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Effect and Spectroscopic Analysis of Solutions in Trychloratsetylpyrogallol Synthesis †

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Abstract: The process of interaction of organic substances mainly occurs in the solvent environment. Therefore, the effect of solvents on the o-chloroacetylation process was studied. For this, the reaction process of triatomic phenol-pyrogallol with chloroethyl chloride in various solvents was studied. In order to study the reaction with pyrogallol chloroacetyloride in various solvents, the compound was subjected to chromatographic, UV, IR, and NMR analyses.

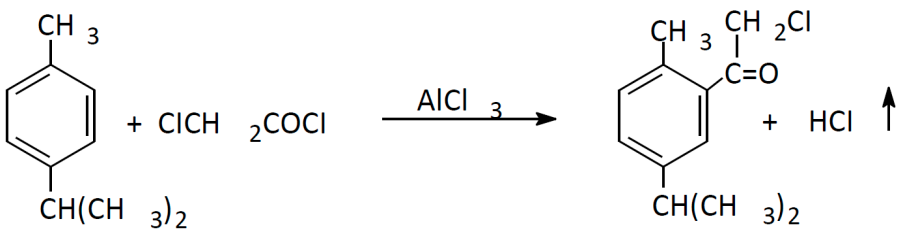
Keywords: chloroacetyl pirogallole; nucleophilic substitution; solvents; UV; IR; and NMR analyses

1. Introduction

The chloroacetylation reaction of an aromatic ring was first studied by Ch Friedel and J.M. Crafts. They carried out the reaction between benzene and chloroacetyl chloride in the presence of an equimolecular amount of AlCI3 in a carbon sulfide solution, and as a result obtained the appropriate chloroketone with a yield of 66% [1]:

O. Gore used monochloroacetic anhydride as an acylating agent in the chloroacetylation reaction of benzene and obtained phenacyl chloride in 88% yield.

They studied the interaction of p-Tsymol and chloroacetyl chloride. 2-methyl-5-isopropylphenacyl chloride was obtained with 30% yield using AlCl3 as a catalyst [2]:



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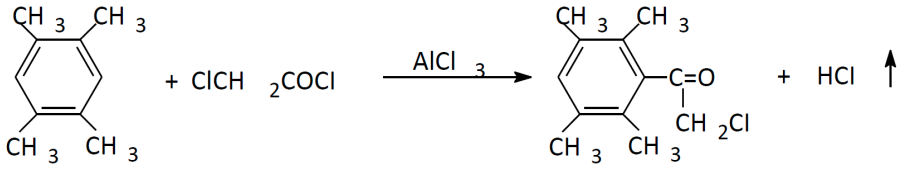
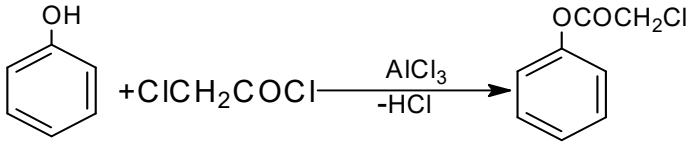
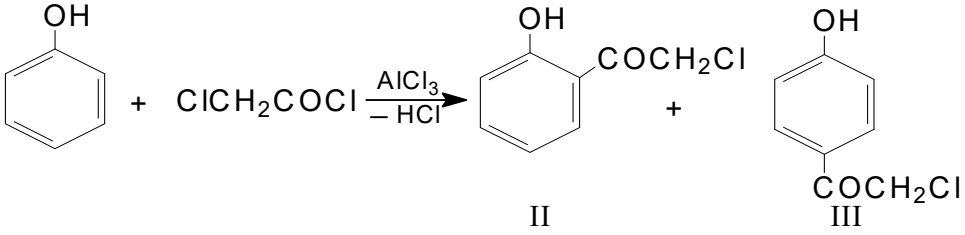
Buy-Khoi and co-workers [3] carried out the chloroacetylation reaction of durol in the presence of AlCI3. They were able to obtain chloroketone with a high yield (78%):



The reaction of chloroacetylation of phenol was first performed by F. Kunkel and F. Johannson studied phenol:chloroacetyl chloride:AlCl3 in a ratio of 1:1:0.7 (CS2, 0 °C) and they determined that phenylchloroacetate is formed as a result of the reaction [4]:

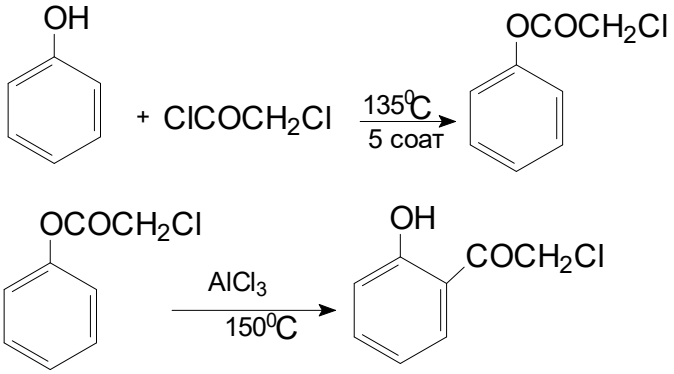


N.M. Cullinan and F.R. When Edwards carried out the same reaction at 10–20 °C and in an excess of phenol, the S-acylation reaction took place and 2- and 4-hydroxyphenacyl chlorides were formed [5]:



K. Fries and A. Fink practically proved that in the reaction of chloroacetylation of phenols, O—acylation reaction takes place first, complex ether is formed, and then regrouping occurs to form S—acylation product-ketone, later this reaction was named "Fries rearrangement" [7].

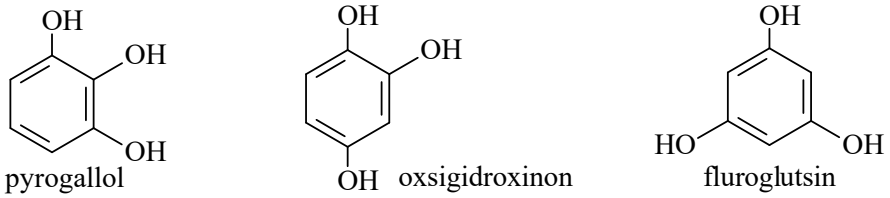
Later K. Fries and V. Pfaffendorfs synthesized phenylchloroacetate by heating a mixture of phenol and chloroacetyl chloride at (1350C) for 5 h and regrouping it (1500C) in the presence of AlCl3, they found that only 2-hydroxyphenacyl chloride was formed as a result of the reaction:



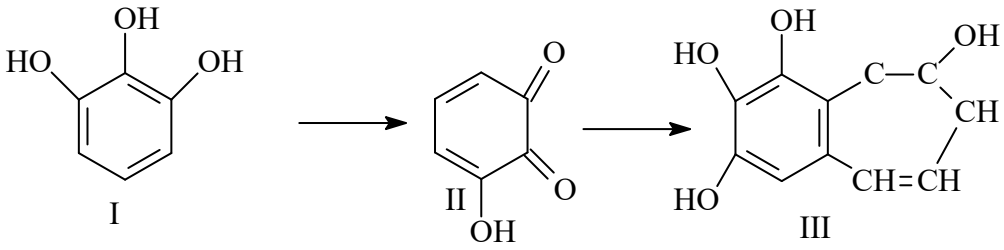
G.N. Dorofenko and E.N. Sodikov [8] also studied the reaction of chloroacetylation of phenol. Unlike the above authors, they heated phenol and chloroacetyl chloride in

equimolecular amounts without catalyst (14 h) and announced the formation of O-acylation product phenylchloroacetate with 79% yield.

Considering the above information, the o-chloroacetylation reaction of triatomic phenols was studied. Pyuragallol (1,2,3-trioxybenzene), oxyhydroquinone, and fluoroglucin (1,3,5-tri oxybenzene) are examples of trihydric phenol compounds:



Pyragallol has a special property among three-atom phenols. Depending on the condition, it easily undergoes an oxidation reaction and turns into a tarry black liquid. Research has revealed that when pyrogallol is oxidized, the following process occurs: pyrogallol is first transformed to orthquinone, then at the conclusion of the process, it is converted to purpurogallin [9–11].



The chemical activity of pyurogallol was increased by a chloroacetylation process. It is well recognized that the chloroacetylation reaction's byproducts are extensively employed in the chemical industry, in medicine, and in several agricultural industries. The national economy therefore places a high value on phenol chloroacetylation goods and items made from their base. Finding practical and affordable ways to synthesize new chloroacetyl products and their derivatives, as well as studying their biological properties, is one of the urgent tasks of organic chemistry.

2. Experimental

To ascertain the composition of the reaction products, Silufol-254 plates were subjected to thin layer chromatography (TLC). In the mobile phase system of benzene and ethyl ether of acetic acid (95:5), TLC was used to assess the reaction's development and the purity of the compounds that were produced during the process. Aluminum plates with a silica gel coating (silica gel 60 F254) purchased from MERCK in India were used for the TLC stationary phase. UV light was used to see how compounds were distributed on TLC plates. Column chromatography was used to clean the reaction mixture, and the yield of the chemical reaction that resulted from isolation was determined. After separation by column chromatography, the reaction mixture was confirmed by TLC using benzene and ethyl acetate (95:5) as the mobile phase. The reaction was subsequently completed, and the liquid was poured into ice-cold water. The solid material that had crystallized was filtered and dried. The starting material was cleaned using column chromatography and petroleum ether and ethyl ester of acetic acid. The FT-IR spectra of the goods were obtained on a Carl Sies (Germany) Specord IR-71 spectrophotometer using the KBr pellet method. TMS was used as the internal standard for the 1H NMR recordings, and chemical shift values were expressed in ppm scale using a Bruker (Germany) 400 MHz NMR apparatus. Using a Mvtec melting point equipment and the open capillary approach, the uncorrected melting points of the produced compounds were determined [12,13].

Synthesis of trichloroacetylpyragallol. Try out the pyrogallol chloroacetylation process. In a 100 mL round flask with a refrigerant (1:3), combine 6.3 g (ops mol) of pyrogallol and 16.95 g (p-1.4 g/mL, 12.1 mL; 0.15 mL) of chloroacetyl chloride. 35 cc of chloroform (along with other solvents) was added before being poured over them. The combination is heated, and it is anticipated that the process will start when the solvent reaches its boiling point. The radiation lasts for 22 h. In reality, the separation of the HCl (as confirmed by wet litmus paper) is evidence of the process' progress. The solvent was released when the process had finished. Tests revealed that the leftover mixture was TLC (0.644).

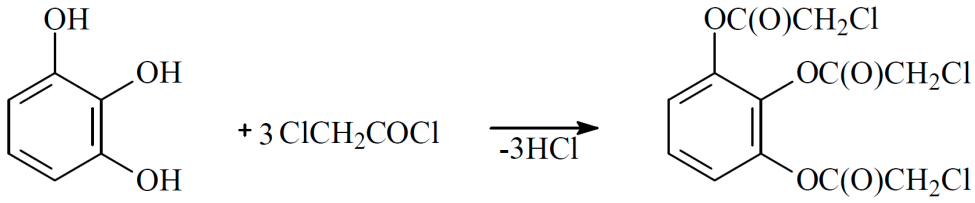
3. Reaction Results and Discussion of Results

When the O-chloroacetylation process is carried out in a chloroform solution, the degree of generality is at its highest. Pyrogallol is chloroacetylated to produce 95% O-chloroacetyl pyrogallol in a chloroform solution.

The sorbed electron density from the chloroacetyl chloride molecule gives the oxygen molecule in the reaction between pyrogallol and chloroacetyl chloride a partial negative charge. The carbon atom interacts with the double electrons of the hydroxyl group in the pyrogallol molecule to form complex I, and the chlorine and oxygen atoms' electrons work to give the element carbon a partial positive charge. Complex II, from which the byproduct of the reaction with hydrogen chloride is removed, is generated during the process when an oxygen-to-carbon valence bond is formed.

Chlorine organic compounds used in the reaction process were more efficient. However, in other solvents (benzene, hexane, and heptane), the reaction was more difficult, and in the process, the product was formed mixed with the oxidation product of pyrogallol. This made the process more complicated.

It is investigated how pyrogallol reacts with trichloroacetypirogallol and chloroacetylchloride.

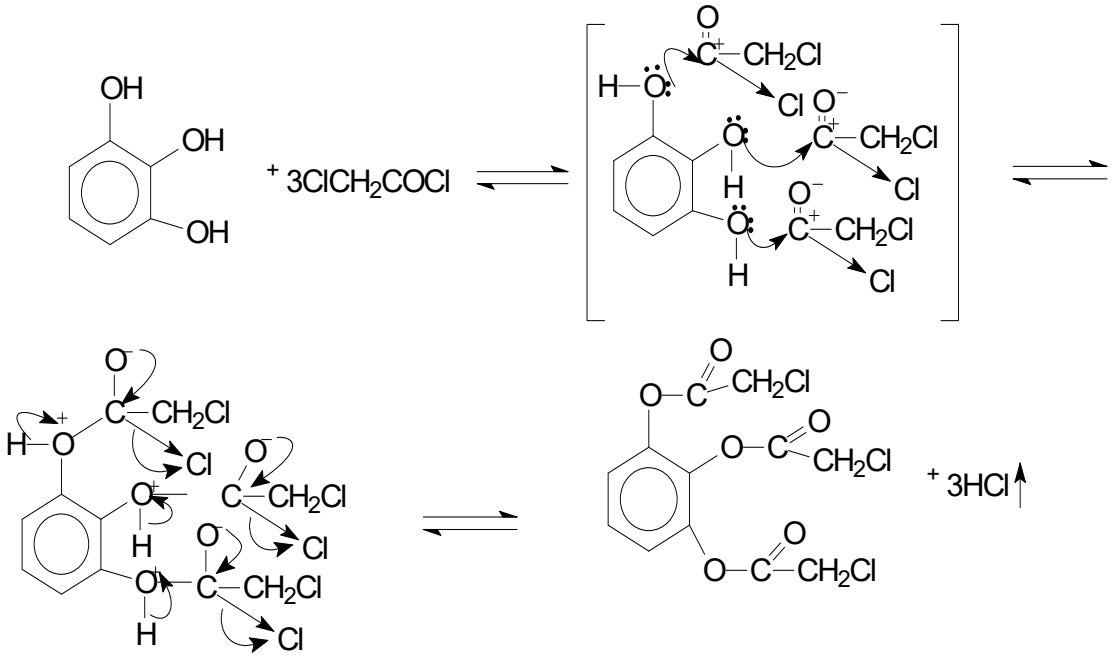


The procedure continues till the conclusion of the HCl elevage as the reaction follows the type of nucleophilic exchange (S_N1). The production yield of the product in chloroform was high, and the procedure was carried out in apraton solvents. Table 1 provides the yield of the reaction in relation to the reducers.

Table 1. Reaction product of the production of trichloroacetylpirogallol with relation to solvents.

Solvents	T_{qay} °C	ϱ g/mL	η %
Xloroform	61.2	1.483	95
Tetraxlormetan	76.75	1.595	90
Dixloretan	83.47	1.253	99
Benzol	80.1	0.879	61.2
Geptan	98	0.6834	60.03
Geksan	68.95	0.6594	60.12

Reaction mechanisms:



UV-spectral data of trichloroacetylpyrogallol: The aromatic ring for pyrogallol exhibits UV absorption spectra in the region of 228 nm ($\pi \rightarrow \pi^*$) and 265 nm ($n \rightarrow \pi^*$) of the OH group linked to the aromatic ring. These absorption regions, however, were not preserved in the molecule we created throughout the reaction. The development of the estimated product is further supported by the fact that the aromatic ring's absorption area relocated to 250 nm and a new absorption region between 295 and 310 nm was created as a result of the synthesis of the carbonyl group (C=O) (Figure 1).

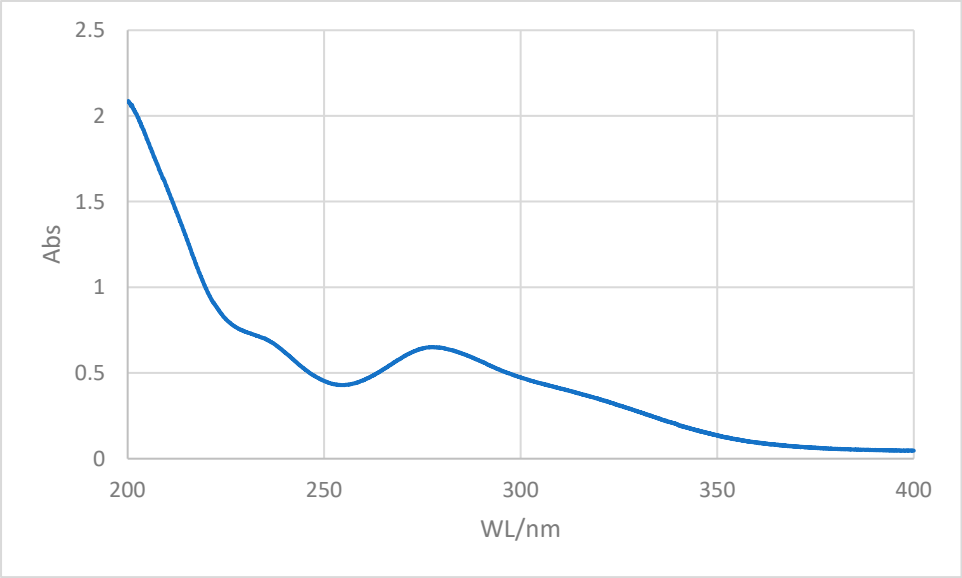


Figure 1. UV spectrum of the chloroacetyl chloride product of pyrogallol.

IR-spectral data of trichloroacetylpyrogallol (Figure 2): (Ar)C-C bond in the range 1500–1400 sm^{-1}, (Ar)C-H bond in the low absorption region 3100–3000 sm^{-1}, Carbonyl group valence oscillation ($\nu_{C=O}$) 1790–1720 sm^{-1} intensity extremely strong field, characterized by a carbonyl group C-O bond 1280–1270 sm^{-1} area, and (Ar) =C-O- bond 1270–1180 sm^{-1} broad intense absorption field In the 800–600 sm^{-1} region of absorption, intense valence bond oscillations of the -CH_2-Cl bond are seen. In the resulting product, the following absorptions are seen: strong, medium-intensity acetyl group valence

oscillations in the region of absorption at 3452.17 sm^{-1}; average weak-intensity absorption valence oscillations particular to group C-H in the aromatic ring: 311.27, 307.25, 3011.65 sm^{-1}; average weak-intensity absorption valence oscillations specific to group C=C in the aromatic ring: 1598.03, 1509.24, 1455.96, 1465.40, 1441.33, 1410.82 sm^{-1}; average weak-intensity absorption deformation oscillations specific to group C-H in the aromatic ring were 947.85, 922.51, 826.57, 769.65, 769.83, 709.45, 734.19, and 654.45 sm^{-1}; average C=O group specific deformation vibration was 1759.51 sm^{-1}; average valence oscillations specific to group C-O in the area of weak absorption was 1054.80; Oscillations unique to the C-Cl group were avoided in the region of average absorption of 522.68 sm^{-1}.

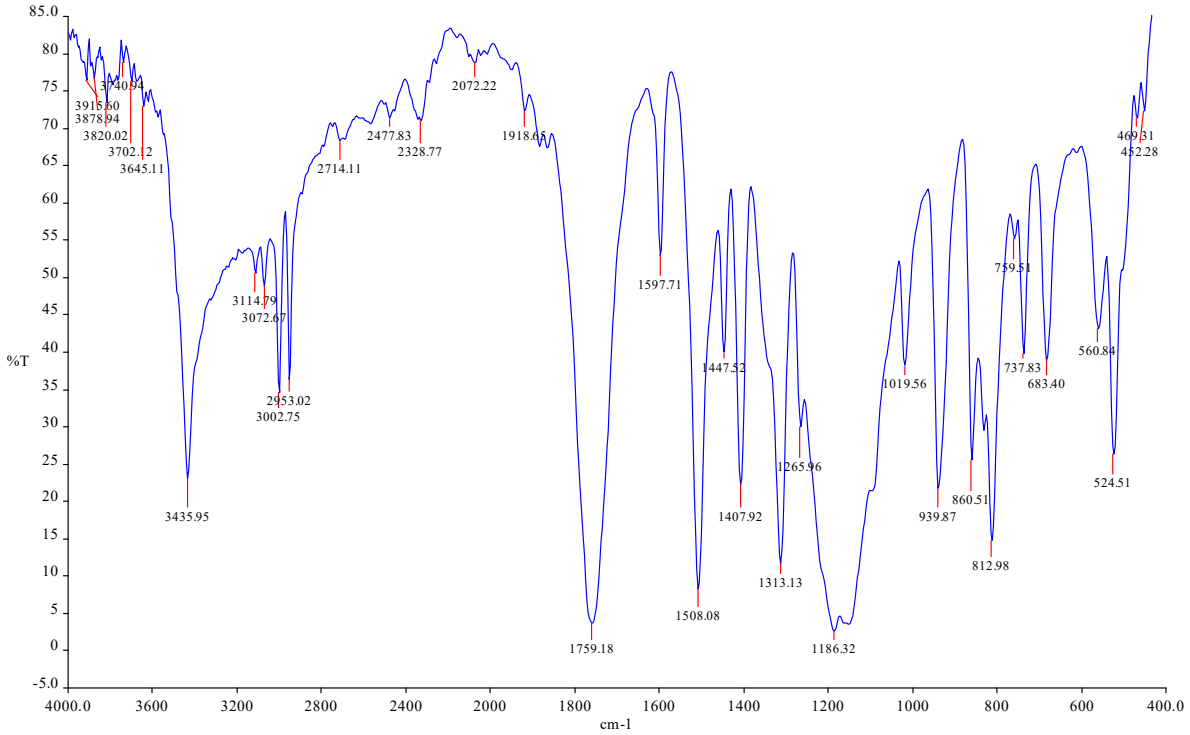


Figure 2. Fourier transform infrared spectrum of O-trichloroacetyl pyrogallol.

^{1}H NMR-spectral data of trichloroacetylpyrogallol: The ^{1}H NMR (400 MHz, $CDCl_3$)spectra of O-trichloroacetyl pyrogallol are presented in Figure 3 and characterize the absorption lines of the hydrogen atoms in the molecule as follows: δ 6.7 (m, 1H, ArH), 7.07 (d, *I* = 8.5 Hz, 1H, ArH), 7.25 (m, 1H, ArH), 12.23 (s, 1H, -OH). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 163.8, 153.0, 136.1, 131.7, 126.2, 121.9, 116.0, 77.5, 26.7, 22.8.

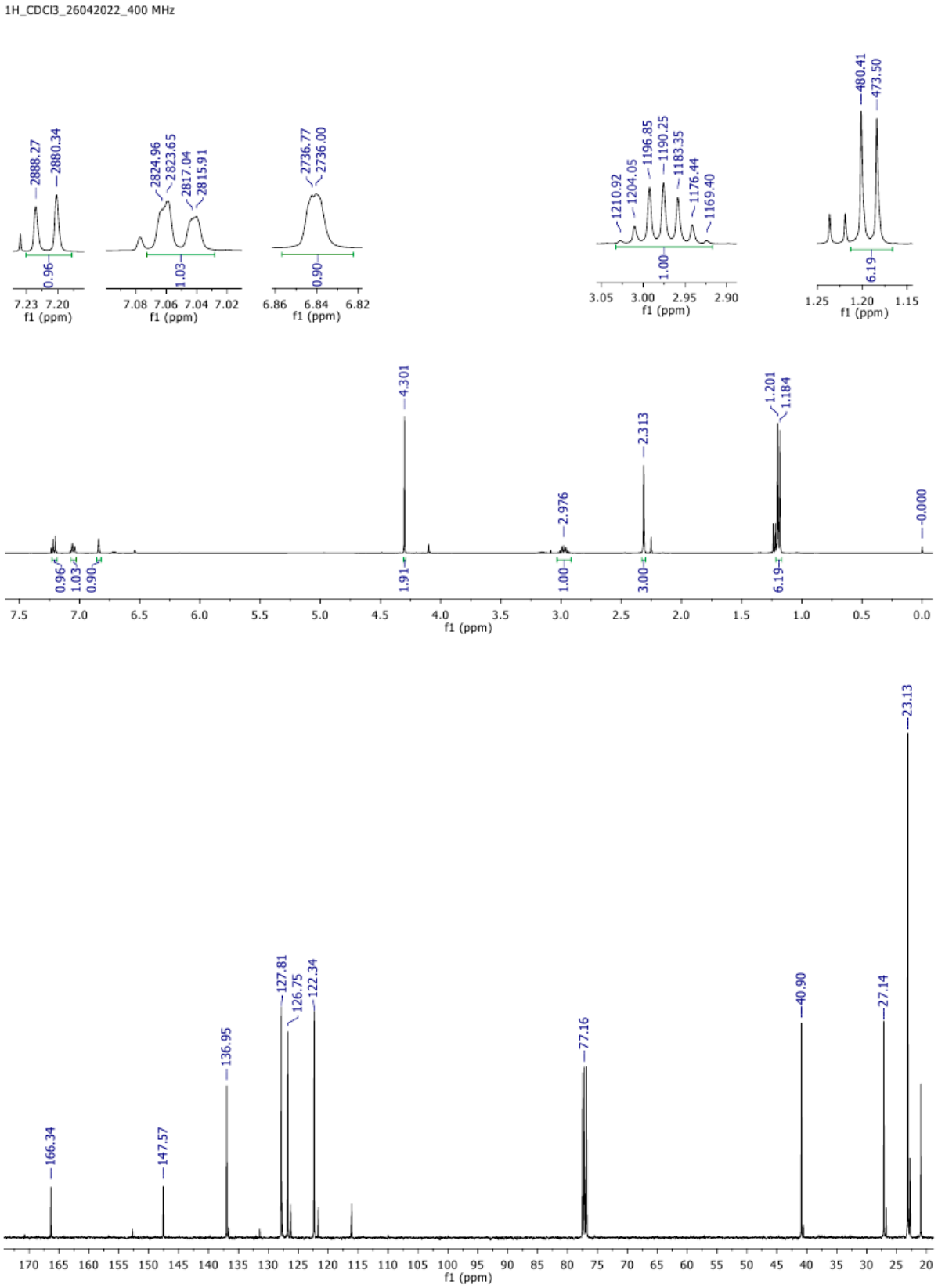


Figure 3. Fourier transform ^{1}H NMR and ^{13}C NMR spectrum of O-trichloroacetyl pyrogallol.

4. Conclusions

As a result of our research, we emphasize that it is necessary to use organochlorine compounds as solvents in the process of o-chloroacetylation of phenols. If heptane,

benzene or hexane is used as an inert solvent, as a result of oxidation of phenols prone to oxidation, various additional compounds appear in the reaction products.

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