

Thermal Decomposition of Maleopimaric Acid in the Presence of Selenium

Short Communication

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During thermal decomposition of maleopimaric acid (**1**) in the presence of selenium a high yield of dehydroabietic acid (**3**) can be obtained, if the selenium is dispersed by sonication. From temperature-dependent side products conclusions are drawn concerning the reaction path.

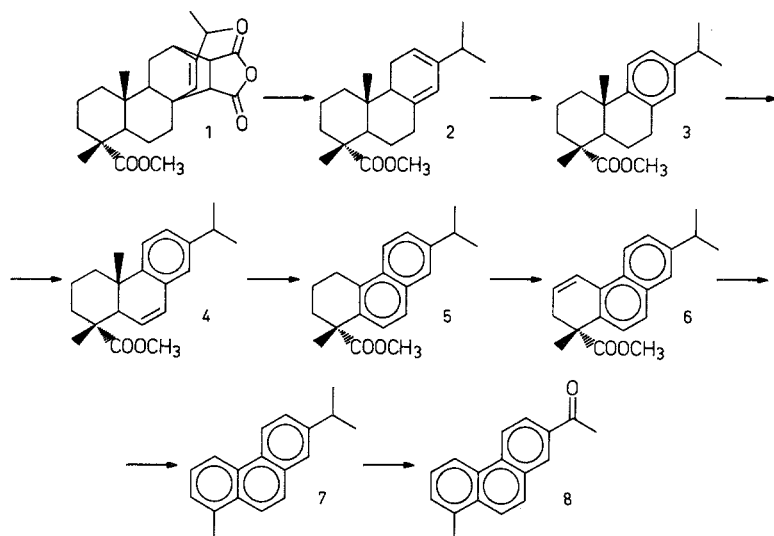
(Keywords: Dehydroabietic acid; Retro-Diels-Alder-reaction; Ultra-sonic)

Thermische Spaltung von Maleopimarsäure in Gegenwart von Selen (Kurze Mitteilung)

Die thermische Spaltung von Maleopimarsäure (**1**) in Gegenwart von Selen liefert in guter Ausbeute Dehydroabietinsäure (**3**), wenn das Selen durch Ultraschall dispergiert wird. Die Temperaturabhängigkeit der Reaktion wird untersucht. Aus den auftretenden Nebenprodukten wird auf den Reaktionsverlauf geschlossen.

Resin acids are attractive starting materials for the synthesis of steroids because their carbon skeletons and configurations are similar to those of steroids. For that purpose a modification of the A-ring and anellation of the D-ring is necessary and several attempts have been made to convert abietic acid or other resin acids to steroids¹.

The main problem during the construction of the D-ring is the modification or degradation of the isopropyl group; it has been shown that the latter is accompanied by epimerisation^{2,3}. However, selective halogenation of the isopropyl group of maleopimaric acid (**1**) can be



performed in high yield⁴. We have therefore studied the retro-*Diels-Alder* reaction of maleopimaric acid which after modification of the isopropyl residue should lead to the desired resin acid derivative. The instable primary product laevopimaric acid (**2**) is immediately dehydrogenated by selenium to stable dehydroabietic acid (**3**). Fig. 1 shows the influence of the reaction temperature by depicting the composition of the reaction mixture after two hours of reaction time. It follows that at temperature above 280 °C—even by excluding oxygen—further dehydrogenation occurs and abietapentaen (**5**) and finally retene (**7**) are formed.

The products can easily be isolated by extraction with ether, because the educt **1** is insoluble. (Fig. 2 shows the composition of the ether soluble products.) It is known that the retro-*Diels-Alder* reaction starts far below 200 °C⁵ but selenium-dehydrogenation is fast only well above 200 °C. To keep the reaction proceeding at the lowest possible temperature and to avoid the formation of side products **5** and **7** we dispersed the selenium by sonication. Thereby the reaction could be carried out at 250 °C with a yield of 60% dehydroabietic acid (i.e. 80% based on reisolation educt).

The reaction mixtures were analysed by glc (using glasscapillar columns) and the products were isolated by column chromatography on silica. All spectroscopic properties as well as the mass spectra are in accordance with the structures given.

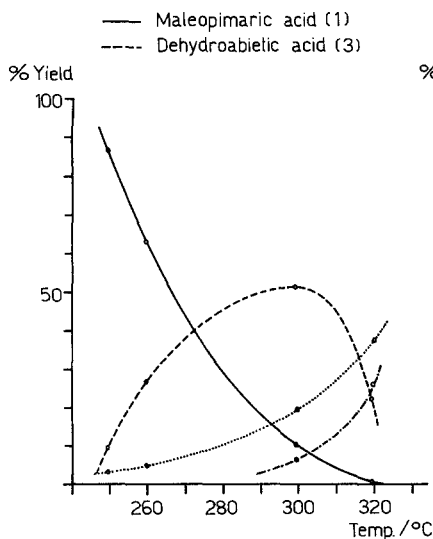


Fig. 1

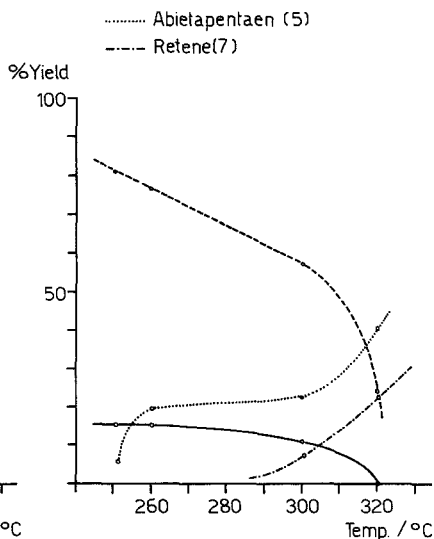


Fig. 2

Fig. 1. Composition of the reaction mixture (maleopimaric acid/Se powder; molar ratio = 1:2) after two hours; the concentration of compounds **4**, **6**, and **8** is less than 1%.

Fig. 2. Composition of the ethereal extract of the reaction mixture from Fig. 1

Acknowledgements

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