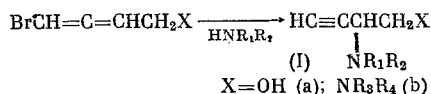


SYNTHESIS OF HYDROXYAMINES OF  
DIACETYLENE SERIES

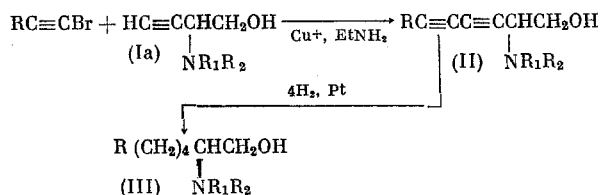
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UDC 542.91:547.362

Previously [1, 2] we have proposed a general method for the synthesis of 3,4-disubstituted 1-butyne derivatives of the (I) type, based on the reaction of the appropriate substituted  $\alpha$ -bromoallenes with various amines



In making a further study of the properties of this class of compounds it seemed of interest to use them in the Cadiot - Chodkiewicz unsymmetrical condensation reaction [3, 4] for the synthesis of various diacetylene derivatives. It proved that 4-hydroxy-3-alkylamino (or dialkylamino) butynes (Ia) easily condense with various bromoacetylenes and give polyfunctional compounds of the diacetylene series (II) in high yield



The best yields of the desired products (70-90%) were obtained by the condensation of (Ia) in methanol solution, in the presence of catalytic amounts of  $\text{Cu}_2\text{Cl}_2$  and aqueous ethylamine solution, with a 1.5 to 2-fold excess of the appropriate bromoacetylene components at a temperature not exceeding 8-10°. Running the reaction at a higher temperature (above 20°) leads to considerable tarring of the end products. The obtained hydroxyamines of the diacetylene series are quite stable compounds, and can be stored at ordinary temperatures. As a rule, the crystalline products are more stable than the liquid products, which lend themselves with great difficulty to distillation. Their structure is corroborated by the elemental analysis and the data of the IR and UV spectra (Table 1).

The IR spectra of these compounds have absorption bands of medium intensity in the 2200-2260  $\text{cm}^{-1}$  region, which correspond to the conjugated substituted diacetylene grouping, and absorption bands that correspond to the stretching vibrations of the functional groups. The UV spectra are characterized by the presence of absorption maxima in the 220-250 nm region, with low intensities that are close in value (not exceeding 1000), which is characteristic for diacetylenic systems of bonds.

When the diacetylenic hydroxyamines are subjected to exhaustive catalytic hydrogenation in alcohol solution, in the presence of Pt catalyst, they easily absorb 4 moles of  $H_2$  with the formation of the previously unknown corresponding hydroxyamines of the aliphatic series (III) (Table 2), for the synthesis of which there have been lacking sufficiently accessible methods up to now.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 5, pp. 1088-1091, May, 1971. Original article submitted June 18, 1970.

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TABLE 1. Hydroxyamines of Diacetylene Series  $RC \equiv CC \equiv CCHCH_2OH$



R	R <sub>1</sub>	R <sub>2</sub>	Yield, %	Mp, °C (recrystallization solvent)	$\lambda_{max}$ , nm (ε)	$\nu$ , cm <sup>-1</sup>	Found N, %	Empirical formula	Calculated N, %
AcOCH <sub>2</sub> CH <sub>2</sub>	H	C <sub>4</sub> H <sub>9</sub>	68	68—70 (petroleum ether)	229, 242, 258, 278 (899, 674, 365, 39)	1740, 2255 3400, 3600	6, 10	C <sub>14</sub> H <sub>21</sub> O <sub>2</sub> N	5, 57
AcOCH <sub>2</sub> CH <sub>2</sub>	H	C <sub>2</sub> H <sub>5</sub>	71	— <sup>*</sup>	240, 252, 266, 282	1742, 2255	6, 35	C <sub>12</sub> H <sub>17</sub> O <sub>2</sub> N	6, 27
C <sub>4</sub> H <sub>9</sub>	H	C <sub>2</sub> H <sub>5</sub>	76	58—59 (petroleum ether)	(569, 510, 528, 160) 242, 256, 286	3440 2257, 3420	7, 41	C <sub>12</sub> H <sub>19</sub> ON	7, 25
C <sub>2</sub> H <sub>5</sub> C(OH)   CH <sub>3</sub>	H	C <sub>2</sub> H <sub>5</sub>	82	— <sup>†</sup>	(555, 429, 152) 234, 243, 258, 290	2250, 3325 3600	7, 18	C <sub>12</sub> H <sub>19</sub> O <sub>2</sub> N	6, 69
C <sub>4</sub> H <sub>9</sub>	H	C <sub>4</sub> H <sub>9</sub>	85	47, 5—49 (hexane)	243, 271, 256, 287 (1090, 940, 741, 890)	2255 3410, 3320	6, 45	C <sub>14</sub> H <sub>23</sub> ON	6, 33
C <sub>2</sub> H <sub>5</sub> C(OH)   CH <sub>3</sub>	H	C <sub>4</sub> H <sub>9</sub>	86	— <sup>‡</sup>	230, 244, 257 (1027, 770, 577)	2252, 3600	5, 37	C <sub>14</sub> H <sub>23</sub> O <sub>2</sub> N	5, 90
HOCH <sub>2</sub> CH <sub>2</sub>	(CH <sub>3</sub> ) <sub>3</sub>	(CH <sub>3</sub> ) <sub>3</sub>	92	— <sup>**</sup>	244, 257 (1550, 850)	2238, 3420 3600	5, 81	C <sub>13</sub> H <sub>19</sub> O <sub>2</sub> N	6, 33
HOCH <sub>2</sub> CH <sub>2</sub>	H	C <sub>4</sub> H <sub>9</sub>	90	77—77.5 (aqueous alcohol)	220, 242, 257 (742, 603, 369)	2235, 3370 3600	6, 62	C <sub>12</sub> H <sub>19</sub> O <sub>2</sub> N	6, 69
CH <sub>3</sub> O <sub>2</sub> CCH <sub>2</sub>	H	C <sub>4</sub> H <sub>9</sub>	(fair)	—	—	1745, 2200 3350			
HOCH <sub>2</sub> CH <sub>2</sub>	H	C <sub>2</sub> H <sub>5</sub> CH <sub>2</sub>	80	110—112 (aqueous alcohol)	244, 259, 265, 269, 286 (657, 472, 222, 166, 55)	2260, 3270 3370	5, 96	C <sub>15</sub> H <sub>17</sub> O <sub>2</sub> N	5, 76
C <sub>4</sub> H <sub>9</sub>	H	C <sub>2</sub> H <sub>5</sub> CH <sub>2</sub>	74	73—74 (hexane)	244, 258, 265, 269 (842, 538, 281, 166)	2252, 3270 3600	5, 49	C <sub>17</sub> H <sub>21</sub> ON	5, 49

\* Oil,  $n_D^{25}$  1.5290.

† Oil,  $n_D^{25}$  1.5244.

‡ Oil,  $n_D^{25}$  1.5160.

\*\* Oil,  $n_D^{25}$  1.5458.

TABLE 2. Hydroxyamines of Aliphatic Series  $R(\text{CH}_2)_4 - \text{CHCH}_2\text{OH}$   
 $\text{NR}_1\text{R}_2$

R	R <sub>1</sub>	R <sub>2</sub>	Bp (in bath), °C (3 mm)	$n_D^{20}$	Found, %			Empirical formula	Calculated, %		
					C	H	N		C	H	N
$\text{HOCH}_2\text{CH}_2$	H	$\text{C}_4\text{H}_9$	175-185	1,4698	66,57	12,37	6,05	$\text{C}_{12}\text{H}_{27}\text{O}_2\text{N}$	66,31	12,52	6,45
$\text{C}_4\text{H}_9$	H	$\text{C}_2\text{H}_5$	130-135	1,4651	71,15	12,97	6,78	$\text{C}_{10}\text{H}_{21}\text{O}_2\text{N}$	71,58	13,52	6,96
$\text{C}_4\text{H}_9$	H	$\text{C}_4\text{H}_9$	130-140*	—	73,39	13,67	6,00	$\text{C}_{14}\text{H}_{31}\text{O}_2\text{N}$	73,30	13,62	6,11
$\text{HOCH}_2\text{CH}_2$	$(\text{CH}_2)_5$	H	120-140†	—	68,25	11,79	6,23	$\text{C}_{13}\text{H}_{27}\text{O}_2\text{N}$	68,07	11,87	6,11
$\text{HOCH}_2\text{CH}_2$	H	H	—	—	54,65	11,83	8,42	$\text{C}_8\text{H}_{17}\text{O}_2\text{N}$	59,59	11,88	8,69
$\text{C}_2\text{H}_5\text{C}(\text{OH})$	H	$\text{C}_4\text{H}_9$	180-190	1,4702	68,34	12,53	5,46	$\text{C}_{14}\text{H}_{31}\text{O}_2\text{N}$	68,52	12,73	5,71
$\text{CH}_3$											

\* Mp. 47-49°.

† Mp. 38-39°.

## EXPERIMENTAL

The IR spectra were taken on a DS-301 double-beam spectrophotometer (Japanese): for the liquid products as such, and for the crystalline products as KBr pellets or in  $\text{CHCl}_3$  solution. The UV spectra were taken on a "Unicam" spectrophotometer (British) in  $\text{C}_2\text{H}_5\text{OH}$  solution.

The starting compounds used in the work, namely (Ia) and the methyl ester of 4-bromo-3-butyric acid, were obtained as described in [1, 5]. The known bromoacetylene derivatives were obtained by the bromination of the corresponding acetylene compounds in potassium hypobromite solution [6]. 1-Bromo-4-acetoxy-1-butyne was obtained by the acetylation of 1-bromo-1-butyne-4-ol with excess acetyl chloride in the presence of triethylamine. Yield 85%, bp 35-38° (3 mm);  $n_D^{21,5}$  1.4800. Found: C 37.95; H 3.75; Br 41.96.  $\text{C}_6\text{H}_7\text{O}_2\text{Br}$ . Calculated: C 37.70; H 3.66; Br 41.88%.

**Preparation of Hydroxyamines of Diacetylene Series (II).** To a solution of 0.01 mole of 4-hydroxy-3-alkyl (or dialkyl)amino-1-butyne (Ia) in 10 ml of  $\text{CH}_3\text{OH}$ , containing 0.002 mole of  $\text{Cu}_2\text{Cl}_2$ , 0.002 mole of hydroxylamine hydrochloride and 0.04 mole of ethylamine (as 40% aqueous solution), in a nitrogen atmosphere, was added in drops, with cooling (8-10°) and vigorous stirring, a solution of 0.015-0.02 mole of the appropriate bromoacetylene derivative in 10 ml of methanol. The reaction mixture was kept at 10-15° for 1 h, treated with 10% HCl solution under ether, and the neutral layer was separated. The acid portion was saturated with  $\text{K}_2\text{CO}_3$  and the reaction product was repeatedly extracted with ether.

The crystalline products were recrystallized from a suitable solvent, while the liquid products were dried well in vacuo. The obtained substituted diacetylenes are listed in Table 1.

**Hydrogenation of Hydroxyamines of Diacetylene Series.** A solution of 0.005 mole of the appropriate hydroxyamine (II) in 20 ml of alcohol was hydrogenated at room temperature in the presence of  $\text{PtO}_2$  until the hydrogen absorption was complete (1.5-2 h). The catalyst was filtered and the hydrogenation product was vacuum-distilled. Some of the compounds obtained by us are listed in Table 2.

## CONCLUSIONS

We synthesized some previously unknown types of polyfunctionally substituted compounds of the diacetylene series by the condensation of 4-hydroxy-3-alkyl (or dialkyl)amino-1-butyne with various bromoacetylenes under the conditions of the Cadiot - Chodkiewicz reaction.

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