

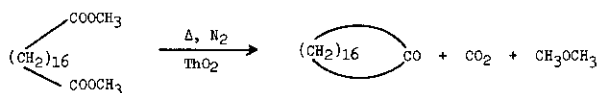
Cycloheptadecanone from Dimethyl Octadecanedioate via a One-Step Catalytic Process

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The search for less expensive routes to synthetic macrocyclic ketones as replacements for natural musk odorants has been studied by various groups for some time. The 15-, 16-, and 17-membered cyclic ketones have desirable odor and fixative properties. The 18-member ketone has an attractive odor but is weaker than that of the 15-17 member rings and at the present time is not of commercial interest. It has good fixative properties which, in the case of toluene, were shown to be due to the formation of a surface-covering of crystalline ketone when the concentration of the ketone reached a critical level of approximately 82%.¹

Many of the routes to the 15- and 16-member rings are based on the expansion of the cyclododecanone ring.² While the chemistry is often quite elegant, each of these procedures involves a number of steps and tend to be tedious and costly.

Another process is based on the acyloin condensation of long chain diesters.³ This route is made more attractive by the increased availability of the dicarboxylic acids through microbial oxidation of n-alkanes,⁴ metathesis of olefinic esters,⁵ and sources not indentified.⁶



A different cyclization of dimethyl octadecanedioate to cycloheptadecanone has been achieved in a single step as illustrated in figure 1. The diester was passed with nitrogen dilution over a high surface area thorium oxide catalyst at

reduced pressure.⁷ When a sample of 10 grams of the diester was put through 18.5 grams (approximately 25 ml) of catalyst at 378°C at a rate of about 0.9 gram of sample per gram of catalyst per hour and a pressure of 2.0 to 3.5 mm, 7.2 grams of mixture was collected overhead.

Gas-liquid chromatography (GLC) indicated that the mixture contained only starting diester and cycloheptadecanone, the structure of which was established by GLC mass spectral analysis. The yield of this macrocyclic ketone was calculated to be 14% based on the GLC. About 28% of the diester feed was lost and was presumed to be held in the catalyst bed, either as starting material or as some form of linear polymer. No study was made of the separation of the ketone from the diester nor were studies made to optimize the yield. Though low, this yield is not greatly different from the overall yield obtained through the steps of the acyloin condensation.

Although the reaction was not studied, it does establish that a one-step conversion of the long chain diesters to the cyclic ketone containing one less carbon atom can occur. It opens the possibility to simpler processes for the preparation of macrocyclic ketones.

References

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