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3.5 - The Reaction of Dinitro Benzoic Acid Buttery Salt with Chloroacetic Acid Esters and Amide

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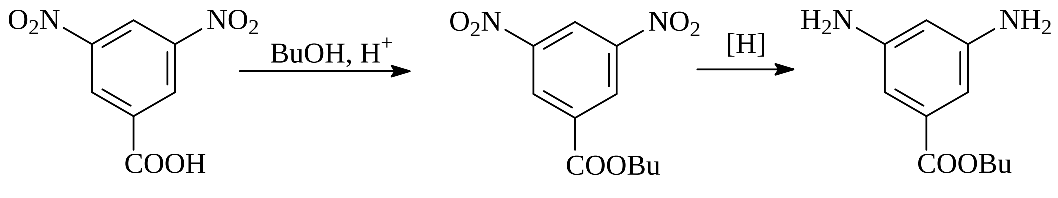
Annotation: Reactions of 3, 5-Dinitrobenzoic acid sodium salt with chloroacetic acid phthalimido ethyl, ethyl ether and amide were carried out in DMF solvent. It was found that 3, 5-Dinitro benzoic acid went by nucleophilic exchange reactions with sodium salt. IK and Chromomass spectrum results of the obtained substances were obtained and the results were analyzed.

Keywords: 3, 5-dinitrobenzoic acid sodium salt, Chloroacetic acid phthalimidoethyl ether, Chloroacetic acid ethyl ether, Chloroacetic acid, DMF, amidoalkylation, complex ester.

Introduction Complex esters of carboxylic acids belong to the class of important compounds used in economy, industry and medicine. Currently, due to the level of resistance of the organism to drugs, the attention to the synthesis of high-quality and new drugs has increased. The body's resistance crisis is mainly caused by overuse of antibiotics and non-compliance with the instructions [1-3]. Also, serious attention is being paid to reducing the negative effects of substances similar to natural compounds and substances used as food addictives . In addition, the synthesis of new therapeutic drugs is an expensive and time-consuming and risky process, and during the trial period, microorganisms may remain unharmed in the developmental stages and resistance to the drug under the study [4].

In particular, sodium or potassium salts of aromatic carboxylic acids are widely used as intermediates in obtaining their complex esters. Such compounds, that is, compounds that give the properties of natural compounds, are mainly esters of carboxylic acids. It is possible to obtain complex esters with high yield as a result of reactions with carboxylic acid salts and alkyl halides. In the literature, many methods of obtaining complex ethers based on the salts of various carboxylic acids are presented, and in these works, dimethylformamide (DMF) is used as a solvent. , dimethylsulfoxide (DMSO), dimethylacetamide (DMAA) and other such aprotic solvents have been used[5,6]. Among these solvents, the most commonly used is dimethylformamide.

The interaction of 3,5-dinitrobenzoic acid with butyl alcohol was carried out in the presence of sulfuric acid and the corresponding butyl ether I was synthesized, as a result of its reduction with hydrazine hydrate in the presence of iron chloride on activated carbon, the butyl ether of 3,5-diaminobenzoic acid II was obtained [7].



I

II

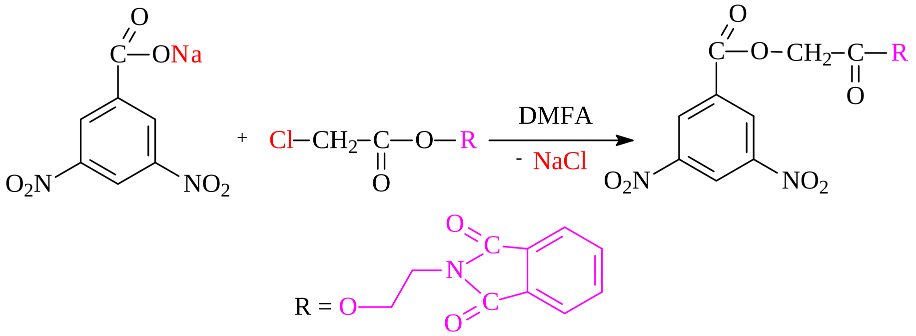
It was observed that DMF is a suitable solvent for the reactions of the sodium salt of p-aminobenzoic acid with chloroacetic acid esters, and the reaction is formed with high yields at temperatures of 70^{0}C and 155^{0}C in the case of 1:1.2 mole ratio of reagents. Reaction equation: [8]

Etherification reaction of benzoic acid with ethyl alcohol is carried out in very high frequency radiation furnaces for 8-10 min. almost 100% yield was achieved during [9].

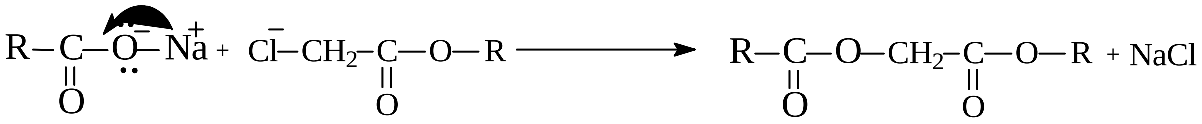
Complex esters of carboxylic acids can be obtained without a catalyst, but it requires high temperature (270-300 ^{0}C). Therefore, the authors used tetraalkyl titanates improved with inorganic reagents as catalysts to carry out the etherification reaction of phthalic anhydride with monoatomic alcohols at low temperatures [10].

Analysis of the reaction of 3,5-dinitrobenzoic acid sodium salt with monochloroacetic acid phthalimidoethyl ether. For the reaction, a mixture of 3,5-dinitrobenzoic acid sodium salt and monochloroacetic acid phthalimidoethyl ether was boiled in dimethylformamide solvent. At first, we took 0.01 mol of 3,5-dinitrobenzoic acid sodium salt, boiled it in 4 ml of dimethylformamide for 10 minutes, then cooled the reaction mixture slightly and added phthalimidoethyl ether of chloroacetic acid. Crystals of NaCl salt formed from the reaction mixture. As the reaction time increases, the amount of separated crystals also increases. The fact that the formed crystals are different from the original sodium benzoate crystals and their insolubility in the reaction medium is one of the most important signs that indicate the progress of the reaction. After removing the solvent from the reaction mixture with dimethylformamide, the residue was cooled and dissolved in water. The ether fraction was separated in a separatory funnel and the aqueous fraction was extracted with benzene. The benzene was removed from the aqueous portion, and the remaining residue was added to the ether layer.

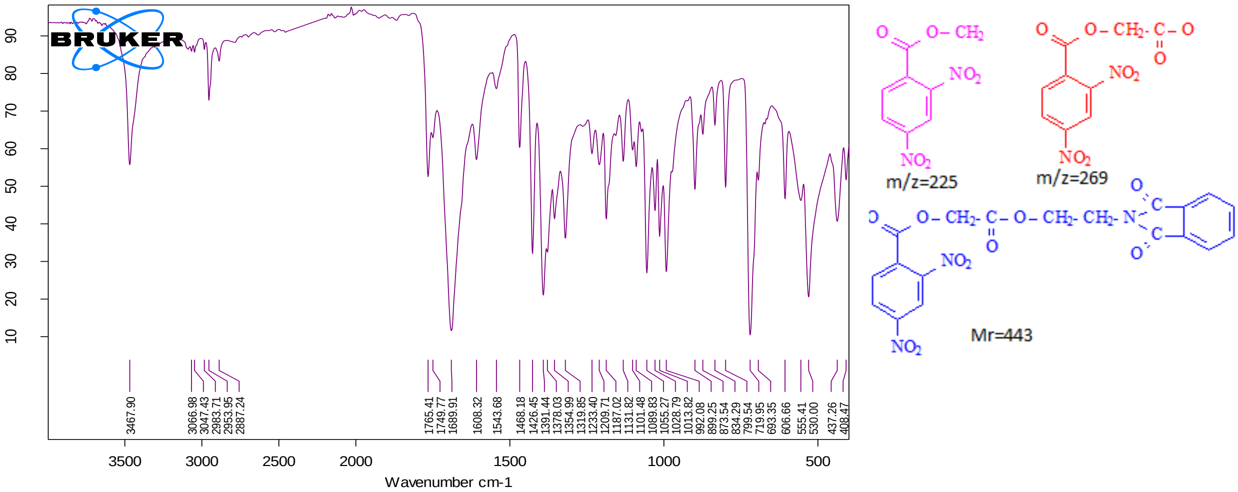
The YUQX method was used to determine the purity of carbthalimidoethoxymethyl-3,5-dinitrobenzoate by recrystallization from alcohol. Silufol was chosen and the ratio of chloroform-benzene-methanol 5:4:1 was chosen as the system, and Rf= 0.75, product yield was 47%, melting temperature was 126-128^{0}C. . One of the most important aspects of the reaction in DMF solvent is the high boiling point and sufficient solubility of the salt. When the same experiment was carried out in DMSO solvent, the yield of the product was 42%, T_{liquid}= 126-128^{0}C Rf= 0.75 (silufol, system chloroform-benzene-methanol (5:4:1)) acetone, it was observed that the reaction almost did not proceed Reaction equation:



The mechanism of the etherification reaction was proposed as follows:

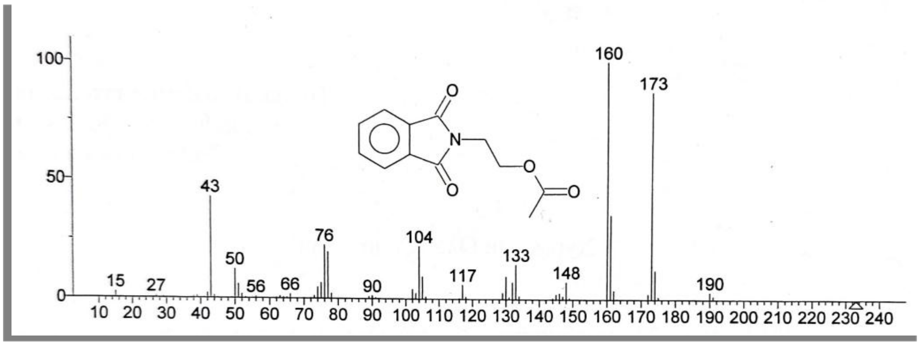


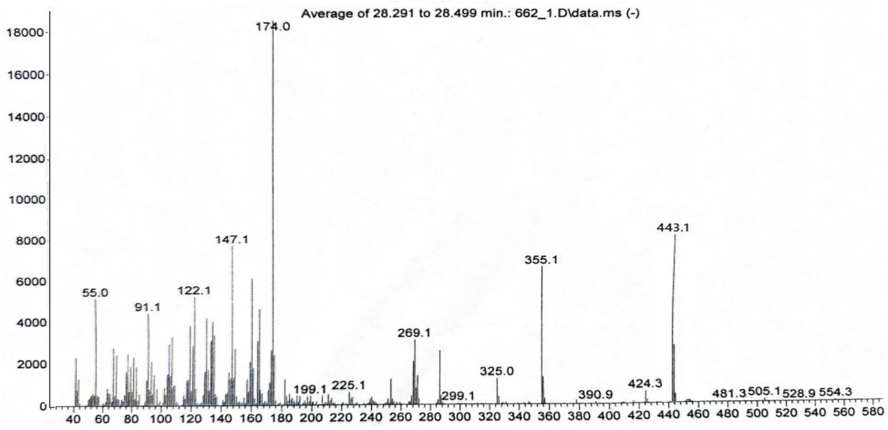
$$R-\underset{\|\atop O}{C}-\overset{-}{\ddot{O}}-\overset{+}{Na} + \overset{-}{Cl}-CH_2-\underset{\|\atop O}{C}-O-R \longrightarrow R-\underset{\|\atop O}{C}-O-CH_2-\underset{\|\atop O}{C}-O-R + NaCl$$



In the cited works, it was found that the desired results can be achieved even when dimethylformamide is taken in small amounts. As a result of the reaction, when determining the structure of carbethoxyphthalimidomethyl-3,5 dinitrobenzoate, IK-spectrum analysis: in the absorption areas of 2953, 3047 sm^{-1}, low intensity absorption lines corresponding to =C-H bonds in the aromatic ring of the substance can be seen. In the 2887 sm^{-1} region, there are symmetric valence vibrations belonging to the $–CH_2$ group, 1055 sm^{-1} to the $–C(O)-O-CH_2$ bond, and in the 1765 sm^{-1} absorption region, there is an intense vibration belonging to the >C=O group valence vibrations, in the region of 720 sm^{-1} (benzene ring)-CH, 1628, 1468, 1417 sm^{-1}, and the ring vibration belonging to the aromatic ring of medium intensity can be observed. In the region of 2887, -1543 sm^{-1} valence vibrations related to the $–NO_2$ groups attached to the aromatic ring were observed.

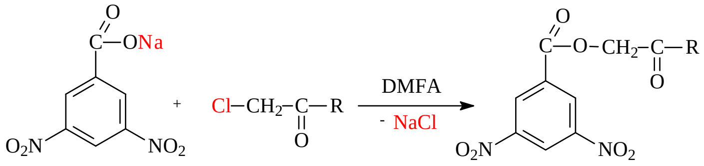
The analysis of the diephyry formed by the sodium salt of 3,5-dinitrobenzoic acid with chloroacetic acid phthalimido ethyl ether was checked by chromo-mass spectrum:





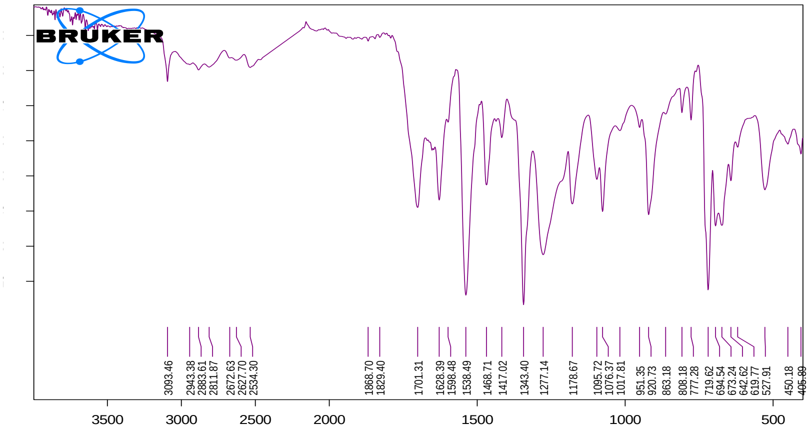
Analysis of the reaction of the sodium salt of 3,5-dinitrobenzoic acid with ethyl ether of monochloroacetic acid. The reaction of sodium salt of 3,5-dinitrobenzoic acid with ethyl ether of chloroacetic acid was studied in dimethylformamide solvent based on the methods mentioned above.

For the experiment, we took 3,5-dinitro benzoic acid sodium salt and dissolved it in dimethylformamide. We added ethyl ether of chloroacetic acid to the resulting reaction mixture and boiled the reaction mixture for a certain time. After completion of the reaction, dimethylformamide was removed under vacuum at 50-60 ^{0}C under low pressure. 10 ml of water is added after the obtained chloroacetic acid ether is cooled, NaCl is soluble in water, but the ether layer is insoluble. The lower ether was separated using a separatory funnel. The resulting ether was recrystallized in alcohol and a brownish yellow oily substance was formed. The general reaction equation is:



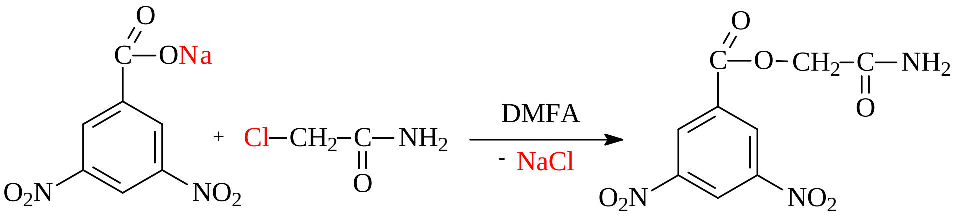
R = O—C_2H_5

The purity of carbethoxymethyl-3,5-dinitrobenzoate was determined in YUQX with Rf= 0.55 (silufol, system Chloroform-benzene-methanol 5:1.5:1), product yield is 77%, and liquefaction temperature Tliquid = 105-110 ^{0}C. When the same experiment was carried out in DMSO solvent, it was found that the product yield did not decrease significantly (68 %) and the physical quantities did not differ. When the biological activity of the obtained products was tested using the PASS program, several properties, mainly inhibitory properties, showed high results. Based on this, we set the goal of our next work to study the biological properties of the obtained compounds.

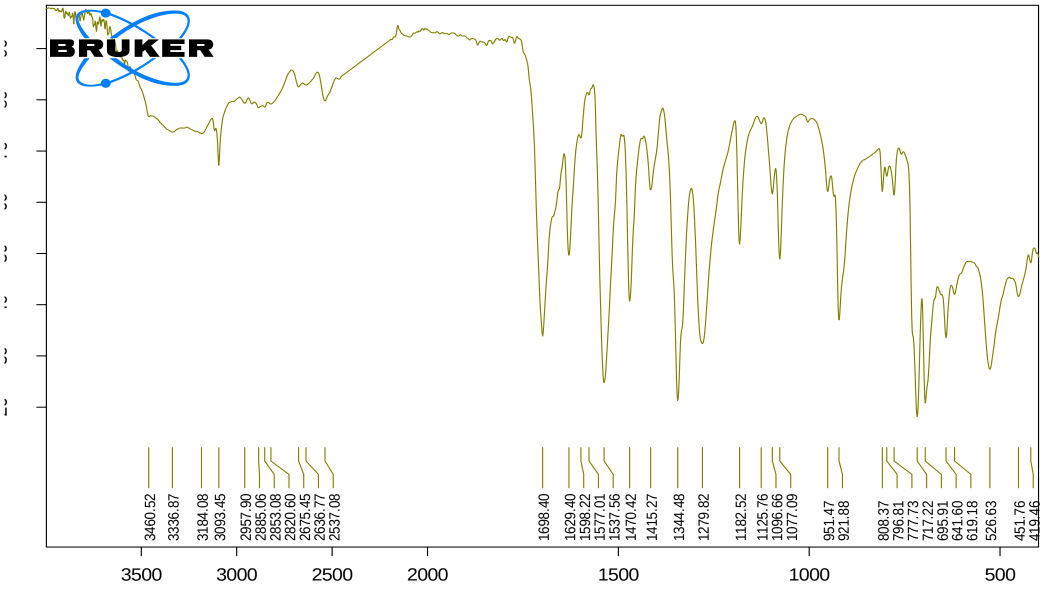


Analysis of the IK spectrum of carbethoxymethyl-3,5-dinitrobenzoate: in the absorption regions of 3093 sm^{-1}, low intensity absorption lines corresponding to =C-H bonds in the aromatic ring of the substance can be seen. In the region of 2883 sm^{-1}, there are symmetric valence vibrations belonging to the $–CH_2$ group, at 1095 sm^{-1} to the $–C(O)-O-CH_2$ bond, in the absorption region of 1701 sm^{-1} there is an intense vibration belonging to the >C=O group valence vibrations, in the region of 720 sm^{-1} (benzene ring)-CH, in absorption regions such as 1628, 1468, 1417 sm^{-1}, a ring vibration belonging to the aromatic ring of moderate intensity can be observed. In the region of 2811, -1538 sm^{-1} valence vibrations related to the $–NO_2$ groups attached to the aromatic ring were observed.

Analysis of the reaction of the sodium salt of 3,5-dinitrobenzoic acid with the amide of monochloroacetic acid. The reaction of sodium salt of 3,5-dinitrobenzoic acid with amide of 2,4-monochloroacetic acid was studied in dimethylformamide solvent based on the methods mentioned above. For the experiment, 3,5 dinitro benzoic acid sodium salt and amide of monochloroacetic acid, DMF was taken as a solvent. The reaction was carried out by boiling at a high temperature of 140-145 ^{0}C. After completion of the reaction, dimethylformamide was removed under vacuum at 50-60 ^{0}C under low pressure. After the obtained benzoic acid ether is cooled, 10 ml of water is added to remove NaCl from the system by dissolving it in water. The ethereal layer was separated and recrystallized in alcohol, and a pale yellow oily substance was formed. The YUQX method was used to determine the purity of carbaminomethyl-3,5-dinitrobenzoate. For this, chloroform, benzene, methanol were selected as silufol and solvent systems. The value of Rf was found to be equal to Rf= 0.5 (Silufol, Chloroform-benzene-methanol 5:1.5:1), and the melting temperature was 175-180 ^{0}C. The product yield was 66% when the same experiment was carried out in DMSO solvent. The general reaction equation is:



Based on the results obtained during the experiments, taking 5 or 6 times more solvent than di-nitrobenzoic acid and conducting the reaction for 5-6 hours shows that it is an alternative for these reactions.



Carbaminomethyl-3,5 dinitrobenzoate

In order to prove the structure of the obtained product (carbaminomethyl-3,5-dinitrobenzoate), it was studied using the IK spectrum. In the IK-spectrum analysis: in the absorption areas of 3093 sm-1, low intensity absorption lines corresponding to =C-H bonds in the aromatic ring of the substance can be seen. 1698 sm^{-1} 1344 sm^{-1} belongs to >C=O, in the area of 1279 sm^{-1} absorption belonging to the –CH2 group is observed, in the area of 717-777 sm^{-1} (benzene ring)-CH, -CH_2-CO = 1415 In the -1470 sm^{-1} area, low valence in the 3184 sm^{-1} area and scissor average vibration in the 1640 sm^{-1} area belong to the NH_2 group, and in the -1537-1577 sm^{-1} area, the valence vibrations belong to the –NO_2 groups attached to the aromatic ring observed.

Reagentlar mo'l nisbatlari:	Reaksiya Unumi: (DMF)	Reaksiya Unumi: (DMSO)	Reaksiya vaqti soat	Sistema Xloroform-benzol-metanol (*a*=5:1.5:1) (*b*=5:4:1)
3,5-dinitrobenzoy kislota natriyli tuzi: xlorsirka kislotasining ftalimidoetil efiri: DMF 1:1,2:5	47%	42%	5	(*b*) Rf=0,75
3,5-dinitrobenzoy kislota natriyli tuzi: xlorsirka kislotasining etil efiri: DMF 1:1,2:5	77%,	68%	5	(*a*) Rf=0,55
3,5-dinitrobenzoy kislota natriyli tuzi: xlorsirka kislotasining amidi: DMF 1:1,2:5	72 %	48%	5	(*a*) Rf=0,5

Chloroacetic acid was made by etherification reactions of phthalimidoethyl, ethyl ethers and amide.

It is known from the literature that bipolar aprotic solvents (DMSO, DMF, TGF, acetone, dioxane) facilitate the progress of bimolecular nucleophilic exchange reactions. But there is no information in the literature about how they affect the reaction when taken in small amounts. Based on the results of our experiments, we can say that when DMF is taken in small amounts, it acts as a catalyst in addition to the solvent. In our experiments, DMF helped to activate sodium benzoate, and thus the reactions proceeded in high yields. In these experiments, we concluded that when using DMSO solvent, the yield of the products did not decrease.

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