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STUDY OF ACYLATION REACTION OF FUNCTIONALLY SUBSTITUTED AROMATIC MONO- AND DIAMINES WITH CHLOROANHYDRIDE OF NAPHTHENIC ACID

M.A.Rustamov, G.A.Mirzayeva, Sh.M.Eyvazova, N. A.Veysova

Azerbaijan Technical University

AZ 1143, H.Javid Ave. 25; e-mail: orqanik_6060@mail.ru

Relevant carboxamide compounds and intramolecular cyclization products – benzimidazole and oxadiapesine derivatives are also produced by acylation reaction of functionally substituted aromatic mono- and diamines with chloroanhydride of naphthenic acid. It was detected that the condition and nature of amine group in amine molecule, as well as other functional group considerably effect on the direction of the reaction and yield of the product.

Keywords: *naphthenic acid, chloroanhydride, carboxyamide, benzimidazole, oxadiapesine.*

Different carbonyl compounds are used a reagent to produce acyl derivatives of amines. For this purpose there are sufficient data on production of carboxamide compounds with different structures using carboxylic acids [1-3], anhydrides of dibasic acids [4-6], complex ethers [7, 8], chloroanhydrides of aromatic and aliphatic acids [9,10] as an acylation reagent. Acylation reaction of alicyclic – cyclohexane row chloroanhydrides of carboxylic acids with amines has been first studied by us [11-13]. We have found that carboxamide compounds based on chloroanhydride of functionally substituted cyclohexane carboxylic acid exhibit the properties of stimulator for bioactive – plants [14], corrosion inhibitor [15]. It was detected that the nature and condition of functional groups in the molecule impact on the properties of carboxamide compounds.considering this in this work we used chloroanhydride of naphthenic acid as an acylation reagent to synthesize new type carboxamide compounds. Naphthenic acid was separated from kerosine cut of oil by distillation. $T_{boil.}$ = 190 -195°C/10 mmHg, n_D^{20} 1.4750, $M_{kriosk.}$ =273.6 . Chloroanhydride (I) of an acid was produced by method [16] under the impact of chlorination reagent (PCl_3). $T_{bil.}$155-160°C/8 mmHg, n_D^{20} 1.4790 .

To perform acylation reaction we used ortho-, meta- and para-phenylenediamine as a substrate. Acylation with ortho-phenylenediamine proceeds by the following scheme.

R - alkyl (hydrocarbon) radical.

As the reaction scheme shows 2-(amine-phenyl)-alkylcarboxamide compound (II) converts to enol-form (A) and forms C-alkylbenzimidazole derivative (III). Unlike ortho-phenylenediamine

mono- (IV) dicarboxamide (V) and diapesine derivative (VI) are produced by the reaction of chloroanhydride (I) with meta-phenylenediamine. The substance (VI) partially converts to enol-form (B) under the reaction of dicarboxamide compound (V) and is formed by intermolecular cyclization. The reaction proceeds by the following scheme.

Unlike ortho- and meta-phenylenediamine only mono- (VII) and dicarboxamide (VIII) compounds are formed by acylation of para-phenylenediamine with chloroanhydride (I).

To study electrophilic reaction of chloroanhydride (I) with functionally substituted aromatic mono- amines we used substrate- para - aminebenzoic acid and its ethyl ether. Since para-aminobnzoic acid exhibit bipolar property its acylation reaction is performed at a basic medium (pH>7).

Like with aromatic diamines acylation of ethyl ether of para-aminobenzoic acid with chloroanhydride (I) proceeds easily at para – xylene medium and relevant carboxamide compound (X) is produced with high yield.

Composition and structure of synthesized substances were confirmed by defining their phsical and chemical constants and IR-spectroscopic analysis.

Experimental part

N-(2-aminephenyl)alkyl carboxamide (II) and 2-alkyl-benzimidazole (III). 70ml of p-xylene and 5.40 g (0.05 mol) of ortho-phenylenediamine are placed into three-necked flask supplied with mechanical mixer, thermometer and reflux condenser and 14.00 g (0.05 mol) of chloroanhydride of naphthenic acid is added drop by drop. When chloroanhydride is added temperature of reaction mass increases up to 47°C. After adding chloroanhydride reaction mass is heated for 50 minutes at the range of 125-130°C. After a day crystal substance is filtered and separated from a liquid part, washed with water and dried. 12.3 g (94.8%) of a substances is produced. Two fractions are obtained in EtOH- H_2O mixture by recrystallization: 2.49 g (18.5%) of N-(2-aminephenyl)alkyl carboxamide (II). Melting temperature is 167-170°C IR-spectrum (v, sm^{-1}): 3230 (NH_2, related), 1710(C=O), 1600, 1560 ($C=C_{ar.}$), 755, 750 ($C=C_{ar.}$ 1,2-substituted). 2) 9.48 g (75.5%) of 2-alkyl-benzimidazole (III). Melting temperature is 117-120°C. IR-spectrum (v, sm^{-1}): characterizes 3400 NH···N type hydrogen bond and shows association of benzimidazole molecule. 1640 (C=N, in cycle), 760, 750 ($C=C_{ar.}$, 1.2-substituted).

N-(3-aminephenyl) alkyl carboxamide (IV) N,N-(1.3-phenylene) -1.3-dialkylcarboxamide (V) and 2.4-(dialkyl-benzoxydiapesine) (VI). Using the above method three

substances are obtained in 70 ml of para-xylene by the reaction of 14.00 g (0.05 mol) of chloroanhydride with 5.40 g (0.05 mol) of meta-phenylenediamine: 1) 9.76 g (45.4%) of N, N-(1.3-phenylene)-1.3-di-alkylcarboxamide (V). Melting temperature is 148-152°C. IR-spectrum (ν, sm^{-1}): 1690 (CO – NH), 1580, 1550 (C=C_{ar}), 780, 750 (C=Car. 1.3-substituted). 2) 3.63(27%) – N – (3-aminephenyl) alkylcarboxamide (IV). Melting temperature is 115-120°C (EtOH-H_2O). IR-spectrum (ν, sm^{-1}): 3330 (-NH_2), 1690 (CO-NH), 1590, 1560 (C = C_{ar}), 775, 760 (C – $C_{ar.}$ 1.3-substituted). 3) 2.76 q (13.4%) 2.4-(diakyl)-benzoxydiapesine (VI). Melting temperature is 93-97°C (EtOH-H_2O). IR-spectrum (ν, sm^{-1}): 1660 (C = C, in cycle), 1645 (C = N, valence vibrations), 1560, 1500 (C = C_{ar}), 1050, 1040 (C – O – C, symmetric valence vibrations), 855, 830 (C = $C_{ar.}$ 1.3-substituted). $R_{f.}$0.46

N-(4-aminephenyl) alkyl carboxamide (VII) and N,N-(1.4-phenylene) -1.4-dialkylcarboxamide (VIII). Using the above method mono- and diamide compounds (VII,VIII) are obtained in 70ml of para-xylene by the reaction of 14.00 g (0.0.5 mol) of chloroanhydride with 5.40 g (0.05mol) of para-phenylenediamine. 1) 10.6 g (35.4%) of N,N-(1.4-phenylene) -1.4-dialkylcarboxamide (VIII). Melting temperature is 167-171°C (EtOH-H_2O). $R_{f.}$ 0.24 IR-spectrum (ν, sm^{-1}): 3230 (NH), 1690 (CO-NH), 1600, 1510 (C=$C_{ar.}$), 860, 830 (C = $C_{ar.}$ 1.4-substituted). 2) 8.56 g (48.6%) of N-(4-aminephenyl) alkylcarboxamide (VII). Melting temperature is 123-127°C (EtOH-H_2O). $R_{f.}$ 0.39 IR-spectrum (ν, sm^{-1}): 3420 (NH_2), 1690 (CO), 1665 (CO – NH), 1600, 1500 (C=C_{ar}), 860, 815, (C=$C_{ar.}$1.4-substituted).

4-(alkylcarboxamide) benzoic acid (IX). Using the above method 16.60 g (84.6%) of 4-(alkylcarboxamide) benzoic acid (IX) is obtained with 2.8 g (0.07 mol) of NaOH solution by the reaction of 14.6 g (0.05 mol) of chloroanhydride (I) with p-aminebenzoic acid. $T_{melt.}$127-129°C (EtOH-H_2O). In IR-spectrum (ν, sm^{-1}): 3360 (– OH), 1690 (– CO – NH –), 1600, 1560 (C = $C_{ar.}$), 860, 820 (C = $C_{ar.}$, 1,4-substituted) absorption bands confirm the structure of the substance (IX).

Ethyl 4-(alkylcarboxamide) benzoate (X). Ethyl ether of 8.25 g (0.05 mol) of p-aminebenzoic acid and 70 ml of p-xylene mixture is placed in three-necked flask and chloroanhydride (I) is added into it drop by drop. When chloroanhydride is added the temperature of the reaction mass increases up to 57°C. Then at the range of 75-80°C it is heated for 45 minutes. After cooling the deposit is filtered and separated from a liquid part. It is recrystallized in water-alcohol mixture and the following is obtained: 16.7 g (79.5%) of ethyl 4-(alkylcarboxamide) benzoate (X). $T_{melt.}$ is 47-49°C (EtOH-H_2O). IR-spectrum (ν, sm^{-1}): 3320 (– NH –), 1720 (– COOAlk), 1580, 1510 (C = $C_{ar.}$), 1240, 1180 (– O – C –) adsorption bands confirm its structure.

IR-spectrum was taken in the form of suspension in vaseline oil in “Nikolet is 10” spectrometer. Thin-layer chromatography analysis was performed on silicagel in petroleum ether – diethyl ether acetic acid (90:10:45) system.

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