$$\begin{bmatrix} Me_2S^+ - OH \end{bmatrix} \xrightarrow{-H_2O} \begin{bmatrix} Me_2S^+ \end{bmatrix} + Me_2SO \iff \begin{bmatrix} Me_2S^+ \end{bmatrix} = SMe_2 \end{bmatrix}$$
(3)  
$$\begin{bmatrix} Me_2S^- OH \end{bmatrix}^0 \xrightarrow{(V)} \begin{bmatrix} (V) & (V1) \end{bmatrix}$$

Change in the ratio of the initial components of the HBr/DMSO system leads to a change in the concentration of the intermediates oxidizing the metal. This also apparently accounts for the extremal dependence of the rate of silver dissolution on the ratio of the starting components. The rate is invariant over time.  $E_{act} = 59.5\pm0.2 \text{ kJ/mole}$  and log A =  $9.2\pm0.6$ .

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REACTIONS OF ESTERS OF 3-PHENYL-3-CHLORO-2-OXOPROPIONIC

ACID WITH 2-AMINOPYRIDINES AND 2-AMINOQUINOLINE

2380

V. A. Mamedov, I. A. Nuretdinov,	UDC 542.91:547.589.4'26:
and F. G. Sibgatullina	547.822.7:547.831.6

The reaction of esters of 3-phenyl-3-chloro-2-oxopropionic acid with 2-aminopyridines and 2-aminoquinoline in chloroform at reflux gave derivatives of imidazo-[1,2-a]pyridine and imidazo[1,2-a]quinoline in high yield.

In the present work, we report the reactions of the methyl and ethyl esters of 3-phenyl-3-chloro-2-oxopropionic acid with 2-aminopyridines and 2-aminoquinoline. The reactions of  $\alpha$ -haloketones with 2-aminopyridines leading to derivatives of imidazo[1,2-a]-pyridine and carried out in water-alcohol mixtures or in the absence of solvent give high yields of the final product [1-3]. We have shown that the reactions of esters of 3-phenyl-3-chloro-2-oxopropionic acid with 2-aminopyridines in chloroform at reflux lead to derivatives of imidazo[1,2-a]pyridine with high yields

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 $\begin{array}{ll} \mathbb{R} = \mathrm{Me} \ (\mathrm{Ia}), \ \mathrm{Et} \ (\mathrm{Ib}); & \mathbb{R}' = \mathrm{H} \ (\mathrm{IIa}), & \mathrm{Br} \ (\mathrm{IIb}); & \mathbb{R} = \mathrm{Me}, & \mathbb{R}' = \mathrm{Me}, & \mathbb{R}' = \mathrm{He}, & \mathbb{R}' = \mathbb$ 

The final products, namely, free bases of imidazo[1,2-a]pyridines are obtained after treatment of salts (III) by 5% aq. sodium bicarbonate. In the case of R = Me and R' = Br, the final product was isolated and characterized as quaternized salt (III). The IR spectrum of this salt contains bands for the carbonyl group and C=N bond at 1740 and 1640 cm<sup>-1</sup>, respectively, and lacks signals for N-H and OH groups. The PMR spectrum shows signals for protons of the pyridine ring and phenyl group at 7.00-8.16 ppm and lacks signals for N-H and OH groups. The elemental analysis data support the formation of 2-methoxycarbonyl-3-hydro-3-phenyl-6-bromoimidazo[1,2-a]pyridinium-4 chloride. We should note that the data on quaternized compounds in such reactions are not unequivocal. Thus, Abighente et al. [3] have shown that the reaction of 3-bromo-1,1,1-trifluoroacetone with aminopyridine gives 2-hydroxy-2-trifluoromethyl-2,3-dihydro-1H-imidazo[1,2-a]pyridinium-4 bromide.

The signals for the protons of the pyridine ring and phenyl group in the PMR spectra of (IVa) - (IVd) are observed at 6.71-7.86 ppm. The introduction of a bromine atom at C<sup>6</sup> in (IVb) and (IVd) significantly simplifies the spectrum of this region. Comparison of the spectra of (IVa) and (IVb) and of the spectra of (IVc) and (IVd) using the data of Paolini [4] and Paudler [5] permit us to assign the signals in this spectral region (data given in the Experimental).

2-Aminoquinoline reacts with methyl 3-phenyl-3-chloro-2-oxopropionate by analogy with 2-aminopyridines to give the corresponding imidazo[1,2-a]quinoline derivatives.



The structures and purity of (IVa)-(IVd) and (V) were confirmed by IR and PMR spectroscopy and elemental analysis.

## EXPERIMENTAL

The IR spectra were taken in vaseline mull on a UR-2 spectrometer. The PMR spectra were taken on a Varian T-60 spectrometer with TMS as the internal standard.

 $\frac{2-\text{Methoxycarbonyl-3-hydro-3-phenyl-6-bromoimidazo[1,2-a]pyridinium-4 chloride (III)}{2-\text{amino-5-bromopyridine}} and 2.1 g (0.01 mole) methyl 3-phenyl-3-chloro-2-oxopropionate (Ia) in 40 ml chloroform was heated at reflux for 6 h. The solvent was distilled off in vacuum. Then, 30 ml ether was added to the residue. The crystals formed were filtered off to give 3.5 g (96%) (III), mp 172-174°C. PMR spectrum in CD<sub>3</sub>OD (<math>\delta$ , ppm): 3.83 s (OCH<sub>3</sub>), 6.23 s (CH), 7.00-8.16 m (protons of the pyridine ring and phenyl group). Found: C, 49.41; Cl, 9.71; N, 7.68%. Calculated for  $C_{15}H_{12}BrClN_2O_2$ : C, 49.00; Cl, 9.65; N, 7.61%.

<u>2-Methoxycarbonyl-3-phenylimidazo[1,2-a]pyridine (IVa)</u>. A solution of equimolar amounts of 2-aminopyridine and methyl 3-phenyl-3-chloro-2-oxopropionate (Ia) in chloroform was heated at reflux for 6 h. Chloroform was removed in vacuum. Then, 5% aq. NaHCO<sub>3</sub> was added to the residue and maintained at 60-70°C for 1 h. The mixture was extracted with chloroform. The extract was washed with water and dried over MgSO<sub>4</sub>. The solvent was removed and ether was added to the residue. The crystals formed were filtered off to give (IVa) in 91% yield, mp 133-135°C. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1710 (C=O). PMR spectrum in CDCl<sub>3</sub> ( $\delta$ , ppm, J, Hz): 3.83 s (OCH<sub>3</sub>), 7.46 s (C<sub>6</sub>H<sub>5</sub>), 6.71 split t (H<sup>6</sup>, 1H), 7.21 split t (H<sup>7</sup>, 1H), J<sub>5,7</sub> = 1.0, J<sub>6,7</sub> = 7.2, J<sub>6,8</sub> = 1.2, J<sub>6,5</sub> = 6.5, and J<sub>7,8</sub> = 10.0. Found: C, 71.21; H, 4.69; N, 11.55%. Calculated for C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>: C, 71.44; H, 4.75; N, 11.10%. Compounds (IVb)-(IVd) and (V) were obtained similarly.

<u>2-Ethoxycarbonyl-3-phenylimidazo[1,2-a]pyridine (IVc)</u> was obtained in 92% yield, mp 88-90°C. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1715 (C=O). PMR spectrum in CDCl<sub>3</sub> ( $\delta$ , ppm, J, Hz): 1.30 t (CH<sub>3</sub>), 4.33 q (CH<sub>2</sub>), 7.46 s (C<sub>6</sub>H<sub>5</sub>), 6.71 split t (H<sup>6</sup>, 1H), 7.20 split t (H<sup>7</sup>, 1H), 7.60 split d (H<sup>8</sup>, 1H), 7.86 split d (H<sup>5</sup>, 1H), J<sub>5,7</sub> = 1.0; J<sub>8,5</sub> = 1.0, J<sub>6,7</sub> = 7.2; J<sub>6,8</sub> = 1.2, J<sub>6,5</sub> = 6.5, J<sub>7,8</sub> = 10.0. Found: C, 71.97; H, 5.12; N, 10.30%. Calculated for C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>: C, 72.19; H, 5.25; N, 10.51%.

 $\frac{2-\text{Ethoxycarbonyl-3-phenyl-6-bromoimidazo[1,2-a]pyridine (IVd)}{(IVd)} \text{ was obtained in 86\%}$ yield, mp 173-174.5°C. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1715 (C=O). PMR spectrum in CDCl<sub>3</sub> ( $\delta$ , ppm, J, Hz): 1.30 t (CH<sub>3</sub>), 4.33 q (CH<sub>2</sub>), 7.48 s (C<sub>6</sub>H<sub>5</sub>), 7.23 split d (H<sup>7</sup>, 1H), 7.52 split d (H<sup>8</sup>, 1H), 7.97 split s (H<sup>5</sup>, 1H), J<sub>5.7</sub> = 2.0, J<sub>7.8</sub> = 10.0, J<sub>5.8</sub> = 0.7. Found: C, 55.51; H, 3.67; Br, 23.21%; N, 5.15%. Calculated for C<sub>16</sub>H<sub>13</sub>BrN<sub>2</sub>O<sub>2</sub>: C, 55.68; H, 3.76; Br, 23.15; N, 8.11%. <u>2-Methoxycarbonyl-3-phenylimidazo[1,2-a]quinoline (V)</u> was obtained in 85% yield, mp 188-190°C. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1710 (C=O). PMR spectrum in CDCl<sub>3</sub> ( $\delta$ , ppm): 3.80 s

 $(OCH_3)$ , 6.93-7.83 m (protons of the quinoline ring and phenyl group). Found: C, 75.62; H, 4.90; N, 9.20%. Calculated for  $C_{19}H_{14}N_2O_2$ : C, 75.51; H, 4.63; N, 9.26%.

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