but the reaction apparently proceeds in at least two stages such as

$$2HCN + H_2O_2 \longrightarrow (CN)_2 + 2H_2O$$
$$(CN)_2 + 2H_2O_2 \longrightarrow (CONH_2)_2 + O_2$$

or, over-all

$$2HCN + 3H_2O_2 \longrightarrow (CONH_2)_2 + 2H_2O + O_2$$

McMaster and Langreck[4] and Radziszewski[2] prepared several amides by the reaction

$$RCN + 2H_2O_2 \longrightarrow RCONH_2 + H_2O + O_2$$

and Wiberg[5] studied the preparation of benzamide from benzonitrile by this reaction. A brief study was made of the reaction of hydrogen cyanide with hydrogen peroxide in an exploration of methods for the preparation of oxamide.

Mixtures of aqueous solutions of hydrogen cyanide and hydrogen peroxide stand quietly with no apparent reaction for an induction period that decreases as the temperature of the cooling bath is raised. The mixtures then begin to effervesce, oxamide crystallizes, and the exothermic reaction becomes quite vigorous unless the mixture is cooled. The effect of the temperature of the cooling bath on the reaction is shown in Table I.

TABLE I

REACTION OF HYDROGEN CYANIDE WITH HYDROGEN PEROXIDE IN AQUEOUS SOLUTION[a]

Temp., °C		Time, min.		% of HCN converted to $(CONH_2)_2$
Bath	Max.	Induction	Reaction	
0	3	205	140	48.5
15	27	68	24	42.9
23	43	40	10	35.3
35	75	15	2	7.5

[a] Charge, moles: HCN 0.1253, H_2O_2 0.4944, H_2O 4.44.

In the runs reported in Table I, the mole ratio H_2O_2:HCN in the charge was 3.95. In tests at 0°, variation in this ratio from 1.65 to 4.70 made no significant difference in the fraction of hydrogen cyanide converted to oxamide (45 to 47%) or in the consumption of hydrogen peroxide, which ranged from 4.0 to 4.9 moles/mole of oxamide produced. Dilution of the reaction mixture with water increased the induction period and decreased the yield slightly.

The spent reaction mixtures contained hydrogen peroxide, but no hydrogen cyanide. The gases evolved during the reaction contained ammonia and carbon dioxide, indicating this side reaction.

$$HCN + H_2O_2 = CO_2 + NH_3$$

The oxamide was a homogeneous, white, crystalline product with the optical properties and powder X-ray pattern of the usual triclinic modification.[6]

Addition of the miscible organic solvents ethanol, methanol, dioxane, tetrahydrofuran, and acetone to the aqueous reaction mixture had no significant effect on the reaction, but N,N-dimethylacetamide both increased the induction period and decreased the yield of oxamide. Addition to the aqueous reaction mixture of small amounts of either sulfuric acid or potassium hydroxide decreased the yield of oxamide but had no effect on either the induction period or the rate of the reaction. Masson[7] reported that oxamide is not formed by the reaction of hydrogen peroxide with potassium cyanide.

When the reaction was carried out at 0° in nonaqueous solvents (ethyl acetate, amyl acetate, or isobutyl alcohol) the results were about the same as those obtained in aqueous solution: from 43.5 to 47.2% of the hydrogen cyanide was converted to oxamide, and 4.8 to 5.4 moles of hydrogen peroxide mole/of oxamide were consumed. The oxamide, however, appeared in a different crystal form which on recrystallization from water yielded the usual triclinic modification.[8]

Experimental

Stock solutions (usually about 10% HCN) were prepared from liquid hydrogen cyanide and chilled solvents. Aqueous hydrogen peroxide solutions were prepared by diluting reagent grade (30%) solutions; solutions of hydrogen peroxide in water-immiscible organic solvents were prepared by shaking mixtures of the solvents with 30% aqueous solutions of hydrogen peroxide and separating and discarding the aqueous phases. These solutions were then dried with anhydrous sodium sulfate and filtered.

Hydrogen cyanide in the stock solutions and spent reaction mixtures was determined by titration with silver nitrate, and hydrogen peroxide was determined by titration with potassium permanganate.

In each test of the reaction, the hydrogen cyanide and hydrogen peroxide solutions were mixed at the bath temperature in 250-ml. wide-necked volumetric flasks. The mixtures were allowed to stand in the cooling bath, with occasional swirling, until the reaction appeared to be complete; they were then filtered and the filtrates were analyzed for hydrogen cyanide and hydrogen peroxide. The precipitated oxamide was washed with small portions of ice–water, rinsed with acetone, dried at 105°, and examined by X-ray analysis.[6]

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The Structure of the Dehydration Product, $C_{10}H_{14}O$, of 2-Hydroxyisopinocamphone[1]

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On dehydrating 2-hydroxyisopinocamphone[2] (1) with anhydrous oxalic acid, Kuwata[3] isolated a terpene ketone (b.p. 205–210°, n^{25}_D 1.5034, d^{25}_4 0.9450) along with the major product, carvacrol, and proposed it to be *p*-mentha-4(8),6-dien-2-one (2). The assignment of structure **2** was based on elementary analyses and nonidentity of the oxime, m.p. 103–104.5°, and semicarbazone, m.p. 183–184°, derivatives with derivatives in the literature. "Isocarvoxime" (3), m.p. 143–144°, the oxime derivative of 2, has been synthesized from

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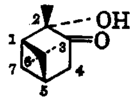
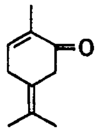
[1] Supported in part by a grant from the Ministry of Education in Japan.

[2] The spatial arrangement of the hydroxyl group at C-2 has been clarified recently by H. Schmidt [*Chem. Ber.*, **93**, 2485 (1960)].

[3] T. Kuwata, *J. Soc. Chem. Ind. Japan*, **40**, 24 (1937); *Chem. Abstr.*, **31**, 3899^4 (1937).



1



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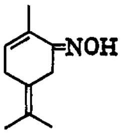

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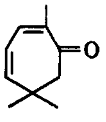

4

carvone[4,5] and clearly is not identical with the oxime derivative of the terpene ketone considered to be 2 by Kuwata.

We have now repeated the dehydration of 1 with anhydrous oxalic acid in accordance with Kuwata's report[3] and have obtained, in 9.8% yield, a terpene ketone, $C_{10}H_{14}O$, whose properties are identical with those reported by Kuwata. An examination of the infrared, ultraviolet, and n.m.r. spectra of the $C_{10}H_{14}O$ ketone demonstrated its identity with eucarvone (4). This identity was further confirmed by the coincidence in melting points of the oxime, semicarbazone, and 2,4-dinitrophenylhydrazone derivatives with those reported for the derivatives of eucarvone (4). The conversion of a pinane derivative to eucarvone by an organic acid is unique.

Experimental

All melting points reported are uncorrected.

(−)-2-Hydroxyisopinocamphone (1).—This compound was prepared from (+)-α-pinene (b.p. 156.7°, $[\alpha]^{25}_D$ 32.72°) by oxidation with potassium permanganate at 0–5° following the method reported.[2,6] The crude compound thus obtained was purified by distillation: b.p. 96.5–96.7° (5 mm.), m.p. 34–35°, $[\alpha]^{25}_D$ −23.26° (*c* 1, ethanol); lit.[3,6] m.p. 35.5–36.5°, $[\alpha]_D$ −18.65° (*c* 1.4, ethanol).

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 69.73; H, 9.37. Found: C, 70.39; H, 9.45.

Preparation of Dehydration Product, $C_{10}H_{14}O$.—A mixture of 1 (200 g.), acetone (266 ml.), and anhydrous oxalic acid (333 g., m.p. 187–189°) was heated under reflux for 6 hr. After acetone was distilled off *in vacuo*, the residue was poured into a large amount of a saturated sodium chloride solution and then extracted with petroleum ether. The petroleum ether solution, after removing carvacrol (82.8 g., b.p. 111.5–112° at 9 mm., identified by infrared spectrum comparison) by washing with 5% potassium hydroxide solution, gave a neutral reaction mixture (98.9 g.). The distillation of the neutral reaction mixture yielded 19.6 g. (9.8% based on 1 taken) of a fraction boiling at 82–84° (10 mm.) and showing the following physical constants: b.p. 205–208°, n^{25}_D 1.5055, d^{25}_4 0.9445.

Structural Confirmation of Dehydration Product.—The further rectification of the fraction boiling at 82–84° (10 mm.) gave a main fraction showing b.p. 84.2° (10.5 mm.), n^{25}_D 1.5050, d^{25}_4 0.9455, and λ^{EtOH}_{max} 303 mμ (log ε 3.81); lit. for eucarvone (4): b.p. 85–87° (12 mm.),[7] $n^{24.8}_D$ 1.5051,[8] d^{20}_4 0.948,[9] λ^{EtOH}_{max} 303 mμ (log ε 3.83).[8] Gas-phase and chromatostrip[10] chromatography indicated this oil to be homogeneous.

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.53; H, 9.22.

The infrared spectrum (neat film) exhibited bands at 1665 (conjugated C=O), 1643, 1601 (C=C), 1425 (—CH₂—CO—), 1390 and 1368 (—CMe₂), 826 (>C=CH—), and 727 (*cis* —CH=CH—) cm.⁻¹. The n.m.r. spectrum (neat, 40 Mc.) showed peaks at τ 8.94 (—CMe₂, relative intensity 6), 8.11 (CH₃—C=C—, 3), and 7.36 (—CH₂—CO—, 2).

The oil gave the following crystalline derivatives, the melting points of which coincided well with those reported for eucarvone (4).

Oxime, m.p. 105–106.5°, λ^{EtOH}_{max} 291 mμ (log ε 4.03), lit.[11] m.p. 106°.

Anal. Calcd. for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.77; H, 8.98; N, 8.38.

Semicarbazone, m.p. 185–186°, λ^{EtOH}_{max} 310 mμ (log ε 4.29); lit.[12] m.p. 186–186.5°, λ^{EtOH}_{max} 309 mμ (log ε 4.22).

Anal. Calcd. for $C_{11}H_{17}N_3O$: C, 63.74; H, 8.27. Found: C, 63.42; H, 8.01.

2,4-Dinitrophenylhydrazone, m.p. 151–152°, λ^{EtOH}_{max} 384 mμ (log ε 4.68); lit.[13] m.p. 151–152°, $\lambda^{CHCl_3}_{max}$ 388 mμ (log ε 4.44).

Anal. Calcd. for $C_{16}H_{18}N_4O_4$: N, 16.87. Found: N, 17.12.

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