

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

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Fischer¹ 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.

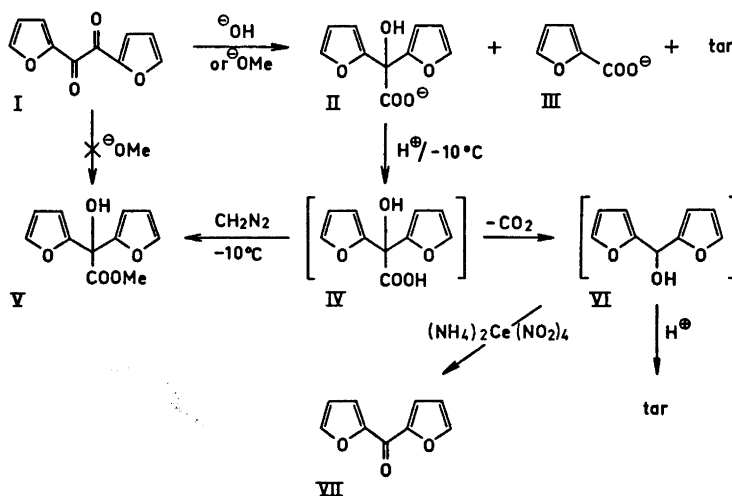
The procedure of Fischer¹ was followed in this reinvestigation and the related reactions with MeONa, *t*-BuOK and Ca(OH)₂ were studied.

The observations by Fischer¹ — 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 CO₂ 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 CH₂N₂ [V: b.p. 135–140°C/7mmHg(decomp.) ν 3480, 3140, 2960, 1730, 870 cm⁻¹; τ 2.57(2H m), 3.63–3.65(4H m), 5.72(1H br. exch. with D₂O), 6.15(3H s)]. The trace compound on the thin layer plate described above after CH₂N₂ 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]thenil⁵ 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) via a Cannizzaro reaction. However, VIII or IX were not isolated.



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 1. The yields of VII and III produced after rearrangement and oxidation.

Base	Yield of VII (%)	Yield of III (%)
KOH	49	17
Ca(OH) ₂	48	18
MeONa	51	23
<i>t</i> -BuOK	32	22

According to this investigation it seems likely that the compound described by Fischer¹ as furilic acid was the cleavage product furoic 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 CH₂N₂.

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Tobacco Chemistry 12 Neutral Volatile Constituents of Greek Tobacco

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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 gel² 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 tobacco³ 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,⁷ shown to be 8,13-epoxylabd-14-en-12-one (8) and 8,13β-epoxylabd-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.¹

The presence of fourteen unsaturated long-chain methyl esters was evident from the mass-spectrometric results. However, since positional isomers exhibit identical mass spectra,⁸ definitive structural assignments could not be achieved. None the less, four of these compounds are in all probability methyl palmitoleate (13), methyl oleate (15), methyl linoleate (19), and methyl linolenate (23) since they