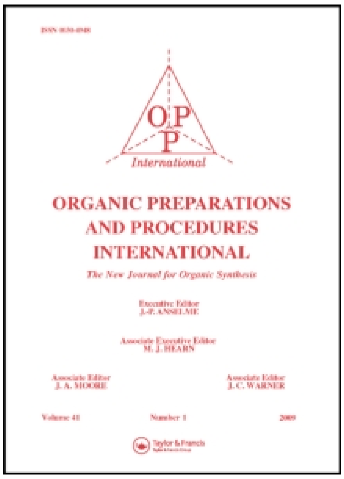

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AN IMPROVED HYDROGENATION FOR THE PREPARATION OF TETRAHYDROFURAN *CIS*-2, 5-DICARBOXYLIC ACID

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AN IMPROVED HYDROGENATION FOR THE PREPARATION OF TETRAHYDROFURAN CIS-2,5-DICARBOXYLIC ACID

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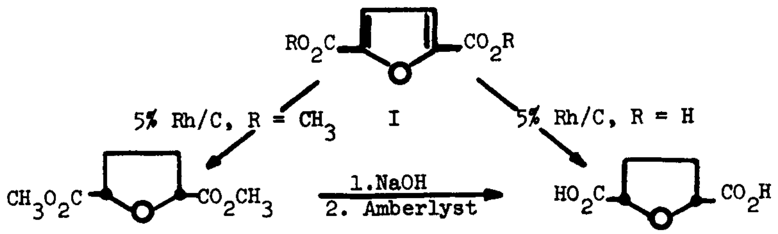
During the preparation of a lactone containing the tetrahydrofuran ring it was necessary to synthesize large amounts of tetrahydrofuran-cis-2,5-dicarboxylic acid (II) and of dimethyl tetrahydrofuran-cis-2,5-dicarboxylate (III). Several methods have been reported for the preparation of II[2-5] and of III,[4,6] but all of these are unsatisfactory.



III

II

The synthesis of II has been accomplished by Na(Hg) reduction of I, R=H (no yield reported;[2] in our laboratory we obtained 3% yield); by hydrogenation of ethyl-5(hydroxymethyl) furan-2-carboxylate over Raney Ni (140°/130 atm, 7 hr) followed by hydrolysis (maximum yield, 48%);[3] by hydrogenation of I, R=H with Raney Ni (235°/135 atm, 8 hrs, no yield reported)[3] by reduction of III over copper chromite (240°/143 atm, 10 hrs) followed by hydrolysis (12% yield);[4] as a by-product of a $LiAlH_4$ reduction of III (15% yield);[4] by the addition of tetracyanoethylene oxide to ethylene and subsequent hydrolysis and partial decarboxylation of the resultant 2,2,5,5-tetracyanotetrahydrofuran (overall yield, 18%).[5]

The saturated diester III has been prepared from I, $R=CH_3$ by Na(Hg) reduction to dimethyl 2,5-dihydrofuran-cis-2,5-dicarboxylate and subsequent hydrogenation over Pd/C (rm. temp/3 atm, 3 hr, 40% yield).[6] Using this involved procedure, Gagnaire and Monzeglio prepared, separated and characterized (NMR) pure cis and trans III. Cope and Baxter[4] hydrogenated I, $R=CH_3$ in one step using Raney Ni (90°/79 atm, 20 hr, 71% yield after distillation). The authors indicate that only the cis isomer is isolated under these conditions.

We now report that one may obtain II in 82% yield by hydrogenation of I, R=H in water in the presence of 5% Rh/C (rm. temp/3atm, 3-4 hr). The diester III may be obtained from I, $R=CH_3$ under similar conditions in 91% yield, after distillation. Saponification of III to II can be readily accomplished in 90% yield. The NMR spectrum of III as isolated indicates the absence of the trans isomer (no signal at 4.71δ).

The reduction of I, R=H when performed in methanol, yields III directly, but better yields and more reproducible results are obtained using I, $R=CH_3$.

EXPERIMENTAL[8]

Tetrahydrofuran cis-2,5-dicarboxylic acid (II). Furan-2,5-dicarboxylic acid (I), 3g (.0192 mole) was suspended in water, 250 ml, in a glass hydrogenation bottle of a Paar hydrogenator (Model 3919). The catalyst, 5% Rh/C (Engelhard Ind.) (0.11g) was added, the reaction mixture was flushed with nitrogen for 10 min and then pressurized with hydrogen to 3 atm. The appropriate amount of hydrogen (0.038 mole) was absorbed after 3 to 4 hr of shaking. The bottle was disconnected from the hydrogenator and the suspension was flushed with nitrogen for 10 min. The rhodium catalyst was removed by filtration. The filtrate was evaporated to give a white solid (2.5g, 83% yield), m.p. 125-126°C (lit.[3] _cis_ acid mp 126°; _trans_ acid mp 93-94°[7]), NMR (DMSO-D_6) δ 2.0 (m 4H-CH_2-ring, δ 4.38 (m 2H (_cis_)-CH-ring).

Dimethyl tetrahydrofuran cis-2,5-dicarboxylate (III).

Dimethyl furan-2,5-dicarboxylate (I, R=CH_3) 3g (0.016 mole) was dissolved in methanol and hydrogenated as previously described for 8-10 hr. The filtrate obtained after removal of the catalyst, was concentrated and the residue was distilled at 70°C (oil bath temperature) and 500μ Hg (lit.[4] 81-83°/0.1mm). A clear liquid was obtained (2.8g, 91% yield), n_D^{25} 1.4511 (lit.[4] n_D^{25} 1.4511) which was shown to be dimethyl tetrahydrofuran-_cis_-2,5-dicarboxylate by spectroscopic analyses, IR (neat), 2950 (CH_3), 1750, 1200 $(-\overset{O}{\overset{\|}{C}}-O-)$, 1090 $(C\overset{O}{\wedge}C)$, 1440, 1360, 1280, 1000, 950, 750 cm^{-1}, NMR (CCl_4) δ 2.16 (m 4H -CH_2-ring), δ 3.67 (s 6H -CH_3), δ 4.36 (m 2H (_cis_)[6] -CH- ring (lit[6] _cis_ δ 4.59; _trans_ δ 4.71).

Saponification of III to II.

III, 10g (0.054 mole) was refluxed overnight with 4.5g (0.11 mole) of sodium hydroxide in 200 ml of water. The resulting solution was passed through a strongly acidic ion exchange column (Amberlyst 15, Mallinckrodt cycled repeatedly with acid and base until a colorless effluent was obtained) and eluted with 700 ml of H_2O. Upon concentration and evaporation a white solid (7.8g, 90% yield) m.p. 125-126°C was obtained.

REFERENCES

1a. To whom correspondence should be addressed.

1b. Goodyear Fellow, 1972-73.

2. H. Hill and A. Wheeler, Am. Chem. J., 23, 463 (1901).

3. W.N. Haworth, W.G.M. Jones and L.F. Wiggins, J. Chem. Soc., 1 (1945).

4. A. Cope and W. Baxter, J. Am. Chem. Soc., 77, 393 (1955).

5. W.J. Linn and R.E. Benson, ibid., 87, 3657 (1965).

6. D. Gagnaire and P. Monzeglio, Bull. Soc. chim. France, 474 (1965).

7. B. Lean, J. Chem. Soc., 77, 103 (1900).

8. Melting points were obtained in open capillaries and are uncorrected. Infrared spectra were recorded as a film on salt plates with a Perkin Elmer Model 137 Infracord. Nuclear magnetic resonance spectra were recorded on a Varian Model T-60 spectrometer with tetramethyl silane as the internal standard.

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