XLVI.—*The Electrolytic Reduction of the Imides of Cyclic Acids (Preliminary Note).*

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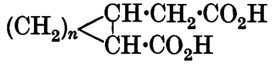
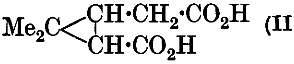
THE methods available for the preparation of cyclic acids of type (I) are somewhat limited in number, and as we have for some time been interested in the synthesis of homocaronic acid (II) we attempted to devise a general method for their preparation. Although our experiments are in many respects incomplete, we have decided to place them on record, since we can no longer collaborate and work in a related field has recently appeared (*J. Indian Chem. Soc.*, 1928, **5**, 549).

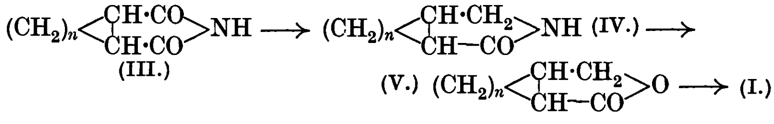
(I.) 

$(CH_2)_n<\begin{array}{l}CH\cdot CH_2\cdot CO_2H\\ CH\cdot CO_2H\end{array}$

 (II.)

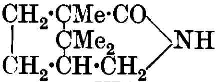
$Me_2C<\begin{array}{l}CH\cdot CH_2\cdot CO_2H\\ CH\cdot CO_2H\end{array}$

After reviewing the literature, the most promising avenue of approach seemed to us to be that indicated by the following scheme :

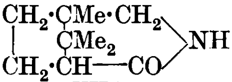


(III.) (IV.) (V.) (I.)

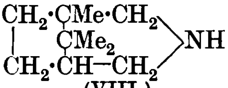
So far as we are aware the only previous description of lactams of type (IV) is that of the isomeric α- and β-camphidones (VI and VII) which were obtained by Tafel and Eckstein (*Ber.*, 1901, **34**, 3274)



(VI.)

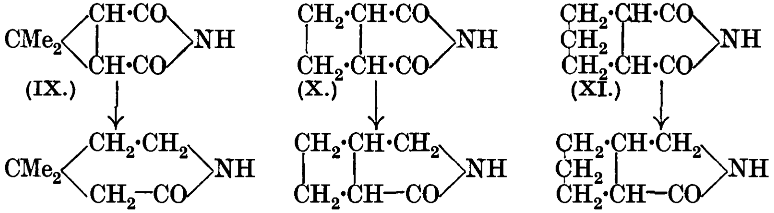


(VII.)



(VIII.)

by the electrolytic reduction of camphorimide, the fully reduced base, camphidine (VIII), being also formed (compare Hope and Lankshear, P., 1913, **29**, 224). We decided, therefore, to investigate the electrolytic reduction of the imides of some typical cyclic acids and selected *caronimide* (IX), cyclo*butane*-1 : 2-*dicarboxylimide* (X),



(IX.) (X.) (XI.) (XII.) (XIII.) (XIV.)

and cyclo*pentane*-1 : 2-*dicarboxylimide* (XI). The reduction of (X) and (XI) proceeded smoothly with formation of the expected lactams (XIII and XIV) and no evidence was obtained of the formation of the fully reduced base corresponding to (VIII); the yield of the reduction product from caronimide, however, was small (5%) and it was found that the reduction had proceeded further with fission of the *cyclo*propane ring and formation of 4 : 4-*dimethyl-2-piperidone* (XII), a substance which should be obtainable more directly from ββ-dimethylglutarimide. The electrolytic reduction of caronimide proceeds, therefore, in a manner analogous to the catalytic reduction of carone (Iyer and Simonsen, J., 1926, 2049) and the reduction of caronic anhydride with sodium and alcohol (Hariharan, Menon, and Simonsen, J., 1928, 431), where also the rupture of the *cyclo*propane ring was observed. The marked instability of this ring to reducing agents is noteworthy but cannot be considered as altogether contrary to views which have been expressed previously as to the effect of substituents on the stability of rings (*inter alia*, J., 1907, **91**, 817; 1914, **105**, 2665, 2685; 1923, **123**, 113; *J. Amer. Chem. Soc.*, 1916, **38**, 1520; 1917, **39**, 1404; *J. pr. Chem.*, 1903, **68**, 156).

The two lactams, which crystallised well, resembled closely in properties the isomeric camphidones. They could not be hydrolysed with barium hydroxide, and with nitrous acid they gave liquid nitroso-derivatives which, on treatment with dilute alkali solution, evolved nitrogen and were converted into the sodium salts of the corresponding hydroxy-acids, which await investigation.

EXPERIMENTAL.

The imides were prepared by treatment of the anhydrides with dry ammonia at 180°. They were readily soluble in water and the ordinary organic solvents.

Caronimide (IX) crystallised from water in long prismatic needles, m. p. 120° (Found: N, 10·4. $C_7H_9O_2N$ requires N, 10·1%).

cyclo*Butane*-1 : 2-*dicarboxylimide* (X) separated from chloroform–light petroleum in plates, m. p. 121° (Found: N, 11·5. $C_6H_7O_2N$ requires N, 11·2%).

cyclo*Pentane*-1 : 2-*dicarboxylimide* (XI) crystallised from light petroleum (b. p. 40—60°) in plates, m. p. 90° (Found: N, 10·2. $C_7H_9O_2N$ requires N, 10·1%).

The following procedure was adopted for the reduction of the imides. The imide (5 g.) in sulphuric acid (50% by weight; 35 c.c.) was reduced for 7 hours at 0—5° with a current of 4·2 amps. ("current concentration" 120 amps.). The ratio of the cathode surface to the cathode space of the reduction apparatus was 1 : 1. On completion of the reaction, the neutral reduction product was isolated by repeated extraction with chloroform, the acid solution, after neutralisation with barium carbonate and filtration, was distilled with the aid of a column under diminished pressure, and the distillate examined for basic products, which, as has already been mentioned, were not found.

4 : 4-*Dimethyl*-2-*piperidone* (XII), obtained (yield, 5%) by the reduction of caronimide, was a thick oil which showed no tendency to crystallise. It gave with phosphotungstic acid a white precipitate and with phosphomolybdic acid a yellow precipitate. For analysis it was purified through the phosphotungstate, since the quantity available was insufficient for distillation (Found: C, 66·1;

H, 10·3; N, 11·3. $C_7H_{13}ON$ requires C, 66·1; H, 10·2; N, 11·0%). The benzoyl derivative, prepared by the Schotten–Baumann reaction, crystallised from dilute alcohol in glistening prisms, m. p. 114°.

γ-Lactam of 2-*Aminomethyl*cyclo*butane*-1-*carboxylic Acid* (XIII).—The lactam (yield, 15%) crystallised from light petroleum (b. p. 40—60°) in plates, m. p. 127—128°. It was precipitated from its aqueous solution by phosphotungstic and phosphomolybdic acids and gave a liquid nitroso-derivative (Found: C, 64·7; H, 8·3; N, 12·6. C_6H_9ON requires C, 64·9; H, 8·1; N, 12·6%).

γ-Lactam of 2-*Aminomethyl*cyclo*pentane*-1-*carboxylic Acid* (XIV).—This lactam was obtained in a more satisfactory yield (25%) than that of the *cyclo*butane acid. It crystallised from light petroleum (b. p. 40—60°) in plates, m. p. 83° (Found: C, 67·1; H, 8·8; N, 11·4. $C_7H_{11}ON$ requires C, 67·2; H, 8·8; N, 11·2%). It was unaffected by treatment with barium hydroxide solution (10%) at 180° (sealed tube), but the liquid nitroso-derivative when warmed with dilute sodium hydroxide solution (10%) evolved nitrogen with formation of the sodium salt of the hydroxy-acid, the lactone of which was deposited on warming the acidified solution. The p-*nitrobenzoyl* derivative, prepared by treatment of the lactam with *p*-nitrobenzoyl chloride in pyridine solution, crystallised from dilute alcohol in glistening leaflets, m. p. 123° (Found: N, 10·5. $C_{14}H_{14}O_4N_2$ requires N, 10·4%).

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