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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Kinetic Features of the Synthesis of an Acid Corrosion Inhibitor, 5-Methyl-1,2,3,3a,4,8b-hexahydrocyclopent[*b*]indole

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Abstract—Kinetic features of thermal cyclization of 2-methyl-6-(cyclopent-2-enyl)aniline hydrochloride at 200–220°C were studied. The cyclization product shows a high performance as acid corrosion inhibitor.

Indoline compounds inhibit oxidation processes and acid corrosion [1, 2]; the highest performance is shown by 2-alkyl- and 2,2-dialkyl-substituted indolines [3]. With the aim of searching for new effective acid corrosion inhibitors, we studied in [4] formation of perhydrocyclopent[*b*]indolines by heterocyclization of hydrochlorides of *o*-(cyclopent-2-enyl)anilines [5] and their *N*-precursors which can be readily prepared from commercially available dicyclopentadiene. Heterocycles of this series, which are potential inhibitors of acid corrosion, are well known, but the kinetic features of their synthesis and the effect of reaction conditions on the product yield are studied insufficiently. In this work we studied some kinetic features of cyclization of 2-methyl-6-(cyclopent-2-enyl)aniline hydrochloride **I** (MCPA) and the inhibiting activity of the reaction product, 5-methyl-1,2,3,3a,4,8b-hexahydrocyclopent[*b*]indole **II**.

EXPERIMENTAL

Tests for protection of structural steels with inhibitor **II** were performed under laboratory conditions in 15% HCl and 20% H_2SO_4. Samples of St.3 steel [GOST (State Standard) 380–87], pretreated for corrosion tests, were placed in a corrosive medium for a prescribed time τ at 20°C. After that, the samples were worked up by an appropriate procedure and weighed with an accuracy of 0.0002 g. The corrosion rate ρ and degree z (%) of metal corrosion protection with the given inhibitor were determined by the formulas

$$\rho = (\Delta m)/S\tau,$$

$$z = (\rho_1 - \rho_2)/\rho_1 \times 100,$$

where Δm is the weight loss (g), S is the sample surface area (m^2), τ is the test time (h), ρ_1 is the corrosion rate without inhibitor (g m^{-2} h^{-1}), and ρ_2 is the corrosion rate in the presence of inhibitor (g m^{-2} h^{-1}).

The kinetic features of intramolecular cyclization of aniline **I** to indoline **II** were studied by the one experiment–one point procedure. The mixture was heated in sealed ampules in a thermostat at a definite temperature for a definite time. The concentrations of reaction products were determined by gas chromatography.

Data on the inhibiting activity of **II** are listed in Table 1. Thus, compound **II** can be regarded as a new inhibitor of acid corrosion of carbon steels.

When developing a synthesis process, it is necessary to elucidate how the reaction conditions (temperature, component ratio, reaction time, etc.) affect the yield of the target product. It was shown previously

Table 1. Performance of indoline **II** as inhibitor of acid corrosion of steel

Inhibitor, wt %	Acid, wt %	ρ, g m^{-2} h^{-1}	z, %
–	HCl, 15	5.0	–
0.4	HCl, 15	0.225	95.5
0.2	HCl, 15	0.585	88.3
0.1	HCl, 15	1.685	66.3
–	H_2SO_4, 20	21.0	–
0.4	H_2SO_4, 20	3.318	84.2
0.2	H_2SO_4, 20	6.279	70.1

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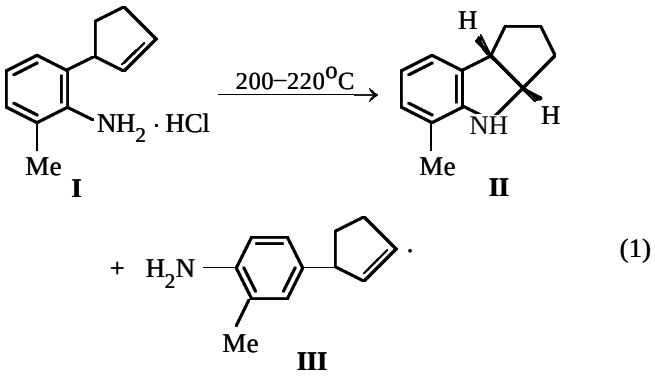
[4] that heating of hydrochloride **I** at 200–220°C in excess *o*-toluidine yields indoline **II** and minor (up to 10%) amounts of 2-methyl-4-(cyclopent-2-enyl)aniline **III**:



(1)

To find how the yield of the target product depends on the initial conditions and heating time, we studied the kinetic features of MCPA **I** consumption and indoline **II** accumulation. As seen from the kinetic curves shown in Fig. 1, the rate of MCPA consumption is the highest in the initial stages, and at 90% MCPA conversion the indoline concentration reaches a certain limit, C_i^∞. The yield of the target product was determined as the ratio of the limiting concentration of indoline **II** to the initial concentration C^0_{MCPA} (Table 2).

The kinetic curves of MCPA consumption are linear in the coordinates of the first-order reaction equation (Fig. 2):

$$\ln C_{MCPA} = \ln C^0_{MCPA} - kt, \quad (2)$$

where C^0_{MCPA} and C_{MCPA} are the initial and current concentrations of MCPA, respectively; k is the apparent rate constant of consumption of **I**.

From the semilog kinetic plots, we determined the rate constants at various temperatures (Table 2) and obtained the Arrhenius equation

$$\ln k = -(20.1 \pm 5.2) - (98.1 \pm 2.2) \times 10^3/RT,$$

where $R = 8.31$ J mol^{-1} K^{-1}.

The activation energy of MCPA transformation, $E_a = 98.1 \pm 2.2$ kJ mol^{-1}, is consistent with published data. It should be noted that this is an apparent quantity, describing transformation of MCPA not only by scheme (1), but also into by-products.

For example, in the experiment performed at 200°C (Table 2) the yield of the target product was low. This may be due to the fact that the runs at 200°C

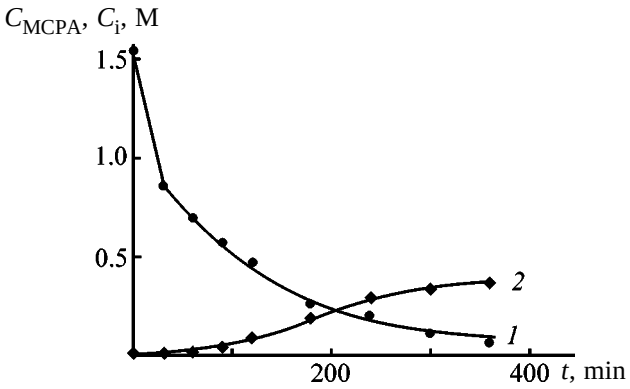


Fig. 1. Kinetic curves of (*1*) MCPA consumption and (*2*) indoline accumulation in intramolecular cyclization of 2-methyl-6-(cyclopent-2-enyl)aniline at 200°C. (C_{MCPA}, C_i) Concentrations of MCPA and indoline, respectively; (τ) time; the same for Fig. 2.

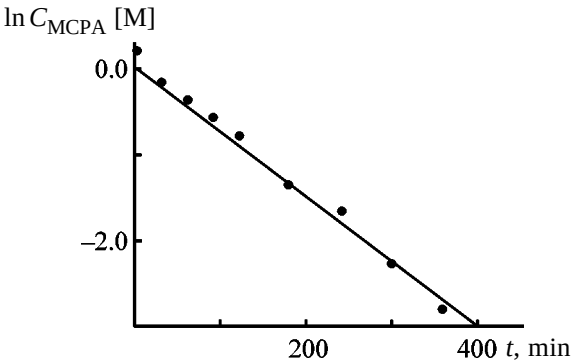
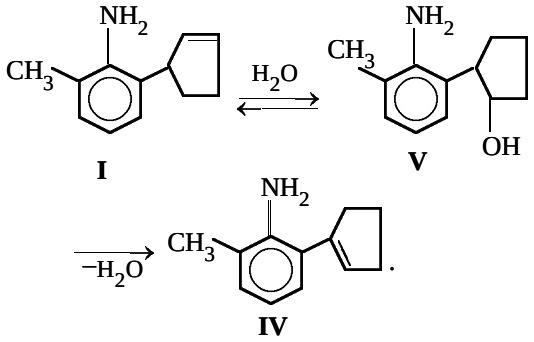


Fig. 2. Kinetic curve of MCPA consumption at 200°C, plotted in semilog coordinates.

were performed with an MCPA sample that had been stored for a month and had taken up moisture. At relatively high temperatures, traces of moisture could initiate the following side reactions:



It was found previously [6] that, indeed, MCPA can transform into 2-methyl-6-(cyclopent-1-enyl)aniline **IV** in both alkaline and acid solutions. At high temperatures in the presence of HCl, this compound undergoes extensive tarring. An intermolecular reaction of 2-(2-hydroxycyclopentyl)aniline with MCPA, decreasing the yield of the target product, cannot be

Table 2. Yield of indoline **II** and apparent rate constant k as influenced by reaction temperature T (C^0_{MCPA} = 1.53 M)

T, °C	C_i^∞, M	C_i^∞/C^0_{MCPA}	$k \times 10^2$, min^{-1}
190	1.16	0.75	0.84
200	0.36	0.24	0.90
210	0.85	0.55	1.38
220	0.77	0.50	2.18
230	0.69	0.45	3.95

Table 3. Apparent rate constant and yield of indoline in isomerization of aniline **I** at 200°C, as influenced by the initial concentration of **I**

C^0_{MCPA}, M	$k \times 10^2$, min^{-1}	C_i^∞, M	C_i^∞/C^0_{MCPA}
1.53	0.9	0.36	0.24
1.15	0.6	0.18	0.16
0.76	0.8	0.05	0.07

ruled out either. Under the experimental conditions (sealed ampules), moisture is not evaporated; therefore, this pathway of MCPA transformation strongly affects the yield of the target product as a function of temperature (Table 2) and initial MCPA concentration (Table 3).

As seen from Table 3, the yield of **II** drastically decreases as the initial MCPA concentration is decreased.

CONCLUSIONS

(1) 5-Methyl-1,2,3,3a,4,8b-hexahydrocyclopent[*b*]-indole inhibits acid corrosion of carbon steels.

(2) The kinetic features of intramolecular cyclization of 2-methyl-6-(cyclopent-2-enyl)aniline were studied. The yield of the target product, indoline, decreases with decreasing initial concentration of the starting compound.

(3) Increase in temperature in the range 190–230°C is accompanied by a decrease in the yield of indoline.

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