SYNTHESIS OF 3-METHYLGLUTARIC ACID

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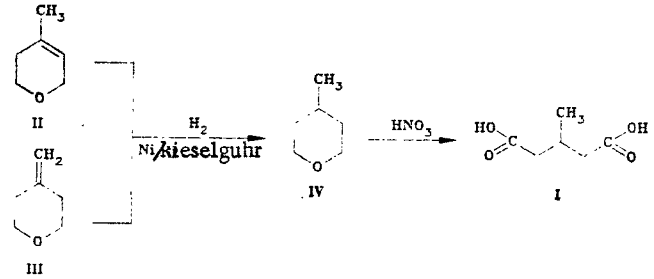
4-Methyltetrahydropyran has been synthesized by catalytic hydrogenation of a mixture of the isomeric 4-methyl-5,6-dihydro- and 4-methylenetetrahydropyrans. Oxidative degradation then led to 3-methylglutaric acid.

3-Methylglutaric acid (I) is used in the production of thermostable lubricants [1], plasticizers, for improving the low temperature properties of plastics [2], and in the synthesis of some anti-ulcer preparations [3]. However, current synthetic methods for industrial preparation of this important acid are based on scarce starting materials — 3- or 4-methylcyclohexanols [4] or 4-methylcyclohexene [5].

With the aim of developing a more convenient synthesis of I we have studied the catalytic hydrogenation of the "pyran" fraction which contains a mixture of 4-methyl-5,6-dihydro-2H-pyran (II) and 4-methylenetetrahydropyran (III). Subsequent oxidation of the tetrahydro derivative (IV) with nitric acid gave I.



The mixture of II and III is a by-product in the synthesis of isoprene from isobutylene and formaldehyde [6] available in large quantity. It is known that hydrogenation of II or III or a mixture can occur to give IV quantitatively using Pd/C catalyst [7]. In this work we have used a more convenient industrial catalyst (nickel on kieselguhr). The optimum yield of IV was achieved by varying the temperature and the rate of addition of starting material at a steady H_2 flow of 120 ml/min (Table 1).

As seen in Table 1 the yield of ether IV was close to quantitative (98%) at 120°C and a volume velocity of 11 h^{-1} for addition of II and III. Increasing the temperature above 130°C lowered the yield significantly and a higher rate of addition caused incomplete conversion of starting material.

Certain studies [8, 9] concern the oxidation of tetrahydropyrans by nitric acid. Glutaric acid is formed in all cases but the yield significantly depends on the structure of the starting ether. In the present work oxidation of IV with 60-65% nitric acid led to the target product in 70% yield. The structure of I was demonstrated by IR and PMR spectroscopy.

Because the hydrogenation product IV was similar to compounds of a reactive classification its oxidation was carried out without further work up.

EXPERIMENTAL

PMR spectra were recorded on a Tesla BS-487C (80 MHz) instrument in d_6-DMSO using HMDS as internal standard. IR spectra were taken on a UR-20 instrument as a suspension in paraffin mull.

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TABLE 1. Conditiona and Results of Pyran Fraction Hydrogenation

T, °C	Rate of addition of starting material, h^{-1}	Yield, %	T, °C	Rate of addition of starting material, h^{-1}	Yield, %	T, °C	Rate of addition of starting material, h^{-1}	Yield, %
100	10	47	140	10	20	120	8	80
110	10	55	120	3	25	120	11	98
120	10	60	120	5	60	120	14	60
130	10	60						

4-Methyltetrahydropyran (IV) Ni/kieselguhr catalyst (10 cm^3) was put into an electrically heated quartz reactor. Initial reduction was with an H_2 stream at 400°C over 2 h and the pyran fraction (mixture of II and III) and hydrogen were fed in. The catalyzate was collected in a vessel with reflux condenser in 98% yield with bp 105°C, n_D^{20} 1.4220, and d_4^{20} 0.8654 g/cm^3.

3-Methylglutaric acid (I) was obtained by a known method [8] from IV in 70% yield with mp 86°C (from 10% HCl). PMR spectrum: 1.15 (3H, s, CH_3), 2.40 (4H, s, 2-CH_2), 2.80 (1H, s, CH), 9.82 (2H, s, 2-OH). IR spectrum: 1700 (C=O), 955, 2800-3000 cm^{-1} (OH).

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