salt [equilibrium (3)] occurs much more rapidly than exchange reaction (2). In principle, such a relationship of the rates of reactions (2) and (3) might have been expected considering that the K_a values of carboxylic acids are, as a rule, from five to seven orders of magnitude greater than the corresponding values for trialkylammonium ions [4].

CAA salts with Me_2NBu-t and $MeN(i\text{-}Pr)_2$ in the free state are colorless syrups, which may be stored without decomposition for 1-2 h at ~20°C or for 24-48 h at −70°C. These salts are highly soluble in chloroform and acetone but have only limited solubility in benzene and are insoluble in hexane. The brucine salt is a white powder, which may be stored in a desiccator without decomposition for several days.

EXPERIMENTAL

The PMR spectra were taken on a Bruker WH-200-SY spectrometer.

Equimolar amounts of CAA and the corresponding amine were dissolved in $CDCl_3$ and the PMR spectrum was taken. In order to obtain the pure salts, 2 mmoles CAA were added to a solution of 2 mmoles amine in 2 ml $CHCl_3$ and stirred for 2-3 min until completely dissolved. The solvent was evaporated in vacuum at 20°C. In the case of the reaction with brucine, the reaction mixture was poured into 15 ml hexane. The precipitate formed was filtered off and dried in a vacuum desiccator. The characteristics and parameters of the PMR spectra of the compounds obtained are given in Table 1.

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SYNTHESIS OF THE ETHYL ESTER OF THE MONONITRILE OF MALONIC ACID BY THE CATALYTIC CARBONYLATION OF BENZENESULFONYLOXYACETONITRILE

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A new method has been developed for the synthesis of the ethyl ester of the mononitrile of malonic acid by the carbonylation of benzenesulfonyloxyacetonitrile in absolute ethanol in the presence of cobalt carbonyl. The yield of the desired product was 30% with 60-90% conversion of the starting compound. The effects of temperature, pressure, and reaction time were studied.

Keywords: carbonylation, dicobalt octacarbonyl, benzenesulfonyloxyacetonitrile, ethyl ester of the mononitrile of malonic acid.

The ethyl ester of the mononitrile of malonic acid (1) is commonly used in organic synthesis for the preparation of plastics, drugs, bioregulators, and pesticides, etc. The major

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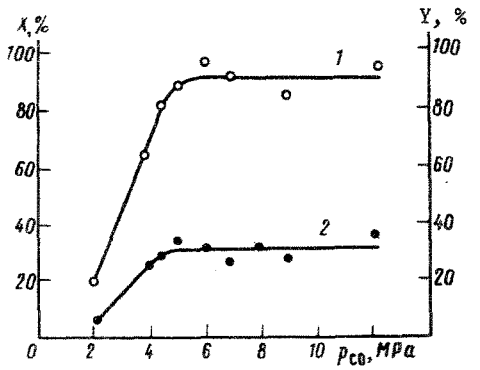

Fig. 1. Dependence of conversion of 2 (1) and yield of 1 (2) on p_{CO} (80°C, τ = 6 h).

method for the synthesis of 1 involves the reaction of chloroacetic acid or its ethyl ester with NaCN [1]. Another synthesis of 1 involves the catalytic carbonylation of monochloroacetonitrile [2, 3]. However, these methods have significant shortcomings. The procedure reported by Kazanskii [1] involves multiple steps and requires careful temperature control since slight overheating heads to tar formation and the loss of HCN. Monochloroacetonitrile, which is the starting reagent for the patent procedures [2, 3], is not readily available and is obtained either by the chlorination of nitriles or dehydration of chloracetamide. In this regard, the search for new methods for the synthesis of 1 has great importance.

In the present work, we studied the carbonylation of benzenesulfonyloxyacetonitrile (2) in absolute ethanol with CO in the presence of $Co_2(CO)_8$ for the preparation of 1:

$$\underset{(2)}{CNCH_2OSO_2C_6H_5}+CO+C_2H_5OH\rightarrow\underset{(1)}{CNCH_2COOC_2H_5}+C_6H_5SO_3H$$

The synthesis of 2 was carried out according to Lichtenberger and Faure [4]:

$$CNCH_2OH+C_6H_5SO_2Cl\rightarrow CNCH_2OSO_2C_6H_5+HCl$$

We have found that not only chemically pure glyconitrile but also its technical aqueous solution, which is an unused waste product produced in large amounts in the coal-tar chemical industry, may be used as the starting reagent for the synthesis of 2. Thus, we propose the synthesis of 1, which is a valuable organic compound, from these toxic wastes.

EXPERIMENTAL

The carbonylation was carried out in a rotating Kh18N10T stainless-steel 0.15-liter autoclave. A charge of 6.0 g (0.03 mole) 2, 15 ml (0.258) ethanol, and 0.65 g (0.001 mole) $Co_2(CO)_8$ was placed into the autoclave in a CO or argon stream. The autoclave was filled with CO to the required pressure and placed into the furnace. The reaction products were analyzed by gas-liquid chromatography on a Chrom-5 chromatograph with a flame ionization detector using a 1200 × 5-mm column packed with 5% XE-60 on Chromaton N-AW-DMCS. The helium gas carrier flow rate was 30 ml/min. The column temperature was raised from 60 to 220°C at 20 deg/min. The quantitative analysis was carried out with p-nitrotoluene as the internal standard. In order to isolate 1, ether was added to the reaction mixture and the precipitate was filtered off. Ether and ethanol were distilled off and vacuum distillation gave 1.0 g (30%) 1. The PMR spectrum was obtained on a Bruker WM-250 spectrometer. PMR spectrum in $CDCl_3$ (δ, ppm): 1.3 t (3H, CH_3), 3.56 s (2H, CH_2), 4.25 q (2H, OCH_2). The ^{13}C NMR spectrum was obtained on a Bruker NJ-300 spectrometer. ^{13}C NMR spectrum in $CDCl_3$ (δ, ppm): 13.86 (CH_3), 24.68 (CH_2), 62.88 (OCH_2), 113.20 (CN), 163.03 (C=O).

RESULTS AND DISCUSSION

Product 1 is formed in the carbonylation of 2 in absolute ethanol in the presence of $Co_2(CO)_8$. The optimum temperature for the reaction is 80-85°C. The reaction rate is very low below this temperature, while the selectivity drops sharply at higher temperatures.

The dependence of the yield of 1 and conversion of 2 on the CO pressure is given in Fig. 1. The greatest yield of 1 (~30%) is achieved for p_{CO} = 4.0 MPa and the yield remains virtually the same with increasing p_{CO} to 12.0 MPa. The maximum conversion of 2 (~90%) is obtained when p_{CO} = 5.0 MPa and the conversion also remains invariant with a further increase in p_{CO}. The reaction time was 6 h. The increase of 1 was unchanged upon doubling the reaction time.

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CATHODIC SYNTHESIS OF ESTERS OF 1,1,2,2-CYCLOALKANETETRACARBOXYLIC ACIDS DERIVED FROM 1,1,2,2-ETHANE- OR ETHYLENECARBOXYLATE ESTERS

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The cathodic electrolysis of esters of 1,1,2,2-ethane- or ethylenetetracarboxylic acids in the presence of dihaloalkanes leads to esters of 1,1,2,2-cycloalkanetetracarboxylic acids.

Keywords: acyclic compounds, esters, alkyl bromides, electrochemical synthesis, electrolytic reduction.

In previous work [1, 2], we have shown that the reduction of active methylene compounds on a platinum cathode under diaphragm electrolysis conditions in the presence of dihaloalkanes proceeds through a Perkin-type reaction, leading to 1,1-disubstituted cycloalkanes. In the present work, we studied the electrochemical synthesis of such compounds starting from the tetramethyl ester of 1,1,2,2-ethanetetracarboxylic acid (1). Esters of 1,1,2,2-cycloalkanetetracarboxylic acids were obtained by the electrochemical cyclization of $(RO_2C)CH(CH_2)_nCH(CO_2R)_2$ tetraesters [3, 4]. The synthesis of the desired tetraesters by the reaction of $(RO_2C)_2CHCH(CO_2R)_2$ with dihaloalkanes in the presence of base has also been described [5, 6].

As proposed, the electrolysis of X_2CHCHX_2 1 (here and subsequently, X = CO_2Me) on a platinum cathode in the presence of dihaloalkanes leads to the corresponding cyclic derivatives 2-4. The mechanism for the formation of these compounds is apparently analogous to our previous proposal for the electrochemical Perkin reaction and proceeds through the consecutive cathodic deprotonation of starting 1 and intermediate $X_2CHCX_2(CH_2)_nBr$ according to the following scheme:

$$X_2CHCHX_2 + \bar{e} \longrightarrow X_2CH\bar{C}X_2 + {}^1/_2H_2$$
$$X_2CH\bar{C}X_2 + Br(CH_2)_nBr \longrightarrow X_2CHCX_2(CH_2)_nBr + Br^-$$
$$X_2CHCX_2(CH_2)_nBr + \bar{e} \longrightarrow X_2\bar{C}CX_2(CH_2)_nBr + {}^1/_2H_2$$
$$X_2\bar{C}CX_2(CH_2)_nBr \longrightarrow X_2C\!\!<\!\!\begin{matrix}(CH)_n\\ 2\text{—}4\end{matrix}\!\!>\!\!CX_2 + Br^-.$$

n=1 (2), 2 (3), 3 (4); X=COOMe.

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