New and Developed Method to Prepare 1,1-Bis (4-chlorophenyl) ethanol and 1,1-Bis (4-chlorophenyl)-2,2,2-trichloroethanol

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Abstract

1,1-Bis (4-chlorophenyl) ethanol and 1,1-Bis (4-chlorophenyl)-2,2,2-trichloroethanol (which are the active ingredient of Qikron and Dicofol pesticides) were synthesized via developed and derived procedure. Treatment of phenyl magnesium bromide (Gringard reagent) with acetophenone gave the 1,1-diphenyl ethanol, chlorination of the obtained product in glacial acetic acid gave 1,1-Bis (4-chlorophenyl) ethanol in good yield. Chlorination of the methyl group in the obtained product in presence of ultraviolet light (UV) and heat gave the 1,1-Bis (4-chlorophenyl)-2,2,2-trichloroethanol in good yield.

The products were identified by physical, chemical, spectroscopic and element analysis. The bioassay was also measured for the obtained compounds.

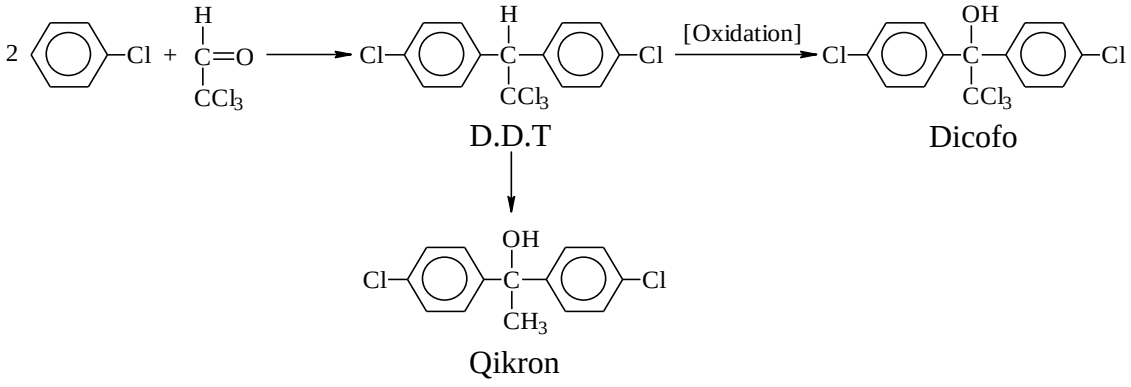
Keywords: Qikron, Dicofol

Introduction

Pesticides are still the speedy effective device to fight different agriculture diseases, where the statistics issued from many developed countries refer to the increasing used amounts of pesticides according to the vital role in increasing agricultural products [1].

Qikron is an acricide which shows an ovicidal effects on eggs of Acari in addition to its effect on other stages of mites. The active ingredients of Qikron characterized by its stability in alkaloids solution but may hydrolyzed in acidic solutions, it is colorless crystals which dissolved in water [2]. While Dicofol is an active Acaricides and in secticides, and its broad spectrum effects led to use as a general pesticides to control a wide range of mites and insects on vegetables, fruits and field crops in addition to its restermany use in controlling ectoparasites on sheeps and cows. Dicofol active ingredient is dry material and brown in color, soluble in water and insoluble in most organic solvents [2].

To our knowledge, and according to the scientific issued references many works to prepare the active ingredient for Qikron and Dicofol which are 1,1- Bis (4-chlorophenyl) ethanol and 1,1-Bis (4-chlorophenyl)-2,2,2-trichloroethanol respectively showed that they were some difficulties and consumptional of chemicals, reagents and solvents in addition to the low percentage of yield [3-6]. The old procedure to prepare the Qikron and Dicofol is shown in Scheme (I) [7].



Scheme (I)

Experimental

Uncorrected melting points were determined using Galkenkamp melting point apparatus. I.R spectra were recorded by using Pye-Unicam SP1100 spectrophotometer as KBr disc. U.V visible were performed on double beam Shimadzu UV (U.V-160) spectrophotometer. ^{1}H-NMR spectra were recorded on a 60 MHz Hitachi-Elmer spectrophotometer in chemistery department College of Education (2001). C.H.N analysis were done on Analyzer type 1106 Carlo-Erba. UV light lamp (250w) was used. The biochemical assay was done in Protecting Plant Department, Agriculture and Forestry College, Mosul University.

Theoretical physical calculation and three dimensional configuration (3D) were pointed out using "ChemOffice" Program Version 7 and MOPAC method [14].

Synthesis of 1,1-diphenyl ethanol (1)

To the reaction mixture of Magnesium metal foil (2.7 gm, 0.1 mole) and bromobenzene (15.7 gm, 0.1 mole) in dry diethyl ether (50 ml).was added one crystals of iodine in order to intiate the reaction. The reaction mixture was heated on steam bath with stirring, then refluxed for 15 minutes. The reaction mixture was allowed to cooled with stirring. Acetophenone (9.6 gm, 0.1 mole) dissolved in dry ether (50 ml) was added drop wise and reflux gently, after adding half the quantity a white precipitate appear. The reaction mixture was continued stirring for 15 minutes until the addition of acetophenone was complete. Cooled in ice bath, the stirring was continued with addition of a solution of ammonium chloride (20 gm) in water (200 ml) dropwise. The aqueous layer separated and the ether layer washed with water (20 ml), dried over anhydrous sodium sulphate (1 gm), filtered and the solvent evaporated. The oily material was left in refrigerator to get white crystals.

m.p. : 78-80 °C (11.6 gm, 73%)

U.V. λ_{max} [EtOH] 298 nm

I.R (KBr disc) ν cm^{-1} 3120 (broad OH), 1620 (C⋯C aromatic)

^{1}HNMR δ($CDCl_3$,TMS) 0.6(s,3H,CH_3), 7.6(m,10H,Ar), 6.3(b,1H,OH)

Synthesis of 1,1-Bis (4-chlorophenyl) ethanol (2)

1,1-Diphenyl ethanol (5.94 gm, 0.03 mole) in glacial acetic acid (75 ml), chlorine gas was passed with stirring at room temperature for 3 hrs. The reaction mixture was lefted cooled at room temperature for 12 hrs, and then added on ice (20 gm) to afforded the product. The crude product extracted by ether (2 × 25 ml), the combine extract were washed with solution of 10% sodium bicarbonate (15 ml) and then with water (25 ml), dried over anhydrous sodium sulphate (5 gm). Evaporation of the solvent under reduced pressure afforded white material, which was washed with petroleum ether (40-60 °C) to give white crystals.

m.p. = 69-70 °C (7 gm, 87.5%)

U.V. λ_{max} [EtOH] 278 nm

I.R(KBr disc) νcm^{-1} 3150-3200(broad OH), 1610(C=C aromatic), 700(C-Cl)

^{1}HNMR δ($CDCl_3$,TMS) 0.7(s,3H,CH_3), 7.5(m,8H,Ar), 6.8(b,1H,OH)

Elemental analysis

	C	H	N
Calcul.	62.92	4.49	-
Found	62.61	4.75	-

Bioassay test

Adult LC = 0.0017

Eggs LC = 0.0031

LC means the concentration killer for 50% for animal test.

Synthesis of 1,1-Bis (4-chlorophenyl)-2,2,2-trichloroethanol (3)

1,1-Bis (4-chlorophenyl) ethanol (2) (2.69 gm, 0.1 mole) was dissolved in carbon tetrachloride (50 ml). An ultra violet light (lamp) was plased near the flask. The reaction mixture was refluxed, chlorine gas was passed. The contents was weighed from time to time until gained in weight about (1.6 gm), for about 10 hrs., cooled and added over ice water (50 gm). The organic layer was separated, dried over anhydrous magnesium sulphate, and after evaporation of the solvent to obtain a pale yellow brown material. The crude was recrystalized from ethanol.

m.p. = 76-78 °C (1.8 gm, 62%)

U.V. λ_{max} [EtOH] 294 nm

I.R (KBr disc) ν cm^{-1} 3200 (broad OH), 1600 (C⋯C aromatic), 3000 (C-H aromatic), 700 (C-Cl)

^{1}H-NMR δ($CDCl_3$,TMS) 7.3-8(m,8H,Ar), 8.5(b,1H,OH)

Element analysis

	C	H	N
Calcul.	44.74	2.39	-
Found	44.33	2.49	-

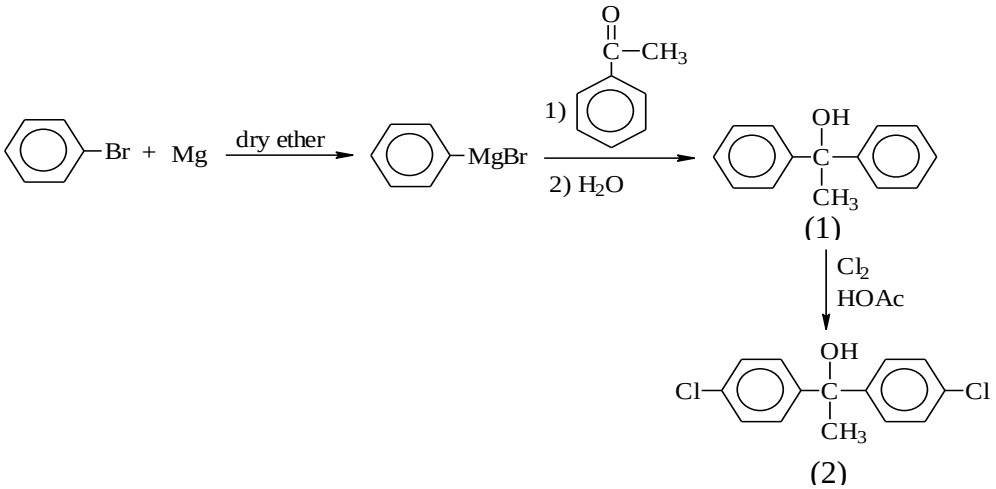
Bioassay test

LC_{50} = 0.0022

Results And Discussion

In the present work the two pesticides, 1,1-Bis (4-chlorophenyl) ethanol and 1,1-Bis (4-chlorophenyl)-2,2,2-trichloroethanol were synthesized in high yield using a developed method.

1,1-Bis (4-chlorophenyl) ethanol (the active ingredient of Qikron pesticide) was synthesized by the reaction of phenyl magnesium bromide with acetophenone, to obtain the 1,1-diphenyl ethanol (1). Chlorination of (1) by chlorine gas [8-10] in the presence of glacial acetic acid gave chiefly 1,1-Bis (4-chlorophenyl) ethanol (2) in a good yield.



Scheme (II)

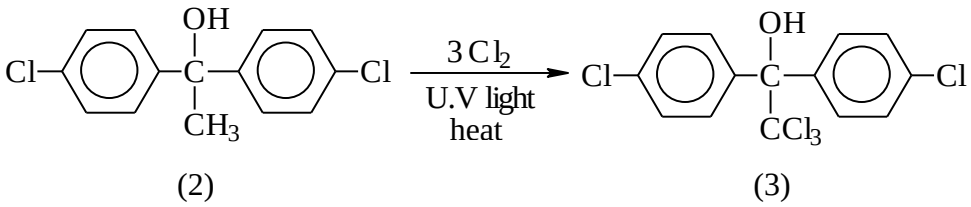
The structure of compound (1) was confirmed on the basis of the following evidences. The infrared spectrum showed a broad band at about 3120 cm^{-1} for hydroxyl group, the ^{1}H-NMR spectrum indicated aromatic protons at δ 7.6 ppm, methyl group at 0.6 ppm and one absorption at 6.3 ppm due to OH proton. The structure of compound (2) was confirmed by the following evidences, the infrared spectrum showed a broad band at about 3150-3200 cm^{-1} for hydroxyl group, and a band about 700 cm^{-1} for (C-Cl).

^{1}H-NMR spectrum which showed a band at 0.7 ppm singlet assigned for methyl group, a band at 7.5 ppm multiplet for eight aromatic protons, and a band at 6.8 ppm broad assigned for one proton of hydroxyl group.

The bioassay test showed the following results: Adult Lc_{50} = 0.0017, Eggs Lc_{50} = 0.0031.

Lc_{50} means the lethal concentration for 50% of the animal tested.

When 1,1-Bis (4-chlorophenyl) ethanol was chlorinated by chlorine gas either by using heat or ultraviolet light [10] yet the chlorination don by heat, the product (3) was obtained.



(2) (3)

The structure of (3) was confirmed on the basis of the following evidences. The infrared spectrum showed broad band at 3200 cm^{-1} for hydroxyl group, 1600 cm^{-1} for C=C aromatic and a band at 700 cm^{-1} for (C-Cl). ^{1}H-NMR spectrum showed a band at 7.3-8 ppm multiplet for eight aromatic hydrogen, and a band at 8.5 ppm broad for hydroxyl group proton.

The bioassay test for the active ingredient gave Lc_{50} = 0.0022.

Further information for the isolated products (2) and (3) was obtained from theoretical calculation which made by means of quantum mechanical semiempirical method (SCF) and molecular mechanics method (MM2) [12,13]. Table I and II give the calculated relevant physical properties of the products. The (3D) configuration [14] for the two isolated products are shown in Figure (1).

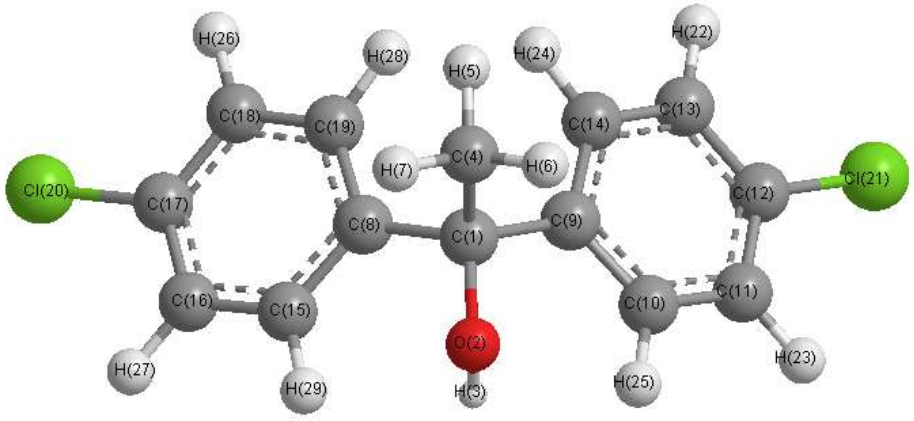


Figure (1) 3D-structure of compound (2)

Table (1) Physical properties of compound (2).

Stretch	Bend	Stretch-bend	Torsion	Non-1,4VDW	1,4VDW	Dipole/dipole	Total
0.8979	1.0719	0.0304	-8.6732	-1.3653	9.9088	1.4498	3.3202

Heat of Formation= -9.08315 kcal/mole
The steric energy 3.3202 kcal/mole

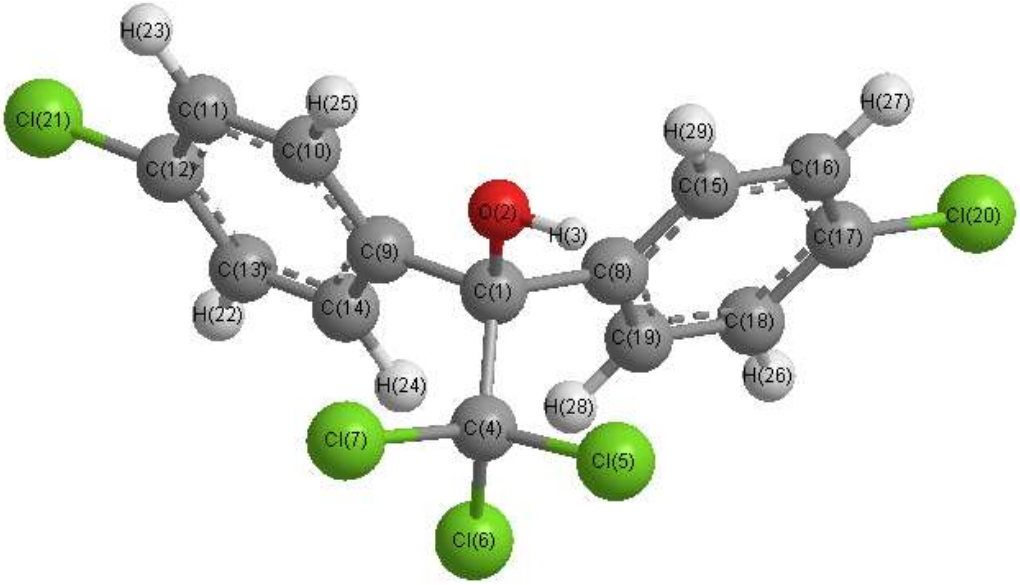


Figure (2) 3D-structure of compound (3)

Table (2) Physical properties of compound (3).

Stretch	Bend	Stretch-bend	Torsion	Non-1,4VDW	1,4VDW	Dipole/dipole	Total
2.5575	3.9734	0.2342	-11.7186	-0.9966	12.3375	5.4217	11.8291

Heat of Formation= -11.50318 kcal/mole
The steric energy: 11.8291 kcal/mole

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طريقة جديدة ومطورة لتحضير ١،١-بس(٤-كلوروفنيل) ايثانول و ١،١-بس(٤-كلوروفنيل)-٢،٢،٢-ثلاثي كلورو ايثانول

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الملخص

١،١-بس (٤-كلورو فنيل) ايثانول و ١،١-بس(٤-كلورو فنيل)-٢،٢،٢-كلورو ايثانول (وهما المادة الفعالة للمبيدين كيكرون ودايكوفول) حضرا عبر طريقة جديدة ومطورة. مفاعلة فنيل مغنسيوم بروميد (كاشف كرينارد) مع الاسيتوفينون يعطي المركب ١،١-ثنائي فنيل ايثانول. كلورة الناتج بوجود حامض الخليك الثلجي يعطي الناتج بكمية جيدة وبنسبة عالية. كلورة مجموعة المثيل بواسطة الأشعة البنفسجية والحرارة في الناتج يعطي المركب الاخير.

شخصت المركبات المحضرة بواسطة الطرق الفيزيائية والكيميائية والطيفية وتحليل العناصر. تم قياس التقييم الحيوي للمركبات الناتجة.

الكلمات المفتاحية: كيكرون ودايكوفول