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The Opening of the Cyclohexane Ring of Pinanones Using Baeyer-Villiger Conditions

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Abstract. Reaction of nopinone (1) with 3-chloroperbenzoic acid in CHCl_3 leads, in a very slow reaction, to the two lactones 2 and 3 in the ratio 9:1. Methylpinone (4) under the same conditions gives the homologous lactones 6 and 7, but in the reverse ratio, together with minor amounts of the stereoisomers 8 and 9 arising from the presence of a small amount of the *trans*-isomer in the starting material. For the successful isolation of some of these lactones, it is essential to remove all traces of EtOH from the solvent CHCl_3 .

Nearly 20 years ago, Joulain and Rouessac obtained the expected lactone 2 from the reaction of 4-nitroperbenzoic acid for 3 weeks on nopinone (1) [1], but had difficulty repeating the result [2]. Another publication claimed the isomeric lactone 3 as a by-product from the ozonolysis of β -pinene (5) [3]. Neither of these papers gave full spectral characterization of the products claimed.

Using 3-chloroperbenzoic acid (MCPBA) in CHCl_3 from which the stabilizing ethanol had been removed, we obtained after 4 weeks at room temperature a 9:1 ratio of lactones 2 and 3 which were separated by flash chromatography and preparative gas chromatography. The structures were secured by NMR spectrometry. In particular, the major lactone 2 had the bridgehead H-C(1) at 4.33 ppm (*dd*, $J = 5$ and 5 Hz), and the $\text{CH}_2(4)$ group at 2.83 and 2.94 ppm. The $^1\text{H-NMR}$ spectrum measured in CCl_4 corresponded to the figures given by Joulain [1]. The minor lactone 3 had a signal at 2.94 ppm corresponding to the bridgehead H-C(1), and the $\text{CH}_2(4)$ at 4.32 and 4.70 ppm; when measured in the CCl_4 , the figures did not fit those given by the Japanese workers [3].

Methylpinone (4), which is mostly the *cis*-isomer 4a with ca. 12% of the *trans*-isomer 4b [5], yielded the homologues 6 and 7 of 2 and 3, respectively, this time with 7 as the major isomer (ca. 70% of the mixture). The $^1\text{H-NMR}$ spectrum of the minor lactone 6 from this reaction had the bridgehead H-C(1) at 4.33 ppm. H-C(4) was at 2.96 ppm, and coupled with the secondary Me group at 1.32 ppm. The major lactone 7 from the reaction had H-C(1) at 2.935 ppm, and H-C(4) at 4.97 ppm. Notable in the $^1\text{H-NMR}$ of the lactones 3 and 7 was the position of the *cis* H-C(5) at 2.49 and 2.15 ppm, respectively, the large shift to lower field being ascribed to the deshielding effect of the C=O group. The attributions of the proton signals

in the methyl-lactones 6 and 7 were also confirmed by NOE measurements. We were unable to separate completely the two lactones 8 and 9 arising from *trans*-methylpinone (4b) except on a capillary GC column, but the similarity of their mass spectra to those of the *cis*-isomers 6 and 7 supported the structures. The NMR spectra will be discussed in the full paper.

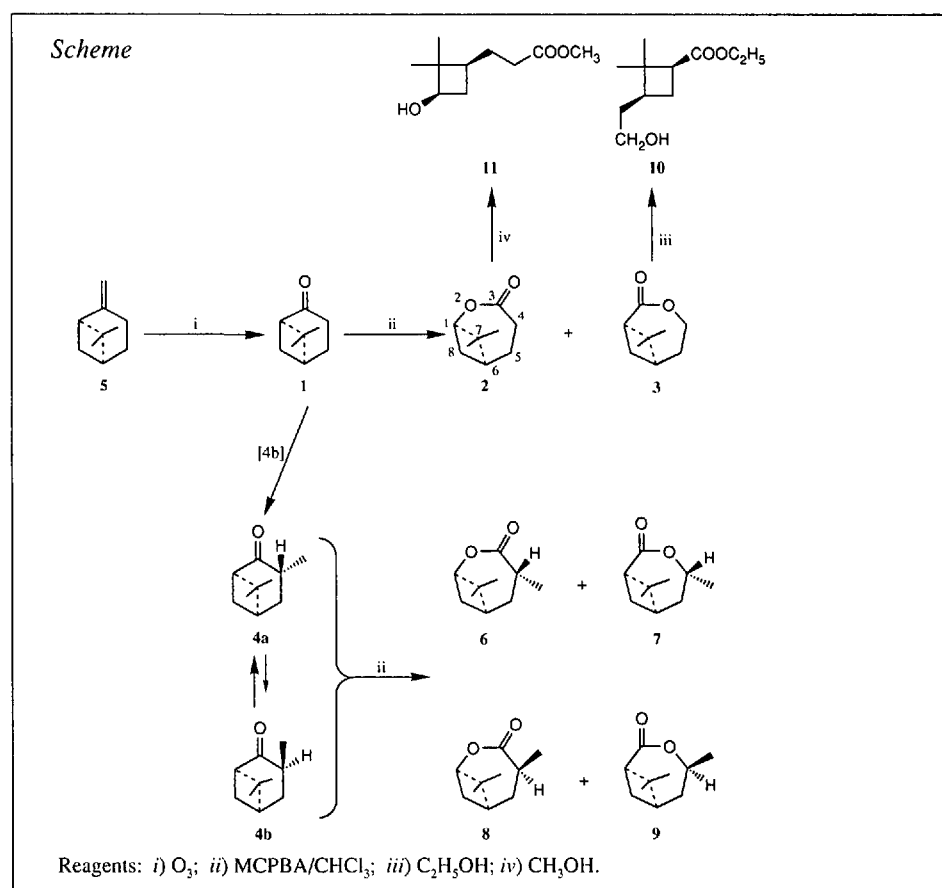
If commercial CHCl_3 was used in the reaction, the minor lactone 2 was not observed; neither was it observed when we tried to accelerate the reaction with CF_3COOH [6]. Instead, we isolated the ester 10. The latter was readily identified from its mass and NMR spectra; in particular the disappearance of the *doublet* due to the *cis*-proton of the CH_2 group in the pinane cyclobutane

ring, and replacement of the two separate signals for the two $\text{CH}_2(4)$ signals of 3 (above) by a *multiplet* centred at 3.57 ppm associated with the CH_2OH group.

The major lactone 2 from nopinone (1) was also converted to the corresponding cyclobutane esters by refluxing with alcohols. Thus, overnight boiling with MeOH yielded the ester 11, a compound that has been identified in the products of the ozonolysis of β -pinene (5) in MeOH [7]. This compound had the carbinol proton at 3.71 ppm, and this was coupled with protons at 1.41 and 2.32 ppm (the CH_2 group of the cyclobutane ring), while the CH_2 group adjacent to the COOMe group appeared as a *triplet* at 2.23 ppm.

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