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THE ALKALINE DEGRADATION OF DEHYDRONORCAMPHOR TO ISOMERIC CYCLOPENTENYLACETIC ACIDS

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Dehydronorcamphor (I) can be prepared by treating -chloro-2-cyano-norbornene-5 with aqueous potassium hydroxide (1). Another product isolated by the author in small amounts from the acidified product mixture was cyclopentenylacetic acid, which gave only one peak in the gas chromatogram of the products isolated from the acidified mixture, but was concluded to be a mixture of two isomers on the basis of the NMR spectrum (see below). From the results of earlier studies (2,3,4) it was concluded that these cyclopentenylacetic acids were formed by the degradation of dehydronorcamphor by aqueous potassium hydroxide. This was confirmed when pure dehydronorcamphor was boiled in an aqueous potassium hydroxide solution for a longer period; the salts of the isomeric cyclopentenylacetic acids were slowly formed.

The conclusion of Cristol and Freeman (3) and Gassmann and Zalar (4) that the degradation of dehydronorcamphor by the action of bases leads to only one isomer, to derivative of Δ^3-cyclopentenylacetic acid (III) is at variance with the preceding observation. For this reason the reactions of dehydronorcamphor with sodamide (2,3) and potassium t-butoxide in a water-dimethyl sulphoxide mixture (4) were re-investigated. The isolated product in each case consisted of an equimolar mixture of Δ^2-cyclopentenylacetic acid (II) and Δ^3-cyclopentenylacetic acid (III) as their amides or potassium salts.

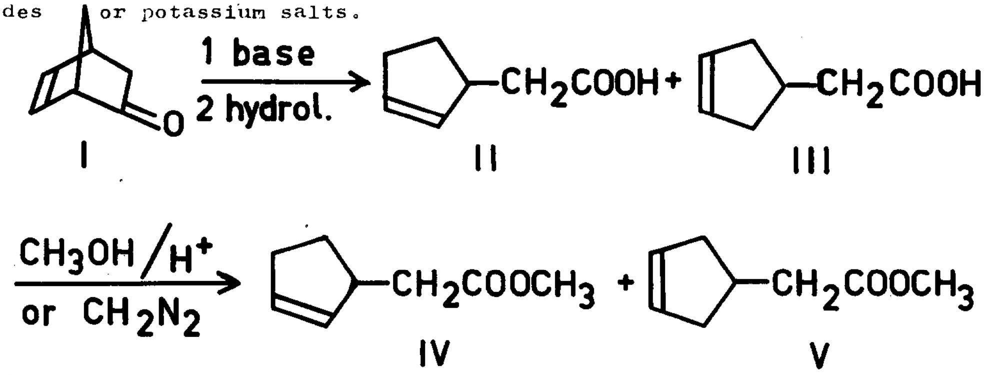
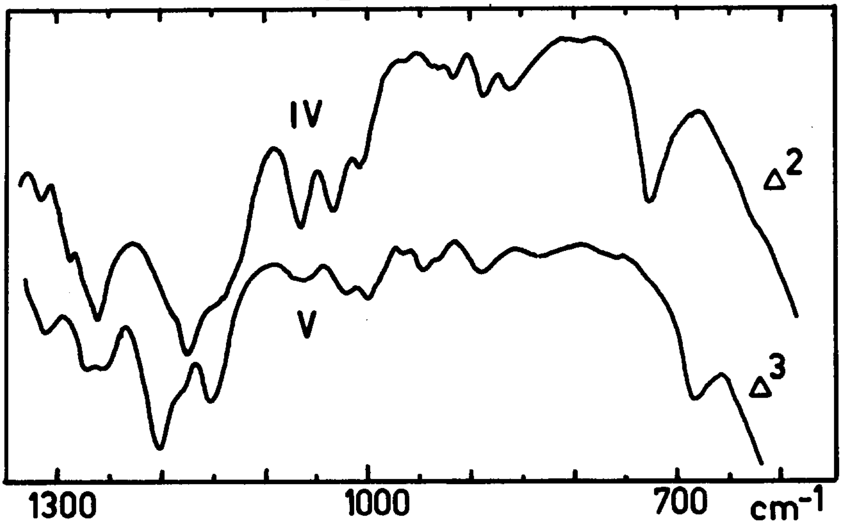
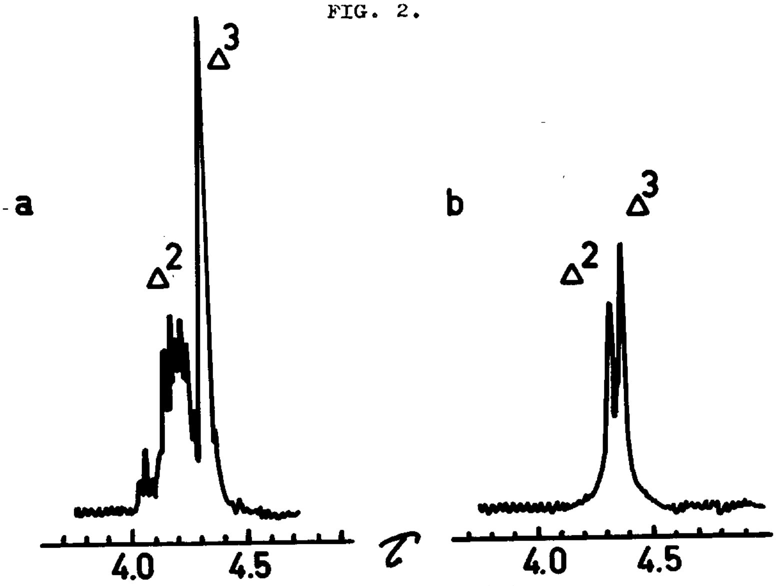


FIG. 1.



Infra-red spectra of the methyl esters of Δ^2-cyclopentenylacetic (IV) and Δ^3-cyclopentenylacetic (V) acids. Perkin-Elmer model 337 spectrometer. The samples were films between sodium chloride plates.

FIG. 2.



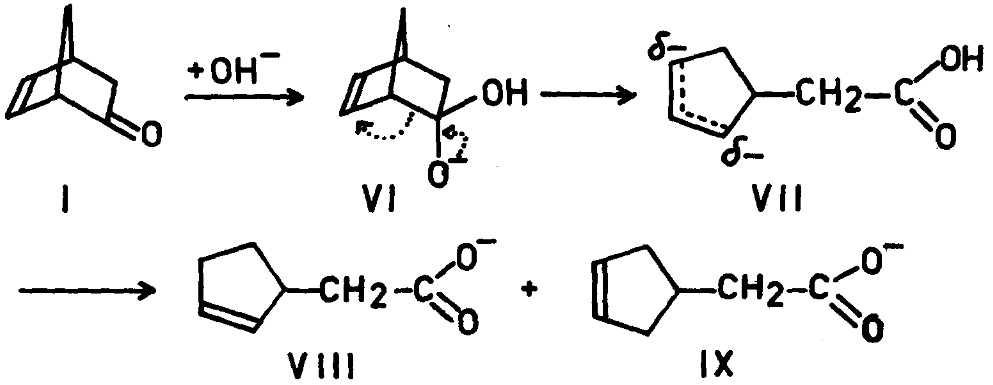
Low-field regions of the NMR spectra of (a) a mixture of isomeric acids (in pyridine) formed in the degradation of dehydronorcamphor in aqueous potassium hydroxide solution and (b) a mixture of the methyl esters of the acids (in CCl_4). The spectra were run on a Varian A-60 NMR spectrometer with TMS as internal reference standard.

This result was confirmed by synthesizing the pure isomeric cyclopentenylacetic acids (II and III) and their methyl esters (IV and V). Δ^2-Cyclopentenylacetic acid was prepared by the method of Noller and Adams (5) and Δ^3-cyclopentenylacetic acid from Δ^3-cyclopentenylcarboxylic acid (6) by the Arndt-Eistert synthesis (7). The methyl esters of the two acids were prepared by allowing the acids to react with methanol containing sulphuric acid and with diazomethane; the esters produced by these two methods were identical.

The infra-red spectra of the isomeric acids II and III and the isomeric methyl esters IV and V were identical in the range 4000-1500 cm^{-1}, but the peaks in the range 1500-600 cm^{-1} were in different locations in the spectra of the Δ^2 and Δ^3 isomers (see Fig. 1). A comparison of the spectra with the spectrum of "Δ^3-cyclopentenylacetic acid" in the dissertation of Freeman (2) revealed that Freeman's product was also a mixture of the isomers II and III as was also the product of degradation of dehydronorcamphor obtained by the present writer.

The presence of two isomers among the products of degradation of dehydronorcamphor in the presence of bases was clearly revealed by the proton resonance spectra. The signal due to protons attached to double-bonded carbon atoms was in a lower field in the spectra of the Δ^2-isomers II and IV than in the spectra of the Δ^3-isomers III and V (see Fig. 2). The signals of protons attached to other carbon atoms were a complex series of peaks in the range τ = 7-9 ppm that were in different locations in the spectra of the Δ^2 and Δ^3 isomers and which hence represent excellent fingerprints for the identification of the pure isomers (7).

The mechanism of the alkaline degradation of dehydronorcamphor is more readily understandable when it is known that the product consists of a mixture of Δ^2-cyclopentenylacetate (VIII) and Δ^3-cyclopentenylacetate (IX) ions than when only one cyclopentenylacetate ion (IX) is known to be formed (3):



The conversion of the mesomeric anion VII, the formation of which was postulated already by Cristol and Freeman, to a mixture of the two anions VIII and IX may be thought to result from the transfer of a proton from any proton donor, e.g. from an identical neighbouring ion, without assuming an intramolecular proton shift to the γ-position (3).

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