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).

MONSANTO CHEMICAL CO.
CENTRAL RESEARCH DEPT.
DAYTON 7, OHIO

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).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIF.

RECEIVED JULY 20, 1950

Pteridine Studies. II. 2-Methylpteridines

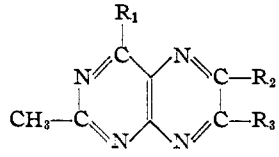
BY EMERY M. GAL[1]

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).