A NEW METHOD FOR PREPARATION OF ALCOHOLS BY THE ELECTRO CHEMICAL REDUCTION OF ALDEHYDES[+]

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ABSTACT

The electro chemical reduction of benzaldehyde and p-tolualdehyde has been achieved by diphenyl ditelluride and diphenyl diselenide as catalysts using undivided cell containing graphite (cathode) and aluminum (anode) electrodes.

The products of electro chemically reduction, are benzyl alcohol and p-methyl benzyl alcohol. They are characterized to melting, boiling points and IR spectra.The yields of alcohol depends upon the kind of dichalcogenides compounds.

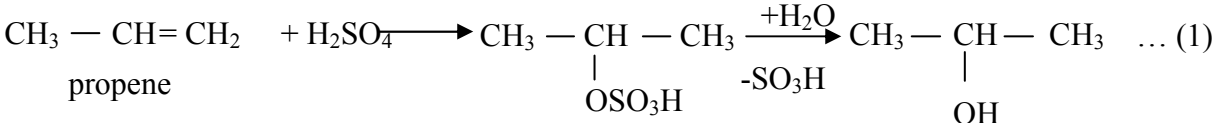
المستخلص

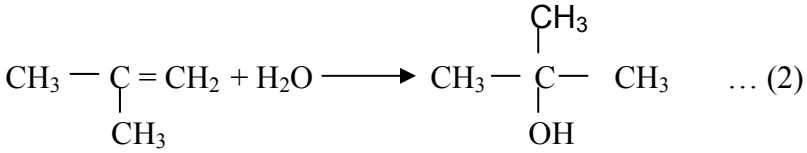
درس اختزال المركبين البنزاليهايد و بارا مثيل بنزاليهايد بواسطة خلية الكترولية غير مفصولة تحتوي على قطبي الكرافيت (الكاثود) و الالمنيوم (الانود) و باستخدام مركبات التلوريوم والسلينوم العضوية كعوامل مساعدة.

تبين من الدراسة تكون الكحولات المقابلة لمركبات الالديهايدات و هي بنزايل الكحول و بارا-مثيل بنزايل الكحول على التوالي، وقد شخصت الكحولات الناتجة بالاعتماد على درجات انصهارها و غليانها و اطياف الاشعة تحت الحمراء.كما تبين من الدراسة ان حصيلة الكحولات الناتجة تعتمد على نوع ثنائي الكالكوجين المستخدم كعامل مساعد.

Introduction

Alcohols can be prepared by a variety of reactions from a number of other functional groups [1].In industry alcohols are prepared by hydration of alkenes [2] by addition of sulfuric acid followed by addition of water according to equation (1) or by direct addition of water (H2O) according to equation (2):





Oxo-Process is one of most important industrial methods for preparation of alcohol from alkene, by the reaction of later with carbon monoxide and hydrogen in the presence of $CO_2(CO)_8$ [3] according to equation (3):

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$$CH_3 — CH = CH_2 \xrightarrow[CO_2(CO)_8]{CO,\ H_2} CH_3CH_2CH_2CHO \longrightarrow CH_3CH_2CH_2CH_2OH \quad \ldots\ldots(3)$$

propene — butraldehyde — butanol

One important source of ethyl alcohol is the fermentation of sugars [3] according to equation (4):

$$(C_6H_{10}O_5)_n \xrightarrow{H_2O} C_6H_{12}O_6 \xrightarrow{\text{fermentation}} 2CH_3CH_2OH + 2CO_2 \quad \ldots(4)$$

starch — glucose — ethanol

Also the reactions of Grignard reagents with carbonyl compounds followed by hydrolysis are produce primary, secondary and tertiary alcohol [3] according to equation (5):

Different types of alcohols are prepared by the reduction of acid chlorides, acid anhydrides, and esters [4].

The reduction of carbonyl compounds (aldehydes and Ketones) [5] is carried out either by using sodium borohydride [5] or by using a strong reducing agent Lithium aluminum hydride [5].

Diorganyl dichalcogenides (Te, Se) / Aluminum system is used for electro chemical reduction of nitro compounds for production of Amines [6][7].

The aim of present work to find a new simple method for synthesis of alcohols from aldehyde.

Experimental

Material and Methods

1- **Power Supply :** using a stabilized power supply type H30/100.

2- **Electrolysis Cell :** the electrolysis cell, which is used in electrochemical reduction, consists of aluminum metal (Anode) and Graphite (Cathode), the electrochemical reduction was carried out under dry and oxygen-free nitrogen atmosphere at(25 ± 2 ºC).

3- **Synthesis of catalysts:** Diphenyl diselenied [8] and diphenyl ditelluride [9] were prepared according to the literature**.**

4- **The electrochemical reduction of aldehyde.**

i- (General Procedure).

The electrochemical reduction of benzaldehyde (1)and p-tolualdehyde (2) were carried out under nitrogen atmosphere as follows:-

(10 mmole) of aldehyde compounds and (0.2 mmole) of Ph_2E_2 (E= Te or Se) were dissolved in methanolic solution of sodium perchlorate (0.2 M)

A current of 0.33 A and Voltage (2.5 V for Ph_2Te_2) and (1.5 V for Ph_2Se_2),were supplied during different periods as shown in Table (1).

ii- Separation of benzyl alcohol [3] and p-methyl benzyl alcohol [4] Air was supplied to cell during 15 min, then the volume of solution was reduced to (5 ml) and distilled water (30 ml) was added.

The reactants and catalyst was extracted with ethyl acetate (3x25 ml) and the water solution (water layer) is separated and distilled by fractional distillation (b.p 205 ºC for benzyl alcohol and 217 ºC for p-methyl benzyl alcohol).

Benzyl alcohol and p-methyl benzyl alcohol were characterized depending on IR spectra and melting and boiling points.

5- Characterization of Products

Infra-Red spectra were recorded as KBr Pellets and discs in the range of 4000-200 Cm^{-1} with a pye-unicam SP3-300S infrared spectrophotometer, melting points were determined on Gallenamp melting point apparatus

Result and Discussion

This work is devoted to find a new method for reduction of aldehyde compounds by electrochemical reduction using organo ditellurides and diselenides as catalyst reduction was achieved in electrolytic cell which consists of two electrodes, the graphite as the cathode and aluminum as sacrificial anode.

In this study the optimum values for both voltage and current were achieved for reduction of the nitro compounds for each catalyst are listed in table (1).

Many experiments were carried out (change voltage, current and time) to find the optimum condition of reduction reaction. It was found that reduction depend upon both the catalyst and the electrical current and no reduction took place in the absence of the catalyst even though the reduction mixture was left for 48 hrs .as well as no reduction was achieved without employing the electrical current in spite of the presence of the catalyst in the reaction mixture for 72 hr.

The electrochemical reduction process was carried out under dry nitrogen atmosphere to prevent the oxidation of $phSe^-$, $phTe^-$ anions to diselenide and ditelluride respectively.

In electrolysis cell, the following reactions may occur:-

(1) At anode, the oxidation process is occurred (loss of electrons)

$$2Al \longrightarrow 2Al^{+3} + 6e^- \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

(2) At cathode, the reduction process occurrs (gain of electrons):-

$3Ph_2Te_2 + 6e^- \longrightarrow 6\ PhTe^-$ …… (6a)

$3Ph_2Se_2 + 6e^- \longrightarrow 6\ PhSe^-$ …… (6b)

Therefore, the general equation for cell is

$2Al + 3Ph_2Te_2 + 6e^- \longrightarrow 2Al^{+3} + 6\ PhTe^-$ ..... (7a)

$2Al + 3Ph_2Se_2 + 6e^- \longrightarrow 2Al^{+3} + 6\ PhSe^-$ ..... (7b)

The main advantage of this method is the easy conversion of organo ditelluride and diselenide compounds to anionic species in addition to the simplicity of catalyst recovery after the reduction processes.

In a previous work, we introduced a new method for the reduction of aldehyde compounds to the corresponding alcohols by using catalyst Ph_2Te_2,

$PhTe^- + H^+ \longrightarrow PhTeH$ …… (8a)

$PhSe^- + H^+ \longrightarrow PhSeH$ …… (8b)

$2Ph_2TeH + PhCHO \xrightarrow[\text{electrochemical reduction}]{N_2} PhCH_2OH + Ph_2Te_2$ …….. (9)

$2Ph_2SeH + PhCHO \xrightarrow[\text{electrochemical reduction}]{N_2} PhCH_2OH + Ph_2Se_2$ ……. (10)

$2Ph_2TeH + P\text{-}CH_3PhCHO \xrightarrow[\text{electrochemical reduction}]{N_2} P\text{-}CH_3PhCH_2OH + Ph_2Te_2$ … (11)

$2Ph_2SeH + P\text{-}CH_3PhCHO \xrightarrow[\text{electrochemical reduction}]{N_2} P\text{-}CH_3PhCH_2OH + Ph_2Se_2$ … (12)

Ph_2Se_2. The catalysts Ph_2Te_2 and Ph_2Se_2 can reduce the aldehyde compounds through there with the protons of solvent (Methanol) of from a tullerol (PhTeH) and selenol (PHSeH) respectively.

Benzyl alcohol and P-methyl benzyl alcohol are characterized by determination its melting points, boiling points (Table 2) and the infrared Spectra are recorded for it (table 3).

Table (1): The optimum conditions (Voltage, Current and Time) and Yield in reduction of aldehyde compounds.

Exp no.	Aldehyde compounds	Catalyst	Voltage (v)	Current (A)	Time hr.	Alcohols	Yield %
1	Benzaldehyde (1)	Ph_2Te_2	2.4	0.033	7	Benzyl alcohol (3)	67
2	Benzaldehyde (1)	Ph_2Se_2	1.5	0.033	6	Benzyl alcohol (3)	79
3	p-tolualdehyde (2)	Ph_2Te_2	2.4	0.033	7	p-methyl Benzyl alcohol (4)	69
4	Tolualdehyde (2)	Ph_2Se_2	1.5	0.033	6	p-methyl Benzyl alcohol (4)	84

Table (2): Melting and boiling points for Alcohols

compounds	b. P. (C^o) present work	b. P. (C^o) literature	M. P. (C^o) present work	M. P. (C^o) literature
Benzylalcohol (3)	205	205	-	-
p-methylbenzylalcohol (4)	217.5	217	59-61	59-61

Table (3): IR data (KBr disc) for Alcohols

compounds	Vas O-H St.	C-O St.	Arom C-H St.	Aliph C-H St.
Benzylalcohol (3)	3505	1250	3030	2890
p-methylbenzylalcohol (4)	3510	1245	3035	2895

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