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R. G. Kostyanovskii, V. F. Bystrov

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Abstract

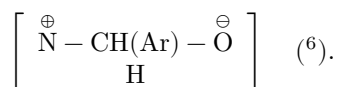
Full Text

R. G. Kostyanovskii, V. F. Bystrov

THE STRUCTURE AND DUAL REACTIVITY OF N-ETHYLENIMINOCARBINOLS

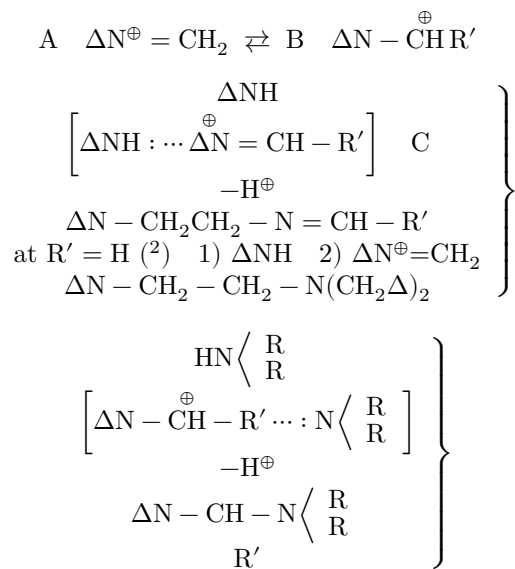
(Presented by Academician V. N. Kondrat'ev, 4 VII 1962)

In (1-3) we reported that ethylenimine (I) with carbonyl compounds forms not oxazolidines (4), but N-ethyleniminocarbinals. 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-β-aminoethylethylenimine (II) (6,7,2). Bestian proposed that these products are formed through an intermediate α-aryl-N-ethyleniminocarbinal, reacting with opening of the ring with I in the form of the zwitterion



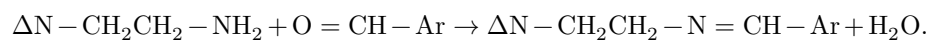
However, this scheme is not in agreement with the data given below. Moreover, it does not follow from (6,7,2) that II is formed under mild conditions (5), and not after distillation of I and interaction of α-aryl-N-ethyleniminocarbinals with the product of their dissociation, I, under the heating conditions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

In the present work it has been established that the reaction of III (3), IV, α-2-furyl-N-ethyleniminocarbinal (V), and α-3-pyridyl-N-ethyleniminocarbinal (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:



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

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):



* 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

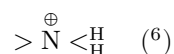
Compound	Yield, mm Hg	b.p., °C	n_D^{20}	d_4^{20}	MRDMRD		C, %	C, %	H, %	H, %	N, %	N, %
					found	calc.	found	calc.	found	calc.	found	calc.
VII. Aziridinyl-CH ₂ CH ₂ -N=CH-C ₆ H ₅	89,4 (86,1)	102	1,55301	1,001655	54,14	75,73; 75,82	8,31; 8,10	16,11; 16,08	16,33			
VIII. Aziridinyl-CH(C ₆ H ₅)-N(CH ₃) ₂	90	69,5	1,52550	0,982855	55,07	75,10; 74,95	9,10; 9,15	15,67; 15,89	15,69			
IX. Aziridinyl-CH(C ₆ H ₅)-N(CH ₂ -CH=CH ₂) ₂	73,7	103,5	1,53500	0,974472	72,62	78,74; 78,89	8,64; 8,83	12,58; 12,27	12,35			
X. Aziridinyl-CH(C ₆ H ₅)-N-cy-clobutyl	72,3	90,5	1,54201	0,24857	57,82	76,29; 76,55	8,54; 8,57	14,96; 14,88	15,07			
XI. Aziridinyl-CH(C ₆ H ₅)-N-cy-clopentyl	58,3	110	1,54271	0,24362	62,11	76,80; 77,18	8,99; 8,97	13,76; 13,85	13,53			
XII. Aziridinyl-CH(C ₆ H ₅)-N-cy-clohexyl	80,4	111	1,54111	0,18966	66,73	78,23; 77,73	9,51; 9,32	12,62; 12,95	12,92			

Compound	Yield, mm Hg	b.p., °C	n_D^{20}	d_4^{20}	<i>MRDMRD</i>		C, %	C, %	H, %	H, %	N, %	N, %
					found	calc.	found	calc.	found	calc.	found	calc.
XIII. Aziridinyl- CH(C ₆ H ₅)- N- mor- pholinyl	59,5	121	1,54731	1,08526	3,81	63,76	71,58; 71,62	71,52	8,28; 8,30	8,31	12,83; 12,83	12,83
XIV. Aziridinyl- CH ₂ CH ₂ - N=CH- furyl	72,5	85	1,53611	1,06024	8,29	47,01	65,32; 65,52	65,82	7,38; 7,44	7,37; 7,44	17,11; 17,06	17,19
XV. Aziridinyl- CH(furyl)- N(CH ₃) ₂	76,6	60	1,48911	1,01604	7,23	47,95	64,99; 64,87	65,03	8,53; 8,52	8,49	17,14; 16,85	17,15
XVI. Aziridinyl- CH(furyl)- N- mor- pholinyl	60,8	107	1,51481	1,24455	8,84	56,63	63,47; 63,52	63,44	7,80; 7,83	7,74	13,40; 13,45	13,51
XVII. Aziridinyl- CH ₂ CH ₂ - N=CH- pyridyl	67,4	129,5	1,52301	1,04605	1,23	52,99	68,41; 68,52	68,54	7,50; 7,58	7,48	23,89; 23,98	23,78
XVIII. Aziridinyl- CH(pyridyl)- N(CH ₃) ₂	62,8	83,5	1,52831	1,03345	2,83	53,41	67,35; 67,42	67,28	4,71; 4,75	4,70	12,89; 13,08	12,96
XIX. Aziridinyl- CH(pyridyl)- N- mor- pholinyl	52,5	135,5	1,54581	1,21361	1,91	62,60	65,61; 65,69	65,73	7,85; 7,91	7,81	19,20; 19,16	19,29

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

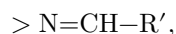
Figure 1: Fig. 1. NMR spectra of compounds: a–VIII, b–XV, c–VII, d–XIV

The dual reactivity of N-ethyleneiminocarbinals 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-orbitals will 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

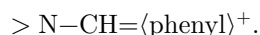


) determines the functional character of the ethylenimine group.

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

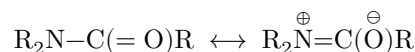


and, when $\text{R} = \text{C}_6\text{H}_5$, also due to the contribution



The proposed scheme is confirmed by the following. First, as a result of p - π -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- β -hydroxyethylethylenimine leads to a slowing of inversion (Fig. 2). Secondly, when N-ethyleneiminocarbinals 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



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).

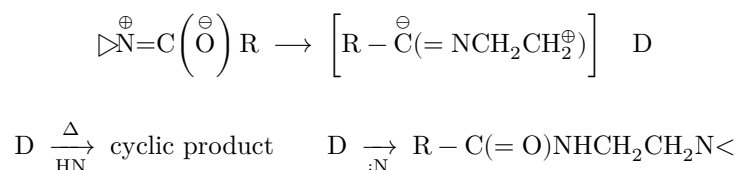
It has been shown by us from the NMR spectra (Fig. 3) that in N-acetylethylenimine (b.p. 44–44.5°/18 mm [6]) the rate of nitrogen inversion is

high (a singlet signal from the protons of the ring), whereas upon rupture of the p - π conjugation in N - β -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 - β -hydroxyethylethylenimine, the rate of inversion decreases sharply.

Fig. 2. Temperature dependence of the NMR spectrum of N - β -hydroxyethylethylenimine

Fig. 3. NMR spectra: a - N -acetylethylenimine, b - N - β -ethyleniminoethyl methyl ketone

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



similarly for $R - SO_2N <$ [9] and



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



and by ethylenimine [9].

Institute of Chemical Physics
Academy of Sciences of the USSR

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