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„SYNTHESIS OF TRICHLOROACETYL ESTERS OF ALDOLS“

„SYNTÉZA ESTERŮ KYSELINY TRICHLOROCTOVÉ S ALDOLY”

Diploma thesis

Universidad de Alcalá,
Faculty of Pharmacy,
Department of Organic Chemistry,
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This work was carried out at the department of Organic Chemistry, University of Alcalá under the supervision of Prof. Dr. Gloria Quintanilla, from September to March during the academic year 2008/2009 in Erasmus programme.

Fair declaration

I declare that I made this diploma thesis myself and mentioned every used sources and used literature.

Date: Signature:

I thank Prof. Dr. Gloria Quintanilla for her advices and good reminds. I also thank Ivan Peréz and Katarzyna Gorécka for their self-sacrificing assist. Special acknowledgement belongs to Ing.Vladimír Kubíček, CSc. for his vasty help and needful support.

CONTENTS

1. ABSTRACT

This diploma thesis describes synthesis of trichloroacetyl esters of aldols which were obtained by a reaction of trichloroacetic acid with formaldehyde and another comercial aldehyde. Used were hydratopaldehyde, isobutyraldehyde, 2-methylpentanal, 2-ethylhexanal and 2-ethylbutanal. Some of these esters were described in the literature but only in part, several of them are new compounds. Excellent yields and clean products prove that the applied method is a good way to achieve these compounds that can be easily used for further processes.

1.1 SOUHRN

Tato práce se zabývá syntézou esterů kyseliny trichloroctové s aldoly. Estery byly získány reakcí kyseliny trichloroctové s formaldehydem, k nimž byl přidán další komerčně dostupný aldehyd. Použity byly tyto aldehydy: hydratopaldehyd, isobutyraldehyd, 2-methylpentanal, 2-ethylhexanal a 2-ethylbutanal. Několik z těchto esterů již bylo popsáno v literatuře, ale pouze částečně, několik z nich jsou však nové sloučeniny. Výborné výtěžky a čisté produkty dokazují, že zvolená metoda je vhodným způsobem pro získání těchto sloučenin, které mohou být výhodně použity pro další procesy.

2. INTRODUCTION

This work was carried out at the department of Organic Chemistry of the University of Alcalá in the group of Prof. Dr. Fructuoso Barba and it is a part of global research of electrochemical behaviour of the carbon-halogen bond in organic compounds.

The research group investigates the synthesis of new organic compounds using electrolysis. One of the most studied process was the reduction of phenylacyl bromide in aprotic medium (DMF/ $LiClO_4$) obtaining 2,4-diarylfuranes in 80 % yield. 3-chloro-4-alkyl (-aryl) coumarines or 1-alkyl-4-alkyl (-aryl)-3-chloroquinolinones were another type of obtained heterocycles. They can be easily prepared by cathodic reduction of the trichloroacetlyesters of o-hydroxyphenones or o-(N-alkyl) aminophenones.

The synthesis of trichloroacetyl esters, which is the main aim of my research, is the first very important step in the series of reactions, because the esters serve as suitable compounds for further reduction of the carbon-chloride bond in order to get interesting new rings. As starting materials the corresponding comercial aldehydes together with either formalin (37 % aqueous solution of formaldehyde) or solid paraformaldehyde are used.

In this diploma thesis I studied various ways of synthesis, improved methods and I focused to achieve the best results with good yields and clean products. I also described the electrochemical properties by cyclic voltammetry which can take advantage for subsequent electrolysis.

3. THEORETICAL PART

3.1 ALDEHYDES

Aldehydes are a class of highly reactive organic chemical compounds containing a carbonyl group with one hydrogen atom attached to the carbon atom.

R-CHO

The word aldehyde is a combination of parts of the words alcohol and dehydrogenated, because the first aldehyde was prepared by removing two hydrogen atoms from ethanol. Aldehydes are very easy to detect by their characteristic smell. Some are very fragrant, and others have a smell resembling that of rotten fruit. A very powerful smelling compound is the decyl aldehyde, which has a scent of orange peel and is present in small concentration in most perfumes. The others are citral with odor of lemon, lauryl aldehyde like lilac or violets, anisaldehyde like liquorice or vanillin like vanilla.

The simplest aldehyde is FORMALDEHYDE (Fig.1).

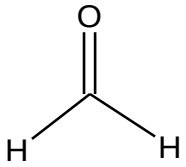


Fig.1 Formaldehyde

It has the central carbon atom in the carbonyl group bound to two hydrogen atoms. Its chemical formula is $H_2C=O$. Formaldehyde, discovered in Russia by A.M. Butlerov in 1859, is a gas in its pure state. It is either mixed with water (sold as formalin solutions) or as a solid polymer called paraformaldehyde. Rather small formaldehyde molecule is very reactive and has found applications in the manufacture of many organic chemicals such as dyes and medical drugs. Formaldehyde is also a good insecticide, and it is used to kill germs in warehouses and ships. In biology laboratories, animals and organs are suspended

in formaldehyde solutions, which are also used as embalming fluid to preserve dead bodies from decay.[1]

3.2 ALDOL REACTION

This reaction is one of the most important processes in the organic synthesis, because it combines two molecules of carbonyl compound to raise C-C bond. The bond is formed only between α-carbon of the first aldehyde, and carbonyl carbon of the second aldehyde. This reaction can be observed also in the group of ketones, but in this case a shift of the chemical equilibrium towards the side of products must be assured for acceptable effect. Mechanism of the reaction consists in base –catalysed production of enolate. The enolate is very strong nucleophile and hits carbonyl group of excess starting compound.

Aldolisation is made usually in the presence of catalytic amount of base. Indeed the process is also possible to occur under acid catalysis. In this case firstly the enol form is formed, which is weaker nucleophile than enolate.

Heating of the reaction mixture containing the aldol at high temperature causes dehydration (water is released) and makes unsaturated ketone or aldehyde with conjugated system of bonds. This is called aldol condensation and it is irreversible. [2]

When an acid catalyst is used (Fig.2), the initial step in the reaction mechanism involves acid catalyzed tautomerization of the carbonyl compound to the enol. The acid also serves to activate the carbonyl group of another molecule by protonation, rendering it to highly electrophilic. The enol is nucleophilic at the α-carbon, allowing it to attack the protonated carbonyl compound, leading to the aldol after deprotonation.

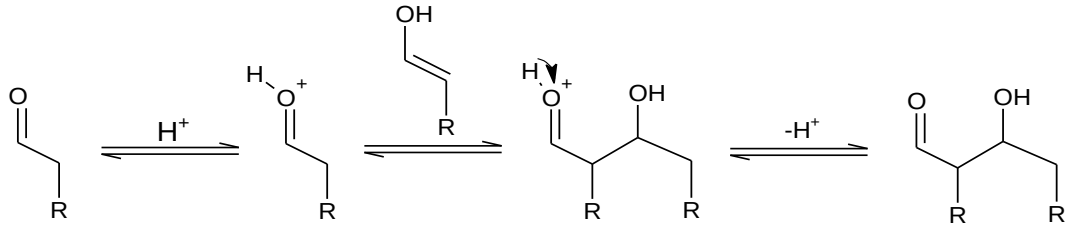


Fig.2 Acid catalyzed aldol mechanism

This usually dehydrates (Fig.3) to give the unsaturated carbonyl compound.

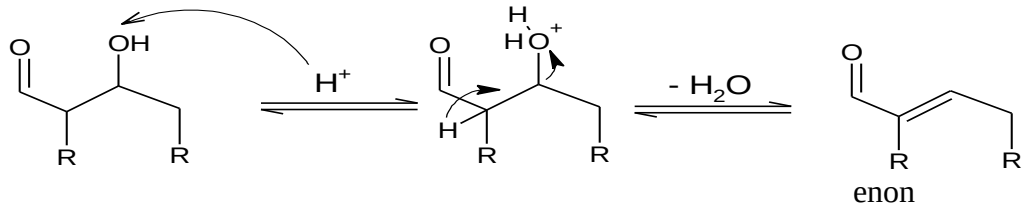


Fig.3Acid catalyzed dehydration

The dehydration is very easy and it is impossible isolate adducts of aldolisation and product is always enon. If the catalyst is a moderate base (Fig.4) such as hydroxide ion or an alkoxide, the aldol reaction occurs via nucleophilic attack by the resonance-stabilized enolate on the carbonyl group of another molecule. The product is the alkoxide salt of the aldol product. The aldol itself is then formed

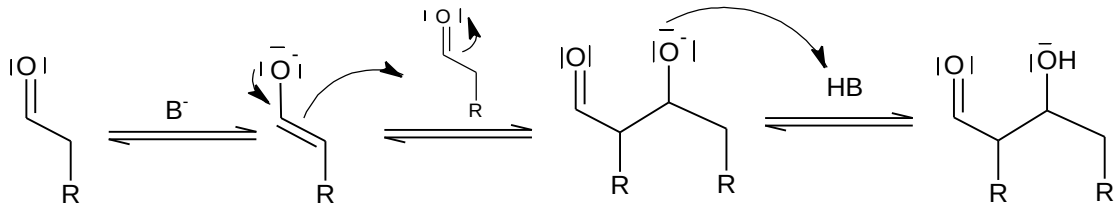


Fig.4 Base catalyzed aldol condensation

and it may then undergo dehydration (Fig.5) to give the unsaturated carbonyl compound.

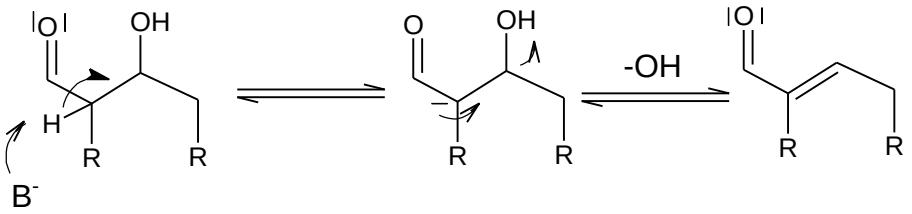


Fig.5Base catalyzed dehydration

When the nucleophile and electrophile are different molecules (the usual case), the reaction is called a crossed aldol reaction.[3]

The aldol reaction was discovered independently by Charles-Adolphe Wurtz[4] and by Alexander Porfyrevich Borodin in 1872. Borodin observed the aldol dimerization of 3-hydroxybutanal from acetaldehyde under acidic conditions. The aldol reaction is used widely in the large scale production of commodity chemicals such as pentaerythritol[5] and in the pharmaceutical industry for the synthesis of optically pure drugs. For example, Pfizer´s initial route to the heart disease drug Lipitor (includes atorvastatin), approved in 1996, employed two aldol reactions, allowing access to multigram-scale quantities of the drug.[6]

In biochemistry, the aldol reaction is one of the key steps of glycolysis, where aldol is catalyzed by enzymes called aldolases. The aldol reaction is particularly valuable in organic synthesis because it produces products with two new stereogenic centers. Modern methods now allow the relative and absolute configuration of these centers to be controlled.[3]

3.3 ALDOLS

An aldol is both an aldehyde and an alcohol and can be formed in aldol reaction. The term aldol is derived from ALDehyde and alcohOL. It can be used to refer to a product of aldol condensation or to describe any molecule containing alcohol (-OH) and carbonyl (-C=O) as main functional groups.[7]

The aldol structural motif is especially common in polyketides, a class of natural product from which many pharmaceuticals are derived, including

the potent immunosuppressant FK506, the tetracycline antibiotics, and the antifungal agent amphotericin B. Extensive research on the aldol reaction has produced highly efficient methods which enable the otherwise challenging synthesis of many polyketides in the laboratory. This is important because many polyketides have medicinally interesting properties, but they occur naturally in such small quantities being impractical for any biological investigations[8]

3.4 CARBOXYLIC ACIDS (CA)

Carboxylic acids are chemical compounds that contain a carboxyl group –COOH(Fig.6).

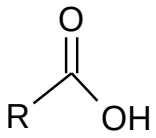


Fig.6 Carboxylic acid

This group is attached to another hydrogen atom (formic acid) or to one end of a larger molecule (R-COOH). Many of them dissolve in water. Their solutions have a sour taste. Carboxylic acids also react with alkalis, or bases.[9]

They play very important role in biology. For example the drug aspirin is a carboxylic acid, and some people are sensitive to its acidity.[4] Aspirin (acetylsalicylic acid) was in use for decades before doctors understood how it worked and before the discovery of the mechanism of its action. Sir John Vane, Sune Bergstrom and Bengt Samuelsson won the Nobel Prize for Medicine in 1982 for these discoveries. This work was first reported in 1971 and showed that aspirin inhibits an enzyme used for the production of prostaglandins. The prostaglandins (a family of compounds) can cause inflammation and also vasoconstriction and platelet aggregation. Aspirin inhibits their formation and thus at low doses aspirin thins the blood and reduces blood clotting; at higher doses it reduces fever and relieves aches and pains.[10] The non-aspirin pain reliever ibuprofen is also

a carboxylic acid. Fatty acids (CA with very long chains of carbon atoms) are important in the formation of fat in the body. Many of them are present in the foods and drinks, like malic acid (found *in apples), tartaric acid (grape juice), oxalic acid (spinach) and lactic acid (sour* milk). The last of the mentioned acid is generated in the muscles of the body during the individual cell´s metabolism of sugars to release energy that can be further used to do some work.[11]

Fatty acids also have industrially important applications – they are present in soaps, detergents and shampoos. In those compounds the carboxyl group is replaced with some metal cation and it is soluble in water, while the long chain of carbons remains soluble in fats, oils, and greases. This double solubility allows water to wash out the dirt.

One of the most important CA is TRICHLOROACETIC ACID, which is prepared by the oxidation of hydrate of chloral by means of nitric acid. It consists of colourless, rhombic deliquescent crystals. In its full strength is a very powerful escharotic and styptic. It is readily soluble in water and alcohol, with an agreeable odour. It coagulates albumin, and its concentrated solutions are powerfully caustic. Diluted solutions cause an increased secretion of saliva, and destroy its power to convert starch into sugar; it also arrests the digestive action of pepsin. As an antiseptic it has been employed in putrid and indolent wounds, in the form of weak solutions, which are unirritating, and promotes healthy granulations and cicatrisation; it has also been employed externally in erysipelas and venereal sores. It is used as a three per cent water solution. It destroys all forms of organic life in such a percentage; and in five per cent solution it arrests the growth of bacteria and other forms of micro-organisms. Internally, it has been administered in cholera, gastric catarrh, etc.[12]

3.5 ESTERIFICATION

Esterification(Fig.7) is the chemical process for making esters, which are compounds of the chemical structure R-COOR´, where R and R´ are either alkyl

or aryl groups. The most common method for preparing esters is to heat a carboxylic acid with an alcohol, while removing the water that is formed. A mineral acid catalyst is usually needed to make the reaction occur at a useful rate.

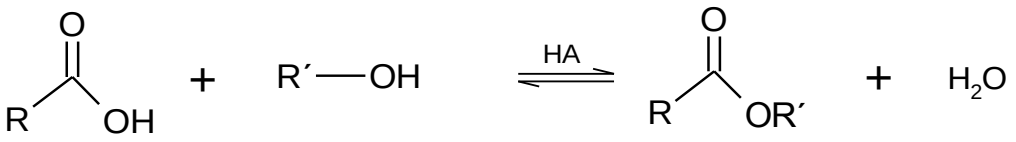


Fig.7 Esterification reaction with an acid catalyst.

Simple alcohols such as methanol and ethanol react very fast with acids because they are relatively small and contain no carbon atom side chains that would hinder their reaction. Nikolay Menschutin first reported these different tares of reaction in 1879-83. He also noted that simple acids such as acetic acid form esters very easily. At the end of the esterification reaction, the acid catalyst has to be neutralized in order to isolate the product. German chemists, during World War II, developed solid acid catalysts or ion exchange resins to be used in the manufacture of esters. These solid catalysts work well with acid sensitive esters because they can be separated from the product by filtration and therefore, the catalyst does not spend very much time in contact with the acid unstable product.

The esterification process has a broad spectrum of uses from the preparation of highly specialized esters in the chemical laboratory to the production of millions of tons of commercial ester products.[13]

3.6 ESTERS

Compounds with carboxyl groups are relatively easily converted to compounds called esters, which have the hydrogen atom of the carboxyl group replaced with a group containing carbon and hydrogen atoms.[14]

The chemical structure of an ester is represented by the general formula R-CO-OR´ (Fig.8).

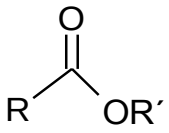


Fig.8 Ester

The R and R´groups can be the same or different. If the R and R´groups are bonded to each other, they form a ring and constitute a cyclic ester or lactone. If an ester group is treated with water, it yields an organic acid and an alcohol. Ester is an organic functional group that forms many sweet-smelling compounds. Low molecular weight esters that produce vinegar or acetic acid when hydrolyzed are used as solvents in coatings or paints on automobiles and inks. Larger esters can be used as a plasticizer, that is, to soften materials that are normally hard or brittle. Esters are also important chemical compounds for various pharmaceutical and agricultural applications.

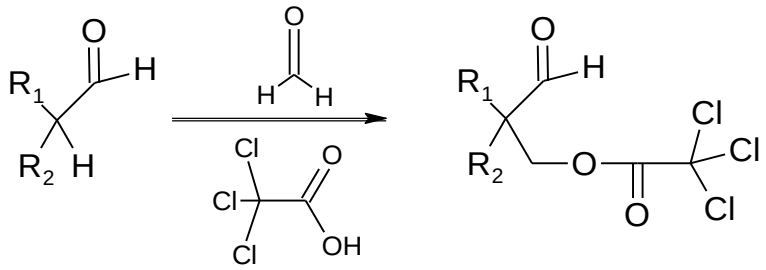
The esters having an acetic acid base are called acetates. They are used extensively as solvents, due to their ability to dissolve various greases.

Esters have characteristic tastes and odours thus carboxyl acids are used commercially as raw materials for the production of synthetic odours and flavours.

In many food and drugs we can find the flavouring esters. These esters are a major constituent of essential oils that are natural flavouring of food. American Indians already knew flavouring esters, using the dried leaves of a fern that commonly grows in the eastern United States, to make wintergreen tea. Scientists later analyzed this essential oil and it is made up almost entirely of the ester methyl salicylate. It can be used to relieve muscular aches and pains and rheumatic conditions. Other very important ester is salicylic acid acetate called aspirin.

Unusual types of esters are macrolides, large rings of lactones or cyclic esters. Most of them are isolated from microorganisms that grow in the soil and are being used as antibiotics in human and veterinary medicine (for example erythromicin).[15]

3.7 SYNTHESIS OF ALDOL TRICHLORACETATES



Compound	R_1	R_2
1	CH_3	CH_3
2	CH_3CH_2	CH_3CH_2
3	CH_3	$CH_3CH_2CH_2$
4	CH_3CH_2	$CH_3CH_2CH_2CH_2$
5	CH_3	Ph

Fig.9 General process

There are just a few references about synthesis of this kind of compounds in the literature. The group of Prof. Dr. Fructuoso Barba studied two different methods:

Method A) Synthesis of the corresponding aldols and further base catalysed esterification with trichloroacetyl chloride.

In the literature the required type of aldols are syntetized starting from aldehydes which present an acid hydrogen atom in α -position (α-carbon trisubstituted), and formaldehyde, as described by Merger et al. [16]

On the other hand, trichloroacetylesters of hydroacetophenone or similar compounds are obtained by treatment with trichloroacetyl chloride and trietylamine in THF.[16]

Previous experiments of the group combined those two reactions in order to obtain esters **1** and **5. (***Fig.10)*

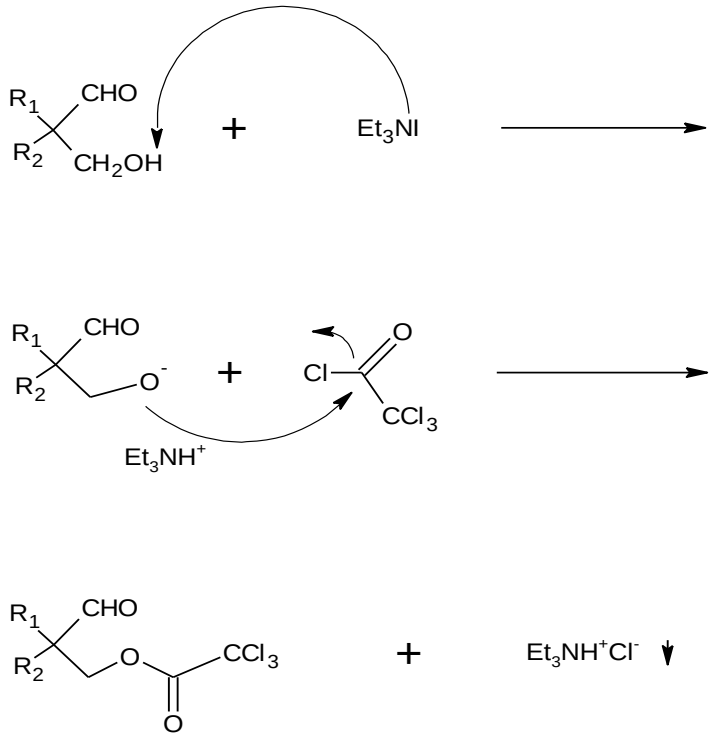


Fig.10 Method A

However the results were not as good as they had been expected: The synthesis of **2, 2-dimethyl-3-hydroxypropanal** (isopropyladehyde with formalin) produces the dimeric aldol (Fig.11), which is not suitable for further esterification.

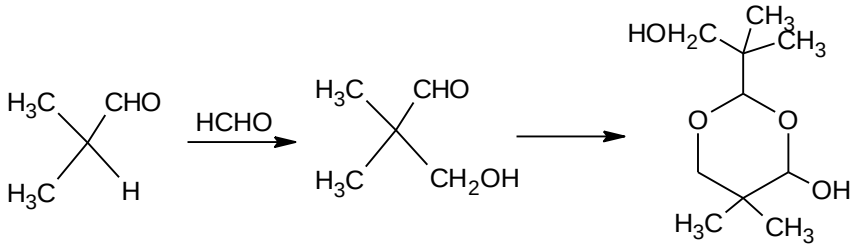


Fig.11 The synthesis of 2,2-dimetyhl-3-hydroxypropanal with rising of dimeric aldol

2-methyl-2-phenyl-3-hydroxypropanal (hydratopaldehyde with formalin) was obtained (Fig.12) with good yield as described in the literature [17] but esterification with trichloroacetate chloride was unsuccesfull.[18]

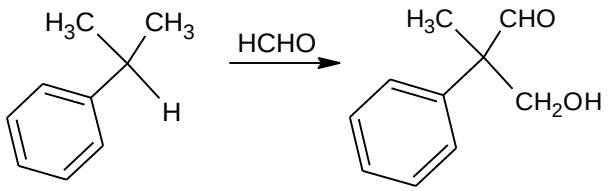


Fig.12 Synthesis of 2-methyl-2-phenyl-3-hydroxypropanal

Method B) One-pot synthesis: direct esterification of aldehydes with either paraformaldehyde or formalin and trichloracetic acid in an acid catalysed esterification. (Fig.13)

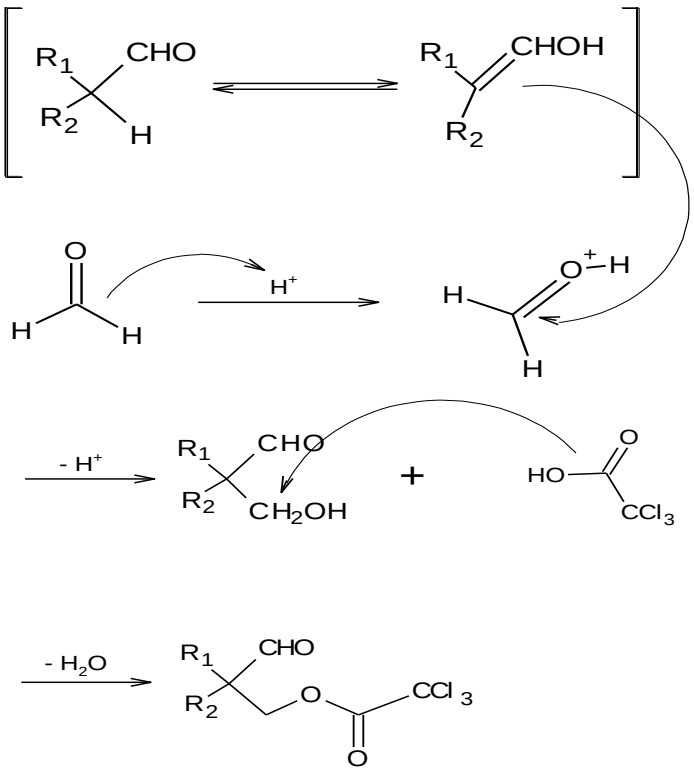


Fig.13 Method B

Merger et al.[16]have described as a patent for the synthesis of the esters **2,2-dimethyl-3-oxopropyl trichloroacetate, 2-methyl-2-propyl-3-oxopropyl trichloroacetate** and **2-butyl-2-ethyl-3-oxopropyl trichloroacetate** using this method in a wide work in which those methods are studied.[16] The spectroscopic properties of those compounds have, however, never been described.

3.8 CYCLIC VOLTAMMETRY

In an electrochemical process an electron transfer (ET) occurs at the interface between an electrode (a conducting piece of matter usually composed of a metal or carbon) and an electrolyte (a conducting liquid phase). Consequently, electrochemistry is dealing with heterogeneous systems. The structure of this interface is a double layer (Fig.14).

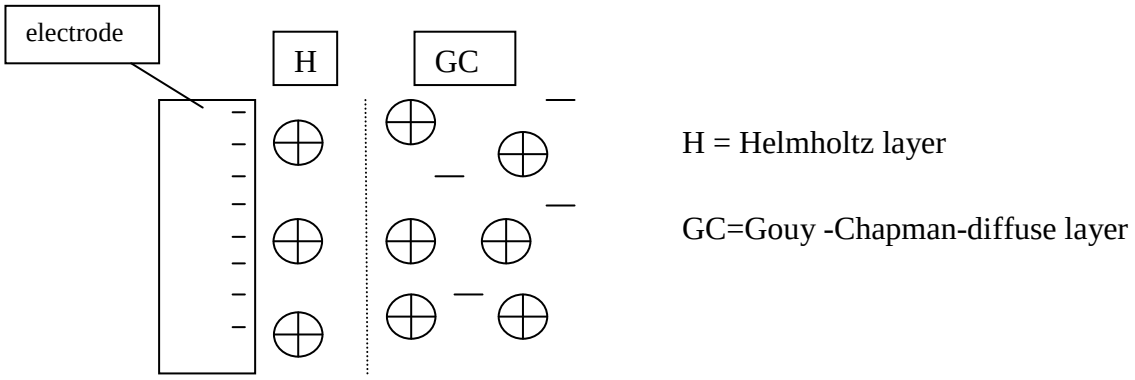


Fig.14 Double layer

On the solution side it is defined by the formation of a Helmholtz layer of closely attached ions and a diffuse layer (Gouy-Chapman). An excess charge on the electrode is complemented by an excess of oppositely charged ions in the electrolyte. The exact composition of the electrochemical double layer depends on the potential difference between the electrode and the electrolyte.

Cyclic voltammetry is one of the most widely used electro analytical techniques. It is based on scanning of working electrode during the experiment.

The method is characterized by continuous increase of potential from the initial value to the terminal value and back to the starting point (Fig.15).

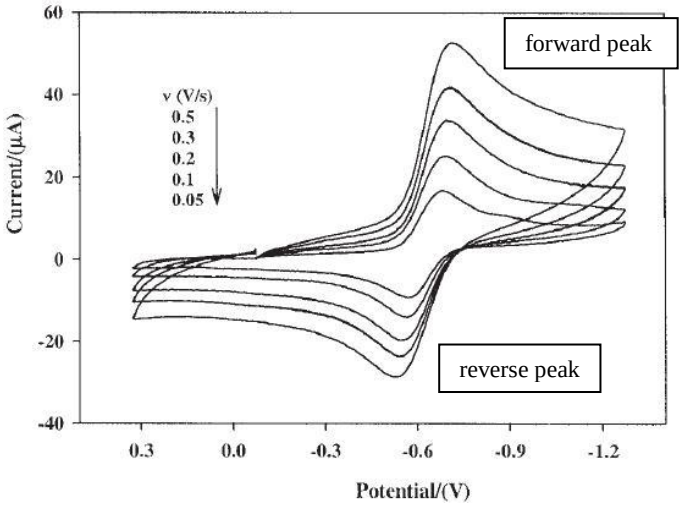


Fig.15 Cyclovoltagramm

The time scale of the CV experiment can be easily varied through the potential scan rate:

$$v = dE/dt$$

Lower limits of v at microelectrodes are about 10mV/s, while at the upper limit 50V/s can be applied. With UMEs scan rates up to 10^6 V/s have been reached. Commercial instruments typically allow 300 V/s. Since a scan extends over potential ranges of a few tenths of a volt to a few volts, a cycle is completed within a few minutes (low v) or in less than a μ s (high v).

Consider a substrate susceptible to a simple ET without coupled chemical or adsorption steps. Upon scanning E, potentials are reached where the substrate undergoes a redox process. Governed by the Nernst equation (1),

$$E = E° + \frac{RT}{nF} \ln \frac{Cox(x=0)}{Cred(x=0)} \quad (1)$$

E-potential, E^o-starting potential, T-temperatura , c_{ox}-concentration of oxidised form, c_{red}-concentration of reduced form, F-Faraday constant, n-number of changing electrons, R-gas constant.

The concentration of the substrate at x=0 gradually decreases, inducing diffusion. Due to interplay between the increase of the concentration profile steepness caused by the potential variation (increasing current), and the relaxation of the profiles similar to chronoamperometric conditions (decreasing current), a peak shaped current–time of current-potential curve (forward peak) is recorded. If the product of the ET is stable, it remains present in the diffusion layer and can be transformed back to the starting compound upon reversal of the scan direction (reverse peak).

In this way, the stability of transient species and products can be assessed. The kinetics of their formation and further reaction(s) may be studied. Furthermore, cyclic voltammetry allows the resolution of redox processes at different potentials, and the determination of redox potentials associated with various oxidation states. Finally, the kinetics of the ET itself, as well as the presence, extent, and rate of adsorption processes are accessible.

A large number of examples have been accumulated in the literature over the years with many different reaction mechanisms coupled to the redox processes at the electrode. Depending on these mechanisms, shapes of cyclic voltammograms widely differ.

Many researchers regard this technique now as a standard tool for the characterization of newly synthesized compounds.[19]

4. EXPERIMENTAL PART

4.1 INSTRUMENTAL

The cyclovoltammetric curves were recorded on VoltaLab PGZ100 using a 0.1 M solution of CH_2Cl_2/ Et_4NCl as SSE and Ag/ AgCl saturated (KCl 3 M) as reference electrode and hanging mercury drop electrode as working electrode.

IR measurements were performed on Perkin-Elmer Model 583 spectrophotometer; liquid samples were measured neat on NaCl plates; solid samples as KBr pellets.

^{1}H-NMR (300 MHz) and ^{13}C-NMR (300 MHz) spectra were recorded on Varian Unity 300 apparat with deuteriochloroform as internal standard; the chemical shifts are given in ppm.

Mass Spectra (EI, ionizing voltage 70 eV) were determined using Hewlett Packard Model 5988A equipped with Hewlett Packard MS Chem. Station. ESI (Electro Spray Ionization) was performed on Automass Multi of ThermoQuest, with mobile phase: MeOH /H_2O + acetic acid 1 %.

4.2 LIST OF CHEMICALS

1. Carbon tetrachloride	CCl_4	Normasolv
	Mr=153.82	d^{20}=1.59 g/cm^3
2.Chloroform D		euriso-top
3. Diethyleter	$C_4H_{10}O$	Scharlau
	Mr=74.12	d^{20}=0.71 g/cm^3
4. 2-ethylbutyraldehyde	$C_6H_{12}O$	Fluka
	Mr=100.16	d^{20}=0.815 g/cm^3
5. 2-ethylhexanal	$C_8H_{12}O$	Aldrich
	Mr=128.22	d^{20}=0.819 g/cm^3

6. Formaldehyde 37 % aqueous s.	HCHO	Sigma-Aldrich
	Mr=30.03	d^{20}=1.083g/cm^3
7. Hexane	C_6H_{14}	Scharlau
	Mr=86.18	d^{20}=0.67 g/cm^3
8. Hydratopaldehyde (2-phenylpropanal)	$C_9H_{10}O$	Aldrich
	Mr=134.18	d^{20}=1.002g/cm^3
9. Isobutyraldehyde	C_4H_8O	Aldrich
	Mr= 72.11	d^{20}=0.794 g/cm^3
10. Magnesium sulphate anhydrous	$MgSO_4$	Panreac
	Mr=120.37	
11. 2-methylpentanal	$C_6H_{12}O$	Fluka
	Mr=100.16	d^{20}=0.809 g/cm^3
12. Paraformaldehyde	$(HCHO)_n$	Panreac
13. Sodium hydrogen carbonate	$NaHCO_3$	Panreac
	Mr=84.01	
14. Toluene	C_7H_8	Normasolv
	Mr=84.93	d^{20}= 0.87 g/cm^3
15. Trichloracetic acid	CCl_3CO_2H	Sigma-Aldrich
	Mr=163.39	d^{20}=1.62 g/cm^3

4.3 SYNTHESIS (Fig.9)

As mentioned above (p.24) the best chosen procedure (by the group of Prof. Dr. Fructuoso Barba) for the synthesis of trichloroacetyl esters was method B (p.22),(Fig.13). This procedure has been the method used in my work for the synthesis of the whole series of thichloroacetates **1-5**, from which compounds **2** and **5** are completely new. To obtain ester **5** (starting from hydratopaldehyde), formalin has been used instead of paraformaldehyde in order to get better results.

The literature reference by Merger et al. describes those steps as follows:

1) While stirring, 486 parts of trichloroacetic acid, 30 parts of paraformaldehyde and 72 parts of isobutyraldehyde in 150 parts by volume of toluene are boiled until completion of water separation (two to three hours).
2) Afterwards the mixture is distilled in vacuum in order to remove the toluene and mainly the enormous excess of trichloroacetic acid[16].

This method has a great disadvantage because the trichloroacetic acid, solid at 40°C, blocks the cooler of the distilling system.

Further attempts of the group to improve the working up process as following described below caused also deficiencies.

a) treating the solution with 5% aqueous solution of $NaHCO_3$ and diethylether and afterwards destilling in vacuum
b) treating the solution with 5% aqueous solution of $NaHCO_3$ and toluene and afterwards destilling in vacuum[18]

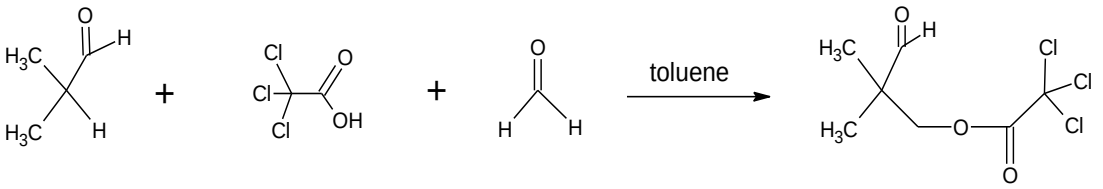
My first task in this project was to improve this step of the synthesis. As a conclusion I accept the following series of steps as the best method:

a) Stirring the corresponding aldehyde with equimolar amount of p-formaldehyde and three times equimolar amount of trichloracetic acid

dissolved in toluene during 4hours at 130°C. The colour changed to dark brown during the heating.

b) Distilling the toluene.
c) Extraction with 5 % aqueous solution of $NaHCO_3$ and diethyleter in order to remove the excess of trichloracetic acid overlefting.
d) Evaporation of diethyleter
e) Distilling the organic phase in vacuum. Small amount of the corresponding unreacted aldehyde and initially formed aldol were collected at lower temperature (about 0.5 ml). Than the main product was obtained.(see details below)

4.3.1 SYNTHESIS OF 2, 2-DIMETHYL-3-OXOPROPYL TRICHLOROACETATE



1

Process:

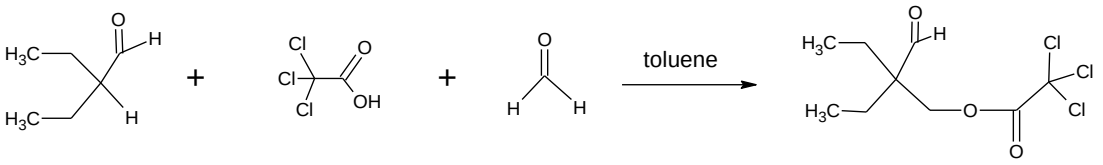
In a one-neck round-bottom flask provided with magnetic stirring bar and refluxing cooler 5.50 ml (0.06 mol, 1 eq) 2-methylpropanal (isobutyraldehyde), 1.85 g (0,06 mol, 1 eq) paraformaldehyde and 30.00 g (0.18 mol, 3 eq) trichloracetic acid are dissolved in 20 ml toluene. The transparent, colourless mixture is stirred 4 hours at 130°C. The colour changes to dark brown during the heating. After the mixture is cooled down, toluene is distilled out (15 mbar, 50°C).

The rest is treated in a beaker with 5 % aqueous solution of $NaHCO_3$ and a little of diethylether (the excessive acid is destroyed). The organic phase is separated in a separatory funnel, dried with $MgSO_4$ 1h and filtered. Ether is removed in the

evaporator. Now the mixture is ready for the vacuum distillation. The vacuum distillation is carried out at 1mbar and 110°C. It is fast and goes very well in good yield.

The obtained product is a bit viscous liquid, transparent and colourless.[16]

4.3.2 DIRECT SYNTHESIS OF 2, 2- DIETHYL-3-OXOPROPYL TRICHLOROACETATE



2

Process:

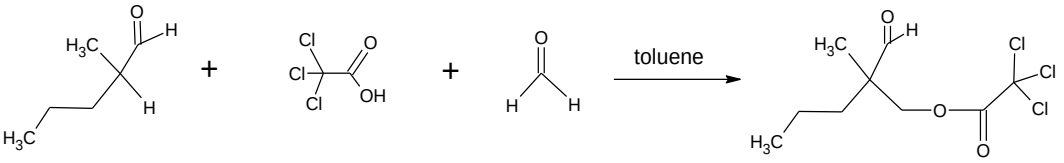
In a one-neck round-bottom flask provided with magnetic stirring bar and refluxing cooler 7.40 ml (0.06 mol, 1 eq) 2-ethylbutanal, 1.85 g (0.06 mol, 1 eq) paraformaldehyde and 30.00 g (0.18 mol, 3 eq) trichloracetic acid are dissolved in 20 ml toluene. The transparent and colourless mixture is stirred 4 hours at 130°C. The colour changes to dark brown during the heating. After the mixture is cooled down, toluene is distilled out (15 mbar, 50°C).

The rest is treated in a baker with 5 % aqueous solution of $NaHCO_3$ and a little of diethylether (the excessive acid is destroyed). The organic phase is separated in a separatory funnel, dried with $MgSO_4$ 1h and filtered. Ether is removed in the evaporator. Now the mixture is ready for the vacuum distillation.

The vacuum distillation is carried out at 1mbar and 120°C. It is fast and goes very well in good yield.

The obtained product is a bit viscous liquid, light yellow.

4.3.3 DIRECT SYNTHESIS OF 2-METHYL-2-PROPYL-3OXOPROPYL TRICHLOROACETATE



3

Process:

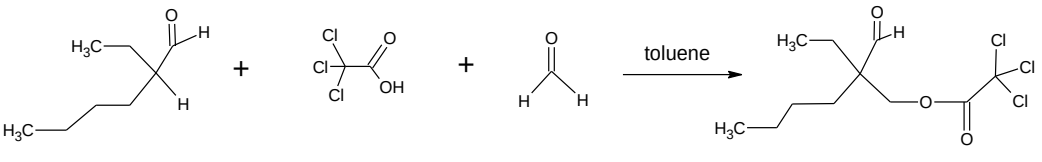
In a one-neck round-bottom flask provided with magnetic stirring bar and refluxing cooler 8.26 ml (0.06 mol, 1 eq) 2-methylpentanal, 1.85 g (0.06 mol, 1 eq) paraformaldehyde and 30.00 g (0.18 mol, 3 eq) trichloracetic acid are dissolved in 20 ml toluene. The transparent and colourless mixture is stirred 4 hours at 130°C. The colour changes to dark brown during the heating. After the mixture is cooled down, toluene is distilled out (15 mbar, 50°C).

The rest is treated in the baker with 5 % aqueous solution of $NaHCO_3$ and a little of diethylether (the excessive acid is destroyed). The organic phase is separated in a separatory funnel, dried with $MgSO_4$ 1h and filtered. Ether is removed in the evaporator. Now the mixture is ready for the vacuum distillation.

The vacuum distillation is carried out at 1mbar and 120°C. It is fast and goes very well in good yield.

The obtained product is a bit viscous liquid, transparent and colourless.[16]

4.3.4 DIRECT SYNTHESIS OF 2-BUTYL-2-ETHYL-3-OXOPROPYL TRICHLOROACETATE



4

Process:

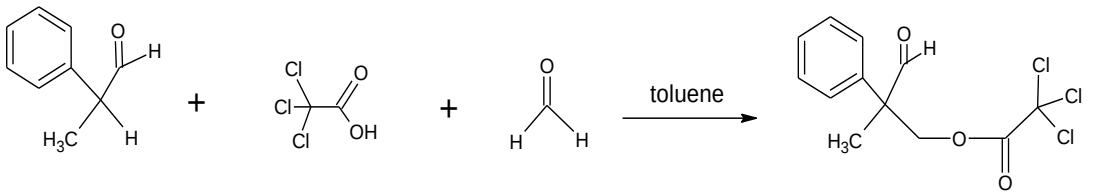
In a one-neck round-bottom flask provided with magnetic stirring bar and refluxing cooler 9.77 ml (0.06 mol, 1 eq) 2-ethylhexanal, 1.85 g (0.06 mol, 1 eq) paraformaldehyde and 30.00 g (0.18 mol, 3 eq) trichloracetic acid are dissolved in 20 ml toluene. The transparent and colourless mixture is stirred 4 hour at 130°C. The colour changes to dark brown during the heating. After the mixture is cooled down, toluene is distilled out (15 mbar, 50°C).

The rest is treated in the baker with 5% aqueous solution of $NaHCO_3$ and a little of diethylether (the excessive acid is destroyed). The organic phase is separated in a separatory funnel, dried with $MgSO_4$ 1h and filtered. Ether is removed in the evaporator. Now the mixture is ready for the vacuum distillation.

The vacuum distillation is carried out at 1mbar and 120°C. It is fast and goes very well in good yield.

The obtained product is a bit viscous yellow liquid.[16]

4.3.5 DIRECT SYNTHESIS OF 2-METHYL-2-PHENYL-3-OXOPROPYL TRICHLOROACETATE



5

Process A):

In a one-neck round-bottom flask provided with magnetic stirring bar and refluxing cooler 9.29 ml (0.06 mol, 1 eq) hydratopaldehyde, 1.85 g (0.06 mol, 1 eq) *p*-formaldehyde and 30.00 g (0.18 mol, 3 eq) trichloracetic acid are dissolved in 20 ml toluene. The transparent and colourless mixture is stirred 4 hours at 140°C. It changes its colour to dark brown during the heating. After the mixture is cooled down, toluene is distilled out (15mbar, 50°C).

The rest is treated in the baker with 5 % aqueous solution of $NaHCO_3$ and a little of diethyleter (the excessive acid is destroyed). The organic phase is separated in a separatory funnel, dried with $MgSO_4$ 1h and filtered. Ether is removed in the evaporator. Now the mixture is ready for the vacuum distillation.

The vacuum distillation is carried out at 1mbar and 170°C, It is slow and very hart.

The obtained product is a yellow viscous liquid.

Process B):

In a one-neck round-bottom flask provided with magnetic stirring bar and refluxing cooler 9.29 ml (0.06 mol, 1 eq) hydratopaldehyde, 5.20 ml (0.06 mol, 1 eq) formalin and 30.00 g (0.18 mol, 3 eq) trichloracetic acid are dissolved in 20 ml toluene. The transparent and colourless mixture is stirred 4 hours at 140°C. The colour changes to gold during the heating. After the dissolution is cooled down, toluene is distilled out (15 mbar, 50°C).

The rest is treated in the baker with 5% aqueous solution of $NaHCO_3$ and a little of diethyleter (the excessive acid is destroyed). Ether is removed in the evaporator. The organic phase is separated in a separatory funnel, dried with $MgSO_4$ 1h and filtered. Now the mixture is ready for the vacuum distillation.

The vacuum distillation was carried out at 1mbar and 170 °C; it was slow and with difficulties.

The obtained product is a yellow viscous liquid.

4.4 CYCLIC VOLTAMMETRY

20 ml of a 0.1 M solution of CH_2Cl_2/ Et_4NCl is placed into a cyclic voltammetry cell. A scan is carried out to 50mV/s from 0 up to -2 V, a blank signal being obtained this way, making sure of the impurities nonexistence. 0.05mg of the product to be analyzed (Tab.1), is added and the same scan is carried out, being obtained this way a voltage/current graph that is typical of the analyzed compound.

As soon as the sign is observed, the area where the reduction takes place is demarcated and a slower scan is realized, between 25 and 10 mV/s, to observe the reduction curve in a more detailed way. The reduction potential of the molecule corresponds with the irreversible reduction peak on the reduction curve.

Tab.1 General conditions of the experiment

Scale of record	50 mV/ s	Reference electrode	Ag/ AgCL
Speed of dropping	300 mV/ s	Counter electrode	Graphite
Temperature	20°C	SSE	0.1 M CH_2Cl_2/Et_4NCl
Sensibility	15 nA/ mm	Working electrode	Hanging mercury drop

5. RESULTS AND DISCUSION

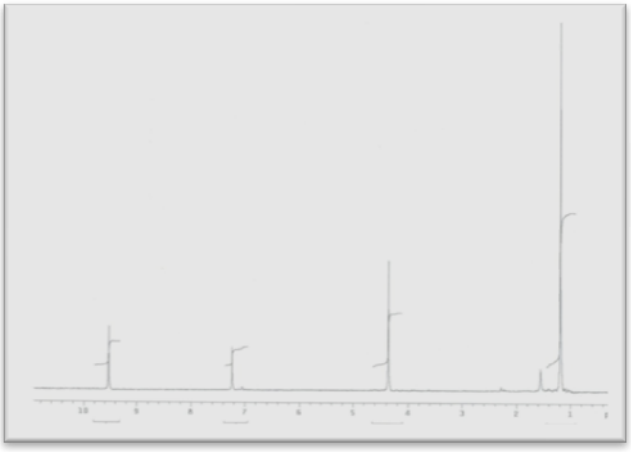
5.1 2,2-DIMETHYL-3-OXOPROPYL TRICHLOROACETATE

The modification of Merger method gives better results than the original procedure[16]. The obtained yield is similar to the yield described[16] but the procedure is much easier and convenient. Therefore I applied the method for the next experiments. Spectral characteristics and the voltammetric curve of the obtained product are shown in following Figs. 16, 17, 18, 19 and 20.

Yield: 9.43 g = 38.1 mmol = **63.5 %**

Fig.16

^{1}H-NMR (300MHz, $CDCl_3$, 300K)
δ = 1.19 (s, 6H, **CH_3**)
δ = 4.37 (s, 2H, **CH_2**)
δ = 9.53 (s, 1H, **CHO**) ppm



^{13}C-NMR (75,4 MHz, $CDCl_3$, 300K)
δ = 18.87 **(-CH_3)**
δ = 46.49 (**C** quaternary)
δ = 71.88 (-**CH_2**-)
δ = 129.00 (**CCl_3**)
δ = 162.00 (**C=O**)
δ = 202.17 (**CHO**) ppm

Fig.17

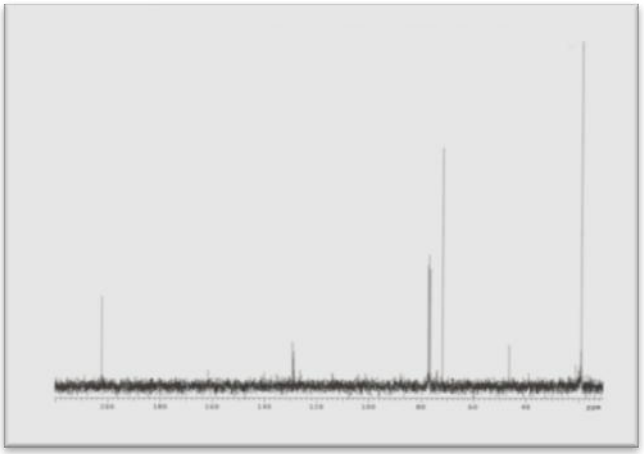


Fig.18

IR (NaCl, [$\tilde{\nu}$ cm^{-1}]):

$\tilde{\nu}$ = 2973.46 - 2715.40 (**C_{sp3}-H**)

$\tilde{\nu}$ = 1769.08 (**C=O ester**)

$\tilde{\nu}$ = 1732.56 (**C=O aldehyde**) cm^{-1}

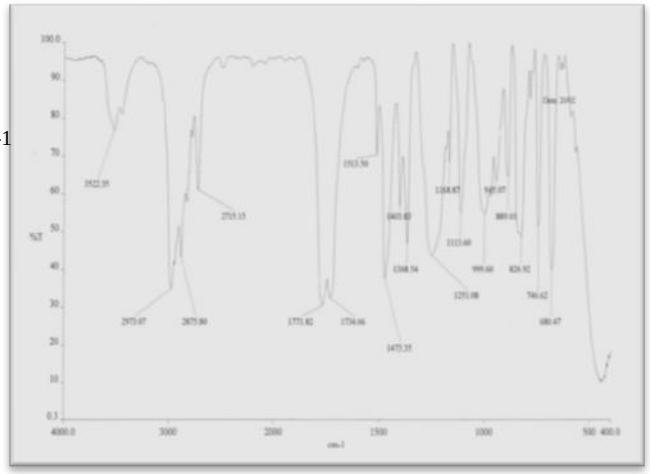


Fig.19

EI-MS: m/z (%):

247, 249, 251 (**4, [M]$^{+}$**)

233, 235, 237 **([$C_6H_6O_3Cl_3$]$^{2+}$)**

213, 215 **([$C_7H_9O_3Cl_2$]$^{2+}$)**

117,119,121 ([**CCl_3**])

85 ([**C_5H_9O**])

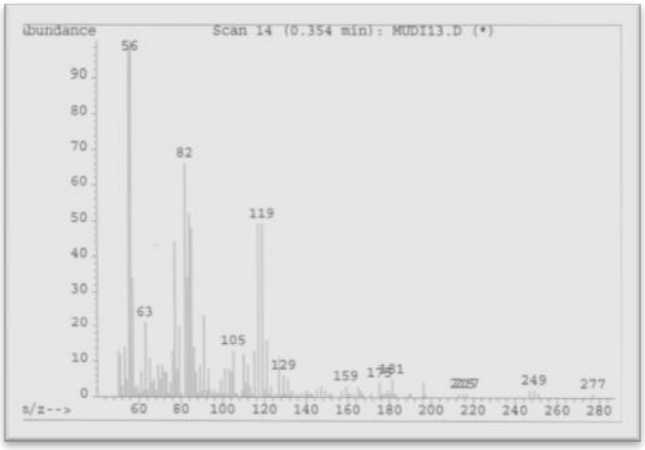
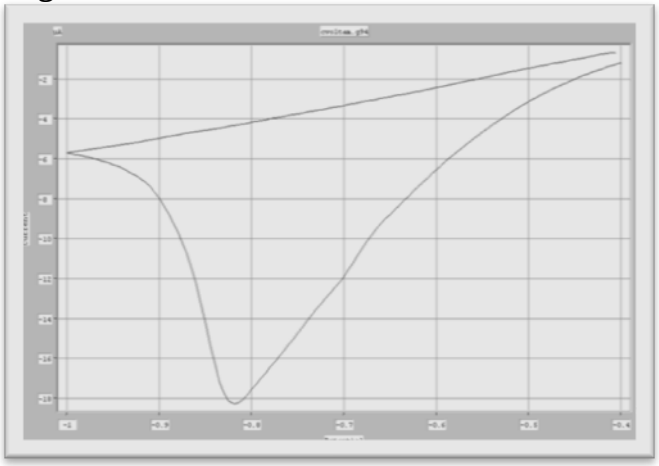


Fig.20

CV:

irreversible reduction peak – 0.8 V



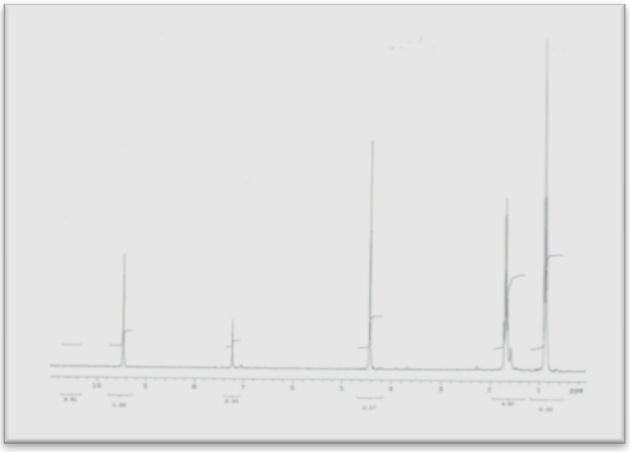
5.2 2,2-DIETHYL-3-OXOPROPYL TRICHLOROACETATE

The modification of Merger method produces good results also in this case when the product is completely new compound. The obtained yield is similar to the yield of described compounds[16]. Spectral characteristics and the voltammetric curve of the obtained product are given in following Figs. 21, 22, 23 and 24.

Yield: 11.00 g = 39.93 mmol = 66.78 %

Fig.21

^{1}H-NMR (300MHz, $CDCl_3$, 300K)
δ = 0.93 (t, 6H, J=7.6Hz, -CH_2-**CH_3**)
δ = 1.74 (q, 4H, J=7.6Hz, -**CH_2**-CH_3)
δ = 4.44 (s, 2H, **CH_2**)
δ = 9.47 (s, 1H, **CHO**) ppm



^{13}C-NMR (75.4 MHz, $CDCl_3$, 300K)
δ = 7.80 **(**-CH_2-**CH_3)**
δ = 23.25 (-**CH_2**-CH_3**)**
δ = 53.16 (**C** **quaternary**)
δ = 67.68 (-**CH_2**-)
δ = 124.00 (**CCl_3**)
δ = 161.73 (**C=O**)
δ = 203.39 (**CHO**) ppm

Fig.22

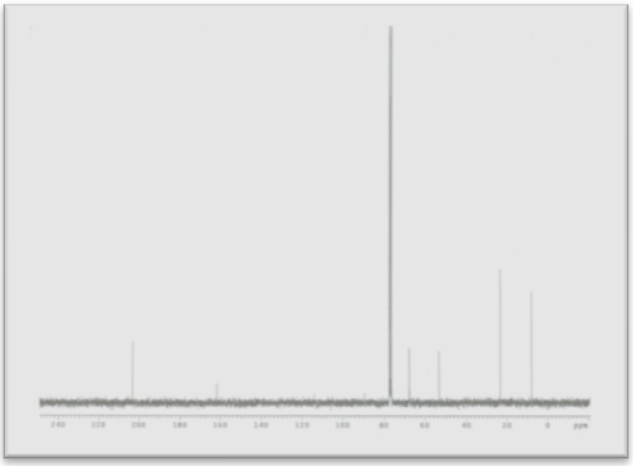


Fig.23

IR (NaCl, [ṽ cm^{-1}]):
ṽ = 2971.24 – 2881.25(**C_{sp3}-H**)
ṽ = 1769.25 (**C=O ester**)
ṽ = 1728.55 (**C=O aldehyde**)cm^{-1}

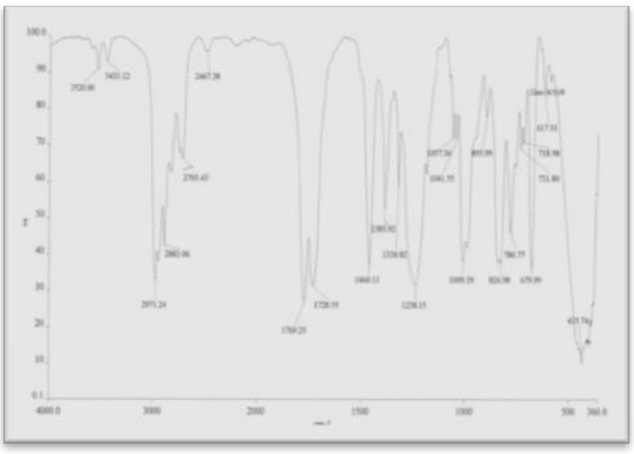
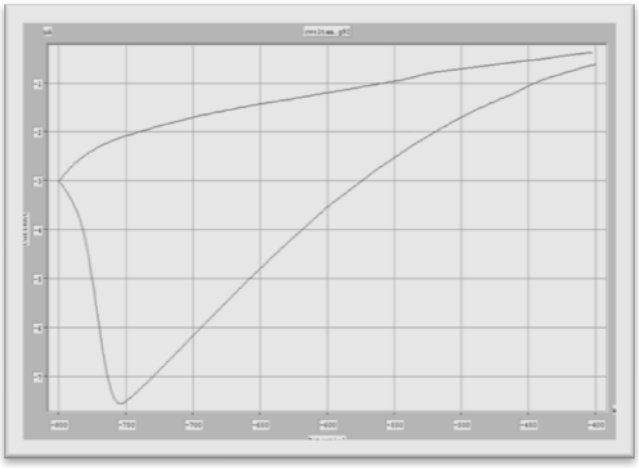


Fig.24

CV:
irreversible reduction peak – 0.75 V



5.3 2-METHYL-2-PROPYL-3-OXOPROPYL TRICHLOROACETATE

The modification of Merger method produces better results than the original procedure[16]. The obtained yield is similar to the yield described[16] but the procedure is much easier and convenient. Spectral characteristics and the voltammetric curve of the obtained product are given in following Figs. 25, 26, 27, 28 and 29.

Yield: 11.03 g = 42.60 mmol = 71.00 %

Fig.25

^{1}H-NMR (300MHz, $CDCl_3$, 300K)

δ = 0.92 (t, 3H,J= 7.1Hz, -CH_2-CH_2-**CH_3)**

δ = 1.17 (s, 3H, **CH_3**)

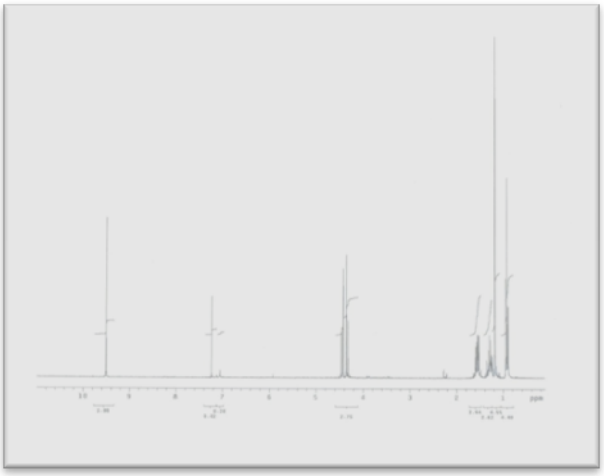
δ = 1.23 - 1.36 (m, 2H, -CH_2-**CH_2**-CH_3**)**

δ = 1.52 - 1.59 (m, 2H, -**CH_2**-CH_2-CH_3**)**

δ = 4.37 (d, 1H, J= 11.2Hz, -**CH_2**)

δ = 4.44 (d, 1H, J= 11.2Hz, -**CH_2**)

δ = 9.51 (s, 1H, **CHO**) ppm



^{13}C-NMR (75.4 MHz, $CDCl_3$, 300K) **Fig.26**

δ = 14.58 (-CH_2-CH_2-**CH_3)**

δ = 16.85 **(-CH_3)**

δ = 35.09 (-CH_2-**CH_2**-CH_3**)**

δ = 50.00 (-**CH_2**-CH_2-CH_3**)**

δ = 66.00 (**C** **quaternary**)

δ = 70.68 (-**CH_2**-)

δ = 140.00 (**CCl_3**)

δ = 162.00 (**C=O**)

δ = 202.71 (**CHO**) ppm

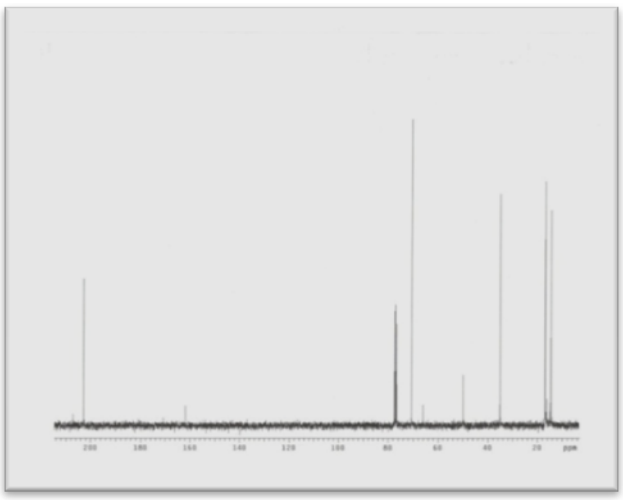


Fig.27

IR (NaCl, [ṽ cm^{-1}]):

ṽ = 2963.39 – 2875.33(**C_{sp3}-H**)

ṽ = 1769.67 (**C=O ester**)

ṽ = 1730.14 (**C=O aldehyde**) cm^{-1}

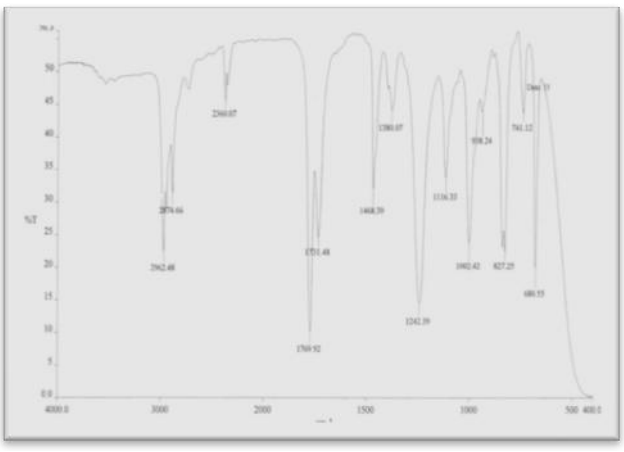


Fig.28

EI-MS: m/z (%):

275, 277, 279	($[C_9H_{13}0_3Cl_3]^+$)
245, 247, 249	($[C_8H_{12}O_2Cl_3]^{2+}$)
95,97,99	($[C_6H_{11}O]$)
113	($[C_7H_{13}O]$)

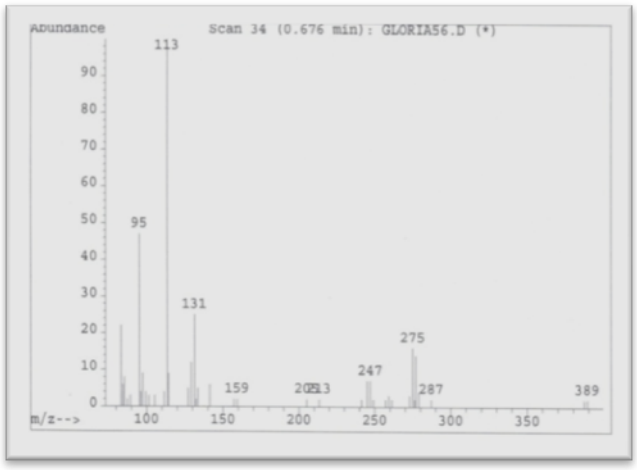
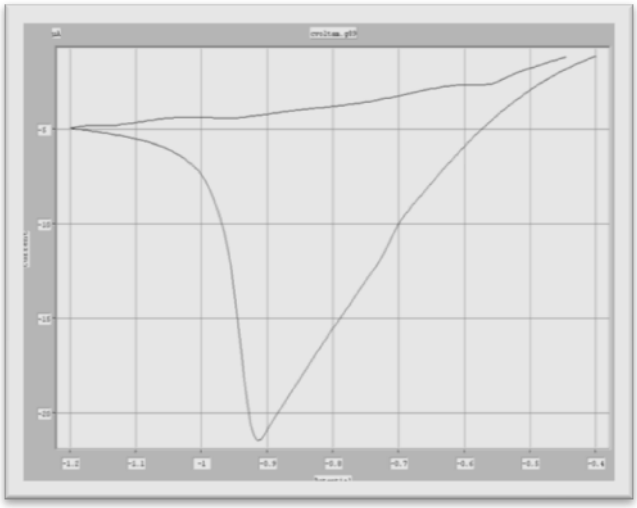


Fig.29

CV:

irreversible reduction peak – 0.9 V



5.4 2-BUTYL-2-ETHYL-3-OXOPROPYL TRICHLOROACETATE

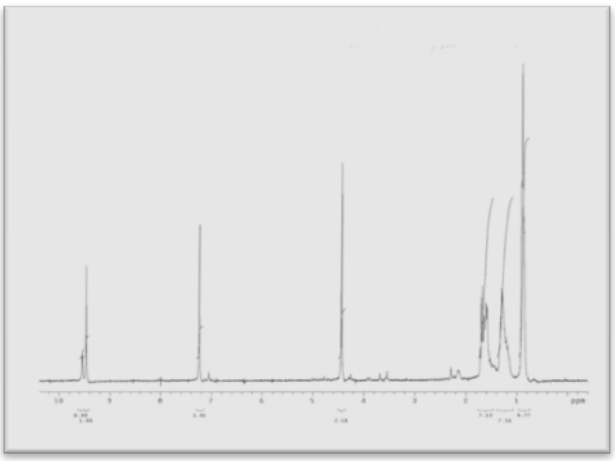
The modification of Merger method produces better results than the original procedure[16]. The obtained yield is similar to the yield described[16] but the procedure is much easier and convenient. Spectral characteristics and the voltammetric curve of the obtained product are given in following Figs. 30, 31, 32 and 33.

Yield: 4.20g = 14.74 mmol = 23.09 %

Fig.30

^{1}H-NMR (300MHz, $CDCl_3$, 300K)

δ = 0.89 (t, 6H, -**CH_3**)
δ = 1.18-1.32 (m, 4H, -**CH_2**-)
δ = 1.52-1.72 (m, 4H, **-CH_2-)**
δ = 4.44 (s, 2H, -**CH_2**-**O**-)
δ = 9.47 (s, 1H, **CHO**) ppm



^{13}C-NMR (75.4 MHz, $CDCl_3$, 300K)

Fig.31

δ = 7.86 (-CH_2-CH_2-CH_2-**CH_3)**
δ = 13.83 **(-**CH_2-**CH_3)**
δ = 23.15 (-CH_2-CH_2-**CH_2**-CH_3**)**
δ = 23.62 (-CH_2 -**CH_2**-CH_2-CH_3**)**
δ = 25.48 (-**CH_2**-CH_2-CH_2-CH_3**)**
δ = 30.23 **(-CH_2**-CH_3**)**
δ = 59.92 (**C** **quaternary**)
δ = 67.94 (-**CH_2**-)
δ = 129.00 (**CCl_3**)
δ = 161.66 (**C=O**)
δ = 203.39 (**CHO**) ppm

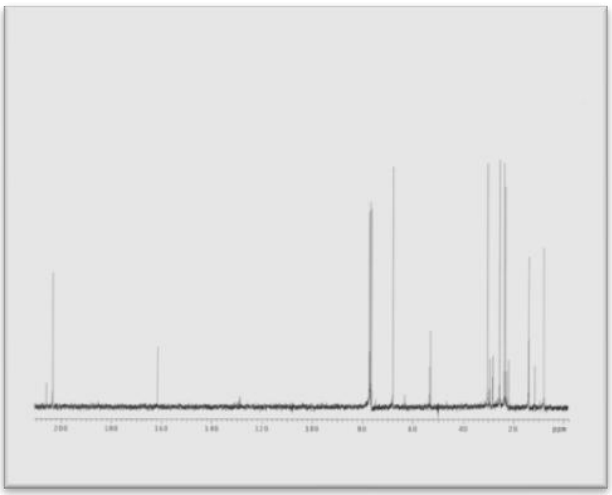


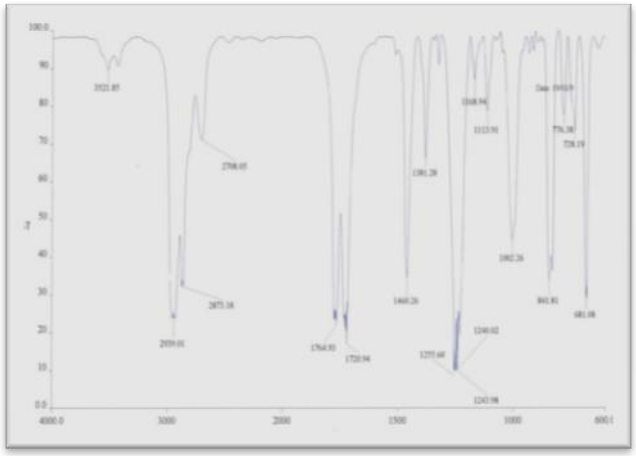
Fig.32

IR (NaCl, [ṽ cm^{-1}]):

ṽ = 2939.00- 2873.55(**C$_{sp3}$-H**)

ṽ = 1764.95 (**C=O ester**)

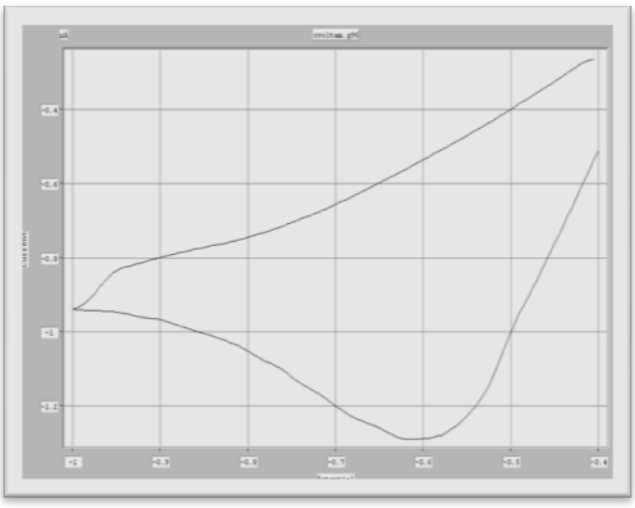
ṽ = 1720.93 (**C=O aldehyde**)cm^{-1}



CV:

irreversible reduction peak -0.6 V

Fig.33



5.5 2-METHYL-2-PHENYL-3-OXOPROPYL TRICHLOROACETATE

Process A)

Yield: 4.93g = 15.93 mmol = 24.85 % this product isn´t clean

The yield of this reaction is, compared to the above described aliphatic aldehydes, quite small. Moreover the spectroscopic methods showed that the product is not pure.

A rest of aldol and more impurities from the reaction contaminate it. There are two possible reasons:

1) Steric hindrance: The big size of aromatic ring in the formed nucleophilic hydratopaldehyde anion might cause difficulties in its approaching to the polymeric paraformaldehyde.
2) Less nucleophility: The delocalisation of the negative charge of the hydratopaldehyde anion (Fig.16) (by a mesomeric effect) reduces its nucleophility. Hence its reactivity towards the aldehyde carbonyl group is much weaker.

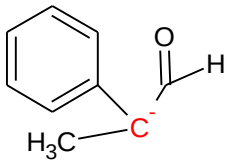


Fig.16 Hydratopaldehyde anion

To solve the first problem I used formalin (37 % aqueous solution of formaldehyde) instead of paraformaldehyde. That facilitates the approach of the anion to the formaldehyde. The second problem cannot be solved, because the stabilization of the negative charge by a mesomeric effect cannot be affected. Therefore the yield in the aromatic case (**5**) is always lower than in the cases with aliphatic aldehyds (**1, 2, 3, and 4**).

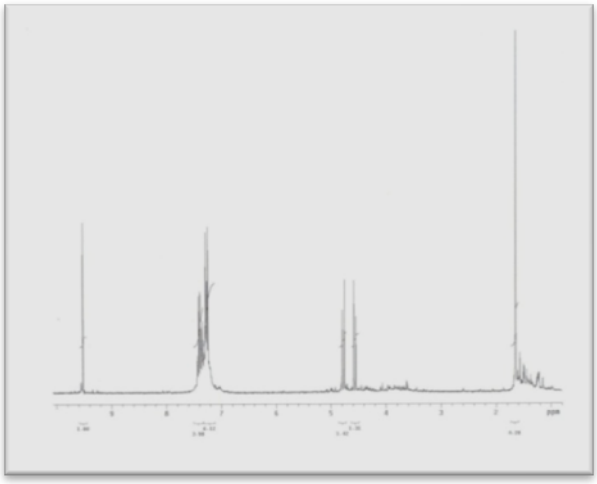
Process B)

Yield: 9.82g = 31.74 mmol = 49.53 %

The fraction collected during the distillation showed a presence of unreacted aldol and other impurities only. But the rest that remained in the flask was unusually big. After performing the ^{1}H-NMR of this rest I found it to be the required product, obtained in a sufficient purity and in a good yield. The impurities were distilled out and the product remained inside of the flask.

The modification of Merger method produces good results also in this case when the product is new compound. This method is convenient though the obtained yield is a little smaller in comparison with the compounds described above. Spectral characteristics and the voltammetric curve of the obtained product are given in following Figs. 34, 35, 36, 37 and 38.

Fig.34



^{1}H-NMR (300MHz, $CDCl_3$, 300K)

δ = 1.65 (s, 3H, **CH_3)**
δ = 4.57 (d, 1H, J= 10.9Hz, **-CH_2**)
δ = 4.78 (d, 1H, J= 10.9Hz, **-CH_2**)
δ = 7.20- 7.43 (m, 5H**, -Ph)**
δ = 9.59 (s, 1H, **CHO**) ppm

^{13}C-NMR (75.4 MHz, $CDCl_3$, 300K)

δ = 16.80 **(-CH_3)**
δ = 54.08 (**C** $_{quaternary}$)
δ = 71.36 (**-CH_2-**)
δ = 127.17 (**CCl_3**)
δ = 128.71 (**-Ph)**
δ = 161.52 (**C=O**)
δ = 198.98 (**CHO**) ppm

Fig.35

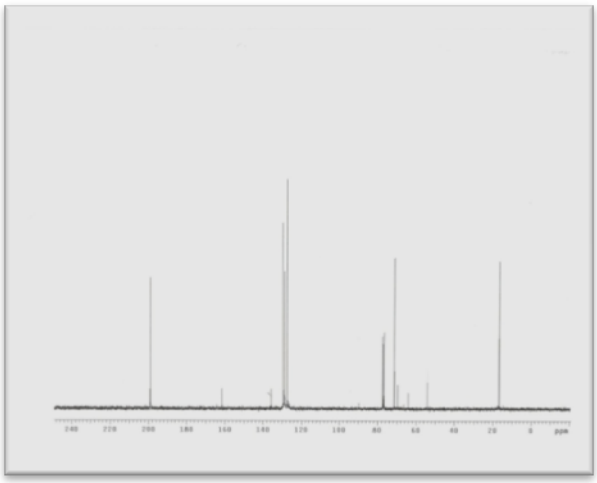


Fig.36

IR (NaCl, [ṽ cm^{-1}]):

ṽ = 2980.25 – 2817.84(**C_{sp3}-H**)

ṽ = 1764.97 (**C=O ester**)

ṽ = 1724.82 (**C=O aldehyde**)cm^{-1}

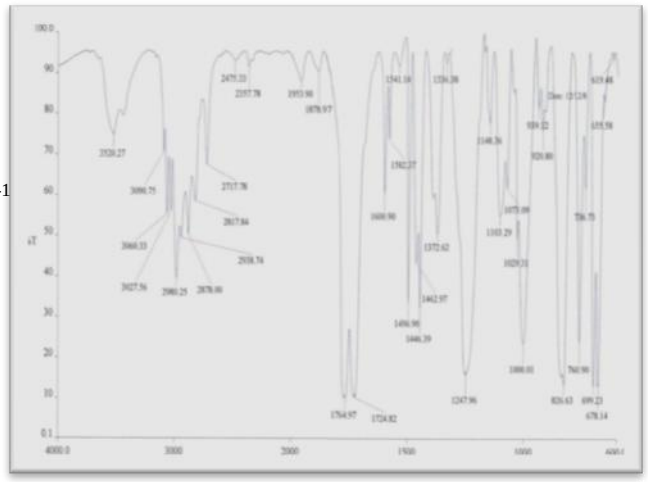


Fig.37

EI-MS: m/z (%):

309, 311, 313 ($[C_{12}H_{11}O_3Cl_3]^+$)

147 ($[C_{10}H_{11}O]^{2+}$)

133, 135 ($[C_9H_9O]$)

135 ($[C_9H_{10}O]$)

117, 119, 121 ($[CCl_3]$)

177 ($[C_{10}H_8O_3]$)

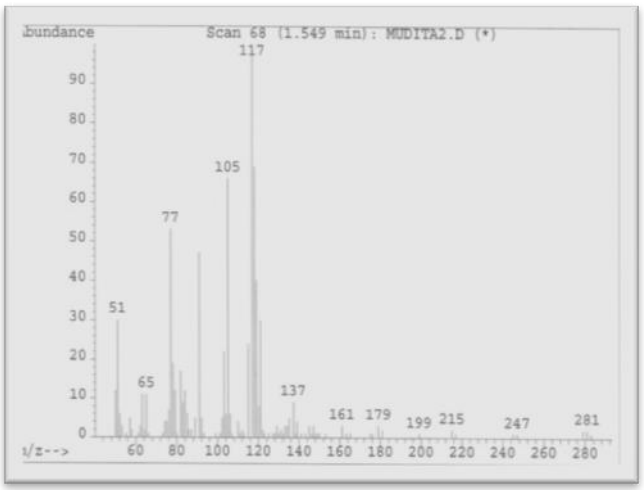
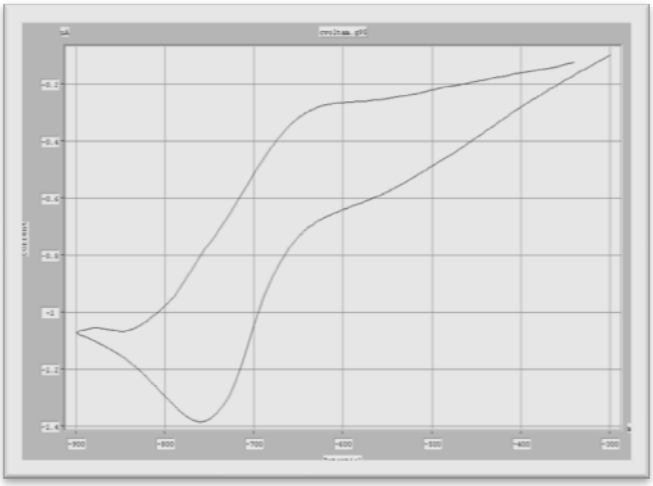


Fig.38

CV:

irreversible reduction peak – 0.75 V



5.6 OVERAL DISCUSION:

Compounds **1-5** have been characterized by their analytical and spectroscopic properties. In IR spectroscopy (Tab.2) they present two carbonyl bands at 1770 and 1730 cm^{-1} (as media values) corresponding respectively to the trichlorocarboxy and aldehyde carbonyl groups, as much as the peak at 2710 cm^{-1}(as a medium value) of C_{sp2}-H stretch in the aldehyde group. Aromatic derivative **5** presents also C=C stretch bands at 1600, 1582 and 1497 cm^{-1}.

Tab.2: Survey of wavenumbers (cm^{-1}) in IR spectra of the obtained esters.

Compound	R_1; R_2	Csp^3-H	C=O ester	C=O aldehyde
1	R_1=R_2=CH_3	2973.46-2715.40	1769.08	1732.56
2	R_1=R_2= CH_2-CH_3	2971.24-2881.25	1769.25	1728.55
3	R_1=CH_3 R_2= CH_2-CH_2-CH_3	2963.39-2875.33	1769.67	1730.14
4	R_1= CH_2-CH_3 R_2= CH_2-CH_2-CH_2-CH_3	2939.00-2873.55	1764.95	1720.93
5	R_1=CH_3 R_2= Ph	2980.25-2817.84	1764.97	1724.82

^{1}H-NMR spectra (Tab.3) present the aldehyde peak at δ= 9.50 ppm and the signals corresponding to the aliphatic or aromatic rest. It is very interesting to observe the different type of signals for the methylene group in α-position of ester obtained when the substituents R_1 and R_2 are either identical (esters **1, 2**) or non identical (**3, 4, 5**). In the first case, the two protons are represented by a singlet at 4.35ppm (**1**) or 4.44ppm (**2**), whereas in the second case the methylene group presents two doublets (J gem= 11Hz) of the two diasterotopic protons due to the vicinity of the asymmetric carbon atom. Compound **4** surprisingly presents a singlet at 4.44 ppm for the methylene group in spite of having two different substituents R_1(Et) and R_1 (n-Bu).

Tab. 3: Survey of chemical shifts (ppm) in ^{1}H-NMR spectra of the obtained esters.

Compound	R_1; R_2	-CHO	- CH_2	- R_1	- R_2
1	R_1=R_2=CH_3	δ = 9.53 s, 1H	δ = 4.37 s,2H	δ = 1.19 s, 6H	
2	R_1=R_2= CH_2-CH_3	δ = 9.47 s, 1H	δ = 4.44 s, 2H	δ = 1.74 q(J=7.6Hz) δ = 0.93 t(J=7.6Hz)	
3	R_1=CH_3 R_2= CH_2-CH_2-CH_3	δ = 9.51 s 1H	δ = 4.44 d(J=11.2Hz) δ = 4.34 d(J=11.2Hz)	δ = 1.17 s, 3H	δ = 0.92 t(J=7.1Hz) δ = 1.23-1.36 m,2H δ = 1.52-1.59 m,2H
4	R_1= CH_2-CH_3 R_2= CH_2-CH_2-CH_2-CH_3	δ=9.47 s, 1H	δ= 4.44 s, 2H	δ= 0.89 t(J=6.8Hz), 6H δ= 1.32-1.18, m, 4H δ= 1.72-1.52, m, 4H	
5	R_1=CH_3 R_2= Ph	δ = 9.59 s, 1H	δ = 4.78 d(J=10.9Hz) δ = 4,57 d(J=10.9HZ)	δ = 1.65 s, 3H	δ = 7.20 – 7.43 m, 5H

^{13}C-NMR spectra (Tab.4) show characteristic peaks for the two carbonyl groups: 202 ppm, for the aldehyde and 162ppm for the ester group (as media values). Other remarkable values are the trichloromethyl (circa 129 ppm. or 140 in **3**), the methylene carbon (around 70 ppm.) and the tetrasubstituted carbon (with values between 46.49 and 66ppm.).

Tab.4: Survey of chemical shifts (ppm) in ^{13}C-NMR spectra of the obtained esters.

Compound	R_1; R_2	Cq	CCl_3	CO	CHO	$-CH_2-O-$	R1	R2
1	$R_1=R_2=CH_3$	46.49	129.00	162.00	202.17	71.88	18.87	
2	$R_1=R_2= CH_2-CH_3$	53.16	124.00	161.73	203.39	67.68	CH_3- 7.80 $-CH_2$- 23.25	
3	$R_1=CH_3$ $R_2= CH_2-CH_2-CH_3$	66.00	140.00	162.00	202.71	70.68	16.85	CH_3- 14.58 $-CH_2$- 35.09 $-CH_2$- 50.00
4	$R_1= CH_2-CH_3$ $R_2= CH_2-CH_2-CH_2-CH_3$	59.92	129.00	161.66	203.39	67.94	CH_3- 13.83 $-CH_2$- 30.23	CH_3- 7.86 $-CH_2$- 23.15 $-CH_2$- 23.62 $-CH_2$- 25.48
5	$R_1=CH_3$ $R_2=$ Ph	54.08	127.17	161.52	198.98	71.36	16.80	128.71

Both ^{1}H-NMR and ^{13}C-NMR spectra present also the peaks corresponding to the different substituents.

6. CONCLUSION

In this work the syntheses of the new compounds with carbon-halogen bond are studied. The trichloroacetyl esters **1-5** are obtained by the reaction of the corresponding aldehydes with formaldehyde and trichloroacetic acid. Method used in my experiment is a relatively cheap and quite easy way to obtain this type of compounds. In addition it does not require any sophisticated equipment; therefore this synthesis can be commonly carried out in an ordinary laboratory. In a case of aliphatic aldehydes it is better to use solid paraformaldehyde to achieve higher efficiency even though paraformaldehyde is more expensive in comparison with formalin. On the other hand formalin is more suitable for aromatic aldehydes due to better reactivity.

In general we can say that the method described above for syntheses of all mentioned esters gives reasonable good yields and clean enough products.

All obtained esters have been characterised by their spectroscopic properties. Thus IR, ^{1}H-NMR, ^{13}C-NMR and MS spectra were according with proposed structures (see results).

The electrochemical properties were studied by cyclic voltammetry. They showed an irreversible reduction peak at -0.6 volts. For this reason those esters are suitable material for further electrochemical reactions especially for forming new rings by electro reduction.

During my laboratory work I have learned many useful skills and new laboratory methods that I have never done before. Now I am familiar with different types of spectroscopy, methods how to conduct these experiments and how to operate with different apparatus.

7. LIST OF ABBREVIATIONS

A	Ampere
CA	carboxylic acid
$CDCl_3$	chloroform D
CU	sample
CV	cyclic voltammetry
Et_4NCl	tetraethylamonium chloride
d	doublet
DCM, CH_2Cl_2	dichloromethane
DMF	dimethylformamide
EI-MS	mass spectroscopy
ET	electron transfer
Fig.	Figure
Exp.	Experiment
H_2O	water
K	Kelvin
$LiClO_4$	lithiumperchlorate
m	multiplet
M	molar
MeOH	methanol
NMR	nuclear magnetic resonance
s	singlet
t	triplet
V	Volt
$\tilde{\nu}$	wavenumbers
δ	chemical shift
SSE	solvent-supporting electrolyte system
THF	tetrahydrofurane
UME	ultramicroelectrode

8. LITERATURE

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