ELECTROLYTIC REDUCTION OF N-METHYLSUCCINIMIDE AND N-ETHYLSUCCINIMIDE.

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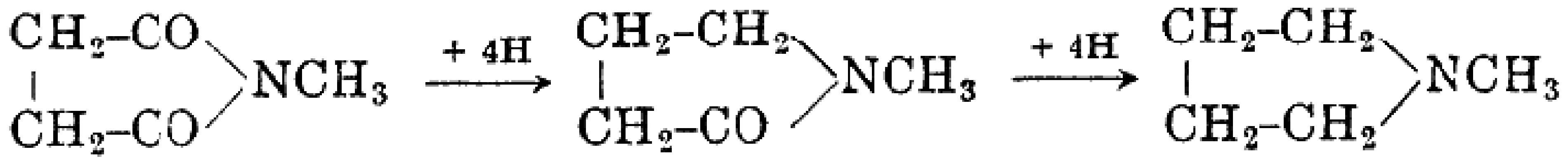
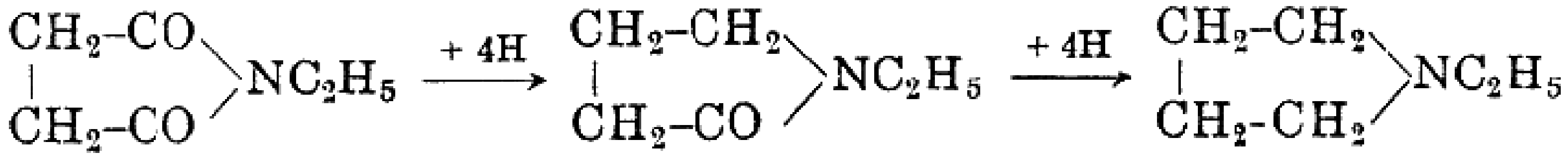
The reduction, especially total reduction, of the cyclic imides of aliphatic acids is very difficult, and it seems to be almost impossible to carry out such reduction through purely chemical methods alone. But it may be accomplished electrolytically by using a lead or a zinc amalgam cathode, which has a strong reducing power. As reported in the preceding paper⁽¹⁾ the present writer carried out electrolytic reduction of succinimide using a zinc amalgam cathode and succeeded in its total reduction with a fairly satisfactory yield of pyrrolidine; and then he proceeded to similar reduction with *N*-methylsuccinimide and *N*-ethylsuccinimide. In these cases reduction goes through the same process as in the case of succinimide:



N-Methylsuccinimide *N*-Methylpyrrolidone *N*-Methylpyrrolidine



N-Ethylsuccinimide *N*-Ethylpyrrolidone *N*-Ethylpyrrolidine

E. Spath⁽²⁾ and his collaborator reduced several derivatives of succinimide using a very high current density and a lead cathode prepared with special care, and succeeded in total reduction, corresponding reduction products being obtained. A. Luckes⁽³⁾ reduced *N*-methylsuccinimide in sulphuric acid solution with a current of 0.1 amp./sq. cm., and obtained *N*-methylpyrrolidone.

The present writer tried electrolytic reduction of *N*-methylsuccinimide, using a zinc amalgam cathode⁽⁴⁾ in a 50% sulphuric acid solution, at a current density as high as 100–125 amp./100 sq. cm., all the while avoiding any rise of temperature, and thus could carry the reduction over the stage of *N*-methylpyrrolidone and obtain *N*-methylpyrrolidine.

As for *N*-ethylsuccinimide, as far as the present writer knows, no reports on its electrolytic reduction have been published. In the first place a 10% sulphuric acid solution, a lead cathode, and a current of 2.5 amp./100 sq. cm. were used, and the cathodic solution was extracted with chloroform without

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(1) B. Sakurai, this Bulletin, **10** (1935), 311.
(2) E. Spath and F. Breush, *Monatsh.*, **50** (1928), 349.
(3) R. Luckes, *Collection Czechoslov. Chem. Comm.*, **2** (1930), 531-44.
(4) B. Sakurai, this Bulletin, **7** (1932), 155.

interfering with its acidity following the example of Lyman(5), the reduction product being thus easily separated. The product was subjected to distillation under reduced pressure. A liquid, which distilled at 107° under 20 mm. was ascertained to be *N*-ethylpyrrolidone by its chemical properties and the results of analysis. Then the concentration of sulphuric acid was increased to 50%, the current density was raised to 100 amp./100 sq. cm., and a zinc amalgam cathode was used to effect a powerful reduction and the experiment resulted in the formation of *N*-ethylpyrrolidine.

Experimental.

The materials for electrolysis were prepared according to the method of Ladenberg(6).

1. **Complete Reduction of N-Methylsuccinimide.** Cathode: zinc amalgam placed in a cylindrical vessel of biscuit, area 15 sq. cm.; cathodic solution: 3 g. of methylsuccinimide dissolved in 100 c.c. of 50% sulphuric acid; anode: cylindrical lead; anodic solution: 50% sulphuric acid; current density: 133 amp./100 sq. cm.; temperature: below 30°; time of electrolysis: 8 hours; current quantity: 224 F./mol.

As the rise of temperature has a harmful influence upon electrolysis as in the case of succinimide, a spiral lead tube was inserted in the cylindrical vessel of biscuit which contained the solution, cold water was passed rapidly through the lead spiral, and the apparatus was immersed in water, so that it was cooled from both inside and outside, while the cathodic solution was constantly stirred throughout the electrolysis.

When the electrolysis was over, the cathodic solution was taken out and shaken with a small quantity of chloroform, unchanged substances and *N*-methylpyrrolidone being thus extracted. The solution was then made strongly alkaline by adding a caustic soda solution and then was subjected to steam distillation. *N*-Methylpyrrolidine, the complete reduction product, distilled over with vapour. The distillate was made acid with hydrochloric acid. From the solution the gold salt of *N*-methylpyrrolidine was obtained in a bright yellow substance in the yield of 8.86%. The gold salt melted at 215°. (Found: Au, 46.5. Calc. for $C_6H_{12}N\cdot AuCl_4$: Au, 46.3%.) Its picrate was found to melt at 220°.

2. **Partial Reduction of N-Ethylsuccinimide.** Cathode: cylindrical lead plate of 100 sq. cm. placed in a cylindrical vessel of biscuit; cathodic solution: 10 g. of ethylsuccinimide dissolved in 100 c.c. of 10% sulphuric acid solution; anode: lead plate; anodic solution: 10% sulphuric acid solution; current density: 3.0 amp./100 sq. cm.; temperature: 28°; time of electrolysis: 21 hours; current quantity: 29.9 F./mol.

The electrolytic apparatus was placed in water, but this time the cooling from inside was dispensed with. Stirring was again continued during electrolysis.

After the electrolysis was finished, the cathodic solution was treated with chloroform to extract *N*-ethylpyrrolidine. When the chloroform was distilled off, about 8 g. of a liquid remained. When this liquid was subjected to vacuum distillation, 6 g. of a liquid distilling at 107° under 20 mm. was obtained. Its specific gravity was 1.0553, and when it was dissolved in 50% sulphuric acid and was oxidized with potassium permanganate solution, it changed back into *N*-ethylsuccinimide. On the other hand, when it was dissolved in 50% sulphuric acid and was electrolytically reduced under the conditions which will be described in the next experiment, it changed into *N*-ethylpyrrolidine. (Found: C, 62.3; H, 10.2; N, 11.98. Calculated for $C_6H_{11}ON$: C, 63.7; H, 9.37; N, 12.39%.) From the above results this substance was evidently *N*-ethylpyrrolidone where only one carbonyl group had undergone reduction.

3. ***Complete Reduction of N-Ethylsuccinimide.*** *The conditions of the electrolysis and* the treatment of the product after electrolysis were almost the same as in the case of N-methylsuccinimide. The double gold chloride of *N*-ethylpyrrolidine obtained in the yield of 18.3%. (Found: Au, 44.84. Cal. for $C_6H_{14}NAuCl_4$: Au, 44.87%.) Its picrate, closely resembling that of *N*-methylpyrrolidine, was bright yellow needle crystals and melted at 185°. These and other properties all well agree with those observed by Brown(7).

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(5) Lyman, *J. Am. Chem Soc.*, **55** (1933), 295-8.
(6) Ladenberg, *Ann.*, **215** (1882), 211.