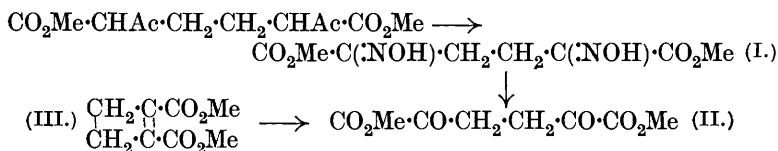


454. *Derivatives of  $\alpha\alpha'$ -Diketoadipic Acid.*

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THE publication of a paper by Sutter (*Annalen*, 1932, 499, 47) makes it desirable to place on record the preparation of methyl and ethyl  $\alpha\alpha'$ -diketoadipates. These were obtained from the corresponding acetyladipe esters by treatment with nitrosylsulphuric acid in two stages (cf. Bouveault and Locquin, *Bull. Soc. chim.*, 1904, 31, 1049). The crude esters were characterised by their *diphenylhydrazones*, that of the methyl ester (II) being identical with the diphenylhydrazone of the ozonisation product of methyl  $\Delta^1$ -cyclobutene-1 : 2-dicarboxylate (III) (Perkin, J., 1894, 65, 950) :



The diketo-esters cannot be distilled without decomposition and give on mild alkaline hydrolysis an acid, m. p. 192°, which is still under investigation.

*Ethyl  $\alpha\alpha'$ -Dioximinoadipate.*—To 163 g. of ethyl diacetyladipe (Perkin, J., 1890, 57, 204) in 179 c.c. of conc.  $\text{H}_2\text{SO}_4$  kept below 0°, 145 g. of nitrosylsulphuric acid in 150 c.c. of conc.  $\text{H}_2\text{SO}_4$  were added during 4 hr. When the frothing had subsided, the mixture was poured on ice, and the oximino-ester (analogous to I) extracted, washed ( $\text{Na}_2\text{CO}_3$ ), and dried in  $\text{Et}_2\text{O}$  and obtained in 76% yield as an undistillable reddish-brown oil.

*Ethyl  $\alpha\alpha'$ -Diketoadipate.*—A solution of 80 g. of the oximino-ester in 160 c.c. of  $\text{HCO}_2\text{H}$ , 23 c.c. of  $\text{H}_2\text{O}$ , and 350 c.c. of  $\text{Et}_2\text{O}$  was treated below 0° (2.5 hr.) with 80 g. of nitrosylsulphuric acid. After the evolution of nitrous fumes had ceased, the solution was allowed to reach room temp., then again cooled

to 0°, and poured on ice. The Et<sub>2</sub>O layer was evaporated under red. press. to remove HCO<sub>2</sub>H, and the residue taken up in Et<sub>2</sub>O, washed with Na<sub>2</sub>CO<sub>3</sub> aq., dried, and recovered, giving 40 g. of the crude diketo-ester. The *diphenylhydrazone*, plates from acetone, had m. p. 150° (Found: C, 64.1; H, 6.2. C<sub>22</sub>H<sub>26</sub>O<sub>4</sub>N<sub>4</sub> requires C, 64.4; H, 6.3%).

The crude diketo-ester (7 g.) was kept over-night with 20 c.c. of 15% KOH aq. and 20 c.c. of EtOH; 100 c.c. of 20 vol. H<sub>2</sub>O<sub>2</sub> were then added, and the solution kept for 12 hr.; 3 g. of succinic acid were obtained.

*Methyl aa'-Diacetyladipate*.—This was prepared from methyl acetoacetate by the method used by Perkin (*loc. cit.*) for the ethyl ester and purified in the same way (Found: C, 55.8; H, 6.9. C<sub>12</sub>H<sub>16</sub>O<sub>6</sub> requires C, 55.8; H, 7.0%). Methyl *aa'*-diketoadipate (II) was prepared from this in the same way as the ethyl ester and gave the same acid on hydrolysis and succinic acid on oxidation. The *diphenylhydrazone* formed fine plates from acetone, m. p. and mixed m.p. with the diphenylhydrazone of the ozonisation product of methyl Δ<sup>1</sup>-cyclobutene-1:2-dicarboxylate, 130—131° (Found: C, 62.5; H, 6.1. C<sub>20</sub>H<sub>22</sub>O<sub>4</sub>N<sub>4</sub> requires C, 62.8; H, 5.8%).

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