

The reactions of both *t*-butylmethylcarbinol and *t*-butylethylene over aluminum sulfate were accompanied by small amounts of sulfur and hydrogen sulfide with the deposition of a dark tarry material on the surface of the catalyst; however, no low boiling partial oxidation products were detected in the olefin mixture. Very clean reactions were obtained with activated alumina.

### Summary

A study has been made of the vapor phase catalytic conversion of *t*-butylmethylcarbinol and *t*-butylethylene over activated alumina and anhydrous aluminum sulfate to yield the three isomeric hexenes, *t*-butylethylene, unsym-methylisopropylethylene, and tetramethylethylene.

In contrast to results obtained by liquid phase reactions with acid catalysts, the dehydration of

*t*-butylmethylcarbinol over activated alumina yields *t*-butylethylene rather than tetramethylethylene as the principal olefin. This reaction is largely independent of the reaction temperature.

In accord with results obtained in liquid phase reactions with acid catalysts, tetramethylethylene is the principal olefin formed by the vapor phase dehydration of *t*-butylmethylcarbinol over anhydrous aluminum sulfate.

*t*-Butylethylene was passed unchanged over alumina, whereas over aluminum sulfate the olefin is rearranged to give the same mixture of hexenes as obtained from *t*-butylmethylcarbinol over the same catalyst.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

## The Synthesis and Bactericidal Properties of Some 5-*n*-Alkylresorcinols

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Interest in the 5-alkylresorcinols arises from two sources. Degradation of the depsides obtained from lichens<sup>1</sup> has shown that they are derivatives of carboxylic acids which upon loss of carbon dioxide yield 5-*n*-alkylresorcinols, the alkyl group always containing an odd number of carbon atoms. In addition to the long-known orcinol, *n*-propylresorcinol (divarinol),<sup>2</sup> *n*-amylresorcinol (olivetol)<sup>3</sup> and *n*-heptylresorcinol (spherophorol)<sup>4</sup> have been isolated and identified. The other incentive to the investigation of the 5-alkylresorcinols was the desirability of comparing their bactericidal properties with those of the much-studied 4-alkylresorcinols.<sup>5</sup>

The naturally occurring 5-alkylresorcinols have been prepared previously in small amounts for purposes of identification but the *n*-butyl and *n*-hexyl compounds have not been reported. The *n*-amyl and *n*-heptyl homologs were first obtained<sup>3,4</sup> by condensation of ethyl *n*-caproylacetate and caprylacetate, respectively, with ethyl acetonedicarboxylate followed by fusion of the reaction mixtures with solid potassium hydroxide. No yields were given. 5-*n*-Propyl-

resorcinol has been synthesized in several ways. Mauthner<sup>6</sup> condensed 3,5-dimethoxybenzoyl chloride with ethyl iodide by means of zinc and reduced the ketone but apparently obtained too little of the diether to carry out the demethylation. The dimethoxy ketone was later<sup>7</sup> prepared more satisfactorily by alkylation and hydrolysis of the ethyl 3,5-dimethoxybenzoylacetate obtained by a Claisen condensation. Reduction of the ketone by the Clemmensen method followed by demethylation with hydriodic acid gave a small yield of the alkylresorcinol. More recently the *n*-amyl compound<sup>8</sup> has been obtained through reduction of the dimethoxyphenyl *n*-butyl ketone by a modified<sup>9</sup> Wolff-Kishner method followed by demethylation. Asahina<sup>10</sup> has also reported that the dimethoxyalkylbenzenes may be prepared by the sodium and alcohol reduction of 3,4,5-trimethoxyphenyl alkyl ketones whereby the 4-methoxy group is eliminated.

In the present investigation the possibility of synthesis of the alkylresorcinols through hydrolysis of the 3,5-dibromoalkylbenzenes was first studied. However, *sym*-tribromobenzene could not be induced to yield a Grignard reagent or

(1) For a summary of the many investigations in this field see Asahina, *Acta Phytotchim.*, **8**, 83 (1934); *C. A.*, **29**, 147 (1935).

(2) Hesse, *J. prakt. Chem.*, **83**, 22 (1911).

(3) Asahina and Asano, *Ber.*, **65B**, 475 (1932).

(4) Asahina and Hashimoto, *ibid.*, **67B**, 416 (1934).

(5) (a) Johnson and Lane, *THIS JOURNAL*, **43**, 348 (1921); (b) Dohme, Cox and Miller, *ibid.*, **48**, 1688 (1926).

(6) Mauthner, *J. prakt. Chem.*, **87**, 403 (1913); **103**, 396 (1922).

(7) Mauthner, *ibid.*, **107**, 104 (1924); **108**, 276 (1924). See also Sonn and Sheffer, *Ber.*, **57B**, 959 (1924).

(8) Asahina and Nogami, *ibid.*, **68B**, 1500 (1935).

(9) Rabe and Jantzen, *ibid.*, **54B**, 928 (1921).

(10) Asahina, *ibid.*, **69B**, 1643 (1936).

lithium derivative, and indirect preparation of the dibromo compounds from the alkylbenzenes or from the *p*-aminophenyl alkyl ketones did not prove practicable. It was reported by Riesz and Frankfurter<sup>11</sup> that the action of chlorosulfonic acid on acetophenone led to 3,5-disulfonation. Reduction of the keto group of such a compound should give an alkylbenzenedisulfonic acid that easily could be converted into the 5-alkylresorcinol. It developed, however, that the structure originally proposed for the sulfonation product was erroneous, one of the sulfo groups being in the side chain.<sup>12</sup> The preparation method finally adopted involved the reaction of 3,5-dimethoxybenzamide with an alkylmagnesium halide according to the procedure described by Jenkins<sup>13</sup> in his work on aryl benzyl ketones. The yields of dimethoxyphenyl alkyl ketones ranged from 80 to 88% based upon the amide. Since the reaction is slow because of the immediate precipitation of the magnesium salt of the amide, the action of a Grignard reagent with the diethylamide was investigated. This method was unsatisfactory as the yield of ketone was low and its isolation in a pure state was difficult. These results are not unlike those just reported by Couturier<sup>14</sup> for the action of ethylmagnesium bromide on *p*-methoxybenzamide.

The possibility of preparing the 3,5-dimethoxyphenyl alkyl ketones from the action of zinc or cadmium alkyls<sup>15</sup> upon the acid chloride was likewise investigated. The cadmium compounds proved to be too unreactive, much unchanged acid chloride being present even after a protracted reaction time and only a small yield of ketone was isolated. In the case of the zinc alkyls all of the acid chloride reacted but the product was always a mixture of the ketone and ester. The reaction of di-*n*-butylzinc in toluene apparently gave the *n*-butyl ester. Judging by our experience the preparation of an aryl alkyl ketone is much more readily effected through the action of an alkylmagnesium halide on an amide than by a zinc or cadmium alkyl acting on the corresponding acid chloride.

Various methods for reducing the 3,5-dimethoxyphenyl alkyl ketones were investigated. In studying the reduction of substituted aryl alkyl

ketones Hartung and Crossley<sup>16</sup> observed that *m*-methoxyphenyl propyl ketone reduced very slowly with a palladium catalyst. With two methoxy groups present the reduction, if it occurs at all, is too slow to be useful. After six hours at 30 lb. (2 atm.) of hydrogen the ketone was recovered unchanged. As already mentioned Asahina<sup>10</sup> has reported the reduction of 3,4,5-trimethoxyphenyl alkyl ketones with sodium and alcohol. Attempts to reduce 3,5-dimethoxyphenyl alkyl ketones by this method using a variety of experimental conditions always resulted in a low yield of an impure product. Application of Martin's<sup>17</sup> variation of the Clemmensen method to the dimethoxyphenyl *n*-amyl ketone gave only a little alkali soluble material but the yield of reduction product was low. The most satisfactory reduction method found was the decomposition of the hydrazones with potassium hydroxide.

The phenol coefficients for the 5-alkylresorcinols against *Staph. aureus*<sup>18</sup> at 37° are practically identical with those for the 4-isomers up to and including the *n*-amyl compound. Above this the symmetrical isomers are less effective. The figures are listed in Table I.

TABLE I

PHENOL COEFFICIENTS; <i>Staph. aureus</i> AT 37°		
Alkylresorcinol	4-Isomers <sup>1b</sup>	5-Isomers
<i>n</i> -Propyl	4	5
<i>n</i> -Butyl	10	10
<i>n</i> -Amyl	30	35
<i>n</i> -Hexyl	98	49
<i>n</i> -Heptyl	280	128

Against *B. typhosus* at 20° 5-*n*-hexylresorcinol gave the phenol coefficient<sup>19</sup> of 22 as compared with about 50 for the 4-isomer. It appears from recent work on the alkylcatechols<sup>20</sup> that a change from the resorcinol to the catechol structure modifies the bactericidal properties even more than varying the location of the alkyl group. This marked difference in the bactericidal effectiveness of isomers makes desirable a careful comparison of their physical properties because of the bearing such data would have on theories of bactericidal action.

(16) Hartung and Crossley, *THIS JOURNAL*, **56**, 158 (1934).

(17) Martin, *ibid.*, **58**, 1439 (1936).

(18) We are indebted to Dr. Maurice L. Moore of the Research Laboratories of Sharp and Dohme for these results.

(19) We wish to thank Charlotte Epple Smith of the Northwestern University Dental School for this determination.

(20) Miller, Hartung, Rock and Crossley, *THIS JOURNAL*, **60**, 7 (1938).

(11) Riesz and Frankfurter, *Monatsh.*, **50**, 68 (1928).

(12) Evidence for the structure of this sulfonation product will be reported later.

(13) Jenkins, *THIS JOURNAL*, **55**, 703, 1618, 2895 (1933).

(14) Couturier, *Compt. rend.*, **202**, 1994 (1936); **205**, 800 (1937).

(15) Gilman and Nelson, *Rec. trav. chim.*, **55**, 528 (1936).

TABLE II  
 3,5-DIMETHOXYPHENYL ALKYL KETONES

Alkyl	Yield, %	B. p., °C.	Mm.	M. p., °C.	Anal.			
					Calcd., %		Found, %	
					C	H	C	H
Ethyl	84	162-163	11	32.5 <sup>a</sup>	..	..	..	..
<i>n</i> -Propyl	88	157-158	7	33.5-34	69.2	7.75	69.4	7.74
<i>n</i> -Butyl	80	175-177	11	42.5 <sup>b</sup>	..	..	..	..
<i>n</i> -Amyl	88	175-176	7	53	71.1	8.54	71.1	8.67
<i>n</i> -Hexyl	85	161-161.5	3	30.5-31 <sup>c</sup>	72.0	8.87	71.7	9.07

<sup>a</sup> *n*<sup>26</sup>D (supercooled) 1.5358. Mauthner [*J. prakt. Chem.*, **107**, 104 (1924); **108**, 276 (1924)] reported m. p. 34-35°.

<sup>b</sup> Asahina<sup>8</sup> reported m. p. 42-43°. <sup>c</sup> *n*<sup>26</sup>D (supercooled) 1.5175.

### Experimental

**3,5-Dimethoxybenzamide.**—Benzoic acid was sulfonated with 30% oleum essentially according to the method of Lock and Nottes.<sup>21</sup> The barium salt was fused with a mixture of equal weights of sodium and potassium hydroxide to give a 63% yield of the dihydroxy acid, m. p. 230°. <sup>22</sup> A wide range of melting points has been reported for the pure acid, Lock and Nottes giving 237-240°. For the methylation a combination of the method of Seka and Fuchs<sup>23</sup> with that of Mauthner<sup>6</sup> was employed. From the action of 134 g. (1.06 moles) of methyl sulfate upon 50 g. (0.325 mole) of the acid dissolved in 60 g. of sodium hydroxide in 300 cc. of water followed by the addition of a further 35 g. of sodium hydroxide and refluxing there was obtained 52-60 g. (86-93%) of the crude dimethoxybenzoic acid. This was converted to the acid chloride by treatment with slightly less than the theoretical amount of solid phosphorus pentachloride.<sup>6</sup> The use of chloroform or carbon disulfide as a solvent gave a much less satisfactory product. The reaction mixture was treated with dry ether, the insoluble material filtered off and the ether solution saturated with dry ammonia at 0°. The precipitate containing the amide and ammonium chloride was washed with ether to remove colored impurities and then with cold water to dissolve the ammonium chloride. Recrystallizing the residue from hot water gave a 72% yield of 3,5-dimethoxybenzamide, m. p. 146°. Mauthner<sup>6</sup> has reported 148-149°.

***N,N*-Diethyl-3,5-dimethoxybenzamide.**—To an ether solution of the 3,5-dimethoxybenzoyl chloride prepared from 70 g. (0.385 mole) of the acid as described above was added gradually with stirring 65 g. (excess) of diethylamine in 100 cc. of dry ether, the temperature being kept below 10°. After removing the precipitate of diethylammonium chloride the ether solution was washed with water, dried and distilled. After removal of the ether there was obtained 67 g. of material distilling at 166.5-167° (3.5 mm.) having *n*<sup>25</sup>D 1.5295 and *d*<sup>25</sup><sub>20</sub> 1.0985. This is a 74% yield.

*Anal.* (Kjeldahl). Calcd. for C<sub>18</sub>H<sub>19</sub>O<sub>5</sub>N: N, 5.91. Found: N, 6.02.

**3,5-Dimethoxyphenyl Alkyl Ketones.**—The ketones were all prepared according to the procedure given here for the *n*-propyl derivative. To a solution of *n*-propylmagnesium bromide in 200 cc. of ether prepared with the usual precautions from 123 g. (1 mole) of *n*-propyl

bromide and 24.3 g. of magnesium, was added 46 g. (0.25 mole) of 3,5-dimethoxybenzamide as rapidly as the refluxing of the ether would permit. A further 300 cc. of ether was added and the reaction mixture was refluxed and stirred in a hydrogen atmosphere for fifty hours. After hydrolysis with a mixture of ice and water containing 80 cc. of concentrated sulfuric acid and drying and distilling the ether layer there was obtained 48 g. of ketone, b. p. 157-158° (7 mm.), *n*<sup>26</sup>D 1.5285, which soon solidified. After crystallizing from dilute alcohol it melted at 33.5-34°. The yield of distilled product was 88%.

Essential data for the ketones including analyses<sup>24</sup> for those not previously prepared are given in Table II.

The ketones were all characterized by conversion to their semicarbazones. The properties of these are listed in Table III.

TABLE III

### 3,5-DIMETHOXYPHENYL ALKYL KETONE SEMICARBAZONES

Alkyl	M. p., °C.	Anal., NH <sub>3</sub> nitrogen <sup>a</sup>	
		Calcd., %	Found, %
Ethyl	131.5-132 <sup>b</sup>	5.58	5.71
<i>n</i> -Propyl	188	5.28	5.41
<i>n</i> -Butyl	204 <sup>c</sup>	..	..
<i>n</i> -Amyl	183-184	4.78	4.83
<i>n</i> -Hexyl	133.5-134	4.56	4.62

<sup>a</sup> The semicarbazones were decomposed by refluxing with 15% mercuric chloride [Hobson, *J. Chem. Soc.*, 1384 (1929)] in acid solution which liberates two-thirds of the nitrogen as the element. The ammonia nitrogen was then determined by the usual Kjeldahl procedure.

<sup>b</sup> Mauthner (see (a) Table II) reported m. p. 130-131°.

<sup>c</sup> Asahina<sup>8</sup> also reported this value.

When the melting points of the semicarbazones are plotted against the number of carbon atoms in the side chains a smooth curve results with a minimum at three (the methyl ketone<sup>25</sup> melts at 186-187°) and a maximum at five carbons.

**Reaction of 3,5-Dimethoxybenzoyl Chloride with Cadmium and Zinc Alkyls.**—In preliminary experiments diethylcadmium was condensed with benzoyl chloride following closely the directions of Gilman and Nelson.<sup>15</sup> From the reaction of 28.9 g. (0.21 mole) of benzoyl chloride with the diethylcadmium from 33 g. (0.3 mole) of ethyl bromide and 29.3 g. (0.16 mole) of cadmium chloride there were obtained in two runs 26 and 34% yields of

(21) Lock and Nottes, *Monatsh.*, **68**, 51 (1936).

(22) All melting points are corrected.

(23) Seka and Fuchs, *Monatsh.*, **57**, 65 (1931).

(24) The carbon and hydrogen analyses in this paper were determined by Mr. Robert Schuetz under an N. Y. A. grant.

(25) Asahina and Ihara, *J. Pharm. Soc. Japan*, **48**, 28 (1928).

phenyl ethyl ketone, based upon the benzoyl chloride added. These are somewhat less than previously reported. Similar results were obtained with 3,5-dimethoxybenzoyl chloride. For example, from 21.1 g. (0.105 mole) of the acid chloride, b. p. 154° (15 mm.), and 0.08 mole of di-*n*-butylcadmuim there was obtained a 27% yield of the ketone, b. p. 139–149 (6 mm.). Using *n*-butyl ether as the solvent there was more reaction product but the distillation range was even greater.

From refluxing for five hours in ether solution the diethylzinc from 0.15 mole of ethyl bromide with 0.155 mole of dimethoxybenzoyl chloride there resulted 21.2 g. of product most of which distilled at 156–158° (11 mm.). Refluxing 1.058 g. of this distillate with 10% sodium hydroxide produced 0.64 g. of 3,5-dimethoxybenzoic acid, indicating that at least 70% of the product was the ethyl ester rather than the ketone. In another experiment involving di-*n*-butylzinc the ether was first removed by distilling with toluene and the acid chloride was added in toluene solution. The largest fraction, b. p. 185–195° (21 mm.), upon treatment with alkali proved to be at least 48% ester. From the distillation range this was probably the butyl ester although some ethyl ester may have been present as undoubtedly a small amount of ethyl ether would be retained in the reaction mixture.

**Reaction of *N,N*-Diethyl-3,5-dimethoxybenzamide with *n*-Butylmagnesium Bromide.**—To the Grignard reagent from 31.5 g. (0.23 mole) of *n*-butyl bromide was added slowly an ether solution of 47.4 g. (0.2 mole) of the diethylamide. After refluxing and stirring for five hours the mixture was hydrolyzed with dilute sulfuric acid. A strong lachrymator was formed during the hydrolysis but this was not further investigated. After extracting twice with ether the aqueous layer was heated on the steam-bath for an hour and the oil which separated combined with that in the ether extracts. Distillation gave material boiling from 137–170° (3 mm.), the first two fractions, b. p. 137–148°, 148–155°, with  $n_D^{20}$  1.5230 and 1.5257 solidified in the refrigerator but melted below room temperature. The yield of impure ketone was 18.9 g. or 43%. The higher boiling fractions were chiefly the unchanged diethylamide. On the basis of the amide used in the reaction the yield of crude ketone was 79% of the theoretical amount. Increasing the reaction time to twenty hours did not improve the results.

**3,5-Dimethoxy-*n*-alkylbenzenes.**—The ketones were reduced by a procedure similar to that employed by Asahina and Nogami,<sup>8</sup> hence only a brief description of one experiment is given. After refluxing 41.6 g. (0.2 mole) of 3,5-dimethoxyphenyl *n*-propyl ketone, 20.8 g. (0.41 mole) of 100% hydrazine hydrate and 75 cc. of absolute alcohol for six hours the alcohol and excess hydrazine were removed and the residual oil heated with 82 g. of powdered potassium hydroxide in an oil-bath at 200–245° until evolution of nitrogen ceased. Distillation gave 21 g. (54%) of an oil, b. p. 125–128° (6 mm.). A yellow solid remained as a residue after the distillation. This proved to be the ketazine. The amount obtained was 13 g. or 32% of the theoretical amount, which accounted for the low yield of reduction product. After crystallizing from 95% alcohol it melted at 96.5–97°. A molecular weight determination by the camphor method gave 425 (calcd. 412).

*Anal.* Calcd. for  $C_{24}H_{32}O_4N_2$ : N, 6.80. Found: N, 6.60.

The azines were present as by-products in the other reductions but were not characterized. Physical constants and other data for the alkyldimethoxybenzenes are given in Table IV. It is to be noted that the observed values for the molecular refraction are uniformly in excess of those calculated. Both the refractive indices and the densities are straight line functions of the number of carbon atoms in the alkyl side chain.

TABLE IV  
3,5-DIMETHOXYALKYLBENZENES

Alkyl	Yield, %	B. p., °C.	Mm.	$n_D^{20}$	$d_4^{25}$	MR	
						Calcd.	Obsd.
<i>n</i> -Propyl <sup>a</sup>	73	103–105	3	1.5114	1.002 <sup>f</sup>	52.68	53.84
<i>n</i> -Butyl <sup>b</sup>	54	125–128	6	1.5085	0.989	57.30	58.49
<i>n</i> -Amyl <sup>c</sup>	65	133–136	6	1.5056	.978	61.92	63.14
<i>n</i> -Hexyl <sup>d</sup>	57	141–143	7	1.5027	.968	66.54	67.75
		120–122	4				
<i>n</i> -Heptyl <sup>e</sup>	63	162–163	6	1.4990	.956	71.16	72.47

<sup>a</sup> Previously prepared by several investigators but no physical properties other than boiling points were listed.<sup>10</sup>

<sup>b</sup> *Anal.* Calcd. for  $C_{12}H_{16}O_2$ : C, 74.17; H, 9.34. Found: C, 73.90; H, 9.19. <sup>c</sup> Reported by Asahina and Nogami<sup>8</sup> to boil at 114° (2 mm.) and by Asahina<sup>10</sup> at 145° (4 mm.). The latter value is inconsistent with our results. <sup>d</sup> *Anal.* Calcd. for  $C_{14}H_{22}O_2$ : C, 75.62; H, 9.98. Found: C, 75.63; H, 10.30. <sup>e</sup> Reported by Asahina<sup>10</sup> to boil at 150° (5 mm.). <sup>f</sup> Thoms, *Ber.*, **44**, 2134 (1911), reports  $d_{19}^{19}$  1.0194.

Reduction of 3,5-dimethoxyphenyl *n*-butyl ketone by sodium and alcohol according to the procedure used by Asahina<sup>10</sup> in reducing 3,4,5-trimethoxyphenyl *n*-butyl ketone gave a product of wide boiling range (120–145° (5 mm.)) from which a fraction, b. p. 128–129° (5 mm.), amounting to a 30% yield, was obtained. This was not entirely pure as it had  $n_D^{20}$  1.5068. The use of *n*-butyl or isoamyl alcohol in the reduction gave no better results.

**5-*n*-Alkylresorcinols.**—The preparation of 5-*n*-hexylresorcinol is described. A mixture of 5.5 g. (0.025 mole) of 3,5-dimethoxy-*n*-hexylbenzene, 40 cc. of glacial acetic acid and 15 cc. of 48% hydrobromic acid was refluxed for four hours. The reaction mixture was poured into ice water, decolorized with a little sodium bisulfite, neutralized with sodium bicarbonate and the mixture extracted with ether. The ether layer was shaken with 10% alkali, the alkaline solution acidified and extracted with ether. Distillation of this gave 2.4 g. of material, b. p. 192–195° (11 mm.). Since 1.2 g. of unreacted material was recovered from the first ether solution the yield was 65% of the dimethoxy compound utilized. The distillate soon solidified and after three crystallizations from water melted at 49–49.5°. Dehydration in a vacuum desiccator over sulfuric acid proved this to be the monohydrate.

*Anal.* Calcd. for  $C_{12}H_{18}O_2 \cdot H_2O$ :  $H_2O$ , 8.47. Found:  $H_2O$ , 8.56.

In the other demethylations the procedure outlined by Asahina<sup>8,10</sup> using hydriodic acid was employed. An alcoholic solution of the 5-*n*-hexylresorcinol gave a dark green color with ferric chloride. It was found possible to analyze this and the other alkylresorcinols on a semi-

micro scale by titration with potassium bromate-bromide solution. Best results were obtained by modifying the original procedure of Francis and Hill as follows. Approximately 0.05 g. of the resorcinol was dissolved in 10 ml. of glacial acetic acid in a 250-ml. Erlenmeyer flask. An excess (35-45 ml.) of a solution 0.021 molar in potassium bromate and 0.11 molar in potassium bromide was added and the mixture cooled in an ice-bath and acidified with 5 ml. of 50% sulfuric acid. After five minutes sufficient glacial acetic acid was added to dissolve the precipitate, the

flask removed from the ice-bath, 1 ml. of a saturated potassium iodide solution was added and the iodine titrated in the usual way. The bromate-bromide solution was standardized against pure orcinol. The tribromoalkylresorcinols were isolated and their melting points determined.

In Table V are summarized the data for the 5-*n*-alkylresorcinols, results of the previous investigators already mentioned being enclosed in brackets.

### Summary

1. 3,5-Dimethoxybenzamide reacts with *n*-alkylmagnesium bromides to give high yields of the corresponding ketones. These are useful intermediates for the preparation of the 5-*n*-alkylresorcinols.

2. 5-*n*-Butyl- and 5-*n*-hexylresorcinol have been described for the first time.

3. The bactericidal properties of the 5-*n*-alkylresorcinols have been reported.

4. An improved procedure for the bromate-bromide titration of resorcinol derivatives has been developed.

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TABLE V

#### 5-*n*-ALKYLRESORCINOLS

Alkyl	Yield, %	B. p., °C.	B. p., Mm.	M. p., °C. Hydrate	M. p., °C. Anhyd.	M. p., °C. tribromo compd.
<i>n</i> -Propyl	80	148-149	3	47	86.5-87	97.5-98
		[169]	8]	[42-51]	[82-84]	[99]
<i>n</i> -Butyl <sup>a</sup>	66	151-152	3	.....	81.5-82.5 <sup>c</sup>	84-84.5
<i>n</i> -Amyl	72	162-164	5	[40-41]	.....	85
		[164]	5]			[87]
<i>n</i> -Hexyl <sup>b</sup>	65	192-195	11	49-49.5 <sup>d</sup>	.....	75-76
<i>n</i> -Heptyl	60	179-181	6	55-55.5	.....	73.5-74.5
				[57]		[75]

<sup>a</sup> Anal. Calcd. for 0.1043 g. of C<sub>16</sub>H<sub>14</sub>O<sub>2</sub>: 32.60 ml. KBrO<sub>3</sub> soln. Found: 32.56 ml. <sup>b</sup> Anal. Calcd. for 0.0835 g. of C<sub>17</sub>H<sub>16</sub>O<sub>2</sub>·H<sub>2</sub>O: 20.44 ml. KBrO<sub>3</sub> soln. Found: 20.52 ml. <sup>c</sup> Fine needles from toluene. <sup>d</sup> After three crystallizations from water.

[CONTRIBUTION FROM THE JESSE METCALF CHEMICAL LABORATORY AT BROWN UNIVERSITY]

## The Extraction of Germanium and Gallium from Germanite. III. The Recovery of Germanium from the Arsenious Sulfide Sublimates

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In the process developed in this Laboratory for the removal of germanium and gallium from germanite, the finely ground ore is first heated in a stream of dry, oxygen-free nitrogen at 800°<sup>1</sup> to remove all of the arsenic. At the same time a small amount of the germanium, present as germanic sulfide, is volatilized. The partially sintered residue subsequently is heated at 825° in a reducing atmosphere (ammonia) whereupon the germanic sulfide present in the ore is converted to the more volatile germanous sulfide which sublimes to the cooler regions of the apparatus where it collects in the form of very pure crystals. The gallium is recovered by means of a hydrochloric acid extraction of the non-volatile residue.

The loss in weight of the ore in the first operation is about 13.5%, and 75% of the loss is accounted for in a highly colored, yellow-orange, sublimate which is collected in an iron condenser. Analyses of many lots of the sublimate

have shown it to be chiefly arsenious sulfide, containing varying quantities of germanium, occasionally as much as 4%, present as germanic sulfide, GeS<sub>2</sub>. In the particular sample referred to, this quantity of germanium amounted to 8.6% of the total germanium in the ore.

From the treatment of more than 100 kg. of germanite, about 10 kg. of these germanium bearing arsenic sulfide sublimates had been collected. In the most commonly used method of recovering the germanium, the material is oxidized with concentrated nitric acid, the product dissolved in hydrochloric acid, and distilled in a stream of chlorine, whereupon germanium tetrachloride is collected in the receiver. For a complete separation from arsenic, a second distillation is usually necessary.<sup>2</sup>

With large quantities of material, the method outlined is very laborious, and a method was sought in which the complete oxidation of the

(1) Johnson, Foster and Kraus, *THIS JOURNAL*, **57**, 1828 (1935); Foster, Johnson and Kraus, *ibid.*, **57**, 1832 (1935).

(2) See, however, Aitkenhead and Middleton, *Ind. Eng. Chem., Anal. Ed.*, **10**, 633 (1938), published after this work was completed.