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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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.

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(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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Pteridine Studies. II. 2-Methylpteridines

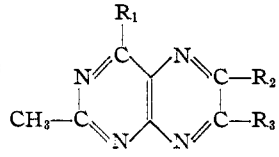
BY EMERY M. GAL[1]

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).

NaOH. Charcoal was then added and the solution was boiled for another five minutes, then filtered hot. The filtrate was acidified with 150 ml. of 2 *N* acetic acid and about 25 ml. of 2 *N* HCl. The yellow precipitate was allowed to settle out. After cooling it was filtered and washed with water, alcohol and ether. It was recrystallized three times from hot alkali and, after thorough washing with water, was dried at 150° *in vacuo*. The compound crystallized with one mole of water which was not lost by prolonged drying *in vacuo*. The light yellow crystals did not melt at 300°.

Anal. Calcd. for $C_7H_6O_3N_4 \cdot H_2O$ (212.0): C, 39.62; H, 3.77; N, 26.41. Found: C, 39.06; H, 3.76; N, 26.03. After 12 hr. of drying at 150°: C, 39.62; H, 3.61; N, 25.79.

4-Amino-6,7-dihydroxy-2-methylpyrimido-(4,5-b)-pyrazine (II).—2.37 g. (0.01 mole) of 2-methyl-4,5,6-triaminopyrimidine sulfate was mixed with a great excess, 9.0 g. (0.1 mole) of anhydrous oxalic acid and 2.68 g. (0.02 mole) of sodium oxalate. The mixture was then heated under vacuum (70 mm.) for three hours, gradually bringing the temperature up to 250°. The yellowish-brown residue was dissolved in 25 ml. of hot 2 *N* NaOH and diluted with distilled water to 100 ml. The solution was heated with charcoal while hot, then filtered into 50 ml. of 2 *N* HCl. After stirring and cooling, the precipitate was collected and this treatment was repeated twice more with just enough 2 *N* NaOH each time to bring about the solution of the pteridine. The final white precipitate was collected, washed with cold water until free of traces of hydrochloric acid and dried *in vacuo* at 100°. This pteridine has no water of crystallization. The resulting white powder did not melt at 300°.

Anal. Calcd. for $C_7H_7O_2N_5$ (193.7): C, 43.28; H, 3.60; N, 36.07. Found: C, 42.98; H, 3.50; N, 35.53.

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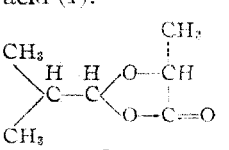
Acid-catalyzed Esterification of Lactic Acid with β-Methallyl Alcohol[1]

BY NORMAN G. GAYLORD[2]

The attempted synthesis of β-methallyl lactate by refluxing excess β-methallyl alcohol with lactic acid in the presence of *p*-toluenesulfonic acid resulted in the isolation of a colorless liquid which was identified as lactic isobutylidene ether ester or isobutyrallactic acid (I).



I

I is insoluble in water and acids but dissolves in hot alkali. It is acidic to moistened litmus, decolorizes bromine water with liberation of hydrogen bromide, decolorizes permanganate but does not take up hydrogen over palladium-on-charcoal. Although it gives a questionable test with Brady reagent (2,4-dinitrophenylhydrazine–HCl) application of the standard procedure[3] for the preparation of the 2,4-dinitrophenylhydrazone gives a solid which was identified by analysis and mixed melting point as the derivative of isobutyraldehyde. Application of the procedure for the preparation of the *p*-phenylphenacyl ester of acids[4] gives a solid identified by analysis and mixed melting point as the derivative of lactic acid.

I could arise from an initial acid-catalyzed rearrangement of β-methallyl alcohol to isobutyraldehyde[5,6] followed by hemiacetal formation and dehydration to the lactone. I is analogous to the previously reported chloralides[7] and the formaldehyde, benzaldehyde[8] and acetone[9] derivatives of hydroxy acids.

The failure of the reaction of I with 2,4-dinitrophenylhydrazine to yield a derivative of lactic acid as well as the 2,4-dinitrophenylhydrazone of isobutyraldehyde, as has been reported[8] in the case of phenylhydrazine and the formaldehyde compounds of malic and tartaric acids, can be reconciled with the fact that, under the experimental conditions, no solid derivative was obtained from 2,4-dinitrophenylhydrazine and pure lactic acid.

The desired β-methallyl lactate can be prepared satisfactorily in the absence of a catalyst.[10]

Experimental

Isobutylidene Ether Ester of Lactic Acid.—Six hundred and thirty-six grams (6 moles) of 85% lactic acid, 1728 g. (24 moles) of β-methallyl alcohol, 8 g. of *p*-toluenesulfonic acid and 300 ml. of benzene were refluxed in a 3-l. round-bottomed flask fitted with a thermometer, mechanical stirrer and a vacuum-jacketed, silvered, fractionating column (45 cm. effective length, 12 mm. i.d.) packed with $^3/_{16}$" glass helices, topped by a water-cooled Dean–Stark tube (Barrett modification) and bulb reflux condenser. Refluxing was continued for 68 hours during which time the aqueous layer was withdrawn from the trap and the benzene continuously returned to the system. The acid catalyst was neutralized with 25 g. of anhydrous sodium acetate, and the Dean–Stark tube and reflux condenser were replaced by a total reflux, partial take-off distilling head. After separation of the forerun consisting of benzene, 380 g. of isobutyraldehyde and 860 g. of β-methallyl alcohol, the fraction boiling at 67–75° at 12 mm. was collected. This fraction was redistilled to yield 625 g. (72%) of product, b. p. 71.0–71.3° at 14 mm., $n^{24.8}D$ 1.4198, $d^{24.8}_4$ 1.0168.

Anal.[11] Calcd. for $C_7H_{12}O_3$: C, 58.31; H, 8.39; MR_D 35.87. Found: C, 58.14; H, 8.23; MR_D 35.77.

The 2,4-dinitrophenylhydrazone prepared in the usual way[3] was the derivative of isobutyraldehyde.

(1) Abstracted from a portion of the dissertation submitted in partial fulfillment of the requirements for the Ph.D. Degree, Polytechnic Institute of Brooklyn, June, 1950.

(2) E. I. du Pont de Nemours & Co., Yerkes Research Laboratory, Buffalo, N. Y.

(3) Shriner and Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

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(6) Tamele, Ott, Marple and Hearne, *Ind. Eng. Chem.*, **33**, 115 (1941); Hearne, Tamele and Converse, *ibid.*, **33**, 805 (1941).

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(10) Fisher, Rehberg and Smith, THIS JOURNAL, **65**, 763 (1943).

(11) Microanalyses by Dr. Francine Schwarzkopf.