A New approach to the synthesis of2- Isopropoxyphenyl N- methyl carbamate

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Abstract

2-IsopropoxyphenylN-methyl carbomate (5) which are the active ingredient of the trade name baygonpesticides had been prepared by reacting equal mole of catechol with 2- chloropropanein a basic medium followed by treatment with carbonyl chloride in dry toluene at zeroC^otogive,2-isopropoxyphenylchloro formate (4). Reaction of the later with methyl amine in presence of base afforded the required product (5).

The structure of the product was diagnosed by comparing it is physical properties and spectral data with the litertures[1]

الخلاصة

2– ايزوبروبوكسي فنيل –N– مثيل كاربميت (وهي المادة الفعالة لمبيد البايكون) حضر عبر طريقة جديدة وذلك من خلال تفاعل الكاتيكول مع 2– كلوروبروبان في وسط قاعدي لنحصل على المركب ايزوبروبوكسي فينول وعند مفاعلته مع المركب كلوريد الكاربونيل حصلنا على 2– ايزوبروبوكسي فنيل كلورو فورميت. حيث تم مفاعلة الأخير مع مثيل أمين بوسط قاعدي من ثلاثي مثيل أمين ليعطي الناتج بكمية جيدة ونسبة عالية.

Introduction

Baygon is a pesticide and it is an insecticide used for extermination and control of many household pets, it is very effective for crickets, ants, carpenter ants, spiders and ather. In 1975, baygon introduced Australia firt for killing cockroaches and crowlinginsects [2-7].

N- Alkyl- carbomates are valuable products and display anuseful activity as plant disease control agents and various type of compositions containing these agents have been recommended. Liquid compositions can be prepared with solid carbomate in two main forms namely as: suspensions and solution. Commerciallycalled propoxur. One of the process is provided for the preparation of N- alky carbomates by direct reaction low molecular alkylisocynatesin particular methyl isocynate and substituted phenolic precursor [8-9] as shown in scheme(1) in an inert organic solvent in presence of basic catalyst and normally selected from ter. amine eq. triethyl amine. The active ingredients of baygon are characterized by its stability in basic mediumbut may hydrolysed in acidic one, colorless crystals which dissolve in most organic solvents.it is an active insecticides and its broad spectrum effect lead to use as a general pesticides to control a wide rang of insects and its low toxicity against mammals incited [10-12].
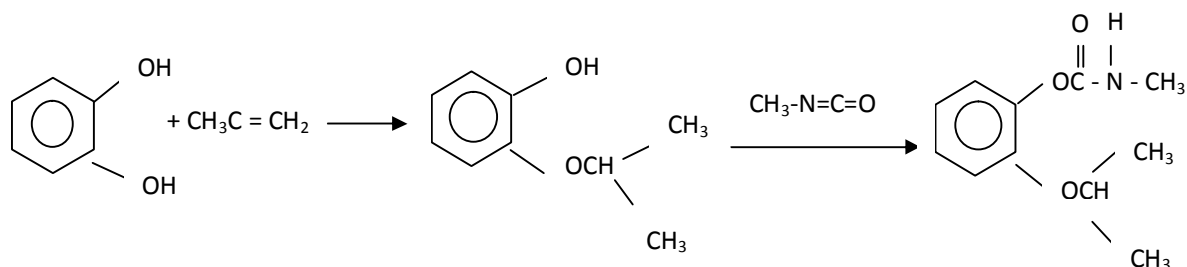
Scheme (1)

Experimental

Uncorrected melting points were determined using Gallenkamp melting points apparatus. IR spectra were recorded by using pye- Unicom sp 1100 spectrophotometer as KBr disc. ^{I}H-NMRspectra were recorded on a 60 MH$_z$ Hitachi- Elmer spectrophotometer in chemistry department college of Education (2001). The biochemical assay was done in protecting plant department. Agriculture and Forestry college. Mosul University.

Theoretical physical calculation and three dimension configuration (3D) were pointed out using " chemoffice" program version and MOPAC method [13-15].

Synthesis of carbonyl chloride:

Don't expose to this material because it is severe toxicity to prepare this material in small quantity in the laboratory. To get rid of any excess of this gas, it is collected in a cooled toluene at zero c^{o}for used in future at thisform. Theexperiment was

conducted under strictlyanhydrous condition.

In a 250 ml 3-necked round bottomed flask containing sulphuric acid (100%) with small quantity of burn celite fitted with a condenser and additionl funnel linked with tube to around bottom flask containing cooled toluene to collect carbonyl chloride gas , the flask connected to atrape containing sodium hydroxide solution in order to get rid of the evolved hydrogen chloride .Heating up the acid to around 120-130^0 with the addition of carbon tetrachloride gradually from the dropping funnel .collect the carbonyl chloride as a gas dissolve in toluene with hydrogen chloride pass through to sodium hydroxide solution trap.

Synthesis of 2-Isopropoxy pheny-lchloroformate (4): A solution of o-is opropoxyphenol (152 g) in water (500 ml) and sodium hydroxide (44g) was stirred for one hour, the reaction temperature is maintained at 85c^0 . Cooled the mixture to 20 c^0 and added gradually 96 part of carbonyl chloride intoluene (300) part over aperiod of one hour at − 50c^0 with continuous stirring for additional one hour at 20-c^0 .The mixture was poured into water and extracted with diethyl ether. Evaporation of the solvent afforded an oil which was purified by chromatog-raphy over alumina eluting with

toluene gave the required compound (4)

2-Isopropoxyphenyl–N-methyl carbamate(5).

The 2- lsopropoxyphenylformate was treated with aqueous methyl amine (40%) with stirring at zero c^0- in presence of triethyl amine (5ml) with continuous stirring for farther one hour at $25c^0$ .The cooled mixture was filtered off to give crystalline solid which was washed with water.Recrystallization from benzene afforded pure compound (5). M.P.=87-90^0 ,yeild 65% . IR (KBr disc) cm^{-1} 1600 c^c=c aromatic),1735 (CO_2), 3100 (C-H aromatic) 3345 (N-H). H-NMR ($CDCL_3$), TMS, Fig (1) , 1.4 (d,$2CH_3$), 2.9 (s,CH_3), 4.5 (m,CH), 5.4 (bs, NH), 7.0 (s,4H, aromatic).

Biological evolution of 2- Isopropoxy phenyl- N- methylcarbomate.

To conduct this study, five cencen-trateion (0.01, 0,004, 0.003, 0.002 and 0.001) of the active ingredient of baygon dissolved in chlorofrom with duplicated of each concentration which contain ten insects from species of sensitive insects (Trogo derma grananium) placed in petridish treated with 1ml of a solution of biological active compound. The control treatment has treated with distill water.

The reading register after four hours and the graph of toxicity of the correcting death rate using a butt equation and calculated the value of concentration of the killed insects for 50% (Lc50)= 0.0125

Results and Discussion

In the present work, the active ingredient of the pesticide, 2- is-opropoxyphenylmethylcarbomate was synthesized following a developed method. Involving conversionof o-isopropoxyphcnylchloroformate (it self

available from the reaction of equal mole of isopropyl chloride with catechol in a basic medium of sodium hydroxide following the method of Williamson for the synthesis of the ether by admixing with methyl amine in presence of triethyl amine to give chiefly o- isopropoxyphenyl –N- methyl carbomate in a good yield.

A plausible reaction path way describe above can be depicted as shown in scheme (2)

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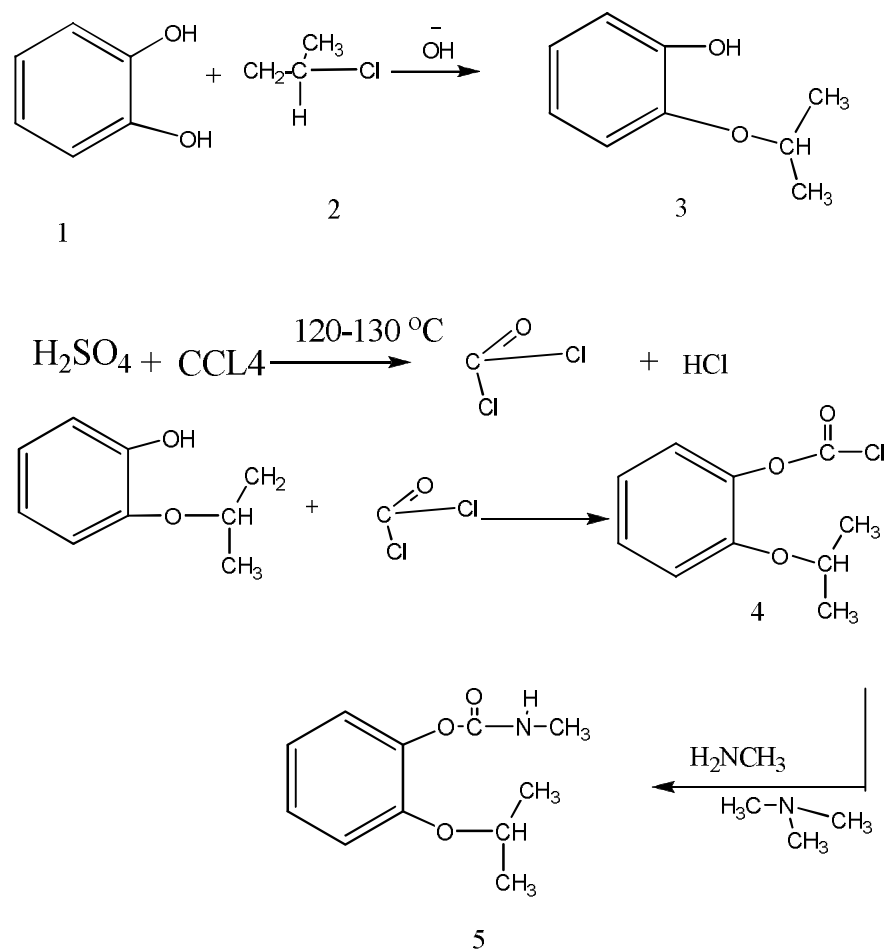
Scheme(2)

The structure of (5) was suggested by spectral data. The infrared spectrum showed absorption band of carbonyl group around 1735 cm^{-1} and aband at 3345cm^{-1} attributed to NH group. H-NMR spectrum which showed a singlet at 7.0 ppm assigned for aromatic protons, one proton broad for NH at 5.4 ppm, a multiplate at 4.0 ppm for methane protons, a singlet peak at 2.9 ppm for methyl group and six protons resonated as a doublet at 1.4 ppm assigned for tow methyl groups Fiq (2).

The possible path way accounting for the formation of the coupound(5) was shown in scheme(3)

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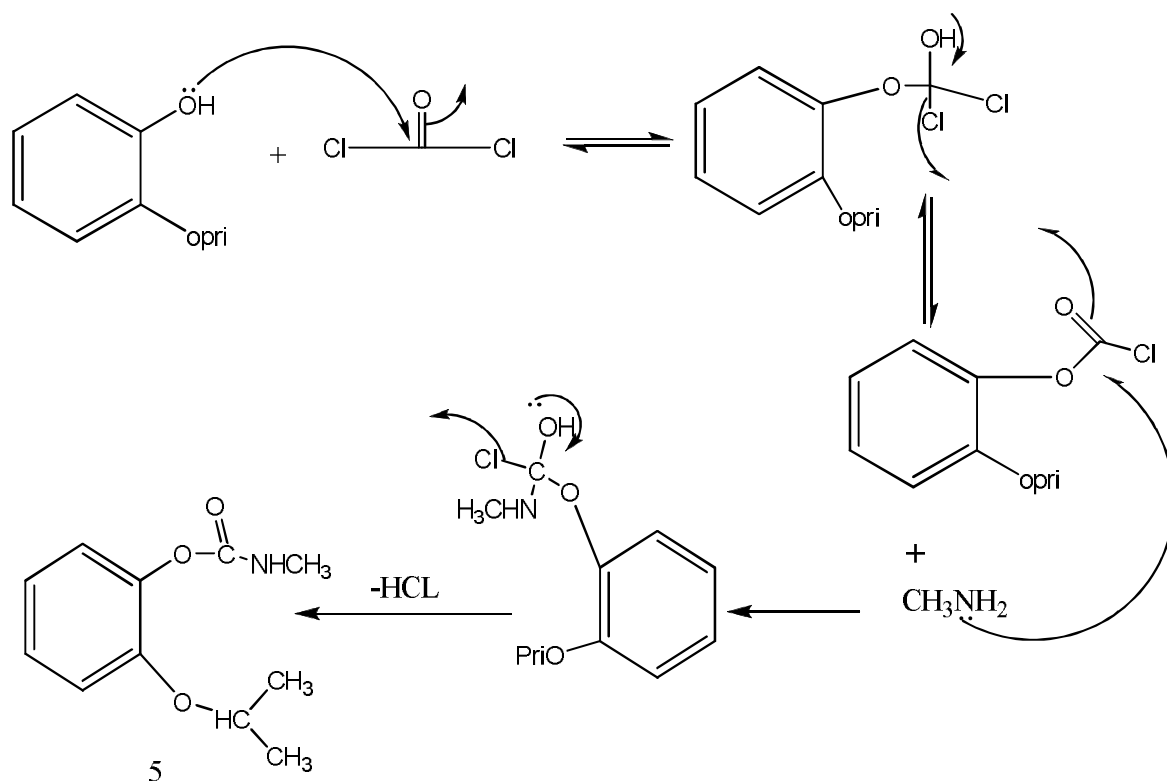
Scheme (3)

The bioassay test for the active ingredient 2- Isopropoxyphenyl –N-methyl carbamate (5) gave $c_{10}=0.0125$. Further information about the isolated products was obtained from theoretical collection which made means of quantum mechanical semi empirical method (SCF) and molecular mechanics method (MM_2). Table (2) and (3,4) gave the calculated relevant physical properties of the products (3) and (4,5).

The 3D.configuration for (3) and (4,5) are shown in Fig (3) and (4,5)
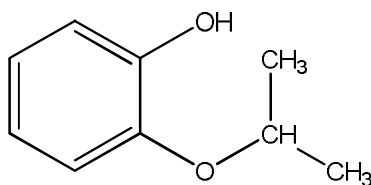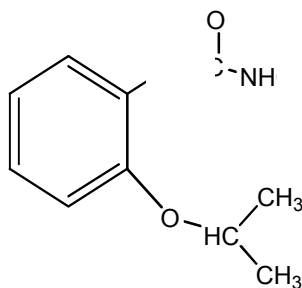
Table (1) physical properties of compound (3)

Stretch	Bend	Stretch bend	Torsion	Non-1,4 VDW	1,4 VDW	Dipole dipole	Total
0.784	5.21	0.0858	-6.576	-1.055	5.7944	-0.3642	3.8818

Critical pressure	Critical Temp	Critical Volume	Gibbs Free	Heat of Formal	Melting Point	Mass Spectra	Mol Weight	MolFormule
38.531	725.466	459.5	-124.75	-307.37	336.06	152.190	152.190	$C_2H_{12}O_2$
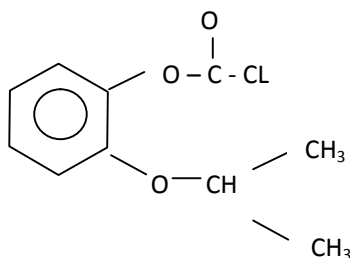
Table (2) physical properties of compound (4)

| Stretch	Bend	Stretch bend	Torsion	Non-1,4 VDW	1,4 VDW	Dipole dipole	Total Steric Energy
1.3697	6.655	0.1340	-5.794	-7656	8.9593	6.963	26.9229 Kcal

Boiling Point	Critical Pressure	Critical Temp	Critical Volume	GibbsFree energy	Heat of Formation	Melting Point	Mass Spectra	Mol Weight	Molecular Formule
510.80 Kelvin	38.531 Bar.	725.466 Kelvin	459.5 cm^3/Mol	-124.75 Kj/Mol	- 307.37Kj/ Mole Kj/Mol	336.06 Kelvin	214.645	214.645	$C_{10}H_{11}CLO3$

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**Table (3) Physical properties of compound (5)**

Water solubility	Mole refractivity	Stretch	Total energy	Steric energy	Heat of Fromal	Critacl temp	Critaclpresurs	Element analysis	Gibs free enegy	Mol. wt
2G/L	5.718	6.5	7.4516K cal/mole	1.2358	-446.62	755.7 K	26.325 BAQR	C,63,14, H,7.23,N ,6.69 O,22.94	138.9 Kal/J	209.24

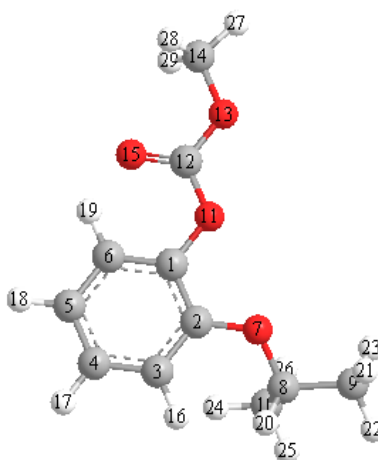| Melting point	Boiling ponint	Stetch	Bend	Steeching bending	Torsion energy	Non-1,4 VDW	1-4 VDW	Dipole dipole	Partition coffecient	Molecular Formula
354.39 K	613.31	0.8889	6.7499	0.08636	-4.941	-3.3089	7.486	-0.1158	3.27	$C_{11}H_{15}NO_3$
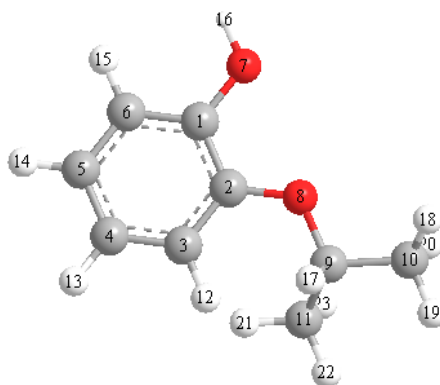
3D-Structure of 2-Isopropoxy phenol   (3)

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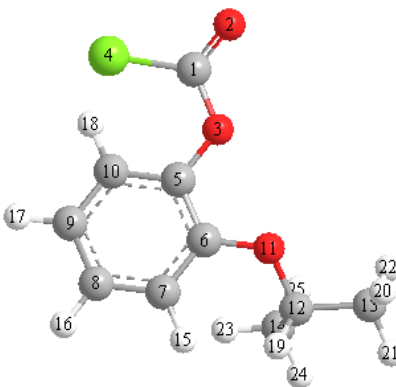
3D-Structure of 2-Isopropoxyphenyl-chloroformate (4)

3D-Structure of 2-Isopropoxyphenyl-N-methylcarbomate (5)

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