Monosubstitution Derivatives of Cadalene. II *

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In a previous paper\(^1\), one of us has shown that the nitration, Friedel-Crafts-acetylation, and bromination of cadalene lead to products with the substituent in the same position. By degradation reactions it was also shown that the entering substituent most probably occupies the 2-position (I; R = NO\(_2\), CH\(_3\)CO, Br resp.), although the 3-position could not be definitely excluded.

![Chemical structure](image)

After that work had been published, a paper by Campbell and Soffer\(^2\) came to our knowledge, where the synthesis of 2-methylcadalene (I; R = CH\(_3\)) is described. By converting one of the substituting groups NO\(_2\), CH\(_3\)CO or Br into CH\(_3\) it would be possible to procure unequivocal evidence of the 2-position for these substituents.

This has now been done by treating the Grignard-reagent from bromocadalene with ethyl orthoformate and hydrolysing the acetal (I; R = CH(OC\(_2\)H\(_5\))\(_2\)), which was not isolated, to the aldehyde\(^3\) (I; R = CHO). This was reduced by Clemmensen-reduction to methylcadalene (I; R = CH\(_3\)). This compound was an oil, but was characterised as the picrate, the trinitrobenzolate, and the styphnate. These had m. p:s in good agreement with the values given by Campbell and Soffer\(^2\) for the corresponding derivatives of

their 2-methylcadalene. Professor M. D. Soffer was kind enough to carry out mixed melting point determinations on these derivatives, for which we are grateful. He reported the following m. p:s.

<table>
<thead>
<tr>
<th>Derivative</th>
<th>Present authors</th>
<th>Campbell and Soffer</th>
<th>Mixed melting point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Picrotate</td>
<td>140—140.5°</td>
<td>138.5—139°</td>
<td>139.5—140.5°</td>
</tr>
<tr>
<td>Styphnate</td>
<td>170°</td>
<td>170°</td>
<td>170°</td>
</tr>
<tr>
<td>Trinitrobenzolate</td>
<td>167—168°</td>
<td>169—169.5°</td>
<td>167—169.5°</td>
</tr>
</tbody>
</table>

(The m. p:s of the picrate and the trinitrobenzolate are somewhat lower than the m. p:s reported in the experimental part. This is probably due to partial decomposition of the products on standing.)

As no depression of the m. p:s was observed, it seems safe to assume that the parent hydrocarbons were identical.

Briggs, Gill, Lions and Taylor 4 have, in a somewhat different way, also been able to connect the derivatives obtained by direct substitution of cadalene with the synthetic 2-methylcadalene.

The constitution originally assigned to nitro-, acetyl- and bromocadalene and the products obtained from them1 can hence be regarded as correct.

**EXPERIMENTAL**

2-Cadalenealdehyde. The Grignard reagent was prepared with 1.1 g Mg from bromocadalene (13 g) and then ethyl orthoformate (6 g) was added. The ether was distilled off, and the mixture was heated for half an hour on a water-bath. The thick oil obtained was poured into water, a small amount of acetic acid was added, and the acetal extracted with ether. The ether solution was warmed with 2 N hydrochloric acid on a water-bath. The ether was then evaporated and the remaining oil fractionated in a vacuum. The following fractions were obtained:

<table>
<thead>
<tr>
<th>Fraction</th>
<th>boiling point</th>
<th>weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>170°/8 mm</td>
<td>1.1 g</td>
</tr>
<tr>
<td>II</td>
<td>170—180°/8 mm</td>
<td>1.4 g</td>
</tr>
<tr>
<td>III</td>
<td>190—200°/8 mm</td>
<td>3.5 g</td>
</tr>
<tr>
<td>Residue</td>
<td></td>
<td>3.0 g</td>
</tr>
</tbody>
</table>

Fraction III solidified and was recrystallised from light petroleum, m. p. 85.5—86.5°.

C<sub>16</sub>H<sub>18</sub>O (226.2)  
Calc. C 84.88  
Found 85.00

H 8.04  
Found 7.55

The semicarbazone was prepared in the usual way and had after recrystallisation from alcohol m. p. 222—223°.

C<sub>17</sub>H<sub>21</sub>ON<sub>3</sub> (283.2)  
Calc. C 72.06  
Found 71.87

H 7.47  
Found 7.31
2-Methylcadalene. 2-Cadalenealdehyde (3 g) was reduced with amalgamated zinc (10 g) and hydrochloric acid (100 ml; 1 : 1) in the usual way. The reduction product was extracted with ether and steam distilled. 1 g of a colourless oil was obtained. This was without further purification converted into the picrate, stypnate and trinitrobenzolate.

The picrate, red needles from alcohol, had m. p. 143—144°.
The stypnate, orange red needles from alcohol, had m. p. 169—170°.
The trinitrobenzolate, yellow needles from alcohol, had m. p. 170—170.5°.

SUMMARY

The conversion of bromocadalene into 2-methylcadalene is described. The previously proposed structure for bromocadalene, and other derivatives of cadalene is thereby verified.

The analyses were carried out by Mr. K. Salo, University of Helsinki.

REFERENCES


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