merization reaction and the amount of aluminum are observed on nickel-containing amorphous and crystalline aluminosilicates. In the NiO-mordenite catalyst, the same as in the NiOamorphous aluminosilicate catalyst, the active center for C_2H_4 dimerization is probably formed via the involvement of Ni²⁺ and the acid sections.

CONCLUSIONS

When the amount of aluminum in a nickel-containing mordenite with variable degree of dealuminization is increased the total acidity of the zeolite increases, the concentration of the electron-acceptor centers, recorded by the EPR method, passes through a maximum, while the degree of ethylene conversion varies within narrow limits.

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N-NITROSATION OF SECONDARY AMINES

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Nonacidic nitrosating agents (N_2O_4 , NOC1, NOBF₄) react with tertiary amines (trialkylamines, dialkylarylamines) and pyridine in aprotic solvents to give unstable complexes of types (I) and (II) [1-6]:

The literature data on the ability of complexes (I) and (II) to transfer the nitroso group to the N atom of secondary amines is scanty. Only one example of the N-nitrosation of amino acids, containing a secondary amino group, via the use of (II) ($X = BF_4$) is known [7].

The N-nitrosation of secondary amines via the reaction of N2O4 complexes with triethylamine (Ia) and pyridine (IIa) (paths A and B, respectively) is described in the present paper:



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 $R = C_2 H_5$ $NH + \left[\underbrace{N \cdot NO}_{NO_3} - \underbrace{B}_{B_1} \right] = C_2 H_5$ $NH + \underbrace{N + N_2O}_{R}$

The synthesized N-nitrosamines (III) and their yields are given in Table 1. The physicochemical and spectral characteristics of the obtained (III) compounds agree with the literature data.

The (III) compounds were also obtained by treating secondary amines with N_2O_4 in the presence of triethylamine (path C) or pyridine (path D). Also in this case, the N-nitrosation most probably proceeds via the intermediate formation of complexes (Ia) and (IIa).

As can be seen from Table 1, the nitrosation of secondary amines using (Ia) and (IIa) made it possible to obtain nitrosamines (IIIa-d) in high yields. Here (IIId) was obtained previously by known methods [8, 9] in 3-14% yield.

EXPERIMENTAL

<u>General Method for N-Nitrosation of Secondary Amines Using Complexes (Ia) and (IIa)</u> (Methods A and B). To a solution of 0.05 mole of triethylamine or pyridine in 10 ml of dry CH_2Cl_2 , at -60°C, in an inert gas stream, was added in drops a solution of 0.05 mole of N₂O₄ in 15 ml of CH_2Cl_2 , followed by the addition of a solution of 0.05 mole of the secondary amine in 10 ml of CH_2Cl_2 at the same temperature, after which the reaction mixture was al-4 γ lowed to warm up to 20°, recooled to 0°, and 10 ml of water was added. The obtained product was isolated and purified in conventional manner.

<u>General Method for N-Nitrosation of Secondary Amines with N₂O₄ in Presence of Tertiary Amines or Pyridine (Methods C and D).</u> To a solution of 0.05 mole of secondary amine and 0.05 mole of triethylamine or pyridine in 15 ml of dry CH_2Cl_2 , at -60°, in an inert gas stream, was added in drops a solution of 0.05 mole of N₂O₄ in 15 ml of CH_2Cl_2 . Then the reaction mass was allowed to warm up to 20°, recooled to 0°, and 10 ml of water was added. The obtained product was isolated and purified in conventional manner.

CONCLUSIONS

A method was proposed for the N-nitrosation of secondary amines using N_2O_4 complexes in combination with tertiary amines or pyridine.

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REACTION OF CHROMIUM ATOMS WITH ACETOPHENONE

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As a continuation of our research on the direct synthesis of bisarene compounds [1] by the reaction of chromium atoms with acetophenone at 77°K we obtained bis(acetophenone) chromium(0) (i), in 3% yield when based on vaporized metal, and bis(acetophenone) chromium tetraphenylborate (II):

$$2C_6H_5COCH_3 + Cr \xrightarrow{77K}_{<10^{-3}} Cr (C_6H_5COCH_3)_2Cr$$
(1)

The IR spectra have absorption bands that belong to the Cr-ring stretching vibrations [2]: 430, 470, 495, 522 cm⁻¹ for (I) and 430, 470, 485 cm⁻¹ for (II), intense peaks at 1655 for (I) and 1700 cm⁻¹ for (II) (C=0 stretching vibrations).

The UV spectrum of bis(acetophenone)chromium hydroxide has three intense bands: 248, 281 nm (absorption of organic ligand), and 347 nm, which is a characteristic band for Aren₂Cr⁺ cations [3]. The EPR spectrum of the paramagnetic (PhCOCH₃)₂Cr⁺ has a hyperfine structure due to the coupling of the unpaired electron with ten protons, with $a_{\rm H}$ = 3.3 Oe and a g factor equal to 1.986, which testifies to a sandwich structure and symmetrical substitution in the complex. An acetone solution of (II) gives an identical EPR signal. The mass spectrum of (I) has weak peaks of the molecular ion (m/e 292) and chromium (m/e 52), and also intense peaks of the fragments, m/e: $172 - C_6H_5 \operatorname{COCH}_3\operatorname{Cr}$, $120 - C_6H_5 \operatorname{COCH}_3$, $106 - C_6H_5 \operatorname{CHO}^+$, $105 - C_6H_5 \operatorname{CO}^+$, $77 - C_6H_5^+$, $71 - H_2 \operatorname{CrOH}$, $69 - \operatorname{CrOH}$.

Exothermic heat decomposition is observed during differential thermal analysis in a sealed evacuated ampul, which begins at 160° (maximum at 178°) for (I), and above 100° (maximum at 155°) for (II).

A substantial amount of 2,3-diphenyl-2,3-butanediol (III) was isolated from the reaction by-products of (I), which was identified by elemental analysis, and by comparing the IR spectra and melting points of the (III) crystals, isolated from the reaction products of the chromium atoms with acetophenone, and authentic specimens, which were obtained by the reduction of acetophenone with aluminum amalgam [4]. The mixed melting point was not depressed. It may be assumed that the reductive condensation of acetophenone proceeds via the intermediate formation of the chromium derivative of 2,3-diphenyl-2,3-butanediol:



According to the oxidation-reduction half-wave potentials of $\operatorname{Cr} \xrightarrow{\stackrel{-2e}{\rightarrow}}_{\stackrel{+e}{+e}} \operatorname{Cr}^{3+} \xrightarrow{\stackrel{+e}{\rightarrow}}_{\stackrel{+e}{+e}} \operatorname{Cr}^{3+}$ and $\operatorname{C_6H_5COCH_3} \xrightarrow{\stackrel{+e}{\rightarrow}}_{\stackrel{-e}{-e}} [\operatorname{C_6H_5COCH_3}]^{-} [5], \operatorname{Cr}(0)$ can apparently be oxidized by acetophenone to Cr^{3+} , while acetophenone is reduced to the ketyl anion-radical.

EXPERIMENTAL

Compound (I) was isolated and purified either in an inert atmosphere or in vacuo. The

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