TABLE I (*Concluded*)

Tertiary halide	Cc.	Reagent	Cc.	Conditions	Time, min.	Halogen reacted, %
AmCl	50	5% Na_2CO_3	100	Reflux, stir[a]	480	81.1
AmCl	50	Water	100	Reflux, stir	450	81.8
AmCl	125[b]	Water	125	Stir, cold	540	54.8[c]
		Water	125	Stir, cold	240	24.2
		Water	100	Stir, cold	870	15.4
		Water	100	Stir, cold	420	1.2
		Water	100	Stir, cold	180	0.1
				Total	2250	95.7[d,e]
AmCl	125[f]	1.4 *N* NaOH	125	Stir, cold	540	60.0
		1.4 *N* NaOH	125	Stir, cold	240	23.9
			100	Stir, cold	870	14.8
			100	Stir, cold	420	2.8
				Total	2070	100.5[g]
AmBr	57 g.	Water	150	Reflux,[h] stir	270	87.0[i]
AmBr	57 g.	Water	150	Cold, stir	270	46.5[j]
$MeBu_2CCl$	15 g.	Water	35	Reflux	450	14.0
Bu_3CCl	25 g.	Water	100	Reflux	480	1.2
	25 g.	5% Na_2CO_3	100	Reflux	480	1.3

[a] Vigorous mechanical stirring during the refluxing. [b] In this experiment the organic layer was separated and shaken with a fresh portion of water. This was continued until practically no acid was removed by this treatment. [c] This and the other figures in this experiment were obtained by titration with standard alkali. [d] A Volhard titration of an aliquot part of the combined water layers gave 92%. [e] The combined aqueous layers were fractionated through a 60 × 1.5 cm. packed adiabatic column using a high reflux ratio. The organic layer was similarly fractionated. The result was the isolation of 17.3 g. of trimethylethylene and 8.4 g. of tertiary amyl alcohol (b. p. 100–101°, n^{20}_{D} 1.4050). [f] This was similar to the preceding experiment except that successive batches of standard alkali were used instead of pure water. [g] Fractionation according to *e* gave 12 g. of trimethylethylene and 17.7 g. of tertiary amyl alcohol (b. p. 100–100.6°, n^{20}_{D} 1.4035). [h] The reflux condenser was kept at 40° to allow the trimethylethylene to pass over to a cold condenser as fast as formed. The yield of olefin was 80%. [i] The trimethylethylene boiled at 37–38.5°. Only 1.5 g. of higher boiling material was obtained. [j] The ratio of olefin to carbinol was 1:2.

Summary

1. Experiments have been conducted on the hydrolysis of several tertiary aliphatic halides under various conditions.

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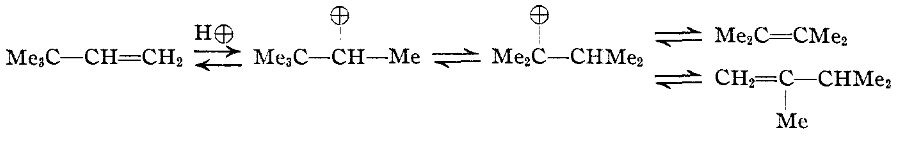
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Isomerization of Olefins. I. Conversion of *t*-Butylethylene, *unsym*-Methylisopropylethylene and Tetramethylethylene to Equilibrium Mixtures of the Three Olefins[1]

BY K. C. LAUGHLIN, C. W. NASH AND FRANK C. WHITMORE

When the dehydration of an alcohol gives more than one olefin, these may be formed directly by the action of the dehydrating agent with the alcohol or one olefin may be formed from another by an isomerizing action of the dehydrating agent. While it has long been known that such "contact isomerization" can shift the position of a double bond in a given carbon skeleton,[1a] it has remained for the present study to prove that this process can also involve the rearrangement of an alkyl group to give a new carbon skeleton.

The dehydration of methyl-*t*-butylcarbinol (pinacolyl alcohol)[2] by a catalyst consisting of phosphorus pentoxide on silica gel in a flow reactor at 300° has been found to give tetramethylethylene, *unsym*-methylisopropylethylene and *t*-butylethylene in the ratio 61:31:3. When each of these olefins was prepared pure and passed over the same catalyst under the same conditions, it gave a mixture of essentially the same composition as that obtained from the alcohol. The interconversion of the olefins probably takes place through the addition of a proton from the catalyst to one olefinic carbon, leaving the other carbon with only six electrons and thus inducing the usual rearrangements.[3] The changes involved may be the following



$$\mathrm{Me_3C{-}CH{=}CH_2} \xrightleftharpoons{H^{\oplus}} \mathrm{Me_3C{-}\overset{\oplus}{C}H{-}Me} \rightleftharpoons \mathrm{Me_2\overset{\oplus}{C}{-}CHMe_2} \begin{matrix} \rightleftharpoons \mathrm{Me_2C{=}CMe_2} \\ \rightleftharpoons \mathrm{CH_2{=}\underset{Me}{C}{-}CHMe_2} \end{matrix}$$

These results show that the formation of a given olefin from an alcohol must not be assumed to be a simple or direct process.

Experimental

The dehydration of dimethylisopropylcarbinol is the best source of *unsym*-methylisopropylethylene. The carbinol was prepared in 41% yield from isopropylmagnesium bromide and acetone. It formed an azeotropic mixture with mesityl oxide formed by the condensing action of the Grig-

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(1) Original manuscript received October 2, 1933.

(1a) Ipatief, *Ber.*, **36**, 2003 (1903).

(2) Whitmore and Meunier, THIS JOURNAL, **55**, 3721 (1933).

(3) Whitmore, *ibid.*, **54**, 3274 (1932).

nard reagent. Treatment of the mixture with β-naphthalene-sulfonic acid gave *unsym*-methylisopropylethylene, b. p. 54.7° (737 mm.), n_D^{20} 1.3904, and tetramethylethylene, b. p. 71.9° (732 mm.), n_D^{20} 1.4121, in the ratio 7 : 5,[4] together with unchanged mesityl oxide.

The *t*-butylethylene was prepared by decomposing the previously distilled methyl xanthate of pinacolyl alcohol.[5] The fraction, 22 g., with b. p. 40.2–40.25° (741 mm.), n_D^{20} 1.3760, was used.

Isomerization of the Olefins and Determination of the Products.—Each of the olefins was passed over the phosphorus pentoxide on silica gel catalyst in the reactor as used for the dehydration of pinacolyl alcohol.[2] The products were carefully fractionated through Column N (see below) at the rate of about 6 cc. per hour using a reflux ratio of 50:1. In each case a small amount of olefin boiling below 50° and having n_D^{20} 1.380 was obtained. This corresponded to *t*-butylethylene, b. p. 40.2° (741 mm.), n_D^{20} 1.376. Each gave a fraction of b. p. 54–60° and n_D^{20} 1.390 in about 15% yield corresponding to *unsym*-methylisopropylethylene, b. p. 54.7° (737 mm.), n_D^{20} 1.390. Each gave a fraction of b. p. 70.6–72.0° and n_D^{20} 1.409–1.413 in about 30% yield corresponding to tetramethylethylene, b. p. 71.9° (732 mm.), n_D^{20} 1.412. In each case a considerable amount of polymerized product was formed. The catalyst which induced isomerization also caused polymerization. Thus with each of the three olefins the chief products were tetramethylethylene and *unsym*-methylisopropylethylene in about 2:1 ratio together with traces of *t*-butylethylene and some polymerized product.

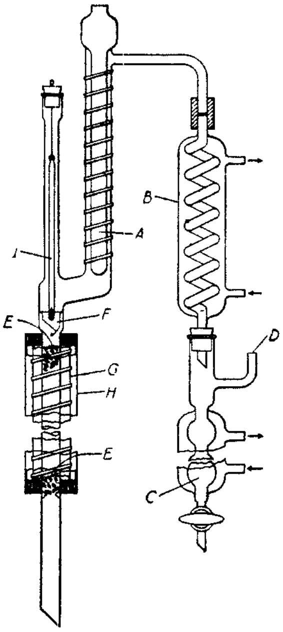

Fig. 1.

Column N has proved so useful in the analytical distillations in this study as well as in other distillations involving numerous components that Fig. 1 and a short description are given. The column is of a partial condensation type. The sealed-in glass condenser well, A, is filled with glycerol, or other suitable liquid, in which is immersed a closely fitting copper condenser which may be raised or lowered by a screw suspension device, thus controlling the amount of reflux. The distillate which passes the condenser well is condensed in the spiral, B, and is collected in the receiver, C, which is an all-glass bulb condenser of about 25-cc. capacity, fitted with a stopcock for removing fractions. . The outlet, D, may be connected to a specially cooled trap, calcium chloride tube, vacuum pump (for distillation under reduced pressure), etc. The reflux liquid is returned to the packed section, E (135 × 1.4 cm.), through the centering device, F, which also serves as a point of reference for determining the reflux. The packing is of the glass helix type[6] and is uniform throughout the column.

Adiabatic conditions are maintained by winding resistance ribbon around the glass tube, G, which is insulated by an outer tube, H. Both tubes are held in position by asbestos tape wound around the inner tube. In order to obtain accurate heat control the column is wound in three equal sections, each with its own rheostat, and a thermometer next to the packed tube. The three heating elements are connected in parallel to a 110-volt lighting circuit, which is controlled by a fourth rheostat. Thus the temperature of each part of the jacket is subject to accurate control. The head of the column, outside the condenser A, is also wound with resistance ribbon (insulated with asbestos tubing), for use with high-boiling liquids. The thermometer, I, is of the Anschütz type, and is supported by a wire through the stopper.

The packed section and head of the column are enclosed in a wood case fitted with a removable glass front and the whole assembly is mounted on a frame which is readily portable. Since for best results the packed section must be perpendicular, this is checked by a spirit level before each distillation. This column has proved very efficient in the separation of liquids of similar boiling points. A test with benzene and carbon tetrachloride[7] showed that the column is equivalent to twenty-three theoretical plates, representing an H. E. T. P. of 5.9 cm. (2.3 in.).

Summary

1. The olefins *unsym*-methylisopropylethylene, tetramethylethylene, and *t*-butylethylene have been isomerized to identical mixtures of the three isomers.

2. A mechanism has been advanced for the above reactions.

3. An efficient laboratory fractionating column is described.

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[4] Schurman and Boord, THIS JOURNAL, **55**, 4930 (1933), have recently found the ratio of these olefins to be 1 : 4 when the dehydration was accomplished by anhydrous oxalic acid.

[5] Fomin and Sochanski, *Ber.*, **46**, 246 (1913).

[6] Wilson, Parker and Laughlin, THIS JOURNAL, **55**, 2795 (1933).

[7] Fenske, Quiggle and Tongberg, *Ind. Eng. Chem.*, **24**, 408 (1932).