Studies on the Furan Series. Part IV. Reinvestigation of the Furil-Furilic Acid Rearrangement

SEppo PEnnanen

Department of Chemistry, Helsinki University of Technology, Otaniemi, Finland

Fischer\(^1\) investigated the KOH-induced furil-furilic acid rearrangement and isolated a compound, purportedly furilic acid, in spite of the fact that an elemental analysis could not be performed. Evans et al.\(^2\) have referred to Fischer's results in their own investigations. The rearrangement is also presented in some organic chemistry textbooks as a fact.

The procedure of Fischer\(^1\) was followed in this reinvestigation and the related reactions with MeONa, t-BuOK and Ca(OH)\(_2\) were studied.

The observations by Fischer\(^1\) — that acidification of the alkaline solution with sulphuric acid produced tars, and that evaporation of an ether extract of the acidified solution gave white crystals which later turned brown — were confirmed. When the crystals were methylated by diazomethane and analyzed by TLC one main compound accompanied by traces of another was found. The main compound was identified as methyl 2-furoate by spectral data and by a comparison with an authentic spectrum.

When, on the other hand, the acidification was done by acetic acid, followed by the quick addition of ceric ammonium nitrate,\(^3\) 2,2'-difurylketone (VII) was produced, proving that the rearrangement had taken place. However, the free furilic acid (IV) is so labile that it decarboxylates very rapidly and spontaneously (evolution of CO\(_2\) was observed during acidification) to 2,2'-difurylcarbinol (VI), which forms tar under acidic conditions or in the presence of oxygen.\(^4\)

IV can be trapped as methyl furilate (V), when acidification is done in ether-water mixture with hydrochloric acid under cooling, followed by a quick addition of ethereal CH\(_3\)N\(_2\) [V; b.p. 135—140\(^\circ\)C/7mmHg (decomp.) \(\nu\) 3480, 3140, 2960, 1730, 870 cm\(^{-1}\); \(\tau\) 2.57 (2H m), 3.63—3.65 (4H m), 5.72 (1H br. exch. with D\(_2\)O), 6.15 (3H s)]. The trace compound on the thin layer plate described above after CH\(_3\)N\(_2\) treatment in Fischer's procedure was found to be V.

The isolation of furoic acid (III) from the reaction mixture shows that the furil-furilic acid rearrangement has a competing reaction, which tends to break the bond between the carbonyls in furil (I). The cleavage presumably occurs analogously to the cleavage of 3,3'-benzo[b]furan\(^{15}\) and ought to give III and furfural (VIII). VIII can form tar or, under strongly alkaline reaction conditions, give more III and furfuryl alcohol (IX) \(\text{via}\) a Cannizzaro reaction. However, VIII or IX were not isolated.

---

\(^1\) Fischer
\(^2\) Evans et al.
\(^3\) Acct. Chem. Scand. 26 (1972) No. 3

---

\[ \text{Furan} \xrightarrow{\text{OH or OMe}} \text{Furil} \]

\[ \xrightarrow{\text{CH}_{2}N_{2}} -10^\circ C \]

\[ \xrightarrow{\text{H}^+\text{Ce}[\text{NO}_2]_4} \text{tar} \]
When MeONa, t-BuOK, and Ca(OH)₂ were used, they all, like KOH in Fischer’s procedure, gave the cleavage product (III) besides rearrangement. The strongest base, t-BuOK, gave the smallest yield of VII (Table 1).

<table>
<thead>
<tr>
<th>Base</th>
<th>Yield of VII (%)</th>
<th>Yield of III (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KOH</td>
<td>49</td>
<td>17</td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>48</td>
<td>18</td>
</tr>
<tr>
<td>MeONa</td>
<td>51</td>
<td>23</td>
</tr>
<tr>
<td>t-BuOK</td>
<td>32</td>
<td>22</td>
</tr>
</tbody>
</table>

According to this investigation it seems likely that the compound described by Fischer as furilic acid was the cleavage product furolic acid, containing some decomposing furilic acid as an impurity. However, the rearrangement does take place, and the quite stable furilic acid salt (II) can be decarboxylated-oxidized to VII or trapped as V with CH₃N₂.

Acknowledgements. Thanks are due to Professor J. Grippenberg, and T. Hase, Ph. D., for helpful comments.

2. Evans, T. W. and Dehn, W. M. J. Am. Chem. Soc. 52 (1930) 252.

Received February 22, 1972.

Tobacco Chemistry 12
Neutral Volatile Constituents of Greek Tobacco
BIARNE KIMLAND, ARNE J. AASEN
and CURT R. ENZELL*

Chemical Research Department, Swedish Tobacco Co., S-104 62 Stockholm, Sweden

To enable identification of minor tobacco flavour constituents, we have extracted a large quantity of Greek tobacco and were recently able to report on the preliminary examination of this extremely complex material.¹ One of the fractions, B 2, has been subjected to further study and the results obtained constitute the subject of the present communication. The GC pattern of this fraction is shown in Fig. 1.

Chromatography of fraction B 2 on silver nitrate-impregnated silica gel furnished nine subfractions which were each examined by GC-MS. The majority of the compounds were identified by comparing their mass spectra and, in many cases, retention times with those of authentic material. In all, twenty-eight new constituents of Greek tobacco were encountered and these are listed in Table 1, except for four which are evidently derived from organochlorine insecticide residues.

Of the compounds listed in Table 1 only one, methyl salicylate (10), has previously been detected in tobacco while none has been found in smoke. Moreover, two new diterpenoid constituents were isolated from subfraction 4 by preparative gas chromatography and, as discussed elsewhere,² shown to be 8,13-epoxyylab-14-en-12-one (8) and 8,13β-epoxyylab-14-en-12-one (9). The occurrence of 2,2,6-trimethylcyclohexanone (6) is of interest since it lends support to the previously discussed concept that many tobacco constituents are formed by degradation of terpenoids.³

The presence of fourteen unsaturated long-chain methyl esters was evident from the mass-spectrometric results. However, since positional isomers exhibit identical mass spectra,⁴ definitive structural assignments could not be achieved. None of the less, four of these compounds are in all probability methyl palmitoleate (13), methyl olate (15), methyl linoleate (19), and methyl linolenate (23) since they

Acta Chem. Scand. 26 (1972) No. 3