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The Preparation of Some 1,2,4-Triazole Ester and Benzotriazole Ester Derivatives

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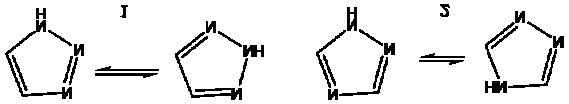
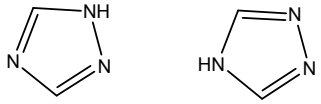
Abstract
We have prepared a 1-chloro ester by a reaction between 4-methoxy Benzaldehyde and Benzoyl chloride, and we have checked the Structure of the produced Compound by IR (Infra Red) and then we have studied the reaction of this compound with Benzotriazole and 1H-1,2,4-Triazole to get the following compounds: (1H-benzo[d][1,2,3]triazol-1-yl)(4-methoxyphenyl)methyl benzoate and (4-methoxyphenyl)(1H-1,2,4-triazol-1-yl)methyl benzoate Then we have purified the produced compounds by re-crystallization, and their structures have been checked by (^{1}H-NMR ,^{13}C-NMR) and FT-IR, Triazole derivatives have a variety of biological applications, therefore the produced compounds should have many important applications.
Keywords: Triazole, esterification, chloro esters.

1 - Introduction

Triazoles are heterocyclic compounds containing three nitrogen atoms in a five membered cyclic structure with the chemical formula $C_6H_5N_3$. There are different structural and positional isomers of Triazoles, this can be one of two types, the 1,2,3-triazoles (1) or the 1,2,4-triazoles (2).

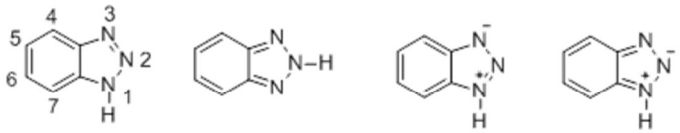


The 1,2,4-triazoles are of considerable biological importance, because most of them are effective in the treatment of different sicknesses.[1] 1,2,4-Triazoles have the two proton transfer tautomeric forms shown below.[2]



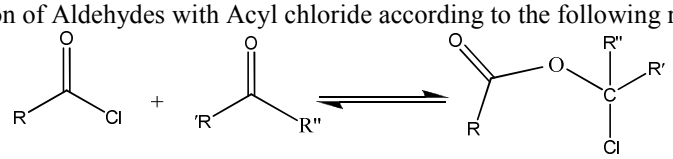
1*H*-1,2,4-triazole A 4*H*-1,2,4-triazole B

Benzotriazole (BTA) has been studied as an example of 1,2,3-Triazole, this aromatic compound is colorless and polar and can be used in many fields, Benzotriazole features two fused rings. Its five membered ring can exist in tautomers A and B, and the derivatives of both tautomers, structures C and D also can be produced.[3]



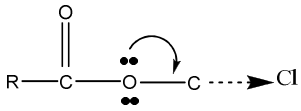
A B C D

Triazoles have been found to have a number of applications as antibacterial agents,[4]Research done by Pattan et al. specifically on 1,2,4-triazoles found antibacterial, antifungal, antitubercular, and anti-inflammatory activity of various substituted compounds.[5], Considering the importance of Triazole and its derivatives we have created Triazole ester derivatives, and we have started this process by synthesizing a 1 -chloro ester compound.1-Chloro esters are compounds that contain an atom of chlorine in the alpha position of the ester, they have the formula RCOOC(Cl)R'R" in which R",R',R are either H , alkyl or aryl. 1-Chloro esters can be prepared by the reaction of Aldehydes with Acyl chloride according to the following reaction :



(R"=H)

The reaction between Acyl chloride and Aldehydes is an important and well known reaction.[6-14], 1-Chloro esters are important medium compounds in the organic preparation because the chlorine atom can be easily inserted in the nucleophilic substitution reactions and the resulting compounds are effective in the fields of anti- tumors and insecticides [15], It is easy to replace the chlorine atom in 1-Chloro esters with another nucleophile because of the polarity of the bond C-Cl resulted from the inductive effect that is given by the oxygen atom.

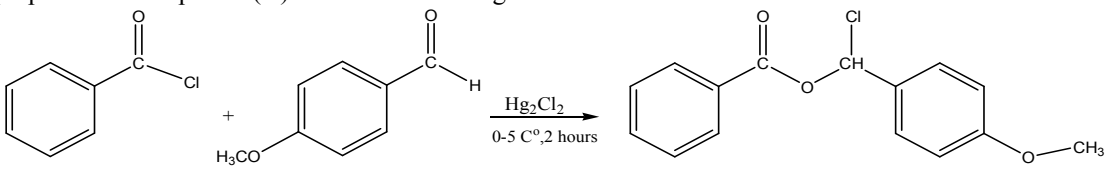


2 - Experiment and results

The experiment includes the following steps:

Step 1 :

The preparation of the chosen 1-Chloro Ester which is Chloro(4-methoxyphenyl)methylbenzoate (A): We prepared the compound (A) in the lab following this reaction :



We put (10mmol, 1.121 ml) of 4-methoxy Benzaldehyde into a flask provided with magnetic stirrer in an ice bath , then we add the catalyst Hg2cl2 , then we add one dose (10mmol, 1.155 ml) of Benzoyl chloride while stirring and we observe the reaction with T.L.C . we notice that the reaction takes 1 hour . Then we put the flask of the reaction in the refrigerator at (2-5C◦) for one day, then we notice the crystallization of ester chloride andwe purify it by recrystallization using hexane .

The resulted compound is a dark violet precipitate and its melting point is (80-82C◦) and its yield is 84% . Its structure was checked by FT-IR

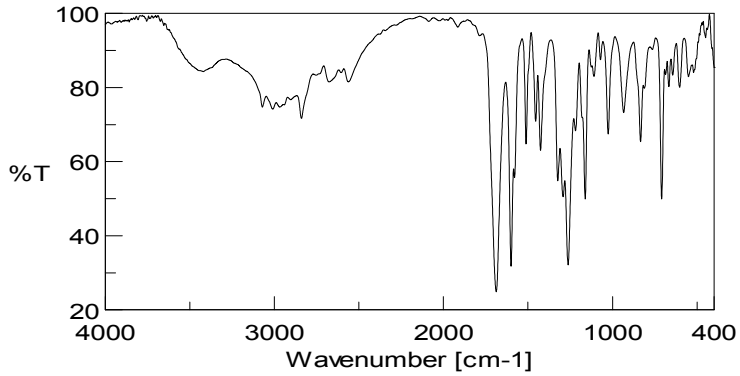


Figure 1. The FT-IR of compound (A)

In the following Chart we see the explanation for the IR Figure :

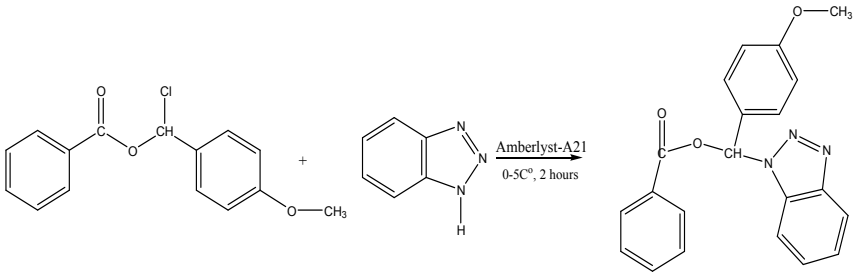
Table1. Characteristic infrared absorption frequencies (cm−1) of the compound (A).

$C_6H_5COOCH(Cl)C_6H_4OCH_3$-4			
Functional group	C_{SP3}–H	C=O	C-O(ester)
Wavenumber (cm^{-1})	3070	1687	1218

Step 2:

Conducting The reaction between compound (A) and the Benzotriazole to get the compound Benzotriazole (4-methoxyphenyl)methyl benzoate (B):

We prepared the compound (B) in the lab following this reaction :



We add (10mmol, 2.76 gr) of ester chloride , newly prepared, dissolved in 20 ml of acetone into a flask equipped with dripping funnel that contains (10mmol, 1.19 gr) of Benzotriazole dissolved in 25 ml of acetone , we put the flask of the reaction in an ice bath . we add Benzotriazole gradually during 40 min under magnetic stirring then we add (10mmol, 0.22gr) of the catalyst basic amberlyst-A21 .

We notice the disappearance of the dark violet color of ester chloride and the appearance of a white color, and the total duration of the reaction is 2 hours . we leave it in the refrigerator for 24 hours at (2-5C◦) , then we purify the precipitate to get the catalyst away from it and we wash it with acetone .

We evaporate the solvent to get yellowish white crystals , then we purify it by recrystallizing it using a mixture of (acetone : chloroform) (2:8).

its melting point is (121-123C◦) with a yield of 85% .

The form(2) shows the IR of (B):

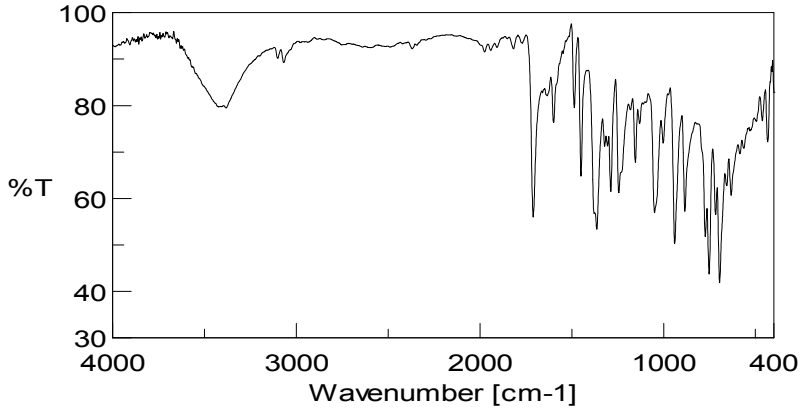


Figure 2. The IR of compound (B)

We see in the chart (2) the explanation of the IR spectrum:

Table2. Characteristic infrared absorption frequencies (cm−1) of the compound (B).

(1*H*-benzo[*d*][1,2,3]triazol-1-yl)(4-methoxyphenyl)methyl benzoate						
Functional group	CSP3–H	Csp2-H	C=O	C=C (Aromatic)	C-O(ester)	C-N
Wavenumber (cm-1)	3069(m)	3101(w)	1710(vs)	1599,1486(v)	1244(vs)	1049(vs)

Figure 3. The ^{1}H-NMR of compound (B) in the solvent $CDCl_3$:

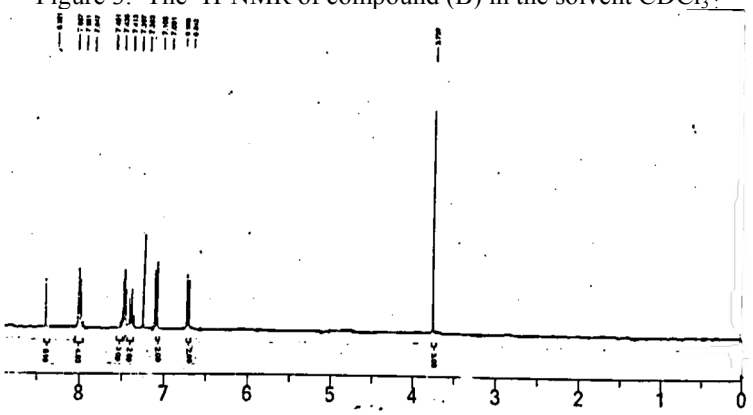
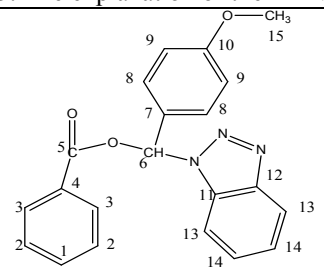


Table 3. The explanation of the ^{1}H-NMR :



(1*H*-benzo[*d*][1,2,3]triazol-1-yl)(4-methoxyphenyl)methyl benzoate

Type	Integration	Splitting	Chemical shift (ppm)	Position Of Hydrogen atom
Aromatic	3H	multi	7,45	1,3
Aromatic	2H	triplet	7,35	2
Aliphatic	1H	singlet	8.35	6
Aromatic	2H	doublet	7,1	8
Aromatic	2H	doublet	6,7	9
Aromatic	4H	multi	7,5	13+14
Aliphatic	3H	singlet	3,70	15

Figure 4. we see the ^{13}C-NMR that shows 15 atoms of carbon

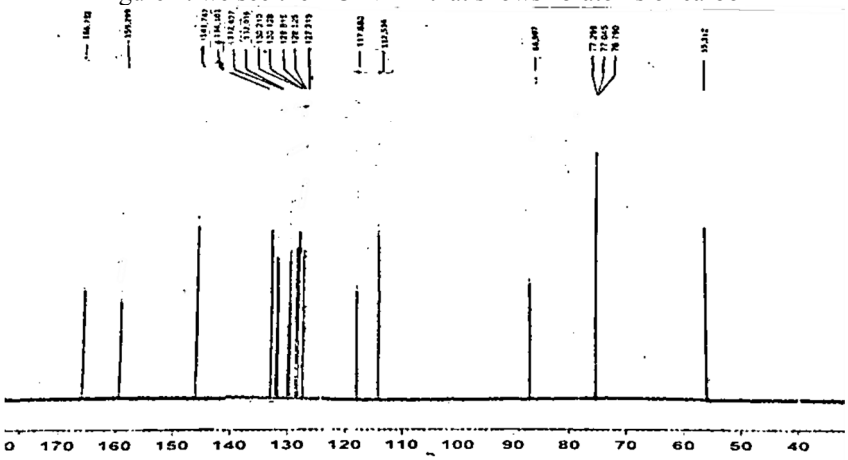
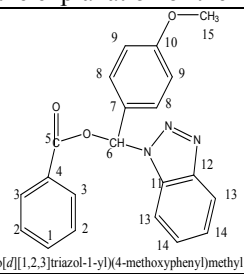


Table 4. the explanation of the ^{13}C-NMR



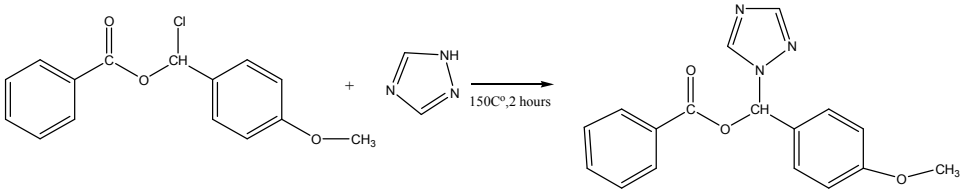
(1*H*-benzo[*d*][1,2,3]triazol-1-yl)(4-methoxyphenyl)methyl benzoate

Type	No. of carbon atoms	Chemical Shift (ppm)	Position of carbon atom
Aromatic	1	130,210	1
Aromatic	2	128,525	2
Aromatic	2	130,125	3
Aromatic	1	134,102	4
carbonylic	1	166,805	5
Aliphatic	1	86,907	6
Aromatic	1	132,497	7
Aromatic	2	128,635	8
Aromatic	2	112,534	9
Aromatic	1	159,299	10
Aromatic	1	132,010	11
Aromatic	1	143,747	12
Aromatic	2	117,880	13
Aromatic	2	127,215	14
Aliphatic	1	55,314	15

Step 3 :

The reaction of compound (A) with 1,2, 4 - Triazole to get the compound 1,2,4-triazole (4-methoxyphenyl)methylbenzoate (C) :

We prepared the compound (C) in the lab following this reaction :



We put (10mmol, 1.121 ml) of 4-methoxy Benzaldehyde into a flask provided with a magnet stirrer, then we add (10mmol, 1.155 ml) of Benzoyl chloride and then (10mmol, 0.69 gr) of 1,2,4-triazole dissolved in acetone, then we put the flask in an oil bath at 150C° .The reaction takes 2 hours and we notice the forming of an orange oil layer. We purify it using column chromatography using the solvent (hexane : chloroform) (1:4), then we freeze-dry the sample for 6 hours and the yield is 80% .

Figure 5. The IR Spectrum of compound (C)

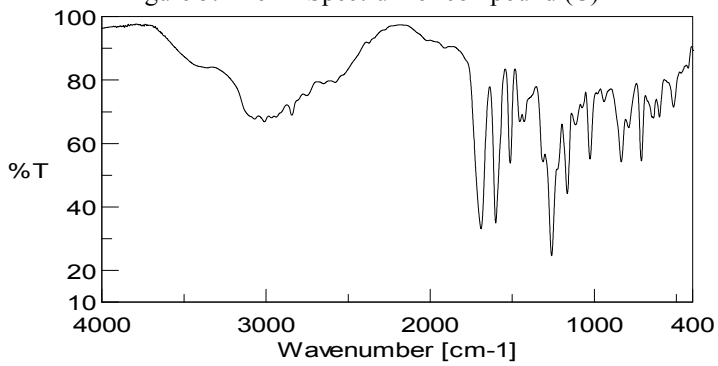


Table5. The explanation for IR Spectrum of compound (C)

(4-methoxyphenyl)(1*H*-1,2,4-triazol-1-yl)methyl benzoate						
Functional group	CSP3–H	Csp2-H	C=O	C=C (Aromatic)	C-O(ester)	C-N
Wavenumber (cm-1)	3075	3110	1715	1610,1500, 1410	1255	1050

The form (6) : The ^{1}H-NMR of compound (C) in the solvent $CDCl_3$

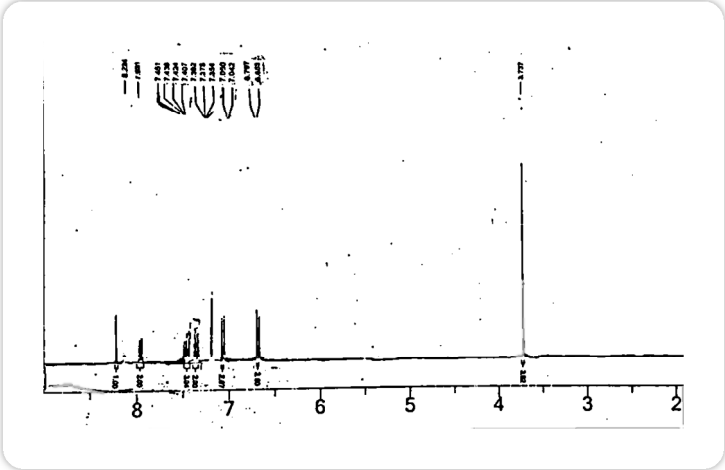
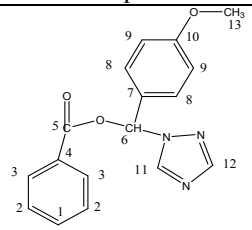


Table 6. The explanation of ^{1}H-NMR



(4-methoxyphenyl)(1*H*-1,2,4-triazol-1-yl)methyl benzoate

type	Integration	Splitting	Chemical Shift (PPM)	Position of hydrogen atom
aromatic	1H	multi	7,45	1
aromatic	2H	multi	7,35	2
aromatic	2H	doublet	7,45	3
aliphatic	1H	singlet	8.25	6
aromatic	2H	doublet	7,1	8
aromatic	2H	doublet	6,7	9
aromatic	2H	singlet	7,95	11,12
aliphatic	3H	singlet	3,7	13

Figure 7. we see ^{13}C-NMR , that shows 13 atoms of carbon

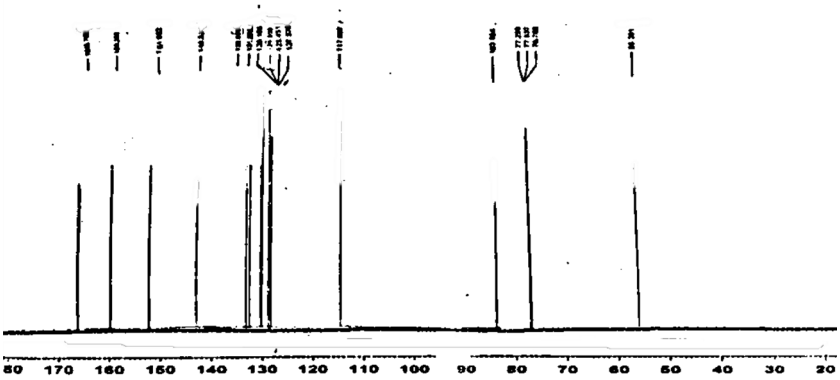
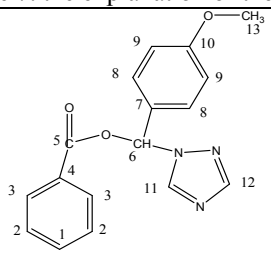


Table 7. the explanation of the ^{13}C-NMR



(4-methoxyphenyl)(1*H*-1,2,4-triazol-1-yl)methyl benzoate

Type	No. of carbon atoms	Chemical Shift (PPM)	Position of Carbon atom
Aromatic	1	132,802	1
Aromatic	2	127,570	2
Aromatic	2	130,165	3
Aromatic	1	132,66	4
carbonylic	1	166,805	5
Aromatic	1	83,054	6
Aromatic	1	131,932	7
Aromatic	2	128,451	8
Aromatic	2	117,014	9
Aromatic	1	159,206	10
Aromatic	1	143,425	11
Aromatic	1	151,962	12
Aliphatic	1	55,314	13

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