 gas-liquid chromatograph at a thermostat temperature of 160° and a vaporization temperature of 220°. The carrier-gas (helium) flow rate was 50 ml/min, the stationary phase was 20% Apiezon M on Chromosorb P, and the column length was 3 m.

 $\frac{2-\text{Methylene-}(\beta-\text{cyanoethylamino})\text{ethyleneimine (IIIa), } 2-\text{Methylene-}(\beta-\text{carbethoxyethylamino})\text{ethylene-}(\beta-\text{carbethoxyethylamino})\text{ethylene-}(\beta-\text{carbethoxyethylamino})\text{ethyleneimine (IIIc). A 0.1-mole sample of II was added to 8.1 ml (0.1 mole) of I in 100 ml of ethanol with cooling (to 15-18°) and stirring, after which the mixture was held at room temperature for 3 h. The solvent was then evaporated, and the oily residue was vacuum fractionated (see Table 2).}$

<u>2-Aminomethyl-1-(β -cyanoethyl)ethyleneimine (IVa)</u>. A 5.3-g (0.1 mole) sample of acrylonitrile was added with cooling (to o°) and stirring to 8.1 ml (0.1 mole) of I, after which the mixture was held at room temperature for 3 h. The product was isolated by vacuum distillation (see Table 2).

 $\frac{2-\text{Methylene-}(\beta-\text{cyanoethylamino})-1-(\beta-\text{cyanoethyl})\text{ethyleneimine (Va), }2-\text{Methylene-}(\beta-\text{carbethoxy-ethylamino})-1-(\beta-\text{carbethoxyethyl})\text{ethyleneimine (Vb), and }2-\text{Methylene-}(\beta-\text{carbomethoxyethylamino})-1-(\beta-\text{carbethoxyethyl})\text{ethyleneimine (Vb), and }2-\text{Methylene-}(\beta-\text{carbomethoxyethylamino})-1-(\beta-\text{carbethoxyethyl})\text{ethyleneimine (Vc). A 0.2-mole sample of II was added at 15-18° to an 8.1-ml (0.1 mole) sample of I in 50 ml of ethanol, after which the mixture was held at room temperature for 3 h. The solvent was then evaporated, and Va-c were isolated by vacuum distillation (see Table 2).$

2-Methyl-3-cyanoethyl-1,3-diazabicyclo[3.1.0]hexane (VIa). A 0.05-mole sample of acetaldehyde was added to 6.25 ml (0.05 mole) of IIIa in 50 ml of ethanol. The method used to carry out the synthesis was

Com-	bp, °C	n _D ²⁰	Empirical formula	Found, %			Calc., %		
pound	(2 mm)			с	н	N	c i	н	N
IIIa IIIb IIIc IVa Va Vb Vc	$129-130 \\ 120 \\ 115-117 \\ 127-129 \\ 142-141 \\ 140-142 \\ 138-140$	1,4850 1,4660 1,4648 1,4780 1,4680 1,4580 1,4560	$\begin{array}{c} C_6H_{11}N_3\\ C_8H_{16}N_2O_2\\ C_7H_{14}N_2O_2\\ C_6H_{11}N_3\\ C_9H_{14}N_4\\ C_{13}H_{24}N_2O_4\\ C_{11}H_{20}N_2O_4\\ \end{array}$	57,4 55,7 53,4 57,5 61,4 57,5 54,1	8,4 9,5 8,5 8,9 8,0 8,4 8,1	33,7 16,0 17,5 33,5 30,5 10,1 11,5	57,6 55,8 53,3 57,6 61,3 57,3 54,0	8,8 9,3 8,7 8,8 7,9 8,8 8,8 8,2	33,6 15,9 17,7 33,6 30,7 10,2 11,5

TABLE 2. Physicochemical Characteristics of IIIa-c, IVa, and Va-c

similar to that described in [3]. Workup gave a product with bp 108-110° (2 mm) and n_D^{20} 1.4832 in 90% yield. IR spectrum, cm⁻¹: 2260 (CN) and 3010 and 3060 (NI) [sic]. Found: C 63.4; H 8.7; N 27.6%. C₈H₁₃N₃. Calculated: C 63.5; H 8.6; N 27.8%.

 $\frac{2-(p-Methoxyphenyl)-3-cyanoethyl-1,3-diazabicyclo [3.1.0]hexane (VIc). A 6.5-g (0.05 mole) sample of anisaldehyde was added to 6.25 ml (0.05 mole) of IIIa in 50 ml of ethanol, after which the mixture was refluxed for 2 h. It was then dried over calcium hydride, the solvent was evaporated, and the residue was vacuum fractionated to give a product with bp 170-172° (2 mm) and n²²_D 1.4952 in 85% yield. IR spectrum, cm⁻¹: 2260 (CN), 3020, 3080 (NI) [sic]. Found: C 69.3; H 7.2; N 16.9%. C₁₄H₁₇N₃O. Calculated: C 69.1; H 7.2; N 17.2%.$

<u>2-Ethylideneaminomethyl-1-(β -cyanoethyl)ethyleneimine (VIIa).</u> A 0.05-mole sample of acetaldehyde was added with stirring and cooling to 10-15° to 6.25 ml (0.05 mole) of IVa in 50 ml of alcohol, after which the mixture was allowed to stand for 2 h. It was then dried over calcium hydride and vacuum distilled to give a product with bp 110-112° (2 mm) and n_D^{22} 1.4739 in 85% yield. IR spectrum, cm⁻¹: 1670 (C = N) and 2250 (C = N). PMR spectrum, τ , ppm (in CCl₄): 2.45 (quartet, CH = N), 8.1 (doublet, CH₃), 6.4-7.2 (multiplet, CH₂N=), 7.48 and 7.58 (AA'BB' system, multiplet, NCH₂CH₂CN), 8.48 (multiplet, C₂H), and 8.65 and 8.37 (two doublets, C₃H₂). Found: C 63.1; N 9.0; N 27.9%. C₃H₁₃N₃. Calculated: C 63.2; H 8.6; N 27.8%.

<u>2-(p-Methylbenzylidene)aminomethyl-1-(β -cyanoethyl)ethyleneimine (VIIb)</u>. This compound, with bp 160-162° (2 mm) and n_D^{22} 1.4786, was similarly obtained in 90% yield from IVa and p-methylbenzaldehyde. IR spectrum, cm⁻¹: 1660 (C = N) and 2260 (C = N). PMR spectrum, τ , ppm (in CCl₄): 1.97 (singlet, CH=), 2.53 and 2.97 (AA'BB' system, multiplet, C₆H₄), 7.73 (singlet, CH₃), 6.2-7.0 (multiplet, CH₂N=), 7.53 and 7.68 (AA'BB', multiplet, -NCH₂CH₂CN), 8.4 (multiplet, C₂H), and 8.74 and 8.37 (two doublets, C₃H₂). Found: C 74.2; H 7.8; N 18.4%. C₁₄H₁₇N₃. Calculated: C 74.0; H 7.5; N 18.4%.

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