

ELECTROLYTIC STUDIES WITH 2-HYDROXYCYCLOHEXANE ACETIC ACID

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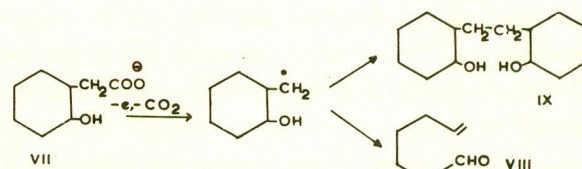
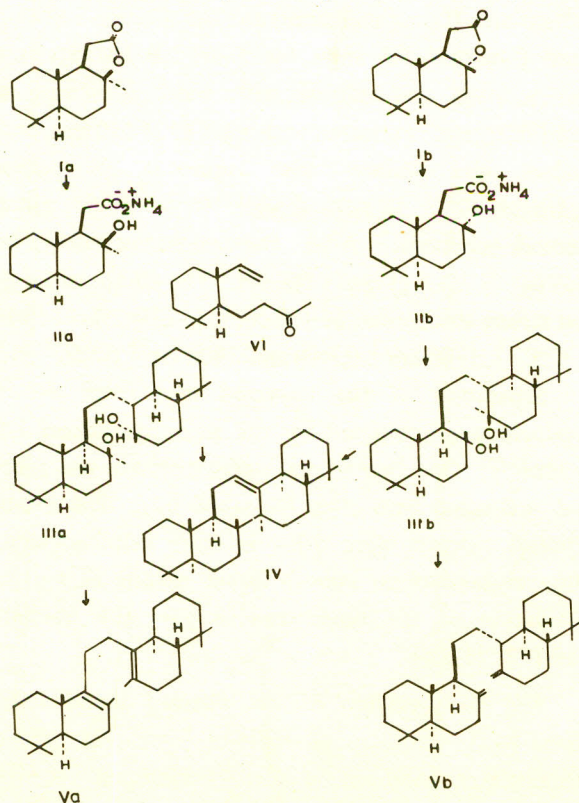
(Received July 7, 1977)

Abstract. It has been shown that in the electrolysis of 2-hydroxycyclohexane acetic acid, apart from the expected diol and hept-6-enal (the product expected on the basis of Corey's [1] work), two other products namely 2-methylcyclohexanone and hept-6-enol, are also formed. Thus it appears that the reaction described by Corey is in fact more complicated than has been previously realised.

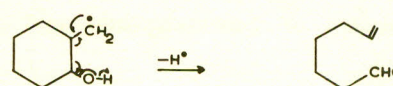
Symmetric anodic coupling has been used in the syntheses of different classes of organic compounds [2,3]. A most elegant use of this has been made by Corey *et al.* [1] in the synthesis of pentacyclosqualene (IV), a compound which has previously only been obtained by partial synthesis from α -onoceradienediol. The epimeric lactones (Ia and Ib) were converted into the corresponding γ -hydroxy acids from which the diols (IIIa and IIIb) were obtained by the electrolytic coupling of the ammonium salts (IIa and IIb). Cyclisation of either diol with perchloric acid in benzene-acetic acid then yielded (+)-pentacyclosqualene (IV). By dehydration of the two diols (IIIa and IIIb) with phosphorus oxychloride-

pyridine syntheses of α - and β -onoceradiene (Va and Vb) were also completed. These Kolbe reactions, which incidentally illustrate very well the retention of configuration associated with both alkyl and hydroxyl substituents, were accompanied by a novel type of elimination reaction leading to the formation of unsaturated ketone (VI). The electrolysis with acetate of IIa and IIb gave no ring opening product. Hence it was deduced by Corey [1] that the hydrogen atom of the hydroxyl group was necessary to the ring opening.

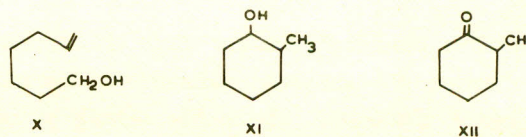
An analogous reaction with 2-hydroxycyclohexane acetic acid (VII) should give an aldehyde (VIII) along with the diol (IX).



A possible route to VIII involves the following mechanism.

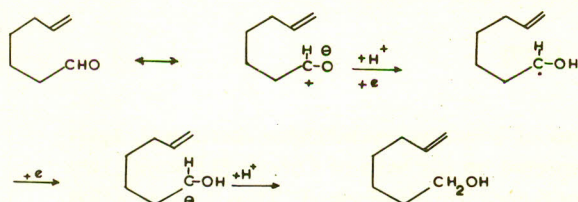


In the present work the electrolysis of 2-hydroxycyclohexane acetic acid was investigated and it was found that apart from the expected diol (IX) and hept-6-enal (VIII) three other products were also formed, viz. hept-6-enol (X), 2-methylcyclohexanol (XI) and 2-methylcyclohexanone (XII).



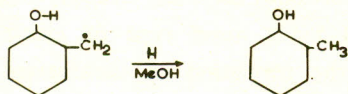
Possible routes to X, XI and XII involve the following mechanisms.

Hept-6-enol presumably arises from the reduction of hept-6-enal at the mercury cathode.



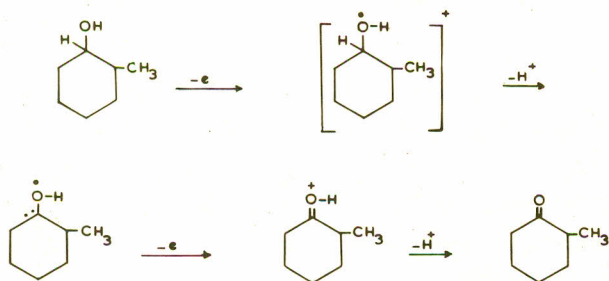
The electrolytic reduction of aldehydes to alcohols has been extensively studied [4,5].

2-Methylcyclohexanol is presumably formed as follows.

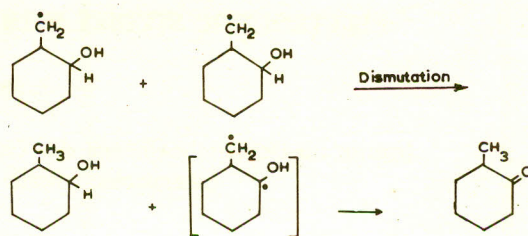


The free radical presumably abstracts a hydrogen atom from the solvent (MeOH). This is quite likely to happen, as according to the free radical theory when the concentration of the free radical formed at the anode is low, it can abstract a hydrogen atom from a molecule of the solvent, but only C-H and not O-H bonds are attacked. The electrolysis of 2-hydroxycyclohexane acetic acid was performed at different current densities but it was found that current density had little effect on the course of the reaction, as no marked increase or decrease in the yields of the diol and 2-methylcyclohexanol was observed. This may be that current density has little effect on the course of the reaction in nonaqueous media.

2-Methylcyclohexanone is presumably formed by the anodic oxidation of 2-methylcyclohexanol as follows:



Another possible mechanism which can account for the formation of 2-methylcyclohexanol and 2-methylcyclohexanone is dismutation of the free radicals as follows:



The above mechanism requires the formation of equal amounts of 2-methylcyclohexanol and 2-methylcyclohexanone. As in the present work the amount of these two compounds formed were different, this suggests that either the cyclohexanol has undergone partial oxidation to the cyclohexanone or vice versa.

EXPERIMENTAL

The electrolytic cell used was based on the design of Dinh-Nguyen [6] and had a rotating circular platinum anode (dia. 4.4 cm) and a mercury cathode; it was fitted with a water jacket for cooling.

Three electrolyses were performed. The results of these three electrolyses are given in Tables 1a and 1b. The experimental detail of one electrolysis is given below.

2-Hydroxycyclohexane acetic acid [7] (20 g) was added to a solution of sodium methoxide (from 2.6 g sodium and 100 ml methanol) and the solution was electrolysed (current 1.4 amps for 7 hr; 2.8 Faradays/mole). The solution was diluted with water (200 ml), acidified (HCl), and extracted with ether (3 × 150 ml), and the extract was washed with aqueous 2% potassium hydroxide (2 × 50 ml) and water (2 × 50 ml) and dried (sodium sulphate). After the removal of ether a liquid residue N (12 g) was obtained. The IR spectrum of N had strong absorptions at 920 cm⁻¹ (-CH=CH₂), 1640 cm⁻¹ (-C=C-), 1700 cm⁻¹ (C=O) and 3400 cm⁻¹ (OH).

Separation of the expected diol from the other products was attempted by the steam distillation of the residue N. One liter of the steam distillate was collected and extracted with ether (3 × 100 ml). The combined ethereal extracts were dried (sodium sulphate) and the ether evaporated to leave a liquid residue (3.9 g). The distillation of the liquid residue gave the fraction bp 155-177° (1.8 g).

The IR spectrum of the distilled liquid obtained above had strong absorptions at 920, 955 cm⁻¹ (-CH=CH₂), 1640 cm⁻¹ (-C=C-), 1700 cm⁻¹ (C=O) and

Table 1a. Electrolysis of 2-hydroxycyclohexane acetic acid.

No. of electrolysis	Wt of acid electrolysed (g)	Current in amps	Electrolysis hr	Faradays/mole	Wt of residue obtained (g)	Wt of N acid recovered (g)	Steam distillation	
							Volatile liquid (distilled)	Nonvolatile crystalline product g / % yield(theory)
1	20	1.4	7	2.8	12		1.8	2.6 /18.1
2	5	1.8	1	2.1	1.8	0.4	0.34	0.25/8
3	55	0.5	3.5	2.0	1.3	0.6	0.28	0.15/4.8

Table 1(b). Electrolysis of 2-hydroxycyclohexane acetic acid. % composition of various products on GLC analysis(20% Carbowax, M20, 130°) of the steam volatile liquid (distilled) / % yield of theory.

No of electrolysis	Hept-6-enal	2-Methylcyclohexanone	2-Methylcyclohexanol	Hept-6-enol
1	33.8/4.2	19.6/2.1	11.5/1.3	29.6/3.5
2	34.2/3.1	19.5/1.7	9.5/0.8	29.9/2.7
3	44.4/3.4	19.6/14	7.5/0.5	19.8/1.3

3400 cm^{-1} (OH). GLC analysis 20% Carbowax, M20, 130° showed four major peaks with the composition 33.8 : 19.6 : 11.5 : 29.6 in order of increasing retention time. These were identified as hept-6-enal, 2-methoxycyclohexanone 2-methoxycyclohexanol and hept-6-enal respectively by mixed GLC analysis with authentic samples.

A portion of the distilled liquid was reduced with lithium aluminium hydride by the method of Elvidge and Sammes [8]. GLC analysis (20% Carbowax M20, 130°) on the reduced material showed two peaks only, identified as 2-methylcyclohexanol and hept-6-enol by mixed GLC analysis with authentic samples. This indicated the conversion of hept-6-enal and 2-methylcyclohexanone to the corresponding alcohols on reduction. The NMR spectrum of the distilled liquid had also indicated absorption at 0.3 (aldehydic proton).

The 2,4-dinitrophenylhydrazone derivative of the distilled liquid was prepared and had m.p. 122-124°. After two crystallisations from ethanol the m.p. was raised to 132-134° (lit [9] gives mp 135-136° for 2,4-dinitrophenylhydrazone derivative of 2-methylcyclohexanone). Mixed mp with 2,4-dinitrophenylhydrazone derivative of 2-methylcyclohexanone was undepressed.

Preparative scale GLC (20% Carbowax, M20, 130°)

was run to isolate the four components of the distilled liquid. The vapours of hept-6-enal and 2-methylcyclohexanone were foggy and difficult to condense. These were, however, collected as their 2,4-dinitrophenylhydrazone derivatives by passing their vapours through traps containing Brady's reagent. The 2,4-dinitrophenylhydrazone of hept-6-enal was obtained as yellow needles mp 90-92° (lit [10] mp 96-96.5°). Mixed mp with an authentic sample 90-92°. The 2,4-dinitrophenylhydrazone of 2-methylcyclohexanone obtained had mp 135-136° (lit [9] mp 135-136°). Mixed mp with authentic sample 135-136°.

The IR spectrum of 2-methylcyclohexanol and hept-6-enal purified above were superimposable on the IR spectrum of their respective authentic samples.

The yield of the crude semi-solid product (6.2 g), obtained as nonsteam volatile portion, corresponded to a 43% yield of theory for the expected diol, 1,2-di-(2-hydroxycyclohexyl)-ethane. After two crystallisations from ethyl acetate this had mp 135-136° (lit [11] mp 135-136°).

Acknowledgement. Helpful suggestions by Professor B.C.L. Weedon, Vice-Chancellor, The University of Nottingham, U.K., and the grant of study leave by the University of Peshawar are gratefully acknowledged.

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