INVESTIGATIONS IN THE IMIDAZOLE SERIES

XXXIX. 2,3-Diphdropyrrolo[1,2-a]imidazoles*

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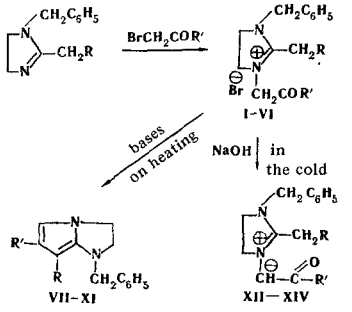
The synthesis of derivatives of 2,3-dihydropyrrolo[1,2-a]imidazole from 1,2-dialkylimidazolines or 1,2-diarylkylimidazolines and phenacyl bromides with subsequent heating of the 1,2-disubstituted 3-phenacylimidazolinium bromides in aqueous or ethanolic solution in the presence of bases has been effected.

A number of 3-oxo derivatives of 2,3-dihydropyrrolo[1,2-a]imidazole obtained by a complex multistage synthesis from aliphatic compounds has been described in the literature [1,2].

Continuing previous investigations [3–7], we have studied the quaternization of 1-benzyl-2-methyl- and 1,2-dibenzylimidazolines with phenacyl bromide and some of its p-substituted derivatives, obtaining in this way previously-unreported quaternary 1-benzyl-2-methyl- or 1,2-dibenzyl-3-phenacylimidazolinium salts (I–VI, table), the structure of which is confirmed by IR spectroscopy [presence of a band at 1690 cm^{-1} (CO) in III].

When the imidazolinium bromides were boiled in an aqueous solution of $NaHCO_3$ (III–VI) or NaOH (III) or in an ethanolic solution of C_2H_5ONa (II), as in the case of the imidazolium halides [3, 4, 6, 7], closure of the pyrrole ring took place with the formation of previously-unknown derivatives of 2,3-dihydropyrrolo[1,2-a]imidazoles (VII–XI, table).

Under the action of NaOH in aqueous solution in the cold on the bromides I, III, and V (and also from I on heating with $NaHCO_3$ in aqueous solution), the corresponding anhydrobases XII–XIV were isolated, as took place in the case of imidazolium halides [5, 7]. Compounds XII–XIV gave qualitative color reactions



with chloranil and picryl chloride. However, these compounds differ from the anhydrobases of the imidazole series in structure and properties. The latter, judging from their IR spectra (absence of an absorption band of a CO group) are O-betaines [7], while compounds XII–XIV have a sharp absorption bands of a CO group (1640 and 1655 cm^{-1}) are, apparently, C-betaines. The UV spectra of XII–XIV have two absorption maxima in the 240 and 310 nm regions. Similar forms of the anhydrobases (O- and C-betaines) have been observed by Kröhnke in the action of caustic soda on phenacylpyridinium bromides [8, 9]. The 2-methyl-3-p-nitrophenacyl-1,4,5-triphenylimidazolium O-betaine that we have isolated previously [7] readily cyclizes on being heated in water into the corresponding pyrrolo[1,2-a]-imidazole. Imidazolinium anhydrobases are also capable of undergoing conversion into derivatives of 2,3-dihydropyrrolo[1,2-a]imidazole. Thus, when XIV was heated in water it gave X.

EXPERIMENTAL

1-Benzyl-2-methyl- and 1,2-dibenzylimidazolines were prepared by published methods [10,11].

1-Benzyl-2-methyl- and 1,2-dibenzyl-3-phenacylimidazolinium bromides (I–VI, table). To a solution of 0.02 mole of the appropriate bromoketone in 35–50 ml of acetone was added 0.02 mole of a 1,2-disubstituted imidazoline (in the case of 1,2-dibenzylimidazoline and p-methylphenacyl bromide, at a temperature not above 0° C). The mixture was boiled for 2 hr (in the preparation of I–III), left at room temperature for 24 hr (V and VI) or kept at 0–2° C for 15–20 min (IV), and then the precipitate was filtered off and washed with acetone. The caramel-like bromide IV was isolated by decanting the solution. The salts obtained were fairly pure and were used for conversion into the dihydropyrroloimidazoles without recrystallization.

2,3-Dihydropyrrolo[1,2-a]imidazoles (VII–XI, table). A) To a solution of 4 M of an imidazolium bromide (III–VI) in 250–300 ml of water was added 4.4 mM of $NaHCO_3$, the mixture was boiled for 2 hr and cooled, and the precipitate (VIII–XI) filtered off and washed with water.

B) To a solution of 4.4 mM of III in 150 ml of water was added 4.8 mM of NaOH. The mixture was boiled and treated as described above. The yield of VIII was 1.2 g (77.5%).

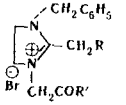
C) To a solution of 8 mM of II in 40 ml of anhydrous ethanol was added a solution of C_2H_5ONa prepared from 8.8 mM of sodium and 10 ml of anhydrous ethanol. The mixture was boiled for 1 hr and cooled, and the precipitate of VII was filtered off.

D) A suspension of 0.1 g of XIV in 10 ml of water was heated to the boil and cooled, and the precipitate was filtered off. The yield of X was 0.08 g (83%), mp 128–129° C (from ethanol). A mixture with the X obtained by method (A) gave no depression of the melting point.

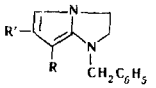
1-Benzyl-2-methyl-3-phenacylimidazolium anhydrobase (XII). A) A solution of 1 g (2.7 mM) of the bromide I in 50 ml of water was treated with 0.25 g (3 mM) of $NaHCO_3$. The mixture was boiled for 1.5 hr and cooled, and after decantation of the aqueous solution the brown oil that had separated out was triturated with ethanol, whereupon it crystallized. The yield of technical XII was 0.6 g (76.5%). Pale yellow crystals with mp 141–142° C (from ethanol), insoluble in water and ether, soluble in benzene and acetone. Gives a crimson coloration with picryl chloride and a blue-green one with chloranil. Found, %: C 77.68; H 6.69; N 9.51. Calculated for $C_{19}H_{20}N_2O$, %: C 78.05; H 6.89; N 9.58. IR spectrum (in paraffin oil): 1640 cm^{-1} (γ_{CO}); UV spectrum: λ_{max} 235 and 306 nm (ε 1.35×10^4 and 1.414×10^4).

B) A cooled solution of 1 g (2.7 mM) of the bromide I in 100 ml of water was treated with 0.12 g (3 mM) of NaOH and left at room tem-

* For part XXXVIII, see [7].



I–VI



VII–XI

Compound	R	R′	Mp, °C*	Empirical formula	Found, %				Calculated, %				Yield, %
					C	H	Br	N	C	H	Br	N	
I	H	C_6H_5	240 (decomp.)	$C_{19}H_{21}BrN_2O$	60.84	5.64	21.48	7.54	61.13	5.67	21.40	7.50	73
II	H	p-$CH_3C_6H_4$	275 (decomp.)	$C_{20}H_{23}BrN_2O$	62.15	5.78	20.49	7.40	62.02	5.98	20.63	7.23	89
III	H	p-BrC_6H_4	275—276	$C_{19}H_{20}Br_2N_2O$	50.60	5.20	35.65	6.08	50.46	4.46	35.34	6.19	93
IV**	C_6H_5	p-$CH_3C_6H_4$	—	$C_{26}H_{27}BrN_2O$	—	—	—	—	—	—	—	—	—
V	C_6H_5	p-BrC_6H_4	202—204	$C_{25}H_{24}Br_2N_2O$	57.41	4.59	30.12	5.31	56.84	4.58	30.25	5.30	50
VI	C_6H_5	p-$O_2NC_6H_4$	200—202	$C_{25}H_{24}BrN_3O_3$	60.40	4.94	16.26	8.20	60.73	4.89	16.17	8.49	52
VII	H	p-$CH_3C_6H_4$	90—91 (decomp.)	$C_{20}H_{20}N_2$	82.73	6.91	—	10.12	83.29	6.99	—	9.72	45
VIII	H	p-BrC_6H_4	126—127	$C_{19}H_{17}BrN_2$	65.22	5.17	22.60	8.15	64.59	4.85	22.62	7.93	64
IX	C_6H_5	p-$CH_3C_6H_4$	113—115 (decomp.)	$C_{26}H_{24}N_2$	85.84	6.79	—	7.48	85.68	6.64	—	7.68	64
X	C_6H_5	p-BrC_6H_4	129 (decomp.)	$C_{25}H_{21}BrN_2$	69.56	4.92	18.71	6.65	69.94	4.93	18.61	6.53	89
XI	C_6H_5	p-$O_2NC_6H_4$	145—147	$C_{25}H_{21}N_3O_2$	75.87	5.59	—	10.40	75.93	5.35	—	10.63	87

*For analysis, the compounds were purified by crystallization: **I-III, V,** and **VI** from anhydrous ethanol, and **VII-XI** from ethanol.

IV is a hygroscopic caramel-like substance; it was not subjected to analysis and was used for the preparation of **IX in the form of the technical product.

perature for 24 hr, after which the oil that had separated out was triturated with ethanol. Yield 0.7 (88.2%), mp 141–142° C (from ethanol).

1-Benzyl-3-p-bromophenacyl-2-methylimidazolium anhydrobase (XIII). This was obtained in a similar manner to **XII** (Method B). Yield 61%. Cream-colored crystals with mp 139–141° C (from ethanol), insoluble in water, soluble in the majority of organic solvents. A mixture with **VIII** melted at 120° C. Found, %: C 61.46; H 5.25; Br 21.85; N 7.68. Calculated for $C_{19}H_{19}BrN_2O$, %: C 61.46; H 5.16; Br 21.52; N 7.55. IR spectrum (in paraffin oil): 1655 $cm^{-1}(\nu_{CO})$. UV spectrum: λ_{max} 245 and 312 nm (ε 1.9×10^4 and 1.514×10^4). Like **XII**, it gave qualitative reactions with picryl chloride and chloranil.

1,2-Dibenzyl-3-p-bromophenacylimidazolium anhydrobase (XIV). This was obtained in a similar manner to **XII** (method B). Yield 71%, mp 58–60° C. On treatment with hydrogen bromide it was converted into the initial bromide **V**. IR spectrum: 1725 cm^{-1} (CO). UV spectrum: λ_{max} 245 nm (shoulder) (log ε 4.13) and λ_{max} 310 nm (log ε 3.67). Found, %: C 67.50; H 5.21; Br 17.68; N 6.08. Calculated for $C_{25}H_{23}BrN_2O$, %: C 67.12; H 5.18; Br 17.87; N 6.26. C 67.12; H 5.18; Br 17.87; N 6.26%.

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