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## Abstract

## Full Text

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# THE STRUCTURE AND DUAL REACTIVITY OF N-ETHYLENIMINOCARBINOLS

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In ([1–3]) we reported that ethylenimine (I) with carbonyl compounds forms not oxazolidines ([4]), but N-ethyleniminocarbinols. Adducts of 2 mol of I to the carbonyl group, which at first were taken for alkylidene- ([5,1]) and arylidene-bis-ethylenimines ([5]), were later identified as derivatives of N-$\beta$-aminoethylethylenimine (II) ([6,7,2]). Bestian proposed that these products are formed through an intermediate $\alpha$-aryl-N-ethyleniminocarbinol, reacting with opening of the ring with I in the form of the zwitterion

$$\left[\begin{array}{c}\overset{\oplus}{\mathrm{N}}-\mathrm{CH(Ar)}-\overset{\ominus}{\mathrm{O}}\\ \mathrm{H}\end{array}\right] \quad ([6]).$$

However, this scheme is not in agreement with the data given below. Moreover, it does not follow from ([6,7,2]) that II is formed under mild conditions ([5]), and not after distillation of I and interaction of $\alpha$-aryl-N-ethyleniminocarbinols with the product of their dissociation, I, under the heating conditions during distillation. The latter is confirmed by the low yields of II ([7,2]) and by the formation of II on distillation of N-ethyleniminocarbinol (III) ([1]) and $\alpha$-phenyl-N-ethyleniminocarbinol (IV).

In the present work it has been established that the reaction of III ([3]), IV, $\alpha$-2-furyl-N-ethyleniminocarbinol (V), and $\alpha$-3-pyridyl-N-ethyleniminocarbinol (VI) ([2]) with compound I (in a sealed ampoule, in benzene, for compound III at 120–130°, for IV–VI at 180–200°, 1-5 hr, with separation of the theoretical amount of water on azeotroping; at 20° no interaction is observed over the course of a month) and the reaction of these same compounds with higher homologs of I and other secondary amines (III ([8]), IV–VI in benzene, 20°, 10 hr, with self-heating and separation of the theoretical amount of water on azeotroping) proceed in the two extreme forms of the system of ethylenimmonium-carbonium ions ([2]) according to the following general scheme:

$$\text{A}\quad \Delta\text{N}^{\oplus}=\text{CH}_2 \;\rightleftarrows\; \text{B}\quad \Delta\text{N}-\overset{\oplus}{\text{C}}\text{H}\,\text{R}'$$

$$\left.\begin{array}{c} \Delta\text{NH} \\ \left[\Delta\text{NH}:\cdots\overset{\oplus}{\Delta}\text{N}=\text{CH}-\text{R}'\right]\quad \text{C} \\ -\text{H}^{\oplus} \\ \Delta\text{N}-\text{CH}_2\text{CH}_2-\text{N}=\text{CH}-\text{R}' \\ \text{at R}'=\text{H}\ (^2)\quad 1)\ \Delta\text{NH}\quad 2)\ \Delta\text{N}^{\oplus}{=}\text{CH}_2 \\ \Delta\text{N}-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_2\Delta)_2 \end{array}\right\}$$

$$\left.\begin{array}{c} \text{HN}\left\langle \begin{array}{c}\text{R}\\ \text{R}\end{array}\right. \\ \left[\Delta\text{N}-\overset{\oplus}{\text{C}}\text{H}-\text{R}'\cdots:\text{N}\left\langle \begin{array}{c}\text{R}\\ \text{R}\end{array}\right.\right] \\ -\text{H}^{\oplus} \\ \Delta\text{N}-\text{CH}-\text{N}\left\langle \begin{array}{c}\text{R}\\ \text{R}\end{array}\right. \\ \text{R}' \end{array}\right\}$$

$$\text{R}'=\text{H}\ (^{2,8}),\quad \text{C}_6\text{H}_5,\quad \text{2-furyl},\quad \text{3-pyridyl}.$$

The structure of the products (Table 1) was confirmed by proton magnetic resonance spectra* (p.m.r.) (VIII, XV, Fig. 1, $a, b$). From the p.m.r. spectra VII, XIV (Fig. 1, $v, g$) and XVII were identified with products of independent synthesis (in benzene, 20°, 1 hr; in Table 1 the yield is in parentheses):

$$\Delta\text{N}-\text{CH}_2\text{CH}_2-\text{NH}_2+\text{O}=\text{CH}-\text{Ar}\rightarrow\Delta\text{N}-\text{CH}_2\text{CH}_2-\text{N}=\text{CH}-\text{Ar}+\text{H}_2\text{O}.$$

* All p.m.r. spectra were measured at 20.529 Mc. The positions of the signals were determined relative to the signal of the internal standard hexamethyldisiloxane (HMDS) (Fig. 1) and benzene (Fig. 2 and 3) and are expressed in millionths fractions (m.f.) of the applied field. The chemical shift of HMDS relative to benzene is +7.07 m.f.

**Table 1**

| Compound | Yield, % | b.p., °C / mm Hg | $n_D^{20}$ | $d_4^{20}$ | $MRD$ found | $MRD$ calc. | C, % found | C, % calc. | H, % found | H, % calc. | N, % found | N, % calc. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| VII. Aziridinyl-$CH_2CH_2$-N=CH-$C_6H_5$ | 89,4 (86,1) | 102 — 102,5 / 1,0 | 1,5530 | 1,0016 | 55,67 | 54,14 | 75,73; 75,75 | 75,82 | 8,31; 8,16 | 8,10 | 16,11; 16,33 | 16,08 |
| VIII. Aziridinyl-$CH(C_6H_5)$-$N(CH_3)_2$ | 90 | 69,5 — 70,5 / 0,3 — 0,5 | 1,5255 | 0,9828 | 55,00 | 55,07 | 75,10; 74,82 | 74,95 | 9,10; 9,27 | 9,15 | 15,67; 15,69 | 15,89 |
| IX. Aziridinyl-$CH(C_6H_5)$-$N(CH_2$-$CH=CH_2)_2$ | 73,7 | 103,5 — 105 / 1,0 | 1,5350 | 0,9744 | 72,96 | 72,62 | 78,74; 78,94 | 78,89 | 8,64; 8,82 | 8,83 | 12,58; 12,35 | 12,27 |
| X. Aziridinyl-$CH(C_6H_5)$-N-cyclobutyl | 72,3 | 90,5 — 91,0 / 1,0 | 1,5420 | 1,0248 | 57,82 | 57,50 | 76,29; 76,41 | 76,55 | 8,54; 8,63 | 8,57 | 14,96; 15,07 | 14,88 |
| XI. Aziridinyl-$CH(C_6H_5)$-N-cyclopentyl | 58,3 | 110 — 112 / 1,0 | 1,5427 | 1,0243 | 62,21 | 62,11 | 76,80; 76,94 | 77,18 | 8,99; 9,11 | 8,97 | 13,76; 13,53 | 13,85 |
| XII. Aziridinyl-$CH(C_6H_5)$-N-cyclohexyl | 80,4 | 111 / 0,8 | 1,5411 | 1,0189 | 66,73 | 66,73 | 78,23; 78,11 | 77,73 | 9,51; 9,59 | 9,32 | 12,62; 12,92 | 12,95 |

| Compound | Yield, % | b.p., °C / mm Hg | $n_D^{20}$ | $d_4^{20}$ | $MRD$ found | $MRD$ calc. | C, % found | C, % calc. | H, % found | H, % calc. | N, % found | N, % calc. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| XIII. Aziridinyl-$CH(C_6H_5)$-N-morpholinyl | 59,5 | 121 – 122,5 / 0,5 | 1,5473 | 1,0852 | 63,81 | 63,76 | 71,58; 71,62 | 71,52 | 8,28; 8,30 | 8,31 | 12,83; 12,89 | 12,83 |
| XIV. Aziridinyl-$CH_2CH_2$-N=CH-furyl | 72,5 (59) | 85 – 86 / 1,5 | 1,5361 | 1,0602 | 48,29 | 47,01 | 65,32; 65,52 | 65,82 | 7,38; 7,44 | 7,37; 7,44 | 17,11; 17,19 | 17,06 |
| XV. Aziridinyl-CH(furyl)-$N(CH_3)_2$ | 76,6 | 60 – 62 / 1,0 | 1,4891 | 1,0160 | 47,23 | 47,95 | 64,99; 64,87 | 65,03 | 8,53; 8,52 | 8,49 | 17,14; 17,15 | 16,85 |
| XVI. Aziridinyl-CH(furyl)-N-morpholinyl | 60,8 | 107 – 107,5 / 1,0 | 1,5148 | 1,1244 | 55,84 | 56,63 | 63,47; 63,52 | 63,44 | 7,80; 7,83 | 7,74 | 13,40; 13,51 | 13,45 |
| XVII. Aziridinyl-$CH_2CH_2$-N=CH-pyridyl | 67,4 (83,7) | 129,5 / 2 | 1,5230 | 1,0460 | 51,23 | 52,99 | 68,41; 68,52 | 68,54 | 7,50; 7,58 | 7,48 | 23,89; 23,78 | 23,98 |
| XVIII. Aziridinyl-CH(pyridyl)-$N(CH_3)_2$ | 62,8 | 83,5 – 84 / 0,5 | 1,5283 | 1,0334 | 52,83 | 53,41 | 67,35; 67,42 | 67,28 | 4,71; 4,75 | 4,70 | 12,89; 12,96 | 13,08 |
| XIX. Aziridinyl-CH(pyridyl)-N-morpholinyl | 52,5 | 135,5 / 1,0 | 1,5458 | 1,1213 | 61,91 | 62,60 | 65,61; 65,69 | 65,73 | 7,85; 7,91 | 7,81 | 19,20; 19,29 | 19,16 |

Fig. 1. NMR spectra of compounds: a–VIII, b–XV, c–VII, d–XIV

Figure 1: Fig. 1. NMR spectra of compounds: a–VIII, b–XV, c–VII, d–XIV

The dual reactivity of N-ethyleneiminocarbinols is explained by the anomalous hybridization of nitrogen in the three-membered ring. It is known that in cyclopropane the hybridization of the carbon endo-orbitals is $sp^4$,[12] while the exo-orwill be $sp^{2,28}$ ([9]). A transition of this type of optimal hybridization of the nitrogen endo-orbitals in the ethylenimine ring I to $sp^2$ in form A (as well as to $sp^3$ in the form

$$> \overset{\oplus}{\mathrm{N}} <^{\mathrm{H}}_{\mathrm{H}} \quad ([6])$$

) determines the functional character of the ethylenimine group.

Attack by cation B in compound I, unlike other secondary amines, is hindered because of the lowering of the $p$-character of its free electron pair. Attack by I is realized in the case of cation C with a localized charge. The activity of cation B is lowered due to delocalization of the charge in the system

$$> \mathrm{N{=}CH{-}R'},$$

and, when $\mathrm{R} = \mathrm{C_6H_5}$, also due to the contribution

$$> \mathrm{N{-}CH{=}\langle phenyl\rangle^+}.$$

The proposed scheme is confirmed by the following. First, as a result of $p$ $-\pi$-conjugation in the planar transition state (form A), compounds III, IV –VI show a sharp increase (in comparison with N-alkylethylenimines) in the rate of nitrogen inversion ([2]); disruption of such conjugation in N-$\beta$-hydroxyethylethylenimine leads to a slowing of inversion (Fig. 2). Secondly, when N-ethyleneiminocarbinols are compared with N-acetylazetidenimine, striking analogies are observed, which are especially valuable in view of the fact that for amides the correspondence to the system:

**Fig. 1.** NMR spectra of compounds: $a$–VIII, $b$–XV, $c$–VII, $d$–XIV

$$\mathrm{R_2N{-}C(=O)R} \longleftrightarrow \mathrm{R_2\overset{\oplus}{N}{=}C(\overset{\ominus}{O})R}$$

has been proved by the method of X-ray structural analysis ([10]) and by the NMR method, from the high barrier of rotation about the N–C bond ([11]).

It has been shown by us from the NMR spectra (Fig. 3) that in N-acetylethylenimine (b.p. 44-44.5°/18 mm [6]) the rate of nitrogen inversion is

high (a singlet signal from the protons of the ring), whereas upon rupture of the $p$-$\pi$ conjugation in N-$\beta$-ethyleniminoethyl methyl ketone (b.p. 65.5-66°/15 mm; $n_D^{20}$ 1.4420; $d_4^{20}$ 0.9564), as in the case of N-$\beta$-hydroxyethylethylenimine, the rate of inversion decreases sharply.

**Fig. 2.** Temperature dependence of the NMR spectrum of N-$\beta$-hydroxyethylethylenimine

**Fig. 3.** NMR spectra: $a$—N-acetylethylenimine, $b$—N-$\beta$-ethyleniminoethyl methyl ketone

It is known that ethyleneamides are prone to N-$\beta$-aminoethylation reactions with ring opening [9], which fit completely into the scheme given above (form A):

$$\triangleright\overset{\oplus}{\mathrm{N}}{=}\mathrm{C}\left(\overset{\ominus}{\mathrm{O}}\right)\mathrm{R} \longrightarrow \left[\mathrm{R}-\overset{\ominus}{\mathrm{C}}(=\mathrm{NCH_2CH_2^{\oplus}})\right] \quad \mathrm{D}$$

$$\mathrm{D} \xrightarrow[\mathrm{HN}]{\Delta} \text{cyclic product} \qquad \mathrm{D} \underset{:\mathrm{N}}{\longrightarrow} \mathrm{R}-\mathrm{C}(=\mathrm{O})\mathrm{NHCH_2CH_2N}<$$

similarly for $\mathrm{R}-\mathrm{SO_2N}<$ [9] and

$$\begin{matrix} \mathrm{R} & \mathrm{O} \\ \backslash & \| \\ \mathrm{R}/ & \mathrm{P} \\ & \backslash \\ & \mathrm{N}< \end{matrix} \tag{12}$$

Moreover, attack of the carbocation D is effected both by amines of the type

$$\mathrm{HN}<^{\mathrm{R}}_{\mathrm{R}},$$

and by ethylenimine [9].

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*Note: Figure translations are in progress. See original paper for figures.*