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Abstract

Full Text

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ALKYLIDENE-BIS-ETHYLENEIMINES

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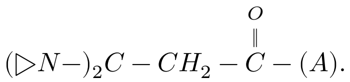
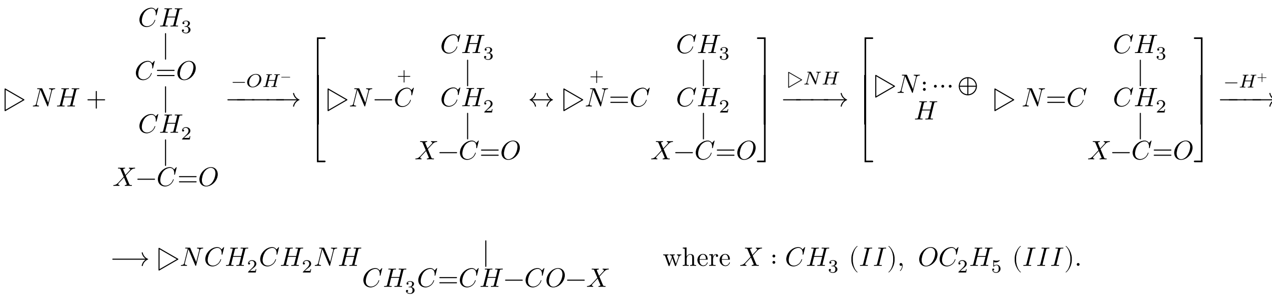
Previously we reported on the impossibility of obtaining alkylidene- and arylidene-bis-ethyleneimines from ethyleneimine (I) and carbonyl compounds (1). However, the products of the reaction of I with certain 1,3-dicarbonyl compounds were postulated by Virling (2) as alkylidene-bis-ethyleneimines of type A:



$$(\triangleright N-)_2C-CH_2-\overset{\overset{\textstyle O}{\|}}{C}-(A).$$

We repeated the work (2) and proved that the products of the interaction of I with acetylacetone and acetoacetic ester are (like the products of condensation of I with two moles of formaldehyde or an aromatic aldehyde) derivatives of β-aminoethylethyleneimine (Table 1):



$$\triangleright NH+\begin{matrix}CH_3\\|\\C{=}O\\|\\CH_2\\|\\X{-}C{=}O\end{matrix}\xrightarrow{-OH^-}\left[\triangleright N{-}\overset{+}{C}\begin{matrix}CH_3\\|\\CH_2\\|\\X{-}C{=}O\end{matrix}\leftrightarrow\triangleright\overset{+}{N}{=}C\begin{matrix}CH_3\\|\\CH_2\\|\\X{-}C{=}O\end{matrix}\right]\xrightarrow{\triangleright NH}\left[\underset{H}{\triangleright N\colon}\cdots\oplus\ \triangleright N{=}C\begin{matrix}CH_3\\|\\CH_2\\|\\X{-}C{=}O\end{matrix}\right]\xrightarrow{-H^+}$$

$$\longrightarrow\triangleright NCH_2CH_2NH\underset{CH_3C{=}CH{-}CO{-}X}{|}\qquad\text{where } X: CH_3\ (II),\ OC_2H_5\ (III).$$

(Scheme 1)

The structure of compounds II and III was proved from NMR spectra (Fig. 1), mass spectra (Fig. 2), and IR spectra: for II and III, respectively, $\nu_{C=C}$ 1580 and 1608 cm^{-1}, $\nu_{C=O}$ 1615 and 1655 cm^{-1}, ν_{C-H} (ring) 3060 cm^{-1}, ν_{N-H} 3200 (diff.) and 3280 cm^{-1}.

Table 1

Compound	Yield, %	b.p., °C/mm Hg	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	C, % found	C, % calc.	H, % found	H, % calc.	N, % found	N, % calc.
II $\triangleright NCH_2CH_2NH$ | $CH_3-C=CH-COCH_3$	47.3^a	96/0.85	1.5373	1.0070	52.1^c	48.65	63.84 64.12	64.02	9.51 9.71	9.59	16.75 16.81	16.66
III $\triangleright NCH_2CH_2NH$ | $CH_3-C=CHCOOC_2H_5$	67.6^b	83–85/0.08	1.5130	1.0315	57.81^d	54.91	60.48 60.75	60.57	9.16 9.31	9.15	14.27 14.31	14.14
IV $\triangleright N\backslash$ $>$ $CH-CH_2CN \triangleright N/$	44.0	m.p. 89.2–89.7 (from ether)	–	–	–	–	61.30 61.18	61.28	8.37 8.56	8.10	30.31 30.90	30.62
V $\triangleright N\backslash$ $>$ $CHCH_2COOCH_3 \triangleright N/$	79.0	92/4.5	1.4702	1.080	43.91	44.24	56.06 56.02	56.46	8.26 8.30	8.23	16.86 16.72	16.47
VI $\triangleright N\backslash$ $>$ $CHCH_2CH_2CH \triangleright N/$	64.9	85/2, m.p. 53–54.5	–	–	–	–	59.46 59.21	59.73	9.84 9.71	9.92	19.78 19.81	19.87

a, b) The reaction was carried out at room temperature without solvent or in ether; the product was dried with barium oxide. The yield increases with increasing reaction time and distillation in a deeper vacuum.
c, d) For β-methylaminocrotonic ester $\Delta MR = 2.79$ (^{3}).

The spectra were measured as follows: NMR on a JNM-C60 instrument at a frequency of 60 MHz, mass spectra on an MX-1303 instrument ($U = 30$ V, $I = 0.7$ mA, $t = 100°$), and IR spectra on a UR-10 spectrometer (in a capillary layer).

Fig. 1. NMR spectra of compounds II and III

Fig. 2. Mass spectra of compounds II and III

For the first time we have succeeded in synthesizing alkylidene-bis-ethyleneimines according to the scheme:

$$\text{aziridinyl-}NCH{=}CH{-}CN \xrightarrow{\text{ethyleneimine}} \text{bis(aziridinyl)}{-}CHCH_2{-}CN \qquad \text{(IV)}$$

$$\text{aziridinyl-}NCH{=}CHCOOCH_3 \xrightarrow{\text{ethyleneimine}} \text{bis(aziridinyl)}{-}CHCH_2COOCH_3 \qquad \text{(V)}$$

$$\text{bis(aziridinyl)}{-}CHCH_2COOCH_3 \xrightarrow[\text{ether}]{\text{LiAlH}_4} \text{bis(aziridinyl)}{-}CHCH_2CH_2OH \qquad \text{(VI)}$$

Scheme 2

The starting products were obtained by us earlier by addition of I to the corresponding acetylene derivatives (^{4}). Since the ethyleneimine group enters into conjugation with an activated double bond to a considerably lesser extent (in comparison with dialkylamino and alkyleneimino groups),

bond $^{(4)}$, the latter remains still quite highly polarized. Therefore addition of a second molecule of I proceeds under mild conditions (one week at room temperature without solvent). The structure of products IV—VI was confirmed by NMR spectra (Fig. 3) and mass spectra (Fig. 4). In the NMR spectra of compounds IV—VI, the protons of the ethylenimine rings give a complex signal (caused by slow inversion of the nitrogen atoms and, apparently, hindered rotation due to steric hindrance by the alkyl substituent), which merges into a singlet signal on heating. It should also be noted that the signal from the proton of the $>CH$— group lies in an unusually high field.

Fig. 3. NMR spectra of compounds IV—VI

The principal type of fragmentation of compounds IV—VI under electron impact corresponds to that for geminal amines $^{(5)}$: in all cases the maximum peak of the fragment ion is $m/e\ M = 42$ (Fig. 4). The reactions studied (Scheme 2) rule out the possibility of intramolecular dehydration in the formation of II and III and thus confirm the reaction mechanism (Scheme 1). The impossibility of dehydration of N-ethyleniminecarbinols was also shown by us on the optimum example of the product of the interaction of ethylenimine with cyclohexanone. As is known, dehydration of the reaction products of aliphatic amines with carbonyl compounds, leading to the formation of enamines, proceeds most readily in the case of cycloalkanones $^{(6)}$.

When we attempted to add strongly basic secondary amines to the methyl ester of β-ethyleniminoacrylic acid, we obtained the corresponding β-aminoacrylic esters:

$$\triangle NCH{=}CH{-}COOCH_3 \xrightarrow{HN<} \begin{bmatrix} \triangle N \cdots H \\ CH{-}CH{-}C(=O) \\ OCH_3 \end{bmatrix} \xrightarrow{-\triangle NH}$$

$$\longrightarrow\ > NCH{=}CHCOOCH_3$$

$$> N- = (CH_3)_2N- \text{ (VII)}, \qquad O(\quad)N- \text{ (VIII)}$$

(Scheme 3)

With dimethylamine (in an ampoule at 110°) VII is formed, yield 84.7% (m.p. 40—40.5°; the product is identical with that obtained earlier via methyl propiolate (2)); with morpholine (at 20°)—compound VIII, yield 98.7%, m.p. 69.5—70.5°.

Found, %:	C 56.19, 56.23;	H 7.67, 7.70;	N 8.07, 8.11
$C_8H_{13}NO_3$. Calculated, %:	C 56.13;	H 7.65;	N 8.18

Fig. 4. Mass spectra of compounds IV—VI

The structures of compounds VII and VIII were confirmed by mass spectra. The proposed reaction mechanism (scheme 3) corresponds to the cleavage of unsymmetrical geminal amines under the action of an electrophilic agent that we studied earlier (5).

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