NOTE

Disproportionation Products of Dehydroabietic Acid with Anhydrous Aluminium Chloride Catalyst

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The Disproportionation of dehydroabietic acid (1a) with anhydrous aluminium chloride catalyst gave six products (2a)~(7a). The reaction pathway of the disproportionation is discussed on the basis of the results obtained under some reaction conditions.

1 Introduction

It is known that catalytic transformation of dehydroabietic acid (1a) with anhydrous aluminium chloride involves not only a sequence of retro Friedel-Crafts reaction at the side chain but also a bond cleavage in the skeleton. On the basis of these studies, we reported already a simple two-step conversion involving the catalytic inversion of the steroidal type A/B ring juncture (dehydroabietic acid) to an antipodal A/B ring juncture system (ent-podocarpic acid) .

In this paper, we would like to describe that the above reaction of (1a) with aluminium chloride involves also a disproportionation mechanism from the results of a structural determination of the reaction products.

2 Experimental

2.1 Analytical instruments

All melting points are uncorrected. IR spectra were obtained in KBr on a JASCO IR-G instrument. 1H-NMR spectra were measured at 100 MHz and 400 MHz, in (2H) chloroform. Chemical shifts are given in ppm, with tetramethylsilane (TMS) as an internal standard (JNM-FX 100 and GX-400 instrument). Mass spectra were recorded on Hitachi M-80 B system at 70 eV. GLC was performed on a Shimazu GC-9A gas chromatograph equipped 2% OV-17 (3 m x 5 mm) at 200°C. HPLC was carried out on Asahipak column (6 mm x 150 mm) using a RI detector with CH3CN-H2O (95:5) as mobile phase. The RRT (relative retention times) in the GLC and HPLC were expressed relative to methyl dehydroabietate (1b), respectively.

2.2 Disproportionation of (1a)

To a solution of dehydroabietic acid (1a) (12 g) dissolved in dried benzene (360 mL) finely pulverized AlCl3 (12 g) was added and the mixture was stirred for maintaining the temperature of the solution at 20°C for 1 h. After decomposition with dil. HCl, benzene layer was separated and after drying over anhydrous Na2SO4, benzene was distilled off.

After methylation of products with diazomethane in dried ether, the ethereal solution was evaporated to dryness. A portion of products was separated on alumina column chromatography and HPLC, while the other portion was analyzed by GLC (Table-1).

3 Results and Discussion

In order to capture intermediates of the isomerization, a reaction of (1a) with aluminium chloride catalyst was carried out in
dry benzene under a milder condition (20°C, 1 h) than the above mentioned one\(^{1a}\) (30–33 °C, 3 h). Reaction products were methylated with diazomethane and subjected to GLC analysis. Results are given in Table–1.

The changing of products by reaction time is shown in Fig.–1. Compound (2\(\text{b}\)), (3\(\text{b}\)) and (4\(\text{b}\)) increased with progress of the reaction, but then decreased rapidly and disappeared after 2 h, affording compounds (6\(\text{b}\)) and (7\(\text{b}\)). Compound (5\(\text{b}\)) increased with the progress of the reaction and existed stably after 2 h. From these results, (2\(\text{b}\)), (3\(\text{b}\)) and (4\(\text{b}\)) were assumed to be reaction intermediates.

Compound (2\(\text{b}\) \(\text{M}^+\), \(m/z\) 314.2221 (C\(_{21}\)H\(_{30}\)O\(_2\))) has a band at 1729 cm\(^{-1}\)(CO\(_2\)C) in its IR spectrum. In the \(^{1}\)H-NMR spectrum, (2\(\text{b}\)) has signals of methyl proton at 1.20 ppm (3 H, s, CH\(_3\)), 1.23 ppm (6 H, d, 
\(J=6.9\) Hz, (CH\(_3\)\(_2\))), 1.65 ppm (3 H, s, vinylic
\(-\text{CH}_3\)), and 3.70 ppm (3 H, s, CO\(_2\)CH\(_3\)). From these spectral data, It would be reasonable to assume that (2\(\text{b}\)) is methyl 9, 10-seco-5 (10), 8, 11, 13-abietan-tetraen-18-oate.

Structures of (3\(\text{b}\)) and (4\(\text{b}\)) were completely not determined at the present time, but the following structures shown in Fig.–2 are tentatively assigned for (3\(\text{b}\)) and (4\(\text{b}\)).

The mass spectrum data of compound (5\(\text{b}\)) \(\text{[M}^+, m/z\) 320.2699 (C\(_{21}\)H\(_{36}\)O\(_2\))\)] indicates molecular formula of methyl perhydroabietaetate. Especially, in the IR spectrum, the absorption spectrum of (5\(\text{b}\)) in the fingerprint region were in good agreement with methyl 8 \(\beta\), 13 \(\beta\) H-tetrahydroabietate in Zinkel’s report\(^{4a}\).

Finally, the structure of (5\(\text{b}\)) has been established by direct comparison with authentic sample\(^{1b,c}\).

The structures of methyl 5 \(\alpha\), 10 \(\alpha\) -podocarpa-8,11,13-trien-15-oate (6\(\text{b}\)) and methyl 5 \(\alpha\), 10 \(\beta\) -podocarpa-8,11,13-trien-15-oate (7\(\text{b}\)) were confirmed by direct comparison with authentic samples\(^{1a}\) which were already confirmed by us\(^{2a,b}\). The physical properties of reaction products were shown in Table–2.

On the base of the reaction products, the pathway of the disproportionation reaction\(^5\)}
In the beginning of the reaction, a $\pi$-complex was formed between (1 a) and aluminium chloride and then produced compound (2 a). Subsequently, deisopropylation of (2 a) gave hydrogen which reduced (1 a) to afforded (5 a). On the other hand, the ring closure of the carbonium ion yielded (6 a) and (7 a). It was assumed that the steric repulsion caused by C-4 and C-10 methyl groups in the molecule leads to the preferential yield of (6 a).

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Table 2 Melting point, chromatographic data, $^1$H NMR data, and IR data of some terpenoids.

<table>
<thead>
<tr>
<th>Terpenoids (mp, °C)</th>
<th>RRT</th>
<th>$^1$H NMR data</th>
<th>IR data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GLC</td>
<td>19-H$_3$ (s)</td>
<td>20-H$_3$ (s)</td>
</tr>
<tr>
<td>1 b (62–63)</td>
<td>1.00</td>
<td>1.20</td>
<td>1.15</td>
</tr>
<tr>
<td>2 b (glassy)</td>
<td>0.79</td>
<td>1.20</td>
<td>1.65</td>
</tr>
<tr>
<td>5 b (44–45)</td>
<td>0.74</td>
<td>1.17</td>
<td>0.79</td>
</tr>
<tr>
<td>6 b (91–92)</td>
<td>0.41</td>
<td>1.20</td>
<td>1.08</td>
</tr>
<tr>
<td>7 b (108–109)</td>
<td>0.49</td>
<td>1.20</td>
<td>1.15</td>
</tr>
</tbody>
</table>

Fig. 3 Proposed pathways for the disproportionation of dehydroabietic acid (1 a).

References
4) a) D. F. Zinkel, L. C. Zank, and M. F. Wesolowski, “Diterpene Resin Acid”, US-
塩化アルミニウム（無水物）を用いるデヒドロアビエチン酸不均化生成物

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塩化アルミニウム（無水物）触媒を用いるデヒドロアビエチン酸 (1a) の不均化反応により、6 種類の生成物 (2a)～(7a) が得られた。
いくつかの反応条件から得られた結果より、不均化反応の反応経路について検討した。
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