

SHORT COMMUNICATIONS

Studies on Chrysanthemate Derivatives. II.¹⁾ Pyrolysis of Pyrethrin-I

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Five compounds were obtained by the pyrolysis of allethrin.²⁾ In this communication we wish to report a new product obtained by the pyrolysis of pyrethrin-I.

Pyrethrin-I, cinerin-I, and jasmolin-I were advantageously separated from the mixtures extracted from pyrethrum flowers,³⁾ using a special column chromatography on silica gel impregnated with silver nitrate. Pyrolysis of pyrethrin-I was carried out at 400°C as reported previously.²⁾ The reaction products were separated into an acidic and a neutral fraction by alkaline extraction.

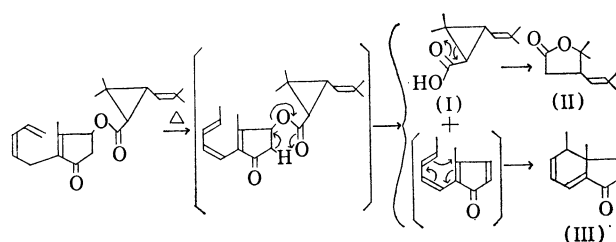
The acidic fraction gave chrysanthemic acid (I) as the only product.

The neutral fraction consisted of pyrocin (II) and a new compound (III) separated by column chromatography on silica gel. Compound III revealed the following spectral data; m/e 160 (M^+) and 145 ($M-15$); IR, $\nu_{\max}$ cm^{-1} : 1680 and 1640; UV, $\lambda_{\max}^{\text{EtOH}}$ $m\mu$ ($\log \epsilon$): 230 (3.50) and 319 (3.64); NMR,⁴⁾ a doublet methyl at 9.39 (3H; $J=7.1$ Hz), a singlet methyl at 8.87 (3H), a multiplet proton on a tertiary carbon at 7.73 (1H), and five olefinic protons at 3.70–3.90 (m, 3H), 3.41 (ddd, 1H; $J=1.0, 2.1$, and 5.0 Hz), and 2.55 (dd, 1H; $J=1.0$ and 6.0 Hz). Heating compound III with concentrated hydrochloric acid afforded a white crystalline substance, mp 84–86°C, which was designated as 4,5-dimethyl-1-indanone (IV) on the basis of the following mass, IR, UV, and NMR spectral data and by comparison with those of the independent synthetic

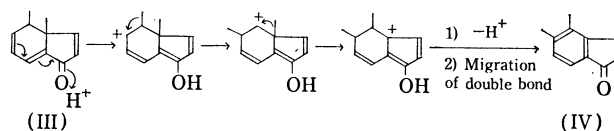
product prepared from *o*-xylene using the method of Hart and Teble;⁵⁾ m/e 160 (M^+), 145 ($M-15$), and 132 ($M-28$); IR, $\nu_{\max}$ cm^{-1} : 1709 and 818 (1,2,3,4-tetrasubstituted phenyl); UV, $\lambda_{\max}^{\text{EtOH}}$ $m\mu$ ($\log \epsilon$): 258 (4.19) and 292 (3.46); NMR,⁶⁾ two singlet methyls at 7.80 (3H) and 7.67 (3H), two multiplet methylenes at 7.48 (2H) and 7.09 (2H), and two aromatic protons centered at 2.95 (d, 1H; $J=4.0$ Hz) and 2.65 (d, 1H; $J=4.0$ Hz).

From these results compound III is presumed to be 4,5-dimethyl-bicyclo[4.3.0]nona-2,6,8-triene.

We propose that the reaction mechanisms for the pyrolysis of pyrethrin-I and for the acid catalyzed rearrangement of compound III to compound IV take place as shown in Scheme 1 and 2, respectively.



Scheme 1



Scheme 2

1) The previous paper²⁾ is regarded as Part I of this series.

2) Y. Nakada, Y. Yura, and K. Murayama, *This Bulletin*, **44**, 1724 (1971).

3) R. M. Sawicki and E. M. Thain, *J. Sci. Food Agr.*, **12**, 137 (1961).

4) NMR spectra were determined at 60 MHz in CCl_4 and chemical shift is expressed in τ from internal TMS.

5) R. T. Hart and R. F. Teble, *J. Amer. Chem. Soc.*, **72**, 3286 (1950).

6) NMR spectra were determined at 100 MHz in CCl_4 .