The residue was dissolved in water and thence extracted into benzyl alcohol and finally partitioned into water as described above. The aqueous solution was lyophilized to yield a chromatographically pure product. The amorphous compound was readily soluble in water, methanol, ethanol, *n*-propanol, benzyl alcohol and the various cellosolves but was insoluble in ether, ethyl acetate, chloroform, benzene or the cellosolve esters.

For crystallization the amorphous compound was dissolved in absolute ethanol. On standing Coprogen separated as clusters of fine, dark brick-red needles. After drying at 110° under reduced pressure, the following analytical values were obtained.

Anal. Found: C, 50.96; H, 6.83; N, 10.26; Fe, 6.61.

Tests for halogen, phosphorus and sulfur were negative. When the compound was dissolved in dilute sodium hydroxide, ferric hydroxide precipitated. Assay with *P. kleinii* indicated that the alkali-treated solution was devoid of growth-promoting activity.

Ultraviolet Absorption Spectra.—Coprogen was dissolved in 50% ethanol at a concentration of 50 mc. per ml. and the ultraviolet absorption spectra was determined with a Beckman Model DU spectrophotometer.

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Synthesis of Cyclobutane by the Dehydroxymethylation Method

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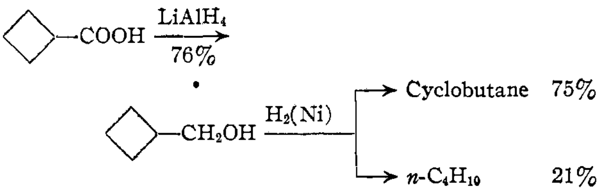
The synthesis of cyclobutane and its intermediates has been widely studied. One of the procedures used in the preparation of cyclobutane involves the oxidation of methylenecyclobutane with performic acid to 1-(hydroxymethyl)-1-cyclobutanol which on cleavage with lead tetraacetate forms cyclobutanone[3]; the latter is then reduced to cyclobutane. The cyclobutanone also was prepared in 30–36% yield by ozonization of methylenecyclobutane.[4] Another method of synthesizing cyclobutanone in good yields consisted of treating ketene with diazomethane.[5] Other procedures of preparation of cyclobutane utilize cyclobutanecarboxylic acid as a starting material. This acid is converted by a series of known reactions to cyclobutylamine, which, by exhaustive methylation and decomposition, yields cyclobutene.[6] The latter is then hydrogenated to cyclobutane.[7] Cason and Way[8] synthesized cyclobutane by bromination of cyclobutanecarboxylic acid to cyclobutyl bromide and then converted the latter to cyclobutane *via* the Grignard reaction. The over-all yield from cyclobutanecarboxylic acid was about 39%.

It has now been found that the preparation of cyclobutane from cyclobutanecarboxylic acid can be achieved in a 57% yield by a two-step synthesis which involves the reduction of the acid to cyclobutylmethanol and the catalytic dehydroxymethylation of the latter to cyclobutane. This can be presented by the equations



n-Butane is the only by-product of the dehydroxymethylation reaction and the formation of this compound could probably be suppressed by adjusting the experimental conditions. The cyclobutane formed is 99–100% pure.

The dehydroxymethylation method, which has been used previously for the preparation of various hydrocarbons,[9] could very well lend itself to the synthesis of various alkylcyclobutanes.

Experimental Part

Cyclobutylmethanol.—It was prepared by the reduction of cyclobutanecarboxylic acid[10,11] according to the general procedure described in the literature[12] with the modification that a slurry of 9.2 g. (0.24 mole) of lithium aluminum hydride in 350 ml. of ethyl ether was added to a solution of 27 g. (0.27 *M*) of cyclobutanecarboxylic acid. The cyclobutylcarbinol distilled at 142–143.5°, n^{20}D 1.4450, yield 76%.

Cyclobutane.—The dehydroxymethylation was made in a 450-ml. capacity rotating autoclave. Cyclobutylmethanol, 17.2 g., and 1.8 g. of UOP nickel-kieselguhr catalyst[13] were placed in the autoclave which was then pressured with 100 atmospheres of hydrogen and heated at 154° for 5 hours. The final pressure at room temperature was 87 atmospheres. The non-condensable gases consisted of 89% hydrogen and 10% methane. The remainder of the product which was distilled on a low temperature Podbielniak column[14] consisted of 75% cyclobutane and 21% *n*-butane and the residue consisted of material boiling above 130°.

The cyclobutane was analyzed on a Consolidated Engineering Corporation Mass Spectrograph Type 21-103.[15] The remarkable agreement with the spectrum of 99–100% purity cyclobutane published in the American Petroleum Institute's Research Project 44 catalog of mass spectra, serial 416, indicates that the cyclobutane prepared was of similar purity.

The infrared spectrum of the cyclobutane was identical with that reported in the literature.[3]

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