REACTIONS OF ACYL ISOCYANATES WITH DISUBSTITUTED AMIDES

B. A. Arbuzov, N. N. Zobova,
A. V. Aganov, and O. V. Sofronova

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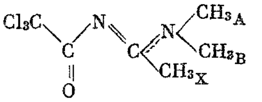
The benzoyl (I) and trichloroacetyl (II) isocyanates react with dimethylformamide to give substituted formamidines [1]. It seemed of interest to study the reaction of the above indicated isocyanates with other disubstituted amides.

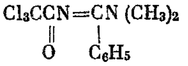
Isocyanates (I) and (II) react with dimethylacetamide (DMAA) to give the substituted amidines (III) and (IV). The IR spectra of (III) and (IV) have the following absorption bands (ν, cm^{-1}) in the region of the stretching vibrations of the C = O and C = N groups: 1695, 1630 for (III); 1690, 1610 for (IV). The NMR spectrum of (IV) made possible additional conclusions regarding the structure of (IV). The spectrum has three lines that correspond to the protons of the three CH_3 groups. The nonequivalence of the chemical shifts of the N-methyl protons in (IV) is caused by the hindered internal rotation around the $C-N\langle$ bond, which has a partial double bond character



$\delta_A = 3.27$, $\delta_B = 3.20$, $\delta_X = 2.40$ ppm, $\Delta\nu = 4.2$ Hz.

Dimethylbenzamide reacts only with (II), with the resultant formation of 1-trichloroacetyl-2-phenyl-3,3-dimethylamidine (V). The IR spectrum of (V) has the absorption bands of the C = O group at 1685 cm^{-1} and the C = N bond at 1600 cm^{-1}. The NMR spectrum of (V) has two broad singlets with δ 3.30 and 3.00 ppm, which belong to the protons of the CH_3 groups on the N atom. The signal with δ 7.53 ppm corresponds to the protons of the phenyl ring. In (V), the same as in (IV), a nonequivalence of the protons of the N-methyl groups is observed due to the fact that the C–N bond has a double bond character.

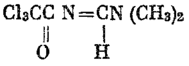
To obtain information on the hindered internal rotation around the C–N bond in the molecules of the obtained amidines we studied the temperature changes in the NMR spectra using 20% solutions of compounds (V) and (VI) in tetrachloroethylene.



$Cl_3C\overset{\underset{\|}{}}{\underset{O}{C}}N{=}\underset{C_6H_5}{C}N(CH_3)_2$

(V)

and



$Cl_3C\underset{O}{C}N{=}\underset{H}{C}N(CH_3)_2$

(VI)

The temperature changes in the spectra of (V) and (VI) are characteristic for spin exchange between the two equally probable equilibrium positions. For (V) a nonequivalence of the chemical shifts of the N-methyl protons is observed at room temperature, which quickly reaches the limiting separation of $\Delta\nu_\infty = 33$ Hz at 293°K. The rate of rotation increases with increase in the temperature, which causes the lines to come closer together until they merge completely at T_m (temperature of merging) = 323°K. The rates were estimated as an approximation of the rapid exchange [2], and gave the following values of the thermodynamic parameters: $E_a = 17.5 \pm 0.5$ kcal/mole, $\Delta F^{\neq}_{323} = 13.5$ kcal/mole, $\Delta H^{\neq}_{323} = 16.9$ kcal/mole, and $\Delta S = \pm 10$ entropy units.

In (VI) the protons of the CH_3 groups are also nonequivalent ($\Delta\nu$ 8 Hz) at room temperature and exhibit coupling with H_X ($^4J_{H_XH_A} = 0.7$ Hz, $^4J_{H_XH_A} = 0.5$ Hz)

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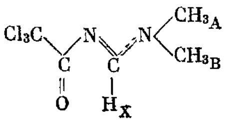
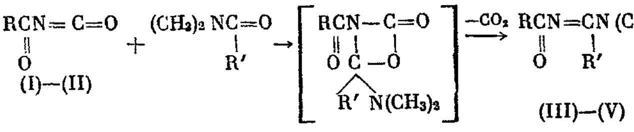


(VI)

$\delta_A = 3.00, \delta_B\ 3.11, \delta_X = 8.43$ ppm.

The signals merge at T_m 388°K. However, a complete separation of the signals could not be achieved even at 233°K (mp of C_2Cl_4). Due to the fact that both $\Delta\nu$ and T_m are strongly dependent on the solvent (at T 313°K $\Delta\nu = 10$ Hz in CCl_4, and 6.4 Hz in C_2Cl_4, while the T_m in CCl_4 is considerably higher than 388°K), a combining of the data for the high and low temperatures, obtained in different solvents, can lead to substantial errors when determining the rates of the process. For an approximate estimate of $\Delta F^{\neq}$ we used the value $\Delta\nu_\infty = 17$ Hz, which was obtained by extrapolation in the region of low temperatures: $\Delta F^{\neq} = 16.5$ kcal/mole (in C_2Cl_4).

Employing the DTA method it was shown that the amidines are formed via the intermediate substituted oxazetidinone



R = C_6H_5 (I), CCl_3 (II), C_6H_5 (III), CCl_3 (IV), CCl_3 (V);
R′ = CH_3 (III), CH_3 (IV), C_6H_5 (V)

One broad exo effect, with T_{init} 283°K and T_{max} 298-303°K, is present on the thermogram of the reaction of (I) with DMAA. Apparently, the superimposition of two exo effects occurred, which led to a broadening of the peak. Two exo effects are present on the thermogram of the reaction of (II) with DMAA. The first exo effect, with T_{max} 244°K, evidently corresponds to the formation of the substituted oxazetidinone, while the second effect, with T_{max} 256°K, corresponds to the formation of (IV). The sulfonyl isocyanates react with disubstituted amides in a similar manner [3].

EXPERIMENTAL METHOD

The IR spectra were recorded on a UR-10 spectrometer as a Nujol mull, while the NMR spectra were recorded on a T-60 spectrometer in $CDCl_3$ solution for (IV), and CCl_4 for (V). The temperature measurements were made on an NA-100D spectrometer in C_2Cl_4 solution for (V), and C_2Cl_4 and CCl_4 for (VI). The thermographic study of the reactions was run on a Kurnakov FPK-59 pyrometer, equipped with a Chromel–Alumel thermocouple, in Stepanov cups at a heating rate of 4-5 deg/min. Ignited Al_2O_3 was used as the standard. The dimethylbenzamide was obtained as described in [4].

1-Benzoyl-2,3,3-trimethylamidine (III). To 2.15 g of benzoyl isocyanate was added 1.27 g of DMAA. CO_2 was liberated at a mixture temperature of 333°K. The temperature dropped to 303°K in 0.5 h and the reaction mixture was kept at this temperature for another 3 h. The obtained viscous liquid was vacuum-distilled, collecting the fraction with bp 453°K (2 mm); n_D^{25} 1.4046; d_4^{25} 1.1364; yield 1.12 g (40%). Found: C 69.60; H 7.37; N 14.74%. $C_{11}H_{14}NO_2$. Calculated: C 69.47; H 7.37; N 14.25%.

1-Trichloroacetyl-2,3,3-trimethylamidine (IV). To 2.74 g of trichloroacetyl isocyanate were added 1.26 g of DMAA and a catalytic amount of BF_3 etherate. The brisk evolution of CO_2 was observed. The temperature of the mixture rose to 353°K. The mixture was kept at 313°K for 2 h. Vacuum-distillation gave 1.81 g (55%) of (IV), bp 428°K (2 mm); d_4^{25} 1.3801; n_D^{25} 1.4178. Found: C 31.42; H 2.72; Cl 46.51%. $C_6H_9ON_2Cl_3$. Calculated: C 31.50; H 2.62; Cl 46.60%.

1-Trichloroacetyl-2-phenyl-3,3-dimethylamidine (V). To 2.1 g of trichloroacetyl isocyanate was added 1.66 g of dimethylbenzamide. The temperature of the mixture rose to 308°K and CO_2 was evolved. Then the mixture was heated at 323°K for 8 h. The reaction mass crystallized completely when cooled. We obtained (V) (~100%) with mp 376°K (from absolute ether). Found: C 44.96; H 3.74; N 9.50; Cl 36.62%. $C_{11}H_{11}ON_2Cl_3$. Calculated: C 44.97; H 3.75; N 9.54; Cl 36.28%.

CONCLUSIONS

1. The benzoyl and trichloroacetyl isocyanates react with dimethylacetamide and dimethylbenzamide to give substituted amidines.

2. The existence of hindered internal rotation around the $=\mathrm{C}-\mathrm{N}\langle$ bond in the molecules of the obtained amidines was detected by NMR spectroscopy.

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