

Hydrogenation of Naphthalene Esters to Tetralin Esters

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Naphthalene esters have been reduced over a nickel-on-kieselguhr catalyst which gives specific reduction to the tetrahydronaphthalene (tetralin) stage. The method is of practical utility, since no monitoring of the hydrogen uptake is necessary.

THE LITERATURE contains much information on the reduction of naphthalene and its derivatives to the corresponding tetralin and its derivatives. Nickel catalysts have been prevalent in the reported work (1, 4, 9, 10), though platinum (4) and copper chromite (2, 6) catalysts have also been used.

The authors were interested in finding a catalyst that would give specific reduction of the naphthalene ring system to the tetralin ring system in a short reaction time, would be nonpyrophoric, would not need activation prior to use, and would be easily regenerable. The catalyst that met these requirements was nickel supported on kieselguhr (G-49A containing 65.5% nickel, from Girdler Catalysts, Louisville, Ky.). Using a stirred autoclave, the uptake of hydrogen was very rapid, and ceased after 2 moles of hydrogen per mole of ester had been consumed. The yields of tetralin products from the hydrogenation of methyl 1- and 2-naphthoates and dimethyl 2,3-naphthalenedicarboxylate were essentially quantitative. On hydrogenating naphthalene under the same conditions used for the esters for 50 minutes—hydrogen uptake ceased after 20 minutes—the product consisted of 98% tetralin, 1% naphthalene, and 1% decalin.

Dimethyl 1,2,3,4-tetrahydro-2,6-naphthalenedicarboxylate has not been reported in the literature. It was obtained as a solid product (m.p. 76–7°C.) by recrystallization from cyclohexane to remove a small amount (7%) of dimethyl decahydro-2,6-naphthalenedicarboxylate impurity. Polyamides and polyesters of 1,2,3,4-tetrahydro-2,6-naphthalenedicarboxylic acid show promise in fibers and films (5).

At 150°C. and 1500 p.s.i.g. pressure, using nickel-on-kieselguhr as catalyst, the naphthalene ring system is specifically reduced to the tetralin ring system. With methyl 1- and 2-naphthoates and dimethyl 2,3-naphthalenedicarboxylate, the unsubstituted ring is more easily reduced. A greater percentage of the 5,6,7,8-tetrahydro isomer is obtained on reducing methyl 2-naphthoate than is obtained with the other two compounds. At higher reaction temperatures, other workers have used G-49 catalyst or similar catalysts to reduce naphthalene derivatives to decalin derivatives (3) and benzene derivatives to cyclohexane derivatives (8). Dimethyl 2,6-naphthalenedicarboxylate can be reduced over nickel-on-kieselguhr (G-49A) at 200°C. and 1500 p.s.i.g. pressure to dimethyl decahydro-2,6-naphthalenedicarboxylate.

EXPERIMENTAL

Gas chromatographic analyses were carried out using a silicone gum rubber column on an F&M Model 720 gas chromatograph with thermal detector. NMR spectra were obtained on a Varian A-60 instrument with tetramethylsilane (TMS) as an internal standard. All melting points are uncorrected and were determined on a Mel-Temp capillary melting point apparatus.

General Hydrogenation Procedure. The weighed sample and solvent—either cyclohexane or methanol—were placed in a 300-ml. Magna-Drive stirred autoclave (Autoclave Engineers, Inc.) with the desired amount of catalyst. The system was sealed, purged several times with hydrogen to remove air, and then pressured with hydrogen to the desired pressure at room temperature. When the desired reactor temperature was reached, the mixture was stirred at 1200 r.p.m. until the hydrogen uptake ceased. The reactor was then cooled to room temperature, vented, purged several times with nitrogen, and the sample removed. The mixture was filtered and the solvent evaporated to recover the hydrogenated product.

Methyl 1,2,3,4- and 5,6,7,8- Tetrahydro -2- naphthoates. Several runs were made following the general procedure and using 10.0 grams of methyl 2-naphthoate, 150 ml. of cyclohexane, and 1.0 gram of Girdler G-49A nickel-on-kieselguhr catalyst. At 150°C. and 1500 p.s.i.g. pressure—initial at room temperature—the reaction was complete in 15 minutes. The tetralin products were identified by NMR and by gas chromatography. In the NMR spectrum, the chemical shift of the alicyclic carbomethoxy protons was 3.60 p.p.m. (TMS = 0.00 p.p.m.) while the aromatic carbomethoxy protons were further downfield at 3.78 p.p.m. Gas chromatographic analysis showed that methyl 5,6,7,8-tetrahydro-2-naphthoate was the higher-boiling component, and in a typical run was 93.6% of the total product. The 1,2,3,4-tetrahydro isomer was lower-boiling, and was 6.4% of the total. Reasonable agreement was obtained between the NMR and GLC analyses.

Methyl 1,2,3,4- and 5,6,7,8- Tetrahydro -1- naphthoates. Several reactions to reduce methyl 1-naphthoate were carried out under conditions identical to those used for the 2-isomer. In this case, the NMR spectrum could not be used to determine isomer distribution, since the difference in chemical shifts of the carbomethoxy protons was not large enough to allow integration of the separate peaks. Assuming that the aromatic ester was higher-boiling—as

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was the case with methyl 2-naphthoate—the product composition in a typical run as determined by gas chromatography was 71.7% methyl 5,6,7,8-tetrahydro-1-naphthoate and 28.3% methyl 1,2,3,4-tetrahydro-1-naphthoate. No other products were present.

Dimethyl 1,2,3,4- and 5,6,7,8-Tetrahydro-2,3-naphthalenedicarboxylates. Several reactions to reduce dimethyl 2,3-naphthalenedicarboxylate were carried out under the conditions used for the naphthoates to give a product in a typical run consisting of 77.8% of dimethyl 5,6,7,8-tetrahydro-2,3-naphthalenedicarboxylate and 22.2% of dimethyl 1,2,3,4-tetrahydro-2,3-naphthalenedicarboxylate, as determined by gas chromatography.

Dimethyl 1,2,3,4-Tetrahydro-2,6-naphthalenedicarboxylate. Several runs to reduce dimethyl 2,6-naphthalenedicarboxylate to its single tetralin product were carried out. In a typical run—150°C., 1500 p.s.i.g. initial pressure at room temperature—a 93% yield of dimethyl 1,2,3,4-tetrahydro-2,6-naphthalenedicarboxylate (m.p. 76–7°C.) was obtained. Anal. Calcd. for $C_{14}H_{16}O_4$: C, 67.72; H, 6.50. Found: C, 67.71; H, 6.48.

The remainder of the product resulted from complete reduction to the decalin diester. The tetralin diester was saponified to the corresponding tetralin diacid [m.p. 358–60°C. (decomposed)]. Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49. Found: C, 65.31; H, 5.47.

Dimethyl Decahydro-2,6-naphthalenedicarboxylate. Dimethyl 2,6-naphthalenedicarboxylate was reduced over nickel-on-kieselguhr at 200°C. and 1500 p.s.i.g. pressure—initial at room temperature—according to the general procedure. There was a notable decrease in the rate of hydrogen uptake at the tetralin stage, but the reaction was continued for another 7 hours. The title compound was obtained in a 79% yield. The presence of several lower-boiling materials indicated that considerable hydrogenolysis had occurred.

Reduction of dimethyl 2,6-naphthalenedicarboxylate over 5% ruthenium-on-charcoal was done at 150°C. and 1500 p.s.i.g. pressure—initial at room temperature—according to the general procedure. The title compound was obtained in 95% yield (m.p. 45° to 60°C.). The reported melting point for the decalin diester is 42° to 56°C. (7). Anal.

Calcd. for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 66.01; H, 8.54.

Under the same conditions, using 5% rhodium-on-charcoal, the yield of the title compound was 98%, and using 10% palladium-on-charcoal, the yield of the title compound was 96%.

The decalin diester was saponified to the corresponding decalin diacid (m.p. 190° to 220°C.). The reported melting point for the decalin diacid is 210° to 222°C. (7).

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The Use of *trans*-Vinylene Diisocyanate for the Identification of Alcohols, Amines, Mercaptans, Thiophenols, and Carboxylic Acids

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Several types of derivatives of *trans*-vinylene diisocyanate were prepared and characterized. The derivatives include bis(alkyl) or (aryl)-*trans*-vinylenedicarbamates and bis(thiolcarbamates), *trans*-1,1'-vinylene bis(3,3'-disubstituted ureas), and *trans*-N,N'-vinylene bis(alkyl or arylcarboxylic acid carbamic acid anhydrides). Yields, melting points, and infrared data are given for the reported compounds.

A WELL-KNOWN method to characterize alcohols (1, 4, 6), phenols (1, 4, 6) and amines (4, 6) is to prepare solid derivatives of these compounds by reaction with aryl isocyanates. The solid urethan or urea derivatives usually are purified readily, and serve as a quick and accurate identification of the alcohol or amine. Recently, the authors prepared several derivatives of *trans*-vinylene diisocyanate in this laboratory.

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Because of the dual functionality of *trans*-vinylene diisocyanate, reaction with alcohols and amines gave high-melting solid derivatives which were characterized easily. Thus, *trans*-vinylene diisocyanate can serve to identify alcohols, amines, and compounds containing active hydrogen in the same manner as α -naphthyl or substituted phenyl isocyanates.

In addition to reaction with alcohols, phenols, and amines, *trans*-vinylene diisocyanate was treated with mercaptans (5), thiophenols, and carboxylic acids (5) to give the addition product characteristic of the reaction.