

room close to the average position of the charges upon the ions into which salting-in could occur. This may be the reason for the order just noted.

The rapid rise of the dielectric constant of the urea-methanol system, with increased percentage of urea, should cause a very marked salting-in effect when salts are added to this system. The authors hope that with the data presented here available, some workers interested in measuring the salting-in or salting-out effect will be encouraged to work with this system and thus test Debye's theory with another non-aqueous system, and one in which prediction has come first and test followed the prediction.

## VI. Summary

Dielectric constant and density measurements have been made on the phenylthiourea-ethanol system at 25.00°, and on ethanol at 28.00°. The salting-in characteristics of this non-aqueous system were found to be at least in qualitative agreement with Debye's salting-out theory.

Dielectric constant, density and saturation data are given for the urea-methanol system at 25.00°. The dielectric constant rises rapidly with increasing concentration of urea, leading to the prediction that if salts are added to the system urea will be strongly salted-in.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES DIVISION, GENERAL MOTORS CORPORATION]

## The Vapor Phase Catalytic Conversion of Tertiary Butylmethylcarbinol and Tertiary Butylethylene

BY PAUL L. CRAMER AND A. L. GLASEBROOK

In the syntheses in this Laboratory of certain isomeric hexenes a search was made for a more convenient method for dehydrating *t*-butylmethylcarbinol. Previous methods,<sup>1</sup> in which acid catalysts and liquid phase reactions were employed, did not appear to be altogether suitable for the dehydration of large amounts of the alcohol. Preliminary experiments on the vapor phase dehydration of *t*-butylmethylcarbinol over activated alumina gave surprisingly different results from those obtained by previous methods. *t*-Butylethylene was found to be the principal olefin formed over activated alumina, whereas previous methods gave only negligible amounts of the normally expected olefin. The liquid phase dehydration of the alcohol with acid catalysts<sup>1</sup> gave the rearranged products, tetramethylethylene and unsym-methylisopropylethylene. These somewhat anomalous results suggested a more detailed study of the vapor phase reactions of both *t*-butylmethylcarbinol and *t*-butylethylene over activated alumina, and also over an acid catalyst, anhydrous aluminum sulfate. Furthermore, a method for the preparation of *t*-butylethylene by the direct dehydration of *t*-butylmethylcarbinol rather than by the thermal decomposition of the

acetate<sup>1,2</sup> or the methyl xanthate<sup>3</sup> of the alcohol was desirable.

An outline of the above experiments together with the analyses of the resulting olefins is presented in Table I.

The order in which the above three olefins are formed by the dehydration of *t*-butylmethylcarbinol by previous procedures<sup>1</sup> is inverted by the vapor phase dehydration of the alcohol over activated alumina. *t*-Butylethylene is formed in yields as high as 64% by volume. The reaction is largely independent of the reaction temperature. Attempts to dehydrate the alcohol over alumina by the static liquid phase method were unsuccessful.

In accord with the results obtained by previous liquid phase procedures with acid catalysts,<sup>1</sup> the vapor phase dehydration of the *t*-butylmethylcarbinol over anhydrous aluminum sulfate gives the rearranged olefins, tetramethylethylene and unsym-methylisopropylethylene. Negligible amounts of the normally expected olefin, *t*-butylethylene, are formed.

*t*-Butylethylene was passed unchanged over activated alumina, whereas, over anhydrous aluminum sulfate, *t*-butylethylene is rearranged to give

(1) For complete references see Whitmore and Rothrock, *THIS JOURNAL*, **55**, 1108 (1933); Whitmore and Meunier, *ibid.*, **55**, 3721 (1933).

(2) Cramer and Mulligan, *ibid.*, **58**, 373 (1936).

(3) Fomin and Sochanski, *Ber.*, **46**, 246 (1913); Schurman and Boord, *THIS JOURNAL*, **55**, 4930 (1933).

TABLE I  
 CATALYTIC CONVERSION OF *t*-BUTYLMETHYLCARBINOL AND *t*-BUTYLETHYLENE

| Name                          | Amt., g. | Rate cc./hour | Temp., °C. | Catalyst  | Olefin yield, % | Olefins, volume %       |                               |                     |
|-------------------------------|----------|---------------|------------|---|-----------------|-------------------------|-------------------------------|---------------------|
|                               |          |               |            |   |                 | <i>t</i> -Butylethylene | unsym-Methylisopropylethylene | Tetramethylethylene |
| <i>t</i> -Butylmethylcarbinol | 178      | 30            | 310        | Al <sub>2</sub> O <sub>3</sub>                  | 85              | 64.2                    | 28.2                          | 7.6                 |
| <i>t</i> -Butylmethylcarbinol | 696      | 60            | 390        | Al <sub>2</sub> O <sub>3</sub>                  | 83              | 61.5                    | 21.6                          | Trace <sup>a</sup>  |
| <i>t</i> -Butylmethylcarbinol | 145      | 50            | 275        | Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> | 74              | 3.5                     | 34                            | 62.5                |
| <i>t</i> -Butylethylene       | 53       | 30            | 275        | Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> | 89              | 4.3                     | 33.3                          | 62.4                |
| <i>t</i> -Butylethylene       | 15       | 20            | 350        | Al <sub>2</sub> O <sub>3</sub>                  | ..              | 100                     | nil                           | nil                 |

<sup>a</sup> A 16.9% distillation loss in this run, which probably occurred near the end of the fractionation, would thus account for the lower amount of unsym-methylisopropylethylene and the negligible amount of tetramethylethylene.

the same mixture of the three hexenes as that which was obtained by the dehydration of *t*-butylmethylcarbinol over the same catalyst. The results obtained with *t*-butylethylene over aluminum sulfate are in agreement with those obtained for the same olefin over phosphoric acid.<sup>4</sup>

The above results, when compared with those obtained by other methods, indicate that the olefin mixture obtained by the catalytic dehydration of *t*-butylmethylcarbinol is influenced little by reaction phase and temperature, but is, to a large extent, dependent upon the rearrangement of the resulting *t*-butylethylene as influenced by acid catalysts.

### Experimental

**Materials.**—*t*-Butylmethylcarbinol was prepared by the reduction of pinacolone<sup>5</sup> by wet ether and sodium.<sup>6</sup> The reduction was carried out in two runs using the following amounts of materials in each run: pinacolone, 674 g.; ether, 2250 cc.; sodium, 500 g. About 250 cc. of water was added to the ether solution of pinacolone. The sodium, cut in medium sized pieces, was added with stirring as fast as the heat of reaction would permit. In order to avoid the loss of pinacolone by condensation reactions, the aqueous alkaline layer was siphoned and fresh water was added frequently. The alcohol, containing a small amount of unchanged pinacolone, boiled at 119–121°. There was a small amount of white crystalline product remaining as a high boiling residue. The yield was 75%.

Commercial activated alumina (4 to 8 mesh) was used in these experiments.

Anhydrous aluminum sulfate was prepared in a Pyrex reaction tube by heating 75 g. of hydrated aluminum sulfate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O) at 285–300° for four hours. The anhydrous aluminum sulfate thus prepared formed a light bulky

mass within the reaction tube. A sample dissolved readily in hot water with only a trace of solid material remaining undissolved, thus indicating that only a slight amount of hydrolysis had taken place during the decomposition of the hydrate.

**The Reactions of *t*-Butylmethylcarbinol and *t*-Butylethylene over Activated Alumina and Aluminum Sulfate.**—An outline of these experiments together with the analyses of the resulting olefins is presented in Table I. These reactions were carried out in Pyrex tubes heated in the conventional type of electric furnace. The reaction products were collected at 0°. The olefin mixture from each run was washed with dilute sodium hydroxide solution and water, and dried over calcium chloride. The fractionation of the hexene mixtures was effected by very efficient spiral columns. Distillation curves for the dehydration products of *t*-butylmethylcarbinol over alumina and aluminum sulfate are shown in Fig. 1. The yields of olefins reported in Table I are for one passage over the catalyst. The physical constants of the pure hexenes

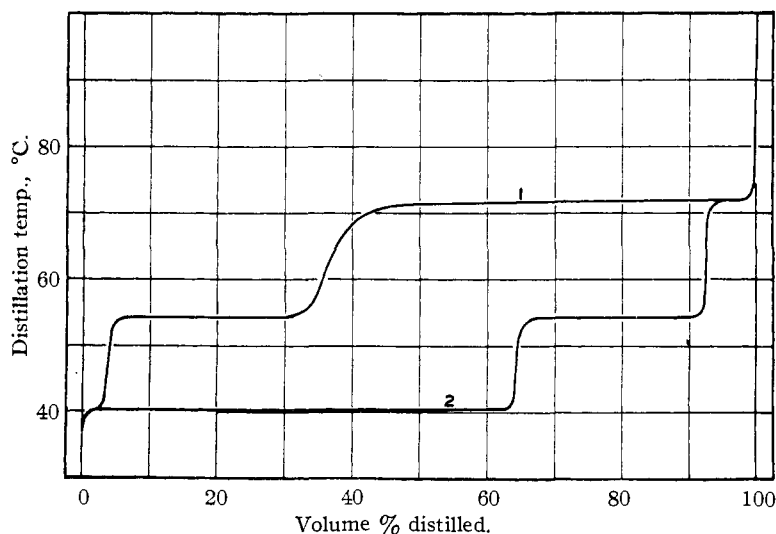


Fig. 1.—Distillation analyses of the olefins, *t*-butylethylene, unsym-methylisopropylethylene and tetramethylethylene, obtained by the catalytic dehydration of *t*-butylmethylcarbinol: curve 1, anhydrous aluminum sulfate; curve 2, activated alumina catalyst.

thus obtained are as follows: *t*-butylethylene, b. p. 41.4°,  $n_{D}^{20}$  1.3765; unsym-methylisopropylethylene, b. p. 55.2,  $n_{D}^{20}$  1.3904; tetramethylethylene, b. p. 72.7,  $n_{D}^{20}$  1.4121.

(4) Laughlin, Nash and Whitmore, THIS JOURNAL, 56, 1395 (1934).

(5) Org. Syntheses, 5, 87, 91 (1925).

(6) Rickard, Ann. chim., 21, 346 (1910).

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

BY C. M. SUTER AND ARTHUR W. WESTON

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).