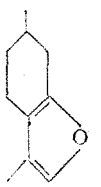
oil (*Mentha piperita*) by several investigators by fractional distillation[1-4] and has been prepared by thermal decomposition of the sultone of 3-hydroxy-3,8(9)-methadiene-9-sulfonic acid which results from sulfonation of pulegone in acetic anhydride.[5]

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 $[\alpha]^{25}D$ +92.5° (pure liquid in 0.25-dm. tube), $n^{25}D$ 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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(1) Carles, *Parfumerie Moderne*, **22**, 615 (1929).
(2) Wienhaus, *Z. angew. chem.*, **47**, 415 (1934).
(3) Bedoukian, THIS JOURNAL, **70**, 621 (1948).
(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] $n^{25}D$ 1.5269–1.5276 ($n^{25}D$ 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] $n^{25}D$ 1.5220–1.5245. A middle fraction, b. p. 115–116° (13 mm.), $n^{25}D$ 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.

(1) (a) Engel, U. S. Patent 2,417,548; *C. A.*, **41**, 3493 (1947); (b) Shortridge, THIS JOURNAL, **70**, 873 (1948).
(2) PB Report No. 81383 (Fiat Final Report No. 1000).
(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.

The 3,5-dinitrobenzoate melted at 88–90°[6] (92°[7]) after one crystallization from ethanol.

When the hydrogenation was attempted in aqueous suspension, no reduction took place and 90% of the dioxane was recovered unchanged.

3-Phenyl-1-butanol was prepared similarly by the hydrogenation of 175 g. of 4-methyl-4-phenyl-1,3-dioxane in the presence of 13 g. of copper chromite at 225–230° and 800–1600 p.s.i. Distillation yielded 100 g. (68%) of 3-phenyl-1-butanol, b. p. 121–123° (13 mm.) (125.5–128.0° at 13 mm.),[8] $n^{25}D$ 1.5165.

(6) Melting point uncorrected.

(7) Shriner and Fuson, "Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 227.

(8) Rupe and Walraven, *Helv. Chim. Acta*, **13**, 361 (1930).

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RECEIVED MAY 27, 1950

On the Kolbe–Schmitt Reaction

BY LLOYD N. FERGUSON,[1] RICHARD R. HOLMES[2] AND MELVIN CALVIN

The recent publication of Cameron, Jeskey and Baine[3] on the Kolbe–Schmitt reaction has prompted us to report an interesting observation from an investigation which included the use of this reaction. At that time, it was desired to carbonate *o*-substituted phenols in the second ortho position. In view of the fact that potassium salts give higher percentages of the para acids in this reaction,[4] a lithium salt was tried, following a suggestion of Dr. R. H. Bailes. It is noteworthy that, under the conditions previously reported for the carbonation of sodium *o*-fluorophenoxide,[5] only the ortho acid was obtained from lithium *o*-fluorophenoxide. In general, only about 30% of the lithium salt was carbonated, and the yields of acid ranged between 65 and 70%, based on unrecovered fluorophenol. On the other hand, potassium *o*-fluorophenoxide yielded the ortho and para acids in a 1:3 mole ratio. Thus, under comparable conditions, there is a decreasing trend in the molar ratios of ortho:para acids of 1:0 from the lithium salt, 3:2 from the sodium salt and 1:3 from the potassium salt.

(1) Howard University, Washington, D. C.

(2) Graduate School, University of Minnesota, Minneapolis, Minn.

(3) D. Cameron, H. Jeskey and O. Baine, *J. Org. Chem.*, **15**, 233 (1949).

(4) H. Kolbe, *J. prakt. Chem.*, [2] **10**, 100 (1874).

(5) L. N. Ferguson, J. C. Reid and M. Calvin, THIS JOURNAL, **68**, 2502 (1946).

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RECEIVED JULY 20, 1950

Pteridine Studies. II. 2-Methylpteridines

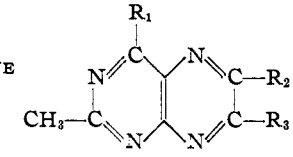
BY EMERY M. GAL[1]

A search of the literature revealed no reports on 2-methyl substituted pteridines with the exception of the 4-hydroxy-2-methylbenzopteridine described among the alloxazines by Gowenlock, Newbold and Spring.[2] Compounds of this type were considered to be of some biological interest because of the analogous structure which exists in thiamine. The 4,5-diamino-6-hydroxy-2-methylpyrimidine and 2-methyl-4,5,6-triaminopyrimidine, prepared according to the methods described in the literature,[3] were used for the condensation with glyoxal bisulfite and oxalic acid. Both 4,5-diamino-6-hydroxy-2-methylpyrimidine and 2-methyl-4,5,6-triaminopyrimidine condensed satisfactorily with oxalic acid, but with glyoxal bisulfite the former gave a product which could not be obtained in a satisfactory state of purity while the latter failed to yield a solid product. These difficulties of condensation are not unusual in working with pyrimidines, as reported by Kuhn and Cook.[4]

Table I lists the pteridines prepared together with their ultraviolet absorption spectra in alkaline solution. Also, their solubility in phosphate buffer is given. It was observed that the introduction of the methyl group in 2-position considerably increased the solubility of the pteridines. The paper chromatographic analysis of the 0.5 *N* NH_4OH solution of the 2-methyl substituted pteridines gave a bright blue fluorescence. The pyrimidine precursors upon paper chromatography not only differed in their R_f values, but did not show any appreciable fluorescence.

TABLE I

THE 2-METHYLPTERIDINE RING



Compound	R_1	R_2	R_3	U.V. spectra in 0.1 *N* NaOH (*p*H 8.55–9.0) Max. Å.	Min.	Soly. in phosphate buffer at *p*H 7.4, mg./100 ml.
I	OH	OH	OH	3460	3070	5
				2940	2690	
				2420	2300	
II	NH_2	OH	OH	3325	3225 shoulder	
				2275	2670	40
					2400 shoulder	
(a)	4,5-Diamino-6-hydroxy-2-methylpyrimidine			2730	2345	
(b)	2-Methyl-4,5,6-triaminopyrimidine			2750	2390	

Experimental

2-Methyl-4,6,7-trihydroxypyrimido-(4,5-b)-pyrazine (I).—One gram of 4,5-diamino-6-hydroxy-2-methylpyrimidine bisulfite, 1.0 g. of sodium oxalate and 5.0 g. of anhydrous oxalic acid were thoroughly mixed and then heated in a container under vacuum, gradually bringing the temperature up to 250°. After three hours of heating the dark brown solid was dissolved in 150 ml. of 2 *N*

(1) U. S. Public Health Special Fellow. This work was supported by a grant from the Cancer Research Grants Branch, U. S. Public Health Service to D. M. Greenberg.

(2) Gowenlock, Newbold and Spring, *J. Chem. Soc.*, 517 (1948).

(3) Lythgoe, Todd and Topham, *ibid.*, 315 (1944).

(4) Kuhn and Cook, *Ber.*, **70**, 761 (1937).