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THE FLASH PYROLYSIS OF D-CAMPHOR

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Abstract—D-Camphor was pyrolysed at 800° for 0·2 sec under high dilution (partial press. of 3×10^{-3} mm Hg) and the structures of the main decomposition products determined.

PYROLYSIS has been used for many years as a technique for the structure determination of organic compounds. Usually, however, the reaction is complicated and is accompanied by extensive polymerization.

Recently a technique of pyrolysis combined with gas chromatography has been developed.[1] This has proved to be useful for the identification of organic substances, particularly those that are non-volatile or poorly-volatile, but little attempt has been made to correlate the structures of the fragments to the original compound structures.

In this study the pyrolysis was carried out in the vapour phase under high dilution and for a very short time, in order to minimize the chance of polymerization of the primarily created active intermediates. The sample was vapourized at 200–250° under a flow of purified nitrogen and the mixture of gases was passed through a hot quartz tube. The pyrolysis was carried out at 750–850° for 0·1–0·2 sec under the partial pressure of the sample of $2\text{–}3 \times 10^{-3}$ mm Hg. Under these conditions diterpene alkaloid delcosine, methyl O-methylpodocarpate, squalane, squalene, methyl oleate, D-borneol and D-camphor were decomposed without any appreciable amount of tarry by-products. The present paper describes the structure determinations of the main fragments obtained from D-camphor (I).

D-Camphor was pyrolysed at 800° for about 0·2 sec under the partial pressure of 3×10^{-3} mm Hg and the pyrolysates were trapped in liquid nitrogen. A pale yellow oil was obtained and this was separated by gas chromatography. The chromatogram is shown in Fig. 1.

Mol. wt. of the fractions A and B were both found to be 152 from their mass spectra.[2] The IR spectrum of the fraction A showed the presence of α,β-unsaturated carbonyl (1676 cm^{-1}), isopropyl (1391 and 1378 cm^{-1}) and terminal methylene (905 cm^{-1}) groups. Furthermore, this fraction exhibited conjugated carbonyl absorption in the UV (λ_{max} 236 and 310 mμ, log ε 3·92 and 1·99, respectively) and was consequently formulated as II. The fraction B was found to be an unconjugated ketone with terminal methylene group, from its UV spectrum (λ_{max} 280 mμ, log ε 1·70) and IR spectrum (1712, 1645 and 898 cm^{-1}) and dihydrocarvone (III) was proposed for this fraction. The fraction C was identified as the original camphor from its m.p.

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[1] For review, S. G. Perry, *J. Gas Chromat.* 54 (1964).

[2] The mass spectra were kindly measured by Dr. N. Wasada with a CEC 21-103C mass spectrometer at the Govern. Chem. Ind. Research Inst. Tokyo.

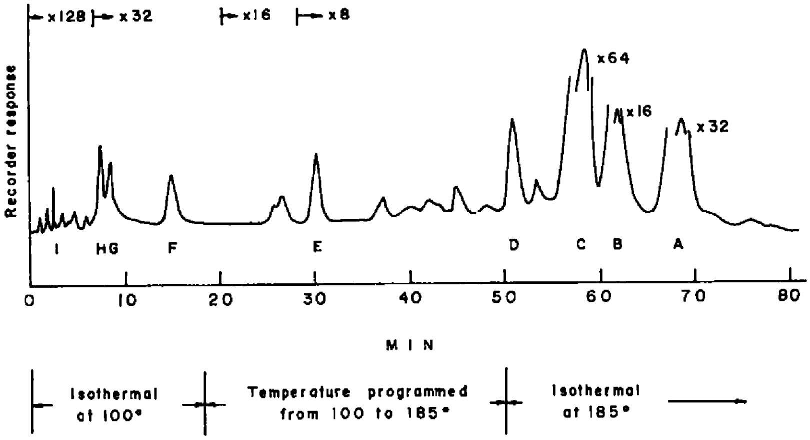
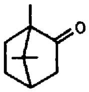
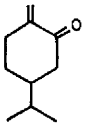


FIG. 1.

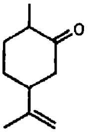
mixed m.p. and IR spectrum. The mass spectrum of the fraction D showed a mol. wt. 108, corresponding to a cresol. From the IR spectrum it was shown to be *o*-cresol.



I

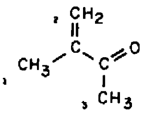


II



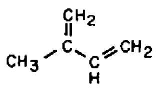
III

The fractions E, F and H were found to be styrene, toluene and benzene, respectively, by comparison of their IR, UV spectra and retention times on gas chromatography with those of the authentic samples. The mass spectrum of the fraction G showed a mol. wt. 84. It was found to be methyl isopropenyl ketone (IV) from its NMR spectrum,[3] in which three protons on C-1 methyl appeared at δ1·82 (quartet, $J \sim 1$ c/s), three protons on C-3 methyl at δ2·26 (singlet) and two protons on C-2 methylene at δ5·68 (multiplet, $J \sim 1$ c/s) and δ5·86 (multiplet, $J \sim 1$ c/s). The α,β-unsaturated



$CH_2{=}C(CH_3){-}C({=}O){-}CH_3$

IV



$CH_2{=}C(CH_3){-}CH{=}CH_2$

V

ketone grouping was verified also from its UV spectrum (λ_{max} 220 and 316 $m\mu$, log ε 3·95 and 1·49, respectively)(4,5) and IR spectrum (1682, 1630 and 930 cm^{-1}).(5,6) The fraction I proved to be isoprene (V) from its UV and IR spectra.

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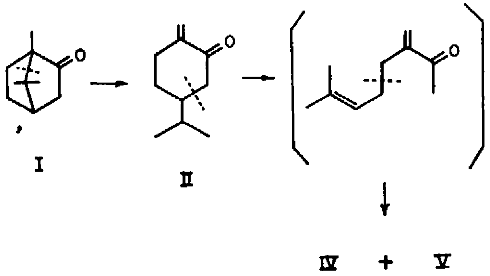
[3] The NMR spectrum was measured in CCl_4 solution on a Varian HR-100 spectrometer. The author is indebted to Dr. H. Yamazaki for the measurement. Chemical shifts are described in ppm downfield from an internal tetramethylsilane reference.

[4] L. K. Evans and A. E. Gillam, *J. Chem. Soc.* 815 (1941).

[5] R. L. Erskine and E. S. Waight, *J. Chem. Soc.* 3425 (1960).

[6] W. H. T. Davison and G. R. Bates, *J. Chem. Soc.* 2607 (1953).

The formations of methyl isopropenyl ketone (IV) and isoprene (V) may be represented schematically as shown below.



The fragmentation processes for more complicated substances by flash pyrolysis are now under study.

EXPERIMENTAL

Pyrolysis. The apparatus for the pyrolysis consisted of a vapourizer of a sample, a pyrolyser and a trap. The vapourizer was a 18 mm i.d. × 25 cm Pyrex tube, half of which was wrapped with heating tape and heated at 250°. The pyrolyser was a 10 mm i.d. × 10 cm quartz tube which stayed in a tubular electric furnace 8 cm in length. The trap was a U-shaped glass tube packed with small pieces of glass in order to minimize the loss during trapping. One gram of D-camphor was evenly put in an aluminium boat 12 cm in length which stayed in the unheated portion of the vapourizer and O_2-free N_2 (passed through a hot column packed with Cu) was introduced from the cold end of the vapourizer at the rate of 460 ml/min. The flow was regulated by a flowmeter. The boat was pushed into the heated portion of the vapourizer in 2 hr. The mixture of the vapourized camphor and carrier gas was directly introduced into the pyrolyser. The temp of the pyrolyser was determined by a thermocouple inserted into the quartz tube. The position of the tip of the thermocouple was adjusted so that it gave the maximum temp and the temp was kept at 800° during the pyrolysis. The mixture gas which left the pyrolyser was immediately cooled by water and passed through the U-shaped trap cooled by liquid N_2. When the trap was warmed to the room temp, a pale yellow oil condensed at the bottom. This was taken out by means of a long pipette and injected into a gas chromatograph.

Gas chromatography. Gas chromatography was carried out on a Shimadzu GC-1B gas chromatograph, equipped with a thermistor detector. The column was a 10 mm i.d. × 3·75 m stainless steel tube packed with Silicone DC 550 absorbed on Shimalite B (60–80 mesh) and was operated isothermally at 100° at the start with H_2 (300 ml/min) as carrier gas. After 18 min, the temp was increased at the rate of 2·65°/min up to 185° and then it was kept constant at this temp until all the materials were eluted. The collection of each fraction was done by attaching a small U-shaped tube, the lower part of which was cooled by liquid N_2, to the heated exit of the gas chromatograph. Each fraction was separately gas chromatographed again in order to secure the purity.

Spectra. IR spectra were measured in CCl_4 and/or CS_2 solution on a Koken DS-301 spectrometer. UV spectra were determined in MeOH on a Shimadzu RS-27 spectrometer.

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