

The Electrolytic Reduction of Alicyclic Ketones (I)

Reduction of Fluorenone and 1-Tetralone

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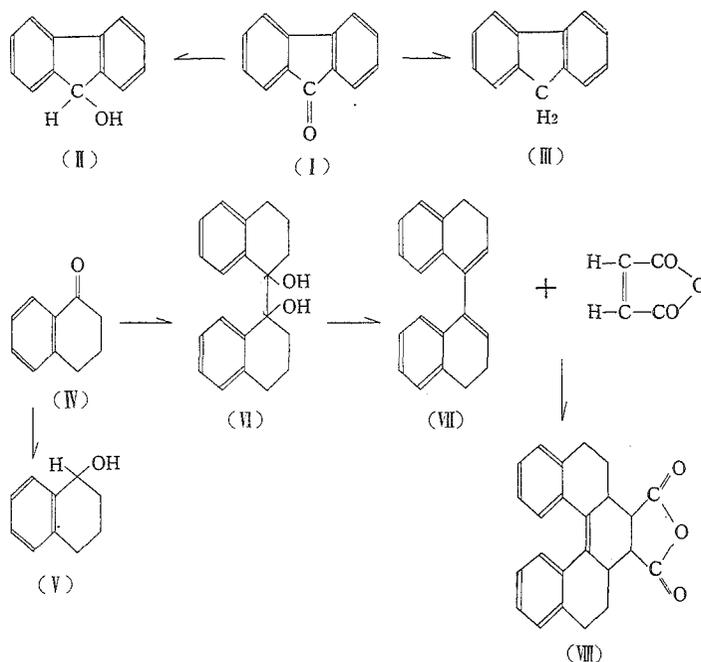
The electrolytic reduction of ketones has been studied concerning many compounds, and it is known that the reduction proceeds to the formation of alcohol, pinacol, or hydrocarbon.

The author has studied also the electrolytic reduction of aromatic and cyclic ketones and in this paper he tries to examine how fluorenone and 1-tetralone will behave in electrolytic reduction and to compare their behaviour with that in the case of purely chemical reduction.

Aromatic ketones, in general, are reduced to secondary alcohols in an alkaline catholyte, and to pinacols in an acidic catholyte at cathodes with high hydrogen overvoltage. They are reduced, also, to hydrocarbons in a sulfuric acid catholyte at a zinc amalgam cathode at high temperatures. For example, benzophenone is reduced to benzhydrol¹⁾ in an alcoholic catholyte containing sodium acetate, to benzpinacolone²⁾ in an acidic catholyte at a high temperature, and to diphenylmethane³⁾ in a catholyte of 70% sulfuric acid at 65°C at a zinc amalgam cathode.

In a purely chemical reaction, fluorenone (I) is reduced to 9-fluorenol (II) with sodium-amalgam or aluminum-amalgam⁴⁾ and aluminum isopropylate⁵⁾, to fluorenonepinacol with a mixture of magnesium and magnesium halide, and to fluorene (III) by heating with hydrazine or zinc dust to a high temperature, or with phosphorous and hydroiodic acid at 160°C.⁷⁾ 1-Tetralone is reduced to 1-tetralol (V) with sodium and alcohol⁸⁾ or aluminum isopropylate⁹⁾, and also reduced to tetraline following Clemmensen reduction. Concerning the pinacol reduction, Weidlich prepared pinacol (VI), by the reduction of 1-tetralone with aluminum-amalgam, as one of the intermediates of synthesis of dibenzylphenanthrene from 1-tetralone, but, in the next step the pinacol obtained was dehydrated with acetic acid without being isolated and then diene compound (VII) was prepared. The nature of pinacol, therefore, was not known. Newman¹¹⁾ also prepared the pinacol of 7-methyltetralone, but the pinacol was dehydrated

similarly without being isolated.



It was thought that fluorenone (I) could be reduced easily owing to its structure. According to the author's experiments, its reduction is similar to that of aromatic ketones, that is, it is reduced to 9-fluorenone (II) in a catholyte of alcohol containing sodium acetate, and to fluorene (III) in a catholyte of 60% sulfuric acid and alcohol at a cathode of mercury or zinc-amalgam at the temperature of 60°C. The reduction of 1-tetralone is also similar to the case of aromatic ketones, being difficult to carry out compared with that of fluorenone. 1-Tetralone (IV) is reduced to 1-tetralol (V) in a catholyte of sodium hydroxide at a cathode of mercury. In a catholyte of sulfuric acid tetrahydrobinaphthyl (VII) is obtained at a high temperature. It seems that pinacol (VI) is prepared at first and then dehydrated easily by the catholyte of sulfuric acid.

Experimental

Material used—Fluorenone¹²⁾ used in this experiment was obtained from

commercial fluorene: fluorene was oxidized with sodium bichromate in an acetic acid solution and then the fluorenone thus obtained was distilled under a reduced pressure followed by recrystallization from benzene-petroleumether. The yield was 65% of crystals melting at 83°C. 1-Tetralone was prepared through air oxidation of tetraline by using copper-chromium oxide as a catalyst, the yield being 50%.

Reduction technique—An electrolytic cell of the usual type was used. A porous pot (44×194mm) was used as a cathode compartment and the cell was immersed in a waterbath and cooled with running water at a low temperature. In the case of high temperature the cell was heated from the outside. A cathode consisted of a metal sheet bent into a form of a cylinder which stood in the cathode compartment (active area 100cm²) and had been treated with a diluted nitric acid or hydrochloric acid solution prior to use. When mercury, which was purified with nitric acid, or zinc-amalgam was used as a cathode, an electrical connection was made at the bottom of a cathode by means of platinum wire sealed in a narrow glass tubing. The catholyte was stirred by a glass stirrer. As an anode a cylindrical lead was employed in the acidic electrolyte, and carbon plate in the alkaline one.

I. Reduction of fluorenone (I) to 9-fluorenol (II)

For this purpose electrolysis was carried out under following conditions; cathode: Ag; catholyte: 120 ml. of 85% alcohol, in which 3 g. of sodium acetate and 2 g. of fluorenone were dissolved; anolyte: a saturated sodium carbonate solution; electric current: 2 amp.; time of electrolysis: 2 hrs.; temp.: 50°C. After the performance of electrolysis the catholyte was made slightly acidic by adding sulfuric acid, and water was also added to it in order to deposit the reduced substance. The deposit was filtered, dried, and recrystallized from benzene-petroleumether. Its yield was about 1.8 g., m. p. 154°C. The crystals were added to a mixture of acetic anhydride and sodium acetate and the mixture was heated a little while. The solution was poured into cracked ice and then the mixture was allowed to stand for a while and the deposits formed were recrystallized from diluted alcohol; m. p. 69°C; this corresponds to the reported value of 9-fluorenolacetate. (m. p. 70°C).¹⁸⁾

II. Reduction of fluorenone (I) to fluorene (III)

Cathode: Zn-amalgam, active area was 15.2 cm²; catholyte: a mixture of 70 ml. of 60% sulfuric acid and 60 ml. of alcohol, to which 2 g. of fluorenone was added; anolyte: 60% sulfuric acid solution; electric current: 5 amp.; temp.: 68°C; time of electrolysis: 1.5 hrs.

After finishing the electrolysis, the catholyte was cooled and by adding

some water needle crystals were deposited. The crystals were filtered, dried, and recrystallized from alcohol, the yield being about 1.2 g., m. p. 114°C. The melting point of this crystal was not depressed by admixture with authentic sample of fluorene, and by nitration of it, 2-nitrofluorene, m. p. 155°C. (reported value, m. p. 155–156°C¹⁶⁾ was obtained.

III. Reduction of 1-tetralone (IV) to 1-tetralol (V)

Cathode: Hg, 15.2 cm²; catholyte: 7 g. of 1-tetralone was added to a mixture of 80 ml. of 5% of sodium hydroxide solution and 40 ml. of alcohol; anolyte: 5% sodium hydroxide solution; electric current: 3 amp.; time of electrolysis: 4 hrs.; temp.: 45°C. The completion of electrolysis was recognized when a small quantity of catholyte, after acidification, gave a negative ketone reaction with sensitive 2,4-dinitrophenylhydrazine reagent. After finishing the electrolysis the catholyte was made slightly acidic and it was extracted with ether and the ether extracts were dried over anhydrous sodium sulfate. The ether was removed and the residue was obtained. This electrolysis was carried out repeatedly three times and the total residue was collected, distilled under a reduced pressure, and the fraction distilling at 132–135°C/12–14 mm was collected. The viscous, colorless oil was obtained which gave a negative ketone reaction: the yield was about 17 g., 80% of theoretical amount. The oil was mixed with phenylisocyanate and the crystals formed were recrystallized from ligroin or alcohol, m. p. 119–120°C; this corresponds to the reported value (m. p. 121–122°C⁸⁾ of phenylurethane of 1-tetralol.

IV. Reduction of 1-tetralone (IV) to 3,4,3',4'-tetrahydro-1,1'-binaphthyl (VII)

Cathode: Hg, 15.2 cm²; Catholyte: 15 g. of 1-tetralone was added to a mixture of 80 ml. of sulfuric acid and 40 ml. of alcohol; anolyte: 30% sulfuric acid solution; electric current: 3 amp.; temp.: 48–50°C; time of electrolysis: 6 hrs. After the current had been passed about three hours, viscous oil floated on the surface of the catholyte and the electrolysis was carried out by stirring the catholyte vigorously. After finishing the electrolysis the catholyte was extracted with ether repeatedly and the ether was evaporated and the residue was dissolved in some ether and then alcohol was added. The solution was cooled and the crystals were obtained, yield being about 6 g.. The filtrate was evaporated and about 8 g. of viscous residue was obtained. Then 2 g. of crystals deposited from it on standing. The crystals were recrystallized from dioxane and dilute alcohol, m. p. 140°C (reported value m. p. 141°C¹⁰⁾. It was further refluxed with acetic acid for two hours and the crystals thus obtained were identical with the former. This compound was tetrahydrobinaphthyl

(VII). A solution of 2 g. of VII and 2 g. of maleic anhydride was refluxed in 20 ml. of nitrobenzene for three hours and the nitrobenzene was then removed by steam distillation. The solid was recrystallized from chloroform-alcohol with charcoal and 2.5 g. of fine needle crystals were obtained, m. p. 252-253°C, this corresponds to the reported value of 1, 2, 2a, 3, 4, 4a, 5, 6-octahydrodi-benzo-(e, g)-phenanthrene-3, 4-dicarboxylic anhydride (VIII), prepared by the addition of maleic anhydride to VII.

Experimental results

Electrolytic conditions for fluorenone were shown in Table 1.

Table 1. Electrolytic conditions for fluorenone

Expt. No.	Cathode	Catholyte	Temp. °C	Elec. Current Amp.	Time hrs.	Product
1	Ag, Cu, Ni	85% EtOH 120ml. NaAc 3g.	50°	2	1	9-Fluorenol
2	Ti, Hg	5% NaOH 70ml. EtOH 60ml.	25°	3	1	"
3	"	"	50°	3	1	"
4	Ag, Cu, Ni	10% NaOH 70ml. EtOH 60ml.	50°	3	1	"
5	Hg, Zn-Hg	60% H ₂ SO ₄ 70ml. EtOH 60ml.	68°	5	1.5	Fluorene
6	Hg	"	25°	5	2	9-Fluorenol
7	Ag, Ni, Ti	EtOH 100ml. 30% H ₂ SO ₄ 10ml.	18°	2	1	Not identified
8	"	"	50°	2	1	"

It was thought that carbonyl group of fluorenone could be reduced easily, and in this experiment fluorenone was reduced in an alcoholic solution containing sodium acetate (Expt. 1) at cathodes of silver, nickel, and copper, which had lower hydrogen overvoltage, and also in a sodium hydroxide solution (Expt. 2, 3, 4), the amount of electric current was three times as much as the theoretical one, but the catholyte in these reductions did not turn from yellow to colorless state perfectly after the elimination of colorless reduced substance. This was due to the formation of water soluble by-product. The effect of

temperature chosen in this experiment was not measured exactly, because the quantity of fluorenone used in the experiment was small. When synthesis of 9-fluorenone was performed in large quantities, one may conclude that the reduction was carried out at a high temperature. Fluorenone was reduced to 9-fluorenone at a low temperature in the catholyte of 60% sulfuric acid (Expt. 6) at a cathode of mercury, but at a high temperature it was reduced to fluorenone (Expt. 5). In the case of aromatic ketones pinacol was obtained in a sulfuric acid catholyte, but fluorenonepinacol could not be obtained in this experiment. In a catholyte of alcoholic solution as shown in Expt. 7, yellow color of catholyte of fluorenone disappeared completely at a low temperature after the current had been passed only for half an hour. The catholyte was poured into water and a white deposit was obtained quantitatively. The deposit was filtered, dried, and recrystallized from benzene-petroleum ether. Then two kinds of products were obtained. One was decomposed into a yellow solution at the temperature of 130–135°C, the other was decomposed slowly at the high temperature above 180°C. It was thought that these compounds were the addition or condensation products of fluorenone and the identification of them will be the object of further investigation. Electrolytic conditions for

Table 2. Electrolytic conditions for 1-tetralone

Expt. No.	Cathode	Catholyte	Ketone g.	Temp. °C	Elec. Current Amp.	Time	Products
1	Hg	5% NaOH 80ml. EtOH 10ml.	7	45°	3	4	1-Tetralol
2	Hg	20% NaOH 80ml. EtOH 40ml.	"	20°	5	4	"
3	Ag, Cu, Ni	"	"	45°	3	4	Unreduced
4	Ti	"	"	50°	3	4	Tar like materials
5	Hg	30% H ₂ SO ₄ 80ml. EtOH 40ml.	15	50°	3	8	Tetrahydro binaphthyl
6	Hg	"	7	25°	4	7	Reduced partially
7	Cd	50% H ₂ SO ₄ 80ml. EtOH 40ml.	"	25°	4	8	Unreduced
8	"	"	"	50°	3	4	Tetrahydro binaphthyl
9	Ni, Cu	30% H ₂ SO ₄ 80ml. EtOH 40ml.	"	60°	3	4	Unreduced

1-tetralone were shown in Table 2. Tetralone behaved similarly as fluorenone in an alkaline electrolyte at a mercury cathode and was reduced to tetralol (Expt. 1, 2). It was not reduced at cathodes of copper and nickel even at a high temperature (Expt. 3). At a mercury cathode it was reduced at a low temperature (Expt. 2) and it seemed that sodium-amalgam prepared by electrolysis had a strong reducing power. The amount of electric current was four times as much as the theoretical one in the alkaline catholyte. In the acidic electrolyte the amount of electric current of about ten times as much as the theoretical one was passed at a low temperature at a cathode of either mercury or cadmium, but the amount of the reduced substance obtained was rather small (Expt. 6, 7). It was reduced easily at a cadmium electrode at a high temperature (Expt. 8). In the case of nickel and copper electrode it was recovered practically (Expt. 9). An attempt to prepare 1-tetralonepinacol in this electrolytic reduction was unsuccessful and dehydrated diene compound was yielded. In a purely chemical method ¹⁰⁾ 1-tetralonepinacol was used for the next step without isolation and dehydrated by refluxing with acetic acid. The result showed that, in this experiment, as the pinacol was dehydrated with 30% sulfuric acid solution at 50°C, it was unstable in an acidic solution and dehydrated easily without rearrangement to pinacoline. Tetraline, which was the fully reduced substance of tetralone, could not be obtained. When pinacol formation was preferential in strong reducing conditions, the fully reduced hydrocarbon was difficult to obtain as shown in a electrolytic reduction of acetophenone.⁸⁾⁹⁾

Summary

The electrolytic reduction of fluorenone and 1-tetralone was studied. The reduction of the both ketones was similar to the case of aromatic ketones. Fluorenone was reduced to 9-fluorenol in an alkaline alcohol catholyte, and fluorene was obtained in the solution of 50% sulfuric acid at a cathode of either mercury or zinc-amalgam at a high temperature, but pinacol could not be obtained.

1-Tetralone was reduced to 1-tetralol in a sodium hydroxide solution at a mercury cathode and in an acidic solution tetrahydrobinaphthyl was prepared by dehydration of the pinacol without rearrangement to pinacoline.

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