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The Preparation of Some Naphthylselen-carboxylic Acids
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In connection with the studies on synthetic plant growth regulators going on at this institute some naphthylsulphide-carboxylic acids have previously been prepared\(^1\) and the plant growth regulating activity has been investigated by Professor B. Åberg at the Royal Agricultural College, Uppsala\(^2\). We have now extended these studies to some naphthylselen-carboxylic acids.

Some phenylselenacetic acids and 1-naphthylselenacetic acid have previously been prepared by reacting the Grignard reagents with selenium and then adding dilute alkali solution and bromoacetic acid\(^4\). As bromobenzene and 1-bromo-naphthalene are readily available this method seems to be convenient for the preparation of phenylselen-carboxylic acids and for 1-naphthylselen-carboxylic acids. For the syntheses of the 2-naphthylselen-carboxylic acids we have tried three methods:

<table>
<thead>
<tr>
<th>Acid</th>
<th>Method</th>
<th>Yield</th>
<th>M.p.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Naphthylselenoacetic</td>
<td>2</td>
<td>50</td>
<td>66—67(^\circ)</td>
</tr>
<tr>
<td>2-Naphthylselenoacetic</td>
<td>1</td>
<td>28</td>
<td>89—90(^\circ)</td>
</tr>
<tr>
<td>2-Naphthylselenoacetic</td>
<td>2</td>
<td>20</td>
<td>89—90(^\circ)</td>
</tr>
<tr>
<td>2-Naphthylselenoacetic</td>
<td>3</td>
<td>75</td>
<td>89—90(^\circ)</td>
</tr>
<tr>
<td>α-(2-Naphthylseleno)-propionic</td>
<td>1</td>
<td>20</td>
<td>118—119(^\circ)</td>
</tr>
<tr>
<td>α-(2-Naphthylseleno)-propionic</td>
<td>2</td>
<td>15</td>
<td>118—119(^\circ)</td>
</tr>
<tr>
<td>α-(2-Naphthylseleno)-propionic</td>
<td>3</td>
<td>77</td>
<td>118—119(^\circ)</td>
</tr>
<tr>
<td>β-(2-Naphthylseleno)-propionic</td>
<td>2</td>
<td>14</td>
<td>105—106(^\circ)</td>
</tr>
</tbody>
</table>

* Morgan and Forrit reported m.p. 54\(^\circ\).

1. Hydrolysis of 2-naphthylselenocyanate\(^5\) and direct reaction with different bromosubstituted acids.
2. Reaction of selenium with the Grignard reagent of 2-iodonaphthalene and further reaction with halogen substituted acids.
3. Reduction with sodiumborohydride of 2,2′-dinaphthylselenide dissolved in a benzene-alcohol mixture followed by reaction with haloesiers.

As can be seen in the table above, method 1 has given a somewhat higher yield (counted on 2-naphthylselenocyanate) than method 2 (counted on 2-iodonaphthalene). However, 2-iodonaphthalene is much easier to prepare than 2-naphthylselenocyanate, and so method 2 is to be preferred. Both in method 1 and 2 some diselenide is formed from which the acids can be obtained in very good yield. If the diselenide is accessible, this method is certainly the best.

Experimental. Method 1. 2-Naphthylselenocyanate was prepared according to Loeve, Frendling and Föhr\(^6\). The naphthylselenocyanate was dissolved in hot alcohol, some glucose and excess of concentrated potassium hydroxide solution were added and the mixture boiled until a homogeneous phase had been obtained. The mixture was cooled and the neutralised bromosubstituted acid was added. After standing in a closed bottle for 12 h warm water was added, the mixture filtered and the solution acidified with hydrochloric acid.
Method 2. 2-Iodonaphthalene was prepared in the usual way. However, the yield and the quality of the product were improved when excess of nitrous acid was removed by potassium permanganate and the diazotized solution filtered before it was treated with potassium iodide.

The Grignard reagent of 0.2 mole 2-iodonaphthalene was prepared in a nitrogen atmosphere using a mixture of dry ether and benzene as solvent. Selenium (0.18 g-atom) was added and the mixture refluxed for 2 h. The flask was then cooled and 200 ml of about 3 M potassium hydroxide was added. A neutralised solution of the bromosubstituted acid was added with vigorous stirring. The stirring was continued for 12 h, the mixture was then treated with hydrochloric acid. The organic phase was extracted with ammonia and the naphthylseleno-carboxylic acid was precipitated with hydrochloric acid. From the ether-benzene phase about 8 g of 2,2'-dinaphthylidiselenide was isolated.

Method 3. The diselenide was dissolved in boiling benzene and alcohol was added until starting turbidity. Sodiumborohydride was added until the solution was almost colourless. After addition of excess of halocester the mixture was refluxed for 2 h, potassium hydroxide solution was added and the alcohol and the benzene were distilled off. The alkaline solution was extracted with ether and then acidified.

All the naphthylseleno-carboxylic acids were recrystallised from carbon tetrachloride and from formic acid. Yield and melting points are given in the table above.

1. Fredga, A. Arkiv Kemi 3 (1951) 123.
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