and the solution was stirred at −70°C for 30 min. It was then decomposed with water and worked up in the usual way to give 0.03 g (3%) of diastereomer IIa and 0.29 g (57%) of diastereomer IIb in a ratio of 5:95.

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C- AND N-ALKYLATION OF 4,5-DIHYDRO-1H-INDENO[1,2-b]PYRIDINE DERIVATIVES

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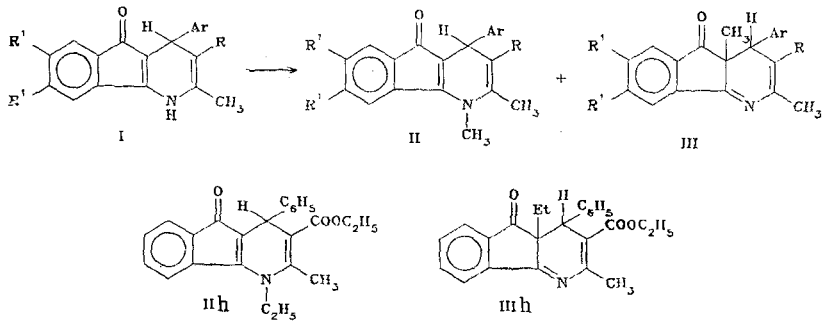
2-Methyl-4-aryl-5-oxo-4,5-dihydro-1H-indeno[1,2-b]pyridine derivatives react with methyl iodide in an aprotic medium in the presence of alkaline agents to give C- and N-alkylation products, viz., 2,4a-dimethyl- and 1,2-dimethyl-4-aryl-5-oxo-4,5-dihydroindeno[1,2-b]pyridines, and with dimethyl sulfate or methyl p-tosylate under the same conditions to give N-methylation products.

1,4-Dihydropyridine derivatives that contain electron-acceptor substituents attached to the $C_{(3)}$ and $C_{(5)}$ atoms and 5-oxo-4,5-dihydroindeno[1,2-b]pyridines are conjugated enamino ketone systems (from the IR spectra [1, 2] and their acidic properties [3]); however, the characteristic chemical properties of these systems have not yet been observed. Aminovinyl ketones of the indene series can be alkylated at one of three centers, viz., O, N, or C, depending on the conditions [4]; however, only N-alkyl derivatives are formed in the alkylation of 3,5-diethoxycarbonyl- [5] and 3,5-diacetyl-1,4-dihydropyridines [6] or 5-oxo-3-alkylthiocarbonyl-4,5-dihydroindeno[1,2-b]pyridine derivatives [3].

We have shown that 4,5-dihydro-1H-indeno[1,2-b]pyridine derivatives (I) in the presence of alkaline agents, i.e., in the anionic form, react with dimethyl sulfate or methyl p-toluenesulfonate to give exclusively N-methyl derivatives II, whereas their dual reactivity is manifested in the reaction with alkyl iodides, and mixtures of N- (II) and C-alkylation (III) products are formed.



I—III **a** R=$COOC_2H_5$, Ar=C_6H_5, R¹=H; **b** R=$COCH_3$, Ar=C_6H_5, R¹=H; **c** R=CN, Ar=C_6H_5, R¹=H; **d** R=R¹=H, Ar=C_6H_5; **e** R=$COOC_2H_5$, Ar=$C_6H_4NO_2$-4, R¹=H; **f** R=$COOC_2H_5$, Ar=$C_6H_4OCH_3$-4, R¹=H; **g** R=$COOC_2H_5$, Ar=C_6H_5, R¹=Cl

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TABLE 1. Quantitative Ratios of Indeno[1,2-b]pyridine Derivatives II and III in Alkylation[a]

Compound	Solvent	Alkylating agent	Percentage in the reaction mixture, %		III : II
			II	III	
Ia	Acetone	CH_3I	26	66	2,5
Ib	"	The same	24	43	1,8
Ic	"	" "	25	27	1,1
Id	"	" "	10	54	5,4
Ie	"	" "	21	37	1,8
If	"	" "	22	57	2,6
Ig	"	" "	13	36	2,6
Ia	THF	" "	30	58	1,9
Ia	DMF	" "	29	65	2,2
Ia	DMSO	" "	23	62	2,8
Ia	Hexametapol	" "	44	52	1,2
Ia	Acetonitrile	" "	22	67	3,1
Ia	Ethanol	" "	6	62	10,3
Ib	"	" "	4	31	8,7
Ib	THF	" "	16	57	3,6
Ia	Acetone	Dimethyl sulfate	65	<1	—
Ib	"	"	61	<1	—
Ia	"	Methyl p-tosylate	71	<1	—

[a]With KOH as the base.

An ambident anion that has reaction centers with different hardnesses is formed in the first step. The hard center of the $N_{(1)}$ anion undergoes reaction with a hard alkylating agent (dimethyl sulfate or methyl tosylate). The milder $C_{(4a)}$ center is preferred in the reaction with mild alkyl iodides, as a result of which C-alkylation products III dominate. The introduction of an electron-acceptor substituent at $C_{(3)}$ and in the 4 position of the phenyl ring increases the yield of the N-methyl derivative (Table 1). Substituents in the indene fragment (Ig) apparently do not affect the reactivity of the ambident anion. Replacement of CH_3I by ethyl iodide in acetone also leads to a mixture of N-alkyl (IIh) and C-alkyl (IIIb) products, although there are data [7] that indicate that this replacement suppresses the formation of the C-alkyl isomer.

The effect of solvents on the ratios of products II and III was investigated in the case of the alkylation of Ia with methyl iodide. In aprotic solvents the IIIa:IIa ratio ranges from 1.1 to 3.0 (Table 1); however, these data do not make it possible to draw conclusions regarding the dependence of the ratios of C- and N-alkylation products on the polarity or basicity of the medium. The amount of C-alkyl product increases sharply (IIIa:IIa = 10) when the alkylation is carried out in a proton-donor medium (ethanol); this is explained [8] by the formation of a hydrogen bond between the solvent and the anion.

No effect of the base used for the formation of the anion on the alkylation was observed. 4,5-Dihydro-1H-indeno[1,2-b]pyridine derivatives I are more acidic than their monocyclic analogs [3], and alkali metal hydroxides can be used in addition to NaH for the formation of the corresponding anions. The transition from NaOH to KOH also does not result in a change in the quantitative ratios of the alkylation products (II:III), although this transition increases the yields of the O-alkyl derivatives in the case of enolate anions [9].

The IR spectra of alkyl compounds III contain an absorption band of a 5-C=O group at 1730 cm^{-1}, which excludes the structure of an O-alkyl derivative. The presence of a ketone C=O group is also confirmed by the ^{13}C NMR spectrum of IIIa, which contains three signals of carbon atoms of CH_3 groups, viz., signals from OCH_2CH_3 at 13.7 ppm, from 4a-CH_3 at 20.6 ppm, and from 2-CH_3 at 21.5 ppm, and a C=O signal at 201.9 ppm (the signal of an ester C=C bond appears at 171.9 ppm). The character of the PMR spectrum (Table 2) of IIId (doublets of 3-H and 4-H protons) makes it possible to exclude alternative C-alkylation products such as those formed by substitution at $C_{(3)}$ or migration of the 4-H proton. The signals of the protons of the 4-C_6H_5 group of III form two multiplets with integral intensities of 2H and 3H, respectively, whereas the protons of the indene fragment form a multiplet (3H) and a doublet (1H) at weaker field, which apparently should be assigned to the 6-H proton.

The PMR spectra of I and II contain similar signals of aromatic protons and 2-CH_3 and 4-H protons; however, the structure of II is confirmed by the absence of a signal of the NH proton and the appearance of an N-CH_3 signal at ~3.65 ppm. The character of the UV absorption of I and II also does not differ; only a 15-nm bathochromic shift of the long-wave maxi-

TABLE 2. PMR Spectra of Indeno[1,2-b]dihydropyridines II-III (ppm)[a]

Compound	2-CH_3 (s, 3H)	4-H (s, 1H)	1-CH_3 (s, 3H)[b]	4a-CH_3 (s, 3H)[b]	3-R	4-Ar	Indene fragment
IIa	2,51	4,99	3,61	—	1,10 (t, 3H); 4,01 (q, 2H);	7,07—7,37 (m, 9H)	
IIb	2,08	4,77	3,63	—	2,32 (s, 3H)	7,11—7,60 (m, 9H)	
IIc	2,28	4,41	3,62	—	—	7,01—7,70 (m, 9H)	
IId	2,04	4,51[c]	3,59	—	5,01 (d, 1H)	7,09—7,44 (m, 9H)	
IIe	2,57	5,09	3,64	—	1,07 (t, 3H); 4,01 (q, 2H)	7,39 (d, 2H); 8,02 (d, 2H)	7,12—7,38 (m, 4H)
IIf	2,54	4,98	3,67	—	1,18 (t, 3H); 4,10 (q, 2H)	3,73 (s, 3H, OCH_3); 6,74 (d, 2H)	7,11—7,44 (m, 6H)
IIg	2,44	4,82	3,69	—	1,11 (t, 3H); 4,02 (q, 2H)	7,19 (s, 5H)	7,40 (s, 1H); 7,74 (s, 1H)
IIh	2,58	5,02	—	—	1,13 (t, 3H); 4,06 (q, 2H)	6,93—7,47 (m, 9H)	
IIIa	2,64	4,23	—	1,32	1,13 (t, 3H); 4,08 (q, 2H)	6,92 (br. s, 5H)	7,38—7,81 (m, 3H); 8,06 (d, 1H)
IIIb	2,48	4,21	—	1,23	2,12 (s, 3H)	6,73—6,98 (m, 2H); 6,94—7,08 (m, 3H)	7,59—7,92 (m, 3H); 8,04 (d, 1H)
IIIc	3,22	3,99	—	1,32	—	6,72—6,90 (m, 2H); 6,98—7,14 (m, 3H)	7,62—7,98 (m, 3H); 8,08 (d, 1H)
IIId	2,27	3,40[c]	—	1,41	5,53 (d, 1H)	7,03 (s, 5H)	7,38—7,81 (m, 3H); 8,10 (d, 1H)
IIIe	2,66	4,30	—	1,34	1,13 (t, 3H); 4,09 (q, 2H)	7,04 (d, 2H); 7,83 (d, 2H)	7,52—7,77 (m, 3H); 8,06 (d, 1H)
IIIf	2,68	4,24	—	1,36	1,21 (t, 3H); 4,13 (q, 2H)	3,40 (s, 3H, OCH_3); 6,54 (d, 2H); 6,87 (d, 2H)	7,51—7,84 (m, 3H); 8,11 (d, 1H)
IIIg	2,59	4,18	—	1,32	1,14 (t, 3H); 4,07 (q, 2H)	6,71—6,89 (m, 2H) 6,98—7,10 (m, 3H)	8,00 (s, 1H); 8,36 (s, 1H),
IIIh	2,67	4,34	—	—	1,20 (t, 3H); 4,12 (q, 2H)	6,98 (s, 5H)	7,47—7,84 (m, 3H); 8,10 (d, 1H)

[a]The PMR spectra of IIa, e, f, h-IIIa, e, f, h and IId-IIId were obtained from solutions in $CDCl_3$, and the PMR spectra of IIb, c, g-IIIb, c, g were obtained from solutions in d_6-DMSO. [b]Compound IIh: 1.46 (s, 3H, CH_3) and 4.14 ppm (q, 2H, CH_2); IIIh: 0.76 (t, 3H, CH_3) and 1.96 ppm (q, 2H, CH_2). [c]Doublet, J_{3H-4H} = 4.5 Hz for IId and 6.5 Hz for IIId. [d]The remaining two protons are overlapped by the multiplet of the indene fragment.

TABLE 3. Characteristics of the Compounds Obtained

Compound	mp, °C	Found, %			Empirical formula	Calc., %			Long-wave λ_{max} of the UV spectrum, nm (log ε)
		C	H	N		C	H	N	
Ig	251—253	63,4	4,0	3,5	$C_{22}H_{17}Cl_2NO_3$	63,8	4,1	3,4	484 (3,38)
IIa	145—147	77,1	5,7	3,9	$C_{23}H_{21}NO_3$	76,9	5,9	3,9	496 (3,45)
IIb	160—161	79,9	5,8	4,3	$C_{22}H_{19}NO_2$	80,2	5,8	4,2	498 (3,48)
IIc	189—191	80,2	5,0	9,1	$C_{21}H_{16}N_2O$	80,7	5,2	9,0	486 (3,45)
IId	137—139	83,3	5,9	4,9	$C_{20}H_{17}NO$	83,6	6,0	4,9	506 (3,51)
IIe	154—156	67,9	4,7	7,0	$C_{23}H_{20}N_2O_5$	68,3	5,0	6,9	486 (3,45)
IIf	135—137	73,8	6,0	3,4	$C_{24}H_{23}NO_4$	74,0	5,9	3,6	488 (3,45)
IIg	173—175	64,2	4,8	3,5	$C_{23}H_{19}Cl_2NO_3$	64,5	4,5	3,3	500 (3,38)
IIh	137—139	76,9	6,3	3,9	$C_{24}H_{23}NO_3$	77,2	6,2	3,7	496 (3,41)
IIIa	126—127	76,9	5,4	4,1	$C_{23}H_{21}NO_3$	76,9	5,9	3,9	316 (3,88), 339 (3,88)
IIIb	153—154	79,9	5,8	4,3	$C_{22}H_{19}NO_2$	80,2	5,8	4,2	320 (3,87), 340 (3,90)
IIIc	181—183	81,0	5,6	9,3	$C_{21}H_{16}N_2O$	80,7	5,2	9,0	316 (3,90), 335 (3,90)
IIId	173—175	84,0	6,2	5,0	$C_{20}H_{17}NO$	83,6	6,0	4,9	305 (3,78), 331 (3,78)
IIIe	153—154	68,0	5,3	7,0	$C_{23}H_{20}N_2O_5$	68,3	5,0	6,9	311 (3,95), 334 (3,90)
IIIf	118—119	73,7	5,6	3,9	$C_{24}H_{23}NO_4$	74,0	5,9	3,6	309 (3,81), 336 (3,79)
IIIg	146—148	64,9	4,8	3,1	$C_{23}H_{19}Cl_2NO_3$	64,5	4,5	3,3	321 (3,93)
IIIh	163—165	77,5	6,0	3,7	$C_{24}H_{23}NO_3$	77,2	6,2	3,7	316 (3,90), 340 (3,89)

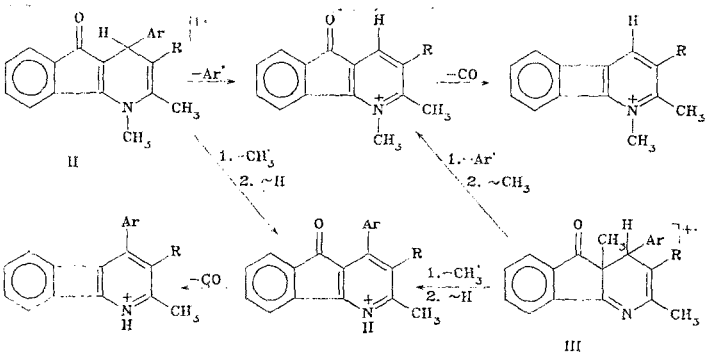
mum is observed for N-alkyl derivatives II (Table 3). Two absorption maxima of equal intensity at ∿310 and ∿340 nm, which merge partially and form a characteristic "hump" at 300-350 nm, are characteristic for the UV spectra of III. The IR spectra of the synthesized N-methyl derivatives II at 1500-1800 cm^{-1} are in agreement with the regularities of the β-aminovinyl ketone system [1, 2].

TABLE 4. Characteristic Ions in the Mass Spectra of II and III

Compound	m/z values (intensities in percent of the maximum ion)											
	$M^{+\cdot}$	$[M-H]^+$	$[M-H-CO]^+$	$[M-CH_3]^+$	$[M-CH_3-CO]^+$	$[M-Ar]^+$	$[M-Ar-CO]^+$	$[M-R]^+$	$[M-R-O]^+$	$[M-CH_4]^{+\cdot}$	$[M-C_2H_5O]^+$	$[M-C_2H_5O]^{+\cdot}$
IIa	359 (28)	358 (25)	330 (44)	344 (17)	316 (7)	282 (100)	254 (44)	286 (33)	270 (7)		314 (11)	313 (3)
IIIa	359 (37)	358 (28)	330 (43)	344 (17)	316 (7)	282 (100)	254 (41)	286 (33)	270 (7)		314 (11)	313 (4)
IIb	329 (49)	328 (8)	300 (9)	314 (68)	286 (24)	252 (100)	—	286 (24)	270 (8)	313 (5)	—	—
IIIb	329 (37)	328 (51)	300 (6)	314 (47)	286 (53)	252 (100)	—	286 (53)	270 (9)	313 (5)	—	—
IIc	312 (10)	311 (12)	—	297 (24)	—	235 (100)	—	—	—	296 (6)	—	—
IIIc	312 (8)	311 (11)	—	297 (23)	—	235 (100)	—	—	—	—	—	—
IId	287 (5)	286 (3)	258 (6)	272 (25)	244 (3)	210 (9)	—	286 (3)	270 (100)	271 (83)	—	—
IIId	287 (26)	286 (50)	258 (4)	272 (67)	244 (4)	210 (100)	—	286 (50)	270 (2)	271 (2)	—	—
IIe[a]	404 (14)	—	375 (2)	389 (1)	—	282 (10)	—	—	—	388 (14)	359 (2)	358 (8)
IIIe	404 (13)	403 (3)	375 (41)	389 (11)	361 (4)	282 (100)	254 (46)	331 (21)	—	—	359 (8)	—
IIf	389 (38)	388 (3)	360 (24)	374 (100)	346 (41)	282 (39)	254 (35)	316 (22)	300 (14)	373 (86)	344 (41)	343 (13)
IIIf	389 (53)	388 (72)	360 (100)	374 (56)	346 (16)	282 (94)	254 (31)	316 (94)	300 (12)	—	344 (21)	343 (9)

[a] m/z 45 (100).

Compounds IIa-f and IIIa-f are characterized mass spectrometrically (Table 4) by medium or high intensities of the molecular ions (8-53% of the maximum peak). The fragmentation of the molecular ions of II and III proceeds via several pathways, of which two typical examples are shown in the Scheme:



The first step in the fragmentation is detachment of an N-methyl (4a-C-methyl) radical and simultaneous detachment of radicals from the 3 and 4 positions. Detachment of the large $C_6H_4R^1$ radical from the 4 position is the dominant process in most cases. This is followed by elimination of CO molecules. Elimination of a molecule of CH_4 occurs at the same time as splitting out of radicals in the case of IIb-f and IIIb, d. If R = $COOC_2H_5$ (IIa, e, f and IIIa, e, f), in addition to splitting out of R$^\cdot$, characteristic (for the ester grouping) detachment of $OC_2H_5^\cdot$ is observed, and ejection of a molecule of C_2H_5OH occurs owing to the ortho effect. The $(M - OCH_3)^+$ and $(M - CH_2O)^{+\cdot}$ fragments do not appear in the mass spectra; this constitutes evidence for the absence of the O-methylated form. Compounds IIf and IIIf, in the mass spectra of which the appearance of these fragments is due to the substituent in the 4-phenyl ring, constitute an exception.

The presence of a para substituent in the 4-phenyl ring complicates the fragmentation somewhat. Thus the ejection of CHO$^\cdot$ and CH_2O fragments, which is characteristic for a methoxy substituent in aromatic compounds, from the molecular ions of IIf and IIIf takes place at the same time as the processes described above. The ejection of not only CO but also NO, which

is characteristic for aromatic nitro compounds, occurs in the fragmentation of IIe and IIIe after primary detachment of radicals.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded with a Brucker WH-90 spectrometer with tetramethylsilane as the internal standard. The UV spectra of $5 \cdot 10^{-5}$ mole/liter solutions of the compounds in ethanol were obtained with a Specord UV-vis spectrophotometer. The mass spectra were recorded with an AEI MS-50 spectrometer at an ionizing-electron energy of 70 eV; the substances were introduced through the direct-input system, and the temperature of the ionization chamber was 150°C. Compounds I were synthesized by the methods in [10, 11]; 2-ethoxycarbonyl-5,6-dichlorindan-1,3-dione and 2-benzylidene-5,6-dichloroindan-1,3-dione, which were obtained in analogy with the known method for the synthesis of compounds of this class [12], were used as starting compounds for the synthesis of Ig. The characteristics of the synthesized I-III are presented in Table 3. All of the solvents were dried and distilled prior to the experiments.

Method for the Determination of the Ratios of the Alkylation Products. A 2-mmole sample of I was dissolved in the investigated solvent, and 0.6 g of ground KOH or 0.2 g of NaH was added. After hydrogen evolution had ceased, 5 mmole of the alkylating agent was added to the dark-blue solution, and the mixture was allowed to stand until the blue coloration vanished. The solution was filtered, the solvent was evaporated in vacuo (except in the case of DMF, hexametapol, and DMSO, 5-10 ml amounts of which were used), and the residue was transferred to a volumetric flask and brought up to the 25-ml mark with ethanol. A 0.03-0.05 ml sample of the investigated solution was applied to ethanol-washed Silufol UV-254 plates in the form of a continuous line and chromatographed in a chloroform–hexane–acetone system (9:7:1). Clearly distinguishable sections I (red), II (dark red), and III (yellow), which were eluted with definite volumes of ethanol, were cut out from the chromatograms after drying. The quantitative determination of the products was carried out by means of measurements of the optical densities at the characteristic long-wave λ_{max} bands of standard compounds under the condition of satisfaction of Beer's law over the range of concentrations of the analyzed solutions.

Column chromatography (on L 100/160 silica gel; the eluent is indicated above) was used for the preparative separation of the mixtures of products II and III. Chromatography was not required in the preparative synthesis of IIIa (55% yield) from Ia in ethanol. Compounds II and III were recrystallized from ethanol.

Synthesis of N-Methyl Derivatives of 4,5-Dihydroindeno[1,2-b]pyridines (II). A 0.36-g (0.015 mole) sample of NaH was added to 0.01 mole of I in the minimum volume of hexametapol. After the anion had formed, 1.9 ml (0.02 mole) of dimethyl sulfate was added, and the mixture was allowed to stand for 1 h. Water (200 ml) was added carefully, and the dark-red precipitate was removed by filtration, washed with water, and crystallized. The yield of products IIa-c, e were 69, 52, 61, and 62%, respectively.

2-Ethoxycarbonyl-5,6-dichlorindan-1,3-dione. A mixture of 10.8 g (0.05 mole) of 4,5-dichlorophthalic anhydride, 7.2 g (0.55 mole) of acetoacetic ester, 160 ml of acetic anhydride, and 15.2 g (0.15 mole) of triethylamine was allowed to stand for 24 h, after which it was poured into a mixture of 200 g of ice and 50 ml of concentrated HCl. The precipitate was removed by filtration and washed with water to give 13 g (91%) of a product with mp 270°C. The product decomposed to give 5,6-dichloroindan-1,3-dione, with mp 284-286°C, upon recrystallization from acetic acid or ethanol. IR spectrum: 1710 cm^{-1} (C=O). PMR spectrum ($CDCl_3$): 3.24 (s, 2H, CH_2) and 8.07 ppm (s, 2H, Ar). Found: C 50.5; H 2.2%. $C_9H_4Cl_2O_2$. Calculated: C 50.3; H 1.9%.

2-Benzylidene-5,6-dichloroindan-1,3-dione. A 14.4-g (0.05 mole) sample of 2-ethoxycarbonyl-5,6-dichloroindan-1,3-dione was dissolved in 10 ml of glacial CH_3COOH, 5 ml (0.05 mole) of benzaldehyde was added, and the mixture was refluxed for 10 min. When the solution was cooled, 10.3 g (68%) of yellow 2-benzylidene-5,6-dichlorindan-1,3-dione, with mp 205-207°C (ethanol), precipitated. IR spectrum: 1720 (C=O) and 1680 cm^{-1} (C=C). PMR spectrum ($CDCl_3$): 7.91 (s, 1H, CH), 8.08 (s, 2H, Ar), 7.44-7.61 (m, 3H, Ar), and 8.33-8.51 ppm (m, 2H, Ar). Found: C 63.0; H 2.5%. $C_{10}H_6Cl_2O_2$. Calculated: C 63.4; H 2.7%.

2-Methyl-3-ethoxycarbonyl-4-phenyl-5-oxo-7,8-dichloro-4,5-dihydro-1H-indeno[1,2-b]pyridine (Ig). A mixture of 9 g (0.03 mole) of 2-benzylidene-5,6-dichloroindan-1,3-dione and 4 g (0.03 mole) of ethyl β-aminocrotonate in 20 ml of glacial acetic acid was refluxed for 5 min, after which it was cooled, and the dark-red precipitate was removed by filtration and recrystallized from ethanol to give 4.8-5.2 g (61-66%) of product.

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NEW METHOD FOR THE PREPARATION OF O-CARBAMOYL DERIVATIVES IN THE 4-HYDROXYAMINOIMIDAZOLIDIN-2-ONE SERIES

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The corresponding 4-(O-carbamoylhydroxyamino)imidazolidin-2-ones were obtained by cyclization of O,N-dicarbamoyl derivatives of N-(3-oximino-2-methyl-2-butyl)- and N-(1-oximino-2-cyclohexyl)methylamines in alkaline media. It was shown that the carbamoylation of 1-methyl-4,5-tetramethylene-3-(3,4-dichlorophenyl)-4-hydroxyaminoimidazolidin-2-one gives, respectively, an O- or N-carbamoyl derivative, depending on whether it is carried out in alkaline or neutral solutions.

Only a few examples of the synthesis of, primarily, unstable O-acylated hydroxylamines have been described in the literature [1-5].

We have found a new method for the preparation of O-carbamoylated hydroxylamines of the heterocyclic series; this method consists in the alkaline cyclization of O,N-dicarbamoyl derivatives (IIIa, b and IVa, b), which, in turn, were obtained by carbamoylation of the E-oximes (I, II) with 2 moles of aryl isocyanates. The 4-(O-arylcarbamoylhydroxyamino)imidazolidin-2-ones (Va, b and VIa, b) are stable at room temperature. Two bands of carbonyl groups at 1630-1680 and 1710-1740 cm^{-1} are observed in their IR spectra. Signals of protons of $C(CH_3)_2$ groups at 1.08 and 1.20 ppm, of $C-CH_3$ and $N-CH_3$ groups at 1.30 and 2.63 ppm, and of two NH groups at 7.95 and 9.60 ppm are present in the PMR spectrum of, for example, Vb.

An attempt to synthesize Va, b and VIa, b by direct carbamoylation of the starting 4-hydroxyaminoimidazolidin-2-one was unsuccessful. Thus the reaction of 1-methyl-4,5-tetramethylene-3-(3,4-dichlorophenyl)-4-hydroxyaminoimidazolidin-2-one (VII) with 3,4-dichlorophenyl isocyanate gave X, which, in contrast to VIb, gives a positive reaction with an alcohol solution of ferric chloride for the presence of a hydroxamic acid fragment in its molecule. Absorption bands of carbonyl groups at 1660-1690 cm^{-1} (i.e., over a range of frequencies lower than 1700 cm^{-1}) are present in the IR spectrum of X; this is characteristic for N-carbonyl derivatives of hydroxylamine. In contrast to the PMR spectrum of VIb, a

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