Pyrolysis of Allethrin

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Pyrolyses of pyrethroidal compounds have been described by Murayama *et al.*,[1,2] but no work has been done in isolation and structure. We have obtained five compounds by pyrolysis of allethrin, the structures of which are reported in this communication.

Pyrolysis of allethrin was carried out in a pyrex glass tube at 400°C under nitrogen. A typical gas chromatograph of the reaction products is shown in Fig. 1. The reaction products were separated into two fractions and a residue by distillation.

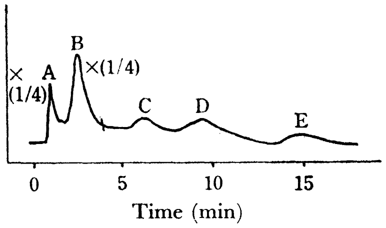


Fig. 1. Gas chromatograph of reaction products. Column: 15%-Silicone XE-60, 191°C.

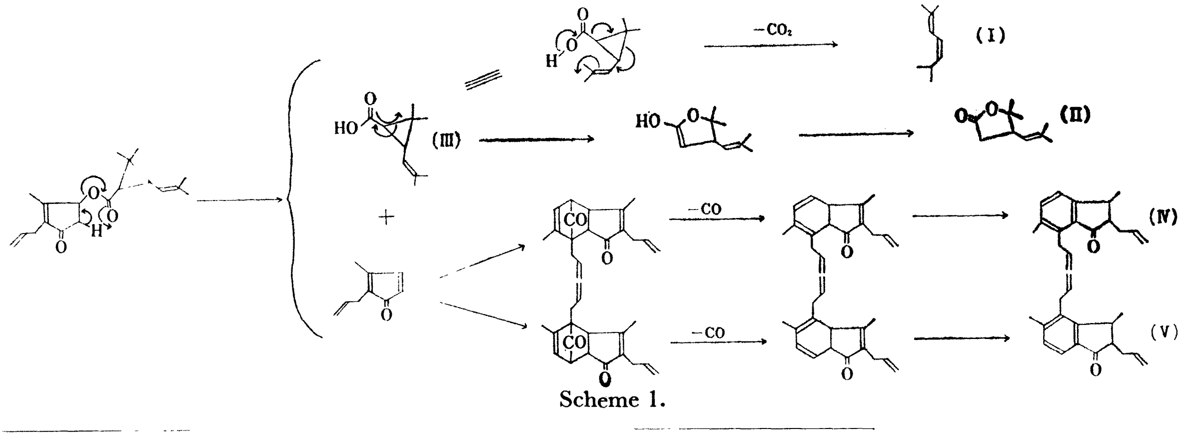
The first fraction, bp 50—60/38 mmHg, corresponding to peak A, mainly consisted of one compound purified by preparative gas chromatography. Identification of this compound (I) as 2,6-dimethylhepta-2, 4-diene was based on the following; m/e 124 (M^+) and 109 (M-15); IR, ν_{max} cm^{-1}: 2910; UV, λ_{max}^{EtOH} mμ (log ε): 238 (3.56); NMR[3]: four methyls at 9.07 (d, 3H), 8.95 (d, 3H), 8.28 (s, 3H), and 8.22 (s, 3H), a proton at 7.70 (m, 1H) and olefinic protons at 4.0—4.9 (m, 3H).

The second fraction, bp 90—120/6 mmHg, peak B, consisting of two compounds, II and III, was identified as pyrocin[4] and crysanthemic acid respectively by comparison with authentic samples.

The distillation residue, with peaks C, D, and E in Fig. 1, was separated into three compounds IV, V, and VI by column chromatography on silica gel. Identification of compound IV, corresponding to peak C, as 2,7-diallyl-3,6-dimethyl-1-indanone was based on the following; m/e 240 (M^+), 225 (M-15), and 199 (M-41); IR, ν_{max} cm^{-1}: 1710 and 821 (1,2,3,4-tetra-substituted phenyl); UV, λ_{max}^{EtOH} mμ (log ε): 252 (4.11) and 315 (3.44); NMR[5]: a doublet methyl at 8.64 (3H, J=3.5 Hz), a singlet methyl at 7.70 (3H), an allylic methylene as a doublet at 6.56 (2H, J=3.2 Hz), two multiplet vinyl singals at 4.8—5.2 (4H) and 4.0—4.4 (2H), and two doublet protons centered at 2.88 (1H, J=4.0 Hz) and 2.76 (1H, J=4.0 Hz) corresponding to the aromatic protons.

The mass, IR, UV, and NMR spectral data of compound V were very similar to those of compound IV; m/e 240 (M^+), 225, and 199; IR, ν_{max} cm^{-1}: 1718 and 830; UV, λ_{max}^{EtOH} mμ (log ε): 262 (4.15) and 293 (3.49); NMR[5]: 8.71 (d, 3H; J=3.7 Hz), 7.67 (s, 2H), 6.55 (dd, 2H; J=2.3 and 1.0 Hz), 4.8—5.3 (m, 4H), 2.88 (d, 1H; J=4.0 Hz) and 2.59 (d, 1H; J=4.0 Hz). An aromatic proton of compound V was found at a lower field than that of compound IV. Thus we concluded that compound V was 2,4-diallyl-3,5-dimethyl-1-indanone, an isomer of compound IV. Compound VI was identified as allethrin by comparison with the retention time (*glc*) and IR spectrum of an authentic sample.

We postulate the reaction mechanism for the pyrolysis of allethrin as shown in Scheme 1.



Scheme 1.

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1) H. Murayama, K. Kyogoku, T. Iguchi, and H. Yamaguchi, *J. Agr. Chem. Soc. Jap.*, **44**, 532 (1970).

2) N. C. Brown, D. Hollinshead, R. F. Phipers, and M. C. Wood, *Pyrethrum Post*, **4**, 13 (1957).

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

4) L. Crombie and S. H. Harper, *J. Chem. Soc.*, **1954**, 470.

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