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PYROLYSIS AND PHOTOLYSIS OF CAMPHOR OXIME*

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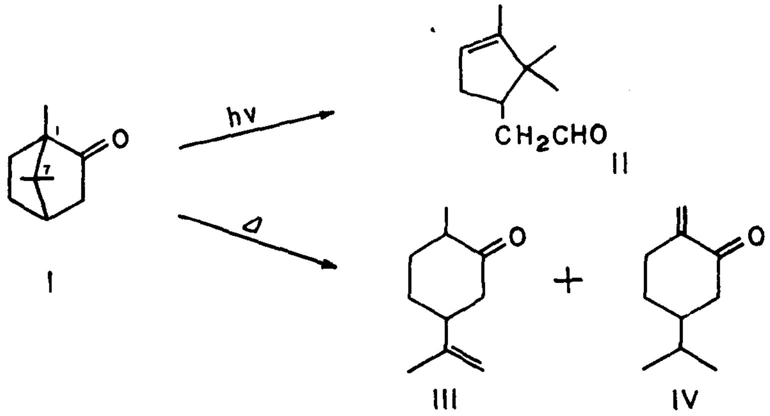
It has been reported that the photolysis of camphor (I) affords α-campholenic aldehyde (II).(1,2) Recently, pyrolysis of camphor was carried out in our laboratory and III, IV and smaller fragments were identified as the products.(3,4) Such a difference between pyrolysis and photolysis could be explained by assuming that the pyrolysis is initiated by C_1-C_7 bond cleavage, while the photolysis is initiated by the excitation of carbonyl group.



In order to investigate the relation between pyrolysis and photolysis, both reactions were carried out on camphor oxime (V). Camphor oxime was kept at 240° for 6-7 min and distilled under a reduced pressure. The distillate (70 per cent wt of camphor oxime) afforded three fractions on gas chromatographic separation (Silicone DC 550 at 180°), the relative amounts(5) being about 1 : 3.8 : 4.4 (in retention time sequence). The first fraction was identified as camphor. The second fraction was found to be VI from the following properties.(6)

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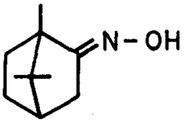
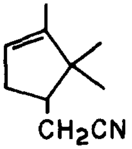
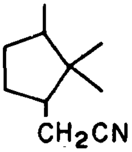
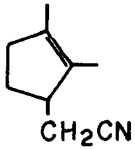
* Part III of a series on the pyrolysis of organic compounds. Part II: Ref. 4.

Mol wt**: 149.1192, calcd for $C_{10}H_{15}N$: 149.1204; IR: 2240 cm^{-1} for CN, 1650 cm^{-1} for C=C, 1392 and 1372 cm^{-1} for $C(CH_3)_2$; NMR: δ 0.85 (3H, singlet) and 1.08 (3H, singlet) for $C(C\underline{H}_3)_2$, δ 1.62 (3H, doublet, J=2 c/s) for $=C-C\underline{H}_3$, δ 2.25 (2H, doublet, J=3 c/s) for $-C\underline{H}_2-CN$, δ 5.22 (1H, multiplet) for $=C\underline{H}-$ and δ 1.7-2.5 (3H, multiplet) for the rest of protons. The third fraction was found to be α-campholanonitrile (VII) by comparing its retention time on the gas chromatogram, IR and NMR spectra with those of the authentic sample.(7)


V


VI


VII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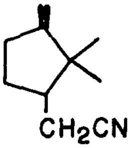
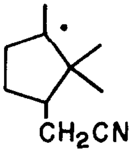

IX


X

When pyrolysis was carried out in the vapor phase at 500° for 1 sec,(8) the principal product was found to be 1,2-dimethyl-3-cyanomethylcyclopentene (VIII) from the following properties. Mol wt***: 135, calcd for $C_9H_{13}N$: 135; IR: 2230 cm^{-1} for CN, 1375 cm^{-1} for CH_3; NMR: δ 1.64 (6H, singlet) for $C\underline{H}_3-C=C-C\underline{H}_3$, δ 2.30 (2H, triplet, J=4 c/s) for $=C-C\underline{H}_2-$, δ 2.34 (2H, doublet, J=4 c/s) for $-C\underline{H}_2-CN$ and complex pattern at δ 1.8-2.7 for the rest of protons.

Photolysis of camphor oxime was carried out in methanol with 100-watt quartz high pressure mercury lamp (Riko, UVL-100P) for 6 hr. The reaction mixture afforded five fractions on gas chromatographic separation (Silicone DC 550 in glass column at 170°),(9) the relative amounts(5) being about 1 : 7.1 : 4.3 : 4.9 : 33 (in retention time sequence). The first fraction was identified as camphor. The second and fourth fractions were found to be VI and VII, respectively, from their spectroscopic behaviors. The third fraction was found to be iso-α-campholenonitrile (IX) from the following properties. Mol wt**:

** Determined on a CEC 21-110B high resolution mass spectrometer.
*** Determined on a CEC 21-103C low resolution mass spectrometer.

149.1217, calcd for $C_{10}H_{15}N$: 149.1204; IR: 2240 cm^{-1} for CN, 1650 and 890 cm^{-1} for $C{=}CH_2$, 1395 and 1373 cm^{-1} for $C(CH_3)_2$; NMR: δ 0.90 (3H, singlet) and 1.12 (3H, singlet) for $C(C\underline{H}_3)_2$, δ 4.75 (2H, distorted triplet, J=1 c/s) for $C{=}CH_2$ and complex pattern at δ 1.3-2.5 for the rest of protons. The fifth fraction was identified as the starting camphor oxime.

Recently, Taylor, Douek and Just(10) reported that the photolysis of some ketoximes gave Beckmann type rearrangement products, cleavage products (amides) and ketones corresponding to the starting material. It is noteworthy that the photolysis of camphor oxime takes a different course from that with other ketoximes. The photolysis products, in case of camphor oxime, are much related to the pyrolysis products, and a radical X seems to be a common intermediate for the pyrolysis and photolysis, which leads to VI and IX by losing H·, to VIII by losing CH_3·, and to VII by abstracting H· from the surroundings. A similar intermediate has been proposed in the photolysis of isobornyl nitrite.(2)

It is of interest to note that the pyrolysis of camphor oxime is apparently analogous to the photolysis, rather than to the pyrolysis, of camphor. These results led us to propose that the pyrolysis of camphor oxime produces >C=N· by an initial N-O bond cleavage, and this radical, which may be comparable to the excited carbonyl group in the irradiated camphor, would initiate the pyrolytic reaction of camphor oxime in a similar fashion as the photolytic reaction of camphor.

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REFERENCES

1. G. Ciamician and P. Silber, Ber., 43, 1340 (1910).
2. M. Nakazaki and K. Naemura, Bull. Chem. Soc. Japan. 37. 532 (1964).
3. T. Sato, Tetrahedron, 21, 2947 (1965).
4. T. Sato, K. Murata, A. Nishimura, T. Tsuchiya and N. Wasada, Tetrahedron, to be published in No. 2 (1967).

5. The relative areas under each peak on the gas chromatogram.
6. IR and NMR spectra were measured in CCl_4 solution. NMR spectra were measured on a Hitachi H-60 spectrometer. Chemical shifts are described in ppm downfield from an internal TMS reference.
7. F. Mahla and F. Tiemann, Ber., **33**, 1929 (1900).
8. For experimental: Ref. 3.
9. Under these gas chromatographic conditions camphor oxime was found to be intact.
10. R. T. Taylor, M. Douek and G. Just, Tetrahedron Letters, **No. 34**, 4143 (1966).