ELECTROLYTIC REDUCTION OF ALKYL-PHTHALIMIDES. IV. COMPLETE REDUCTION.

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When acid imides of dicarboxylic acid, such as phthalimide is subjected to reduction, only one carbonyl group generally enters into reaction and is reduced to the corresponding secondary alcohol group or methylene group according to the conditions under which the reaction takes place, while another carbonyl group remains unaltered. Shortly before Goro Shima⁽¹⁾ succeeded in reducing the carbonyl group in many aldehydes and ketones completely to the corresponding hydrocarbon radical by passing an electric current of high density at the cathode composed of zinc amalgam. This suggests that a similar manner of electrolysis might, with a similar effect, be applied to the complete reduction of both carbonyl groups in the acid imide. With such an anticipation the writer undertook electrolytic reduction of phthalimide, methyl phthalimide, ethyl phthalimide and phenylphthalimide, and succeeded in fulfiling his expectation. Of the four imides above mentioned phenylphthalimide, however, could not be reduced to phenyl dihydroisoindol, as it was hydrolysed into phthalic acid and aniline, before it underwent reduction.

The cathode of zinc amalgam was prepared in the following way:

Into a cylindrical cell having a diameter of 4.5 cm. mercury was introduced to the depth of about 1 cm., and after a conducting wire sealed up in a small glass tube was inserted into mercury a solution of zinc sulphate was poured into the cell as the catholyte. The cell was then placed in a glass cylinder which contained sulphuric acid of 6 normal as the anolyte. Now taking a lead plate as the anode a current of 2 amperes was passed between this and the mercury, which served as the cathode. The electrolysis was continued till the mercury completely solidified as zinc amalgam.

As the electrolyte, 12 normal sulphuric acid or hydrochloric acid was taken, and a current of high density, such as 30–60 amp./100 sq. cm. was passed at 80–90°C. using lead as the anode.

Experimental.

1. **Phthalimide.** The cathodic solution consisting of 120 c.c. of 12 normal sulphuric acid and 5 gr. of phthalimide was electrolysed with

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(1) *Memo. Kyoto Imp. Univ.*, Series A, **12** (1929), 79.

the cathode of zinc amalgams (15 sq. cm.) by passing through it a current of 9.5 amperes. The current density at the cathode thus amounts to 60 am. / 100 sq. cm. The catholyte was kept stirred while electrolysed. Though after the lapse of 3.5 hours, the phthalimide in suspension had completely disappeared, electrolysis was continued as long again to ensure reduction. The temperature of the bath at the end of electrolysis rose to 90°C. On cooling with cold water the catholyte was made alkaline with caustic soda, when a brown oil separated out floating in the surface of the solution. It was extracted with ether and purified, and 3 gr. of an oil boiling at 213°C. were obtained. The material yield is thus 80% of the theoretical. It behaves as a base and easily changes into phthalimide when oxidized with potassium permanganate. On analysing it as its platinum double chloride (M.P. 252°C.) following result was obtained:

0.0619 Gr. of the double chloride gave on ignition 0.0184 gr. of Pt. Pt. = 29.73 %.
Calc. for $C_{16}H_{20}N_2PtCl_6$: Pt = 30.12 %.

These results in all respects precisely agree with pure chemically prepared dihydroisoindol.(1) So there is no doubt that both carbonyl groups were thus completely reduced into the methylene group.

By adding alcohol to the catholyte so as completely to dissolve all phthalimide, the reduction may be made to take place more smoothly and to finish in nearly 3.5 hours. Hydrochloric acid of similar normality may well be substituted for sulphuric acid in the electrolyte, but its use in such an experiment to be worked at high temperature is, of course, inconvenient in every respect.

2. **Methyl Phthalimide.** The conditions used for complete reduction of methyl phthalimide were as follows:

Cathode: zinc amalgam; Cathode solution: 120 cc. of 12 N. H_2SO_4+5 gr. of the imide; Anode: lead; Anode solution: 12 N. H_2SO_4;
Current density: 60 amp./100 sq. cm.; Temperature: 85°C.; Time: 5 Hours.

After about an hour's electrolysis, the methyl phthalimide in the catholyte, which was always kept agitated, completely disappeared. The treatment of the electrolyte after the electrolysis was made in an analogous way as in the previous case, and about 3.2 gr. of an oil were isolated. The yield is calculated to be 80%. On keeping long in a cool place the oil was found partly crystallized into tabular crystals, the melting point of which was roughly determined to lie near 85°C. The melting point

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(1) Gabril and Newmann, *Ber.*, **26** (1893), 526. Gabril and Pinkus, *Ber.*, **26** (1893), 2213. Fränkel, *Ber.*, **33** (1900), 2808. Brown, *Ber.*, **43** (1910), 1353.

of its platinum double chloride was determined as 199–200°C., and the result of the analysis was as follows:

0.0484 Gr. of the double chloride gave on ignition 0.0140 gr. of Pt; Pt = 28.91 %.
Calc. for $C_{18}H_{24}N_2PtCl_6$: Pt = 28.87 %.

These agree well with the methyl dihydroisoindol found by Fränkel.(1) The reduced product, thus identified as methyl dihydroisoindol was also observed to change back to methyl phthalimide, when oxidized with potassium permanganate.

3. **Ethyl Phthalimide.** The reduction experiment of ethyl phthalimide was carried out under the following conditions:

Cathode: Zinc amalgam; Anode: lead; Catholyte: 80 c.c. of 12 N. H_2SO_4 +40 c.c. of alcohol+5 gr. of the imide; Anolyte: 12 N. H_2SO_4; Current density: 38 amp./100 sq. cm.; Temperature: 80°C; Time: 7 hours.

The catholyte after electrolysis was coloured dark at high temperature; but become colourless when cooled. It was neutralized with caustic soda and a dark brown oil thus separated was purified after being extracted with ether. The yied was 2.5 gr., corresponding to 60% of the theoretical. It was analysed as its platinum double chloride (M.P. 192°C.) with the following result:

0.0475 Gr. of the double salt gave on ignition 0.0131 gr. of Pt. Pt = 27.69 %.
Calc. for $C_{20}H_{23}N_2PtCl_6$: 27.71 %.

The oil thus identified as ethyl dihydroisoindol(2) was also confirmed to be oxidizable to ethyl phthalimide.

4. **Phenyl Phthalimide and Ammonium Phthalate.** Phenyl phthalimide and ammonium phthalate were subjected to the complete reduction in a manner analogous to that employed in the previous case, taking a saturated solution of ammonium carbonate as the anolyte. In neither case, however, could completely reduced products be obtained. Phenyl phthalimide was observed to change into phthalic acid and aniline, while ammonium phthalate partly changed to phthalide, but not to phthalane.

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(1) *Ber.*, **33** (1900), 2815.
(2) Scholz, *Ber.*, **31** (1898), 1706.