an hour, was allowed for thermal equilibrium to be established between the tube and the surrounding glass jacket and magnet, otherwise drift in weight of a few hundredths of a milligram occurred during the measurement. Measments were made usually with currents of 6.00, 8.00 and 10.0 amp. In some of the later measurements where the presence of ferromagnetic impurities was suspected measurements were made at 1.00-amp. intervals Following a series of measurements, a small reverse current was passed through the magnet to remove the residual field and a check made on the initial weight of the tube

Measurements with Tube A.—The tube was calibrated with water and with ferrous ammonium sulfate. The density reported is the effective or bed density. Two measurements were made on vitamin B_{12}, the tube being repacked for the second measurement.

Change in weight of material, mg.

Current, amp.	Water (wt. 0.6920 g., *d* 1.00)	B_{12} (0.4570 g., *d* 0.660)	B_{12} (0.754 g., *d* 0.688)	Ferrous ammonium sulfate (0.7119 g., *d* 103)
1	−0.51		+0.05	+ 2.73
2	− .44		+ .20	+10.61
3	− .65		+ .31	
4	− .95		+ .36	+35.96
5	−1.16		+ .37	
6	−1.51	+0.57	+ .37	+56.33
7	....		+ .37	
8	−1.76	+0.55	+ .36	+71.18
9	−1.85		+ .36	
10	−1.90	+0.53	+ .35	+83.06

The observed changes in weight of water and of ferrous ammonium sulfate were more or less linear with the changing current. On the other hand only a small increase in weight (paramagnetic effect) was found for B_{12} for currents up to 6 amp. and at higher currents no increase at all; such behavior is characteristic of a diamagnetic material containing a ferromagnetic impurity. Even by taking the maximum increase in weight of B_{12}, the paramagnetic susceptibility calculates out (on the second measurement) to be a very small value: $\chi = +0.247 \times 10^{-6}$ using water as reference ($\chi = -0.720 \times 10^{-6}$), and corrected for the effect of air in the lower part of tube using $k = +0.029 \times 10^{-6}$, and $+0.246 \times 10^{-6}$ using ferrous ammonium sulfate as reference ($\chi = +31.7 \times 10^{-6}$). Assuming the molecular weight of B_{12} to be 1500, this gives a molar susceptibility of $+370 \times 10^{-6}$ and a magnetic moment of 1.18; the latter value is far below the moment expected for one unpaired electron ($\mu = 1.73$). It is therefore apparent that B_{12} is diamagnetic.

Measurements with Tube B.—The tube was calibrated with water and as a check a measurement was made on bi-(disalicylalethylenediimine)-μ-aquo-dicobalt, the molar susceptibility of which has been reported[5] as $\chi_M = +3160 \times 10^{-6}$.

Change in weight of material, mg.

Current, amp.	Water (Wt. 1.701 g., *d* 1.00)	B_{12} (1.191 g., *d* 0.700)	Bi-(disalicylalethylenediimine)-μ-aquo-dicobalt (0.7429 g., *d* 0.437)
1	−0.20	+0.49	+ 1.89
2	−0.79	+1.23	+ 7.37
3	−1.84	+1.82	+15.64
4	−3.01	+2.19	+25.34
5	−3.98	+2.37	+34.59
6	−4.81	+2.49	+40.04
7	−5.53	+2.49	+45.86
8	−6.15	+2.49	+51.82
9	−6.70	+2.49	+55.28
10	−7.21	+2.49	+59.36

As in tube A vitamin B_{12} exhibited a very small paramagnetic effect varying with the field strength ($\chi = +0.415 \times 10^{-6}$, $\chi_M = +623 \times 10^{-6}$ and $\mu = 1.22$ using the maximum change in weight and reference at 10 amp. and water as reference, and $\chi = +0.283 \times 10^{-6}$, $\chi_M = 424 \times 10^{-6}$ and $\mu = 1.01$, using the cobalt compound as reference). It is therefore necessary to conclude again that vitamin B_{12} is diamagnetic.

Discussion

Since vitamin B_{12} is diamagnetic, it becomes pertinent to ask if the cobalt atom of the molecule may not actually be paramagnetic and its paramagnetism covered by the diamagnetism of the large organic molecule. In the absence of the cobalt-free organic component for direct measure, the diamagnetic moment can only be calculated. Using Pascal's constants[13] and the formula proposed by Brink and co-workers,[14] $C_{62}H_{86-90}N_{14}O_{13}PCo$, gives a value for χ_M of about -780×10^{-6}, the uncertainty amounting to probably $\pm 75 \times 10^{-6}$, owing to the lack of knowledge of the nature of the binding of the oxygen and nitrogen atoms and of the constitutive factors. The minimum magnetic moment for the cobalt atom would correspond to one unpaired electron, $\mu = 1.73$ or at room temperature $\chi_M = 1300 \times 10^{-6}$. The calculated diamagnetic moment would be far short of concealing a paramagetic moment were it present.

The ferromagnetic impurity apparently present in the crystalline vitamin B_{12} used probably does not exceed a few thousandths of one per cent. It will be interesting to repeat the measurement sometime after a recrystallization technique has been worked out which will eliminate the trace of iron or iron oxide probably present.

Inasmuch as it now appears that vitamin B_{12} is diamagnetic and in view of the magnetic character of the coördination compounds of cobalt in its two valence states as reviewed above, it may be concluded that the cobalt is present in the molecule in the trivalent state or in the bivalent state coupled with molecular oxygen.

Acknowledgment.—The authors wish to express their appreciation to the E. R. Squibb and Sons Company for the material used in this study and to the Institute for Atomic Research of the Iowa State College for making available the magnetic susceptibility apparatus.

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(13) Selwood, ref. 1, p. 52.

(14) Brink, Wolf, Kaczka, Rickes, Koniuszy, Wood and Folkers, THIS JOURNAL, **71**, 1854 (1949).

DEPARTMENT OF CHEMISTRY
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RECEIVED MAY 18, 1950

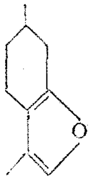
The Isolation of Menthofuran from American Peppermint Oil

BY RICHARD H. EASTMAN

Menthofuran (I) a terpenoid substance of unusual structure has been isolated from peppermint oil (*Mentha piperita*) by several investigators by fractional distillation[1–4] and has been prepared by thermal decomposition of the sultone of 3-hydroxy-3,8(9)-methadiene-9-sulfonic acid which results from sulfonation of pulegone in acetic anhydride.[5]

A convenient method for obtaining methofuran from peppermint oil takes advantage of the easy dissociation[6] of maleic anhydride–furan adducts. Treatment of American peppermint oil with *ca.* 10% of its weight of maleic anhydride with warming causes formation, and, after cooling, separation of the adduct of menthofuran. After purification by crystallization the menthofuran adduct is decomposed by heating in benzene and the maleic anhydride is irreversibly removed from the equilibrium through combination with an appropriate conjugated diene. Alkali extraction removes the adduct of the diene and fractionation of the benzene solution gives excellent yields of menthofuran, based on the weights of adduct decomposed. Both 3-methylpentadiene-1,3 and α-phellandrene have been used as maleic anhydride acceptors with good results.

Depending upon its source American peppermint oil yields from one to eight per cent. of menthofuran. The method described here may prove useful in isolating other naturally occurring furans.



I

Experimental

Fifteen hundred ml. of American peppermint oil was heated to 80° and 60 g. of maleic anhydride was added with stirring. The deep-yellow solution which resulted was allowed to cool to room temperature and then placed at 0–5° for twelve hours. The precipitate which had formed was separated by filtration and washed thoroughly with low boiling petroleum ether to yield 50.5 g. of crude menthofuran–maleic anhydride adduct. The crude product was crystallized from 75 ml. of benzene and gave 39.0 g. of adduct in the form of flat needles, m. p. 132–133°.[3,5]

The purified adduct was boiled under reflux in 100 ml. of benzene containing 27 g. of α-phellandrene for 24 hours. The hot benzene solution was then extracted during three hours of reflux over a solution of 16 g. of NaOH in 150 ml. water. The mixture was cooled, the layers were separated, the benzene layer was dried with anhydrous sodium sulfate and the benzene was removed by distillation on the steam-bath. Fractionation of the residue after benzene removal yielded 6.2 g., b. p. 81–84° (15 mm.) and 17.4 g., b. p. 84–86.5 (15 mm.). The latter material was menthofuran (I) and had $[\alpha]^{25}\mathrm{D}$ +92.5° (pure liquid in 0.25-dm. tube), $n^{25}\mathrm{D}$ 1.4832 (reported,[4] +81, 1.4807, respectively).

Menthofuran prepared in this way has been characterized as its maleic anhydride adduct, and as menthofuran mercurichloride prepared as follows: To a solution of 5.4 g. of mercuric chloride dissolved in 100 ml. of 95% alcohol containing 2.0 g. of sodium acetate was added 3 ml. of menthofuran. After three hours needles were deposited which were separated by filtration and washed with alcohol to yield 2.2 g., m. p. 126–129°. Two crystallizations from alcohol yielded white needles, m. p. 126–127°.

Anal. Calcd. for $C_{10}H_{13}OHgCl$: C, 31.2; H, 3.4. Found: C, 31.2; H, 3.8.

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RECEIVED JUNE 27, 1950

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(4) Schmidt, *Ber.*, **80**, 538 (1947).

(5) Treibs, *ibid.*, **70**, 85 (1937).

(6) Diels and Alder, *ibid.*, **62**, 557 (1929); see also ref. 5.

The Hydrogenolysis of 4-Phenyl-1,3-dioxanes

BY WILLIAM S. EMERSON, RUDOLPH L. HEIDER, RAYMOND I. LONGLEY, JR., AND THEODORE C. SHAFER

4-Phenyl-1,3-dioxane is obtained easily (83–88% yield) from styrene and formaldehyde by the Prins reaction.[1] We have prepared 4-methyl-4-phenyl-1,3-dioxane in 72% yield from α-methylstyrene and formaldehyde by using a dioxane[1b] solvent for the same reaction. Hydrogenation of 4-phenyl-1,3-dioxane in ethanol solution in the presence of a copper chromite catalyst yielded 85% of 3-phenyl-1-propanol. 3-Phenyl-1-butanol was obtained similarly in 68% yield from 4-methyl-4-phenyl-1,3-dioxane. This method, namely, the Prins reaction followed by hydrogenation, appears to be a convenient procedure for converting styrenes to the corresponding 3-aryl-1-alkanols. In view of the reported hydrogenolysis of 4,4,5,5-tetramethyl-1,3-dioxane to 2,2,3-trimethyl-1-butanol,[2] it might be a general synthesis of a number of primary alcohols.

Experimental

Dioxanes.—The dioxanes were prepared by the method of Shortridge[1b] using aqueous formaldehyde. The 4-phenyl-1,3-dioxane was obtained in 83–87% yield, b. p. 120° (10 mm.) to 126° (15 mm.) (121–123° (11 mm.)),[1b] $n^{25}\mathrm{D}$ 1.5269–1.5276 ($n^{25}\mathrm{D}$ 1.5288[1b]). In the reaction between α-methylstyrene and formaldehyde, 1 l. of dioxane was added as a solvent for a 2-molar run and the boiling time was reduced to seven hours. 4-Methyl-4-phenyl-1,3-dioxane was obtained in 72% yield, b. p. 119° (14 mm.), (130–135° (15 mm.),[3] m. p. 33.0–38.5° (39–40°).[3]

3-Phenyl-1-propanol.—A mixture of 249 g. of 4-phenyl-1,3-dioxane, 30 g. of copper chromite and 200 cc. of ethanol was charged to an American Instrument Co. rocking autoclave and hydrogenated at 200–208° and 1500–2600 p. s. i. The catalyst was separated by filtration and the filtrate distilled to give 175 g. (85%) of 3-phenyl-1-propanol, b. p. 110° (13 mm.) to 123° (12 mm.), (119° (12 mm.)),[4] $n^{25}\mathrm{D}$ 1.5220–1.5245. A middle fraction, b. p. 115–116° (13 mm.), $n^{25}\mathrm{D}$ 1.5242 was analyzed.

Anal.[5] Calcd. for $C_9H_{12}O$: C, 79.4; H, 8.82. Found: C, 79.2; H, 8.71.

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(3) Price, Benton and Schmidle, THIS JOURNAL, **71**, 2860 (1949).

(4) Schimmel & Co., German Patent 116,091; *Frdl.*, **6**, 1282 (1904).

(5) Microanalysis by Mr. Donald Stoltz of this Laboratory.