

On a New Method of Synthesis of Bicyclic
Terpenes: Synthesis of Ethyl *cyclohexanone*
2:6-dicarboxylate.

THE synthesis of this ester has been attempted in this laboratory by several methods, one of which, *viz.*, the action of sodium ethoxide upon trimethylene dimalonic ester has now yielded the desired product b.p. 140-42°/1-1.5 mm. The formation of the desired *cyclohexane* ring by this method has been definitely established by hydrolysis and decarboxylation of the ester into *cyclohexanone*.

Recourse has also been taken to another method for the preparation of the desired di-ester from *cyclohexanone*-2:2:6:6-tetracarboxylic ester, b.p. 175°/2-3 mm. (pure product 30% yield) obtained by the action of carbonyl bromide upon the disodium derivative of trimethylene dimalonic ester. The tetra ester on being hydrolysed with alcoholic potash gives the corresponding tetra acid m.p. 246°, and is converted into *cyclohexanone* on being boiled with 50 per cent. sulphuric acid during 16 hours. The

conversion of this tetra ester into the required diacid is being tried under regulated conditions of hydrolysis and decarboxylation. This reaction being of very general applicability has been extended for the preparation of *cyclopentanone* and *cyclobutanone* tetracarboxylic esters by condensing ethylene and methylene dimalonate esters, respectively, with carbonyl bromide. The *cyclopentanone* tetra ester on drastic hydrolysis accompanied by decarboxylation has given *cyclopentanone*. It has been possible to raise the yield of ethyl butane tetracarboxylate from 15 to 65 per cent. by using magnesium amalgam instead of sodium.¹

The *cyclohexanone*-2:6-dicarboxylic ester and the corresponding *cyclopentanone* and *cyclobutanone* diesters with two active hydrogen atoms in 1:3-positions should, it is expected, form convenient starting materials for the synthesis of some interesting bicyclic terpenes.

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May 31, 1934.