centages of morpholine converted to the ether and dimorpholinomethane reported in Table I.

The other 4-morpholinomethyl alkyl ethers were made by the method described above, with the modifications given in the footnotes of Table III which summarizes all of the experimental data.

N-Substituted Morpholines.—The Grignard reagents were prepared in the usual way using 0.12 mole of magnesium and 0.12 mole of halide in 100 cc. of absolute ether. One-tenth mole of 4-morpholinomethyl ethyl ether dissolved in 50 cc. of absolute ether was then added slowly to the solution of Grignard reagent, the mixture refluxed for thirty minutes and allowed to stand overnight. The mixture was hydrolyzed with 10 cc. of concentrated sulfuric acid dissolved in 100 cc. of water. The ether layer was extracted with three 20-cc. portions of 20% sulfuric acid. Ten grams of ammonium chloride was added to the combined acid extracts to which concentrated ammonium hydroxide (about 65 cc.) was added until the solutions were alkaline. The alkaline solution was extracted with four 40-cc. portions of ether. The combined ether extracts were dried over calcium sulfate, the ether distilled and the remaining oil was distilled under reduced pressure. The results are given in Table II.

Summary

The preparation of eight new 4-morpholinomethyl alkyl (or aralkyl) ethers has been described and the amount of dimorpholinomethane formed by a competing reaction has been indicated in each preparation.

Five alkyl (or aralkyl) morpholines have been prepared from 4-morpholinomethyl ethyl ether and Grignard reagents.

BOSTON, MASS. RECEIVED MARCH 14, 1940

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

The Thermal Decomposition of the Acetate of 2,2-Dimethyl-3-pentanol

BY PAUL L. CRAMER AND VERLE A. MILLER

The dehydration of primary and secondary alcohols containing a neopentyl group to form the corresponding olefin is accompanied by a skeletal rearrangement.[1] Thus, the alcohol–olefin–paraffin method in many instances is not applicable in the synthesis of the tetra-alkylmethanes. The thermal decomposition of the methyl xanthate of the alcohol has provided a successful modification of the above method for the preparation of this type of hydrocarbon.[2]

The thermal decomposition of the acetate rather than the methyl xanthate of the alcohol has been employed in the synthesis of 3,3-dimethyl-1-butene.[1,3] The acetate gives much higher yields of the olefin than those obtained by the methyl xanthate procedure. Also the acetate method offers a more simple procedure in which no solvent is required. The main disadvantage of this method is the high temperature required to decompose the acetate, which would be expected to enhance the possible formation of isomeric olefins or other undesirable side reaction products. Thus, it seemed desirable to further test the acetate method as a possible general procedure for the synthesis of the above type of olefins and the corresponding paraffins.

In the present investigation a study has been made of the thermal decomposition of the acetate of 2,2-dimethyl-3-pentanol. As in the case of the acetate of 3,3-dimethyl-2-butanol,[3] a temperature of 400° is required to bring about an 80% conversion at contact times of reasonable length. Only about 12% conversion is obtained at 350°. The reaction is remarkably free of side reaction products, and the unchanged acetate may be recovered almost quantitatively.

4,4-Dimethyl-2-pentene is the principal olefin (93%) formed in the decomposition of the acetate of 2,2-dimethyl-3-pentanol. In contrast with the results obtained with the acetate of 3,3-dimethyl-2-butanol,[1,3] rearrangement occurs in this reaction to the extent of about 7%.[4] The rearranged products consist of a mixture containing about equal amounts of two olefins boiling in the 2,3-dimethylpentene and the 2,4-dimethylpentene range. Due to the very small amounts of these rearranged olefins, their separation and further identification by fractionation was unsuccessful.

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(1) For references see Whitmore and Meunier, THIS JOURNAL, **55**, 3721 (1933).

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

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

(4) To demonstrate that the rearranged olefins were not the result of the decomposition of the 2,2-dimethyl-3-pentanol contained as an impurity in the acetate, the pure alcohol, obtained by the saponification of a portion of the acetate, was found to be stable under the conditions employed in the decomposition of the acetate.

However, from the corresponding heptanes, obtained by the hydrogenation of the rearranged olefin mixture, pure 2,3-dimethylpentane was separated by fractionation. Thus, one of the rearranged olefins is identified as 2,3-dimethylpentene. The boiling point range, and in particular the refractive index curve for the second hydrogenated rearranged product, offer strong evidence in favor of the 2,4-dimethyl isomer. The above distillation analysis is shown in Fig. 1.

It is of interest to note that in the case of the principal olefin, 4,4-dimethyl-2-pentene, only a very small amount of evidence was obtained to indicate the presence of both *cis* and *trans* isomers. The entire distillation range, carried out in a column having an effectiveness equivalent to 100 plates, was only 0.1°. The refractive index of the first 20% of the distillate was slightly higher than that of the main portion. Hydrogenation of the first portion gave pure 2,2-dimethylpentane, Fig. 1. Thus, it seems reasonable to assume that the 4,4-dimethyl-2-pentene obtained by the above method is comprised largely of one form, presumably the higher boiling isomer.

A comparison of the results obtained by the acetate and the methyl xanthate methods in the synthesis of 4,4-dimethyl-2-pentene is shown by the following data: acetate, yield based on the carbinol 70.5%, b. p. 76.6–76.7°, d^{20}_4 0.6884, n^{20}D 1.3983; methyl xanthate,[2b] 44%, 76–76.1°, 0.6881, 1.3986. No rearranged olefins have been reported for the methyl xanthate procedure.

Experimental

Materials.—2,2-Dimethyl-3-pentanol was prepared in the usual manner, namely, the reaction of *t*-butyl-magnesium chloride with propionaldehyde. The yield of the alcohol, b. p. 132–135°, was 35%.

The acetate of 2,2-dimethyl-3-pentanol, previously prepared by the acetylation of the alcohol with acetic anhydride,[5] was prepared here by the acetylation of the alcohol by a 10% excess of acetyl chloride. The acetyl chloride was added slowly to the alcohol with stirring. The reaction mixture finally was heated at 100° for two hours. The acetate was distilled from the reaction mixture. It was washed with water and with sodium bicarbonate solution, and dried over calcium chloride. The yield of acetate, b. p. 153–158°, containing a small amount of unchanged carbinol, was 80%.

The Thermal Decomposition of the Acetate of 2,2-Dimethyl-3-pentanol.—These reactions were carried out in a pyrex tube packed with glass wool, and heated in the conventional type of electric furnace. The reaction products were collected at 0°. The olefin containing unchanged acetate was separated from the acetic acid by washing with water and with sodium bicarbonate solution. After drying over calcium chloride, the olefin was separated by distillation.

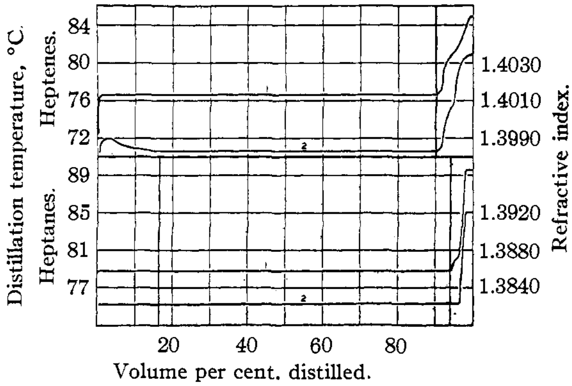

Fig. 1.—Distillation analyses of the heptenes and the corresponding heptanes obtained by the thermal decomposition of the acetate of 2,2-dimethyl-3-pentanol: curves 1, distillation temperature; curves 2, refractive index.

The decomposition of the acetate (238 g.) at 349° with a contact time of one hundred and nine seconds yielded 11.5% olefin. At 401° and a contact time of ninety-nine seconds the yield from 214 g. of the acetate was 77%.

The main portion of the acetate (538 g.), in which the olefins were analyzed by fractionation, was decomposed at 400° and a contact time of one hundred seconds. The yield of olefin, including that obtained from the second passage of the recovered acetate from the main run, was 88%. The main portion of the olefin (90.5%), pure 4,4-dimethyl-2-pentene, was separated by fractionation in a 100-plate column. The hold-up from this column, amounting to about 50 cc., was transferred to a small column having an effectiveness equivalent to 28 plates. In the latter column only a partial separation of a mixture (38 cc.) of 4,4-dimethyl-2-pentene, and two rearranged products, boiling in the 2,3- and 2,4-dimethylpentene range, was effected. The distillation analysis of the heptenes is shown in Fig. 1. The physical constants for 4,4-dimethyl-2-pentene are presented elsewhere in this paper.

The Hydrogenation of the Heptenes.—The hydrogenation of the heptenes was carried out in three separate batches: namely, the first 20%, the middle 70.5% and the last 8% of the total heptene distillate. The hydrogenation was effected by the use of Raney nickel catalyst in the absence of a solvent. The hydrogenated products in each case were purified by washing with water, concd. sulfuric acid, and finally by refluxing and fractionation over sodium. The fractionation was carried out in the 28-plate column. The distillation analysis of the heptanes is shown in Fig. 1. The physical constants for the pure heptanes thus obtained are as follows: 2,2-dimethylpentane, b. p. 78.8°, n^{20}D 1.3823; 2,3-dimethylpentane, b. p. 89.6°, n^{20}D 1.3920.

Summary

A study has been made of the thermal decomposition of the acetate of 2,2-dimethyl-3-pentanol

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[5] Favorsky, *J. prakt. Chem.*, (2) **88**, 672 (1912).

to yield 4,4-dimethyl-2-pentene and acetic acid.

About 7% rearrangement occurred in this reaction. One of the two rearranged olefins obtained in this reaction was identified as a 2,3-dimethylpentene.

In the case of the principal olefin, 4,4-dimethyl-2-pentene, little evidence was obtained of the presence of both *cis* and *trans* isomers.

2,2-Dimethylpentane, 2,3-dimethylpentane and an unidentified isomer were obtained by the hydrogenation of the heptenes.

DETROIT, MICH. RECEIVED MARCH 11, 1940

[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

The Ternary Systems Involving Cyclohexene, Water, and Methyl, Ethyl, and Isopropyl Alcohols

BY E. ROGER WASHBURN, C. LOREN GRAHAM,[1] GEORGE B. ARNOLD AND LAURENCE F. TRANSUE

In continuation of a series of investigations of similar binary and ternary systems the solubility relationships for the systems formed from cyclohexene, water and methyl, ethyl and isopropyl alcohols have been studied at 25.0°. In order to provide an indication of the changes to be expected with changes in temperature the system involving isopropyl alcohol was also studied at 15.0 and 35.0°. The proportions in which the alcohols are distributed between the water-rich and cyclohexene-rich layers have been measured.

Materials.—Good commercial grades of methyl and ethyl alcohol, and isopropyl alcohol from Eastman Kodak Company were dried by refluxing over active lime for many hours. The alcohols were then distilled from the lime into a carefully dried all-glass still. They were then slowly distilled from this still through an efficient fractionating column and preserved in carefully dried glass-stoppered bottles. The specific gravities and refractive indices of the purified materials are listed in Table I.

Several studies carried out in this Laboratory indicate that both the density and the refractive index of cyclohexene change with the passage of time if the material is in contact with oxygen. That this is probably due to the formation of a peroxide is indicated by the fact that while the freshly distilled material fails to liberate iodine from an iodide, the material which has been in contact with oxygen for some time gives positive results when added to an acidified potassium iodide–starch solution. Accordingly our cyclohexene, the better of the two grades sold by Eastman Kodak Company, was repeatedly fractionated through a carefully controlled Snyder column[2] in an atmosphere of purified nitrogen. It was collected in carefully dried, nitrogen-filled bottles and kept under nitrogen until used. It was our experience that the specific gravity and refractive index were constant at the values indicated in Table I as long as tests with potassium iodide and starch indicated no peroxide.

There is little consistency in the recorded values for the specific gravity, or for the refractive index, of cyclohexene. Therefore, since considerable effort was made in this work to obtain material of a high degree of purity, more than the usual amount of interest may attach to the value which we record. In one distillation these observations were made. Three hundred twenty-five cc. of stock material of d^{25}_4 0.80919 was distilled. The first 50 cc. collected had a value of d^{25}_4 of 0.80558, the second fraction (210 cc.) had a specific gravity of 0.80566, while the 50 cc. of residue showed the high value of 0.82152. The second fraction was then fractionated yielding 35 cc. with d^{25}_4 of 0.80564, 55 cc. of 0.80562 and leaving 50 cc. of residue of 0.80576.

A large number of similar distillations carried out by different investigators in this Laboratory lead us to believe that the specific gravity of cyclohexene d^{25}_4 is 0.8056 ± 0.0001.

TABLE I

Material	Specific gravity, d^{25}_4	Refractive index n^{25}_D
Methyl alcohol	0.7866	1.32659
Ethyl alcohol	.7851	1.35942
Isopropyl alcohol	.7809	1.37487
Cyclohexene	.8056 d^{15}_4 0.8151	1.4434

Procedure and Results.—The ternary solubility curves were determined by a titration method similar to that described elsewhere.[3] The titrations were carried out at the temperatures

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[1] Present address: Eastman Kodak Company, Rochester, New York.

[2] Hill and Ferris, *Ind. Eng. Chem.*, **19**, 379 (1927).

[3] THIS JOURNAL, **62**, 579 (1940).