

# Reactivity of selenyl Acrylate to ward cyclopentodieryl

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## Abstract

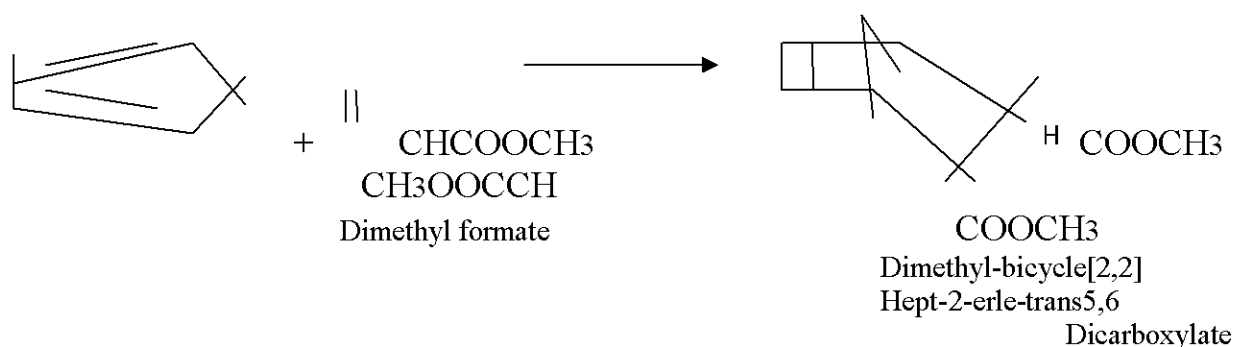
Aselenyl oxide derivatives as a dienophile react with fresh cyclopentadiene as diene to give adduct which is a specific kind of Diels-Alder reaction, the result of this reaction is very important in the organic reaction because of its ability to cyclization and retention (1) of its configuration, this work describes their reactivity in a particular Diels-Alder reaction, and covers the synthesis and characterization of the products by  $^1\text{H-NMR}$ , elemental analysis, chromatography melting points and IR.

## Introduction

A conjugation addition of an alkene to a conjugate diene give a cyclic derivatives classified as (cyclo addition).(2)

The diene must adopt the S-Cis conformation which means "the double bond like in a plane on the same side (Cis) of the single bond connecting the dienes, previous studies of cyclopentadiene with dienes yielded. Bridged cyclic Diels-Alder adduct(3) figure(1)

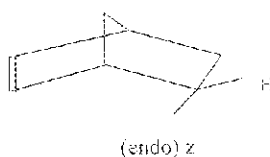
The selenium oxide has a strong reactivity toward the diene system. This reactivity is due to the group electro attractor which activated the carbon-carbon bond, if we add another electro active group like Nitril the system reager as acceptor



Figure(1)

When cyclopentadienyl reacts with dieno phile such as selenium ethylincoxides new six member(3) ring there is one carbon atom of the diene ,this new system called " Cabridge bicycles system"(4) in this system we find that the ligand take endo or exo position < for example figure (2)

To distinguish between endo and exo ligandes for example (Z )ligand.



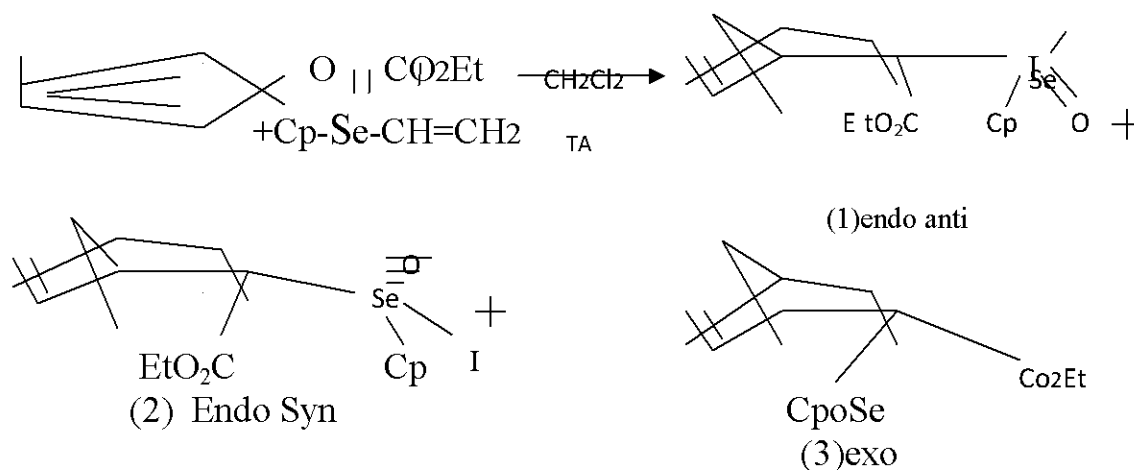
Figure(2)

The (Z) ligand oriented either directly under the diene to form the endo products, or away from the diene, to form the exo product in practice, the endo product is the major product because it allows more interaction between the electron-rich diene and the electron-withdrawing substituent (5)(Z) on the dienophile and energetically favorable arrangement .

This introduction is applied exactly on our work in the field of Diels\_Alder reaction(6)

### Results and discussion

The reaction of selenyl acrylate with cyclopentadiene is very fast at room temperature, in dichloromethane as a solvent, this reaction produces a very good yield, the conformation of the molecule depended on Cp ligand, when it is close to the bond of the produced ring we call it endo, on the contrary, we call it exo conformation, when Cp is away from diene (6). the end ring have two isomers called (7) syn and anti (figure 2)



Figure(3)

**Their name are as follows**

1- cyclopentadiene selenyl (anti) [2,21] bicyclohept-5-ene,2-ethyl carboxylate(endo).

Its obtained with yield 60% (.1.6gm)m.p= 78°C

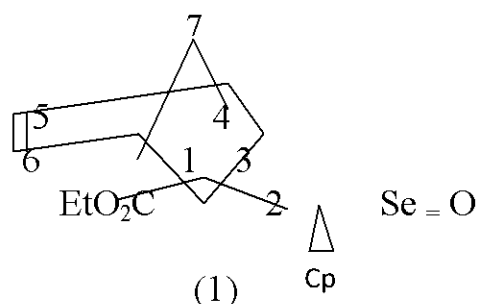
**Analysis C<sub>15</sub>H<sub>17</sub>OSe**

Calc% C:75 H:7 O:33 Se:14.2

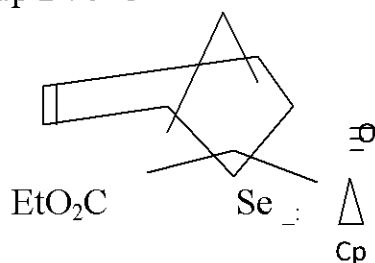
Found % C:75.6 H:7.0 O:32.72 Se:14.82

<sup>1</sup>H<sup>1</sup>NMR(COCl<sub>3</sub>) (Sppm):1,2(3H,t,J= 5Hz) .CH<sub>3</sub> ester (1.53(1Hdm) and (1H.dd):H7:1,8(1H.dd)and 2.53 (1H.dd)H3:3.08 (1H.m)H4:3.61(1H.m)Hz 3.9 (2H<sup>9</sup> J= 7.5Hz) CH<sub>2</sub> ester 6.07 (1H,dd) H5 and H4:7.59 (5H.m) H atom

IR δ<sub>max</sub>: 173 2(C = O) 1629 (C = C) and 1049 (Se = O)



2- 2-cyclopentadiene selenyl (syn) [2,2,1] bi cyclohept-5-ene-2 carboxylate  
Yeild 8% (0.23gm) ethyl m.p = 76°C



<sup>1</sup>H<sup>1</sup>NMR (CDCl<sub>1</sub>) (δppm) 1.07 (3H,t J = 76Hz) CH<sub>3</sub> ester : (1.6H dm) and 1.98 (1H.m)H<sub>3</sub> 1.72 (1H m) and 2.8 (1H.m) H<sub>7</sub>; 3.12(1H.m)H<sub>4</sub> 3.86 (3 A.m) H<sub>1</sub> and CH<sub>2</sub>

Ester; 6.13(1H.dd) and 6.43(1H.dd) H<sub>5</sub> and H<sub>4</sub>; 7.6(5H.m)

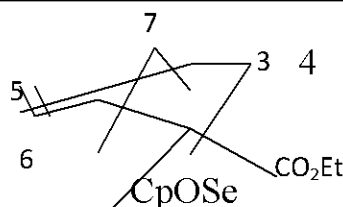
IR δ max . 1723 (C= O) 1632 (C = C) 1051 (Se = O) cm<sup>-1</sup>

**Analysis ; C<sub>15</sub>H<sub>17</sub>OSe**

Calc% C: 70.3 H:76 O: 3.3 Se:12.8

Found% C:70.2 H:752 O:3.2 Se:13

3- 2-cyclopentadiene selenyl [2,2,1] bicyclohept-5-ene-2-ethyl carboxylate (exo) yield 26.1 (o.752 gm) m.p= 85°C



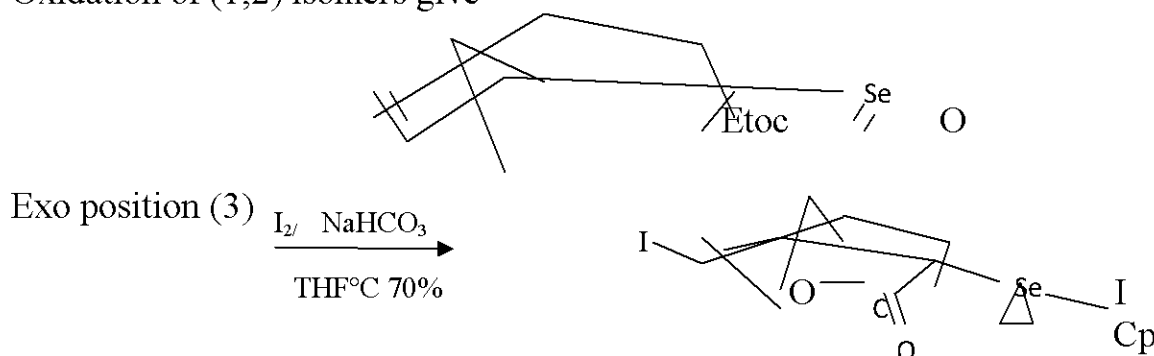
<sup>1</sup>H NMR (CDCl<sub>3</sub>) (δppm)

1.02 (3H,t J = 7.5Hz) CH<sub>3</sub> ester ; 1.34(1H,d) and 1.63(1H,d) H<sub>3</sub>; 2.14 (1H,d) and 2.5 (1H,d) H<sub>7</sub> 3.08(1H,m) H<sub>3</sub> . 4.06(2H,9 J = 7.6 Hz) CH<sub>2</sub> ester 6.33 (1H,d) H<sub>5</sub> and H<sub>6</sub>; 7.58(5H,m) H cyclo

IR δ mas (fi lm) 1718(C = O) , 1635 ( C = C ) and (Se = O) cm<sup>-1</sup>

The exo position is confirmed by the reaction of Iodo lacton ,and the two isomers give the same product when they oxidized .(8)

Oxidation of (1,2) isomers give



### Anti-Bacterial Activity

These compounds were tested for their antibacterial activity against bacterial strains such as (A) Escherichiacoli (B) pseudonomous aerugionsa (C) staphylococcus aurous

Inhibition zone measured in minutes

(1) 5-10 min

(2) ++ 10-15 min

Table (1) anti bacterial data of compound (1,2,3)

1	+	+	+
2	+	+	+
3	+	+	----
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The selenium ion increases the anti – bacterial activity of these compounds du to the effect of the positive charge of the element

This effect leads to the penetration of the complexes in to the cell and block the protein synthesis

### Part Experimental

#### A. Dils alder reaction

A solution of (40 ml) of CH<sub>2</sub>Cl<sub>2</sub> and (1 ml) of fresh C<sub>5</sub>H<sub>5</sub> was added to a solution of (6 gm-2mmol) of selenium oxide in 40 ml of CH<sub>2</sub>Cl<sub>2</sub>, the mixture is

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stirred for 3hr at room temperature ,the evaporation of solvent give residue ,which chromatography

b. method of Iodo lactonization

(2.8 gm-1mmol) of selenium oxide in (10ml) of dichloro methyl was introduced to 4, mixture of (7.6gm-105mmol) of iodo with (7.4mg-4.5mmol) of KI and (1.68 gm-2mmol) of NaHCO<sub>3</sub> in 10ml of H<sub>2</sub>O ,the mixture was stirred at room temperature for (12hr) ,then it dilute with 30ml of H<sub>2</sub>O,the excess of Iodo was destroyed by sodium bisulfite until there is no color ,the aqueous phase was extract with (2x20) hexane ,the organic phase brought a sec by MgSO<sub>4</sub> .we obtained a compound pale yellow yield (89%) (3 mg) mp 65.6°C

FT-IR Spectrum for the products (1,2,3)

Showed bands of (1639 cm<sup>-1</sup>) which can be attributed to the (C = O) bond , also spectrum showed bands of (1630-1050 cm<sup>-1</sup> ) can be attributed to (C = C ,Se = O) ,Spectrum of compound (3),showed different bond position of compound (3) table (2)

<sup>1</sup>HNMR the difference between the two spectry are came from H<sub>1</sub> and H<sub>3a</sub> or H<sub>3b</sub> this effect may be influenced by the cyclopenta diene group which exerce an effect of deblindage onH<sub>3</sub>. the examination of molecular modeles of lewis acid as catalysit make the proportion of products changed hence the Iodo lactone give one adduct but we get three products with cyclopentadiene . the product of the diels –alder reaction of a cyclic 1,3diene is bicyclic ,but the carbon atoms shared by both rings are not adjacent.

That's the bicyclic product differ from the fused rin system obtained when the dienophil is a cycle .

Table (1) Some physical properties of prepared compounds and their reactant quantities

Table(2) Infrared Spectrum of compounds (1,3)

Table (1) some properties of prepared complexes and their reactant quantities

Compound	Yield	Weight of product
1	52%	0.5.7 gm
2	38%	0.23 gm
3	10.8%	0.764 gm
Iodo lacton	89%	0.6 gm

Table (2) Infrared spectrum of compound (1,2)

Compound	C = C	Se = O	C = O
1	1630.14	1050	1725.2
2	162.7	1020.34	16880.71

### Instruments

The following measurement were wed to character the three Products.

Melting point measurement

Stuart melting point apparatus was used to measure the melting point of compounds H' NMR typ JEOL FX a tranformee de Fourier

Mass spectral : apparatus type 3300 Flinnigan

chromatoyraphy : a thin plate, it was made of Awminium thin papers, covered by gel of sill cemerek 5553

Analysis : was measured by CNRS France

Biological activities are performed in the university of Baghdad- science colledge

### Perspective studies

- 1- Preparation of new adducts having six –members ring forms with one carbon atom bridge originated to the  $Sp_3$  hybridization carbon of the diene mot invluded in the reaction
- 2- We utilized a specific Diels-Alder reaction of ethyl selenium oxide with Cyclopentadiene called " bridge bicycles system
- 3- When endo and exo adducts possible , the endo product is preferred
- 4- There is a biological activities for the compounds tested for their antibacterial activity

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### الخلاصة

تم تحضير مركبات عضوية من تفاعل مشتقات لاوكسيد السلينيوم كداينوفيل مع السايكلوبنتادايين كدايين كحالة خاصة من تفاعل ديلز الدر حيث تتكون حلقة سباعية لذا فان هذا التفاعل مهم في تفاعلات تكوين الحلقات ذات ترتيب فراغي مماثل للمركب الاصللي علما ان هذا النوع من التفاعلات شغلت مجالا واسعا في الكيمياء العضوية كونها تعطي مركبات حلقيه نوعية وتم التحقق بواسطة  $H^1$ NMR، الكروماتوغرافيا، IR، تحليل العناصر ، درجة الانصهار ، ولقد وجدت لها فعالية بايولوجية كما سيوضح لاحقا.