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Reactions of 1-Cyanoimidazole and 1-Cyanobenzimidazole with Aliphatic Alcohols

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Abstract — Alkyl imidazole-1-carboximidates and alkyl benzimidazole-1-carboximidates were synthesized by reaction of 1-cyanoimidazole and 1-cyanobenzimidazole with aliphatic alcohols. The reaction time and the product yield depend on the structure of the alcohol.

We previously described the reactions of 1-cyanobenzimidazole with amines, which led to formation of benzimidazole-1-carboxamidines [1]. The present communication reports on the results of our study of the reactions of 1-cyanoimidazole (**I**) and 1-cyanobenzimidazole (**II**) with a series of aliphatic alcohols. Cyanoazoles **I** and **II** reacted with excess anhydrous alcohols **III**–**X** at 64–65°C to give alkyl azole-1-carboximidates **XI**–**XXVI**:

$$\underset{\textbf{I, II}}{\text{Ht–C}\equiv\text{N}} + \underset{\textbf{III–X}}{\text{ROH}} \xrightarrow{64-65^\circ\text{C}} \underset{\textbf{XI–XXVI}}{\text{Ht–C(=NH)–OR}},$$

I, **XI**–**XVIII**, Ht = 1-imidazolyl; **II**, **XIX**–**XXVI**, Ht = 1-benzimidazolyl; **III**, **XI**, **XIX**, R = Me; **IV**, **XII**, **XX**, R = Et; **V**, **XIII**, **XXI**, R = Pr; **VI**, **XIV**, **XXII**, R = *i*-Pr; **VII**, **XV**, **XXIII**, R = Bu; **VIII**, **XVI**, **XXIV**, R = *i*-Bu; **IX**, **XVII**, **XXV**, R = *t*-Bu; **X**, **XVIII**, **XXVI**, R = *iso*-C_5H_{11}.

Cyanoazoles **I** and **II** readily react with primary alcohols **III**–**V**, **VII**, **VIII**, and **X**. The reactions take 2–3 h, and the corresponding alkyl azole-1-carboximidates are formed in more than 80% yield. The structure of the hydrocarbon radical in primary alcohols has no appreciable effect on the reaction rate and product yield. The rate of the reaction of cyanoazoles **I** and **II** with secondary and tertiary alcohols **VI** and **IX** is lower by a factor of 5–10, and the yields of the products do not exceed 20%. The conversion of the substrates in the reactions with 2-propanol (**VI**) does not reach 20%, and with *tert*-butyl alcohol (**IX**) it is as low as 10%. Azolecarboximidates **XI**–**XXVI** are colorless crystalline or oily substances, which decompose on prolonged storage (for 3–4 weeks) as follows from the IR spectral data.

Taking into account published data on alcoholysis of nitriles [2] and cyanic acid esters [3–6], we presume that the reaction of cyanoazoles **I** and **II** with aliphatic alcohols **III**–**X** occurs as nucleophilic addition at the cyano group. The structure of imidates **XI**–**XXVI** was proved by the ^{1}H NMR and IR spectra (Table 1) and elemental analyses (Tables 2, 3). The IR spectra of **XI**–**XXVI** lack cyano group absorption at 2295–2265 cm^{-1}, but a strong band appears in the region 1700–1670 cm^{-1}, which corresponds to stretching vibrations of the newly formed C=N bond. A narrow medium-intensity band at 3300–3240 cm^{-1} belongs to stretching vibrations of the N–H bond in the imino group. Absorption bands in the range from 3160 to 3020 cm^{-1} are typical of heterocyclic C–H bond vibrations, and bands at 2990–2840 cm^{-1} arise from stretching vibrations of aliphatic C–H bonds. The ^{1}H NMR spectra of **XI**–**XXVI** (Table 1) contain characteristic signals from alkyl protons, protons of the imidazole or benzimidazole ring, and the NH proton at δ 6.19–6.31 ppm; the latter appears as a broadened singlet.

EXPERIMENTAL

The IR spectra were measured on an IKS-29 spectrophotometer in KBr or in thin films on KBr support. The ^{1}H NMR spectra were recorded on a Bruker WP-200SI instrument at 200.13 MHz in DMSO-d_6 using TMS as internal reference. The purity of the products was checked, and the progress of reactions was monitored by TLC on Silufol UV-254 plates; acetone and acetone–petroleum ether (1:1) were used as eluents; spots were detected under UV light.

Alkyl imidazole-1-carboximidates XI–**XVIII (***general procedure***).** Preliminarily sublimed 1-cyanoimidazole, 0.063 g, was dissolved in 6 ml of the corresponding anhydrous alcohol. The solution was heated for several hours on a water bath at 64–65°C, and excess alcohol was removed under reduced pres-

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Table 1. IR and ^{1}H NMR spectra of alkyl azole-1-carboximidates **XI**–**XXVI**

Comp. no.	IR spectrum, ν, cm^{-1}		^{1}H NMR spectrum, δ, ppm	Comp. no.	IR spectrum, ν, cm^{-1}		^{1}H NMR spectrum, δ, ppm
	N–H	C=N			N–H	C=N	
XI	3260	1700	3.64 s (3H, CH_3O), 6.23 br.s (1H, NH), 6.82 s, 7.45 s (2H, 4-H, 5-H), 8.86 s (1H, 2-H)	**XX**	3260	1670	1.19 t (3H, CH_3, *J* 7.00 Hz), 3.95 q (2H, CH_2O, *J* 5.88 Hz), 6.30 br.s (1H, NH), 7.11 m (2H, 5-H, 6-H), 7.51 d, 7.55 d (2H, 4-H, 7-H, *J* 1.8 Hz), 8.46 s (1H, 2-H)
XII	3270	1680	1.13 t (3H, CH_3, *J* 6.6 Hz), 3.89 q (2H, CH_2O, *J* 5.6 Hz), 6.19 br.s (1H, NH), 7.00 s, 7.62 s (2H, 4-H, 5-H), 8.88 s (1H, 2-H)	**XXI**	3250	1680	0.78 t (3H, CH_3, *J* 8.0 Hz), 1.58 m (2H, CH_2), 4.01 t (2H, CH_2O, *J* 6.2 Hz), 6.25 br.s (1H, NH), 7.11 m (2H, 5-H, 6-H), 7.51 d, 7.54 d (2H, 4-H, 7-H, J 1.8 Hz), 8.42 s (1H, 2-H)
XIII	3260	1680	0.74 t (3H, CH_3, *J* 7.7 Hz), 1.50 m (2H, CH_2), 3.99 t (2H, CH_2O, *J* 6.1 Hz), 6.23 br.s (1H, NH), 6.91 s, 7.55 s (2H, 4-H, 5-H), 8.15 s (1H, 2-H)	**XXII**	3240	1670	–
XIV	3270	1670	–	**XXIII**	3260	1670	0.73 t (3H, CH_3, *J* 7.3 Hz), 1.23 m (2H, CH_2), 1.49 m (2H, CH_2), 4.07 t (2H, CH_2O, *J* 6.6 Hz), 6.31 br.s (1H, NH), 7.11 m (2H, 5-H, 6-H), 7.50 d, 7.54 d (2H, 4-H, 7-H, *J* 1.7 Hz), 8.45 s (1H, 2-H)
XV	3280	1690	0.73 t (3H, CH_3, *J* 7.3 Hz), 1.26 m (2H, CH_2), 1.48 m (2H, CH_2), 4.05 t (2H, CH_2O, *J* 6.5 Hz), 6.25 br.s (1H, NH), 6.79 s, 7.48 s (2H, 4-H, 5-H), 8.37 s (1H, 2-H)				
XVI	3290	1700	0.75 d (6H, 2 CH_3, *J* 6.6 Hz), 1.84 m (1H, CH), 3.82 d (2H, CH_2O, *J* 6.5 Hz), 6.25 br.s (1H, NH), 6.83 s, 7.50 s (2H, 4-H, 5-H), 8.00 s (1H, 2-H)	**XXIV**	3275	1670	0.79 d (6H, 2 CH_3, *J* 6.7 Hz), 1.92 m (1H, CH), 3.88 d (2H, CH_2O, *J* 6.5 Hz), 6.23 br.s (1H, NH), 7.12 m (2H, 5-H ,6-H), 7.51 d, 7.55 d (2H, 4-H, 7-H, *J* 1.7 Hz), 8.50 s (1H, 2-H)
XVII	3300	1675	–				
XVIII	3270	1680	0.68 d (6H, 2 CH_3, *J* 7.7 Hz), 1.25 m (1H, CH), 1.49 m (2H, CH_2), 4.00 t (2H, CH_2O, *J* 7.3 Hz,), 6.66 br.s (1H, NH), 7.44 s, 7.62 s (2H, 4-H, 5-H), 8.09 s (1H, 2-H)	**XXV**	3300	1670	–
				XXVI	3270	1675	0.72 d (6H, 2 CH_3, *J* 6.6 Hz), 1.21 m (1H, CH), 1.46 m (2H, CH_2), 4.10 t (2H, CH_2O, *J* 6.3 Hz), 6.26 br.s (1H, NH), 7.13 m (2H, 5-H, 6-H), 7.50 d, 7.54 d (2H, 4-H, 7-H, *J* 1.7 Hz), 8.47 s (1H, 2-H)
XIX	3240	1680	3.76 s (3H, CH_3O), 7.13 m (2H, 5-H, 6-H), 7.50 d, 7.53 d (2H, 4-H, 7-H, J 1.7 Hz), 8.41 s (1H, 2-H)				

Table 2. Reaction times and yields, melting points or TLC data, and elemental analyses of alkyl imidazole-1-carboximidates **XI**–**XVIII**

Comp. no.	Reaction time, h	Yield, %	mp, °C (R_f[a])	Found, %		Formula	Calculated, %	
				C	H		C	H
XI	3–3.5	85	(0.25)	47.96	5.69	$C_5H_7N_3O$	47.99	5.64
XII	2.5–3	88	68–69	51.74	6.54	$C_6H_9N_3O$	51.79	6.52
XIII	2.5–3	86	(0.32)	54.87	7.31	$C_7H_{11}N_3O$	54.89	7.24
XIV	11	18	(0.27)	–	–	–	–	–
XV	2–2.5	78	(0.30)	57.43	7.89	$C_8H_{13}N_3O$	57.46	7.84
XVI	2–2.5	85	(0.40)	57.39	7.90	$C_8H_{13}N_3O$	57.46	7.84
XVII	17–18	10	(0.32)	–	–	–	–	–
XVIII	2–2.5	64	(0.36)	59.57	8.41	$C_9H_{15}N_3O$	59.64	8.34

[a] For oily products; eluent acetone–petroleum ether, 1:1.

Table 3. Reaction times and yields, melting points or TLC data, and elemental analyses of alkyl benzimidazole-1-carboximidates **XIX**–**XXVI**

Comp. no.	Reaction time, h	Yield, %	mp, °C (R_f[a])	Found, %		Formula	Calculated, %	
				C	H		C	H
XIX	5–6	82	109.5–110.5	61.68	5.21	$C_9H_9N_3O$	61.70	5.18
XX	2.5–3	84	79.5–80.5	63.43	5.93	$C_{10}H_{11}N_3O$	63.48	5.86
XXI	2.5–3	85	96.5–97.5	64.98	6.44	$C_{11}H_{13}N_3O$	65.01	6.45
XXII	11	15	(0.75)	–	–	–	–	–
XXIII	2–2.5	77	(0.73)	66.28	6.99	$C_{12}H_{15}N_3O$	66.34	6.96
XXIV	2–2.5	75	(0.75)	66.30	6.98	$C_{12}H_{15}N_3O$	66.34	6.96
XXV	20–20.5	9	(0.76)	–	–	–	–	
XXVI	2–2.5	64	(0.69)	67.43	7.47	$C_{13}H_{17}N_3O$	67.51	7.41

[a] For oily products; eluent acetone.

sure (water-jet pump). The oily residue was dissolved in 2 ml of dry benzene, and 1 ml of dry petroleum ether was added. The precipitate was filtered through a glass filter, and the filtrate was evaporated. The reaction time and yields, melting points, TLC data, and elemental analyses of the products are given in Table 2.

Alkyl benzimidazole-1-carboximidates XIX–XXVI (*general procedure*). Preliminarily sublimed 1-cyanobenzimidazole, 0.100 g, was dissolved in 10 ml of the corresponding anhydrous alcohol, and the solution was heated for several hours on a water bath at 62–65°C. Excess alcohol was removed under reduced pressure (water-jet pump), the precipitate was dissolved in 2 ml of dry benzene, and 2 ml of dry petroleum ether was added. The precipitate was filtered off through a glass filter, and the filtrate was evaporated. The reaction time and yields, melting points, TLC data, and elemental analyses of products **XIX**–**XXVI** are given in Table 3.

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