made to prove the absence of free halogen acids in the sample of halogen compound used. These substances were all soluble in water and insoluble in benzene, ligroin and ether. Their solubility in acetone and chloroform varied considerably.

Summary

Several aryl substituted β-bromoethyl phenyl ethers have been prepared including the mono derivative of hydroquinone. These halogen compounds have been converted into substituted phenyl ethers of choline. All of them were less active than the unsubstituted phenyl ether in stimulating respiration and blood pressure.

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The Dehydration and Rearrangement of Certain Pinacolyl Alcohols and Related Compounds

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The dehydration and rearrangement of pinacolyl alcohols have been studied in only four cases in which all the groups involved are aliphatic, namely, pinacolyl alcohol itself (*tert*-butylmethylcarbinol),[2] *tert*-butylethylcarbinol,[3,4] *tert*-amylmethylcarbinol[4] and *tert*-butylisopropylcarbinol.[5] With only the first of these substances has anything approaching a complete study been made. The present investigation was undertaken in connection with theoretical studies on the mechanism of rearrangements.[6] The pinacolyl alcohols selected were 6,6-dimethyldecanol-5 (I) and 3-methyl-3-butylheptanol-2 (II) because of their availability and the variety of courses which their rearrangements might follow. These were prepared by reducing the pinacolones obtained by Meerwein[7] from the rearrangement of the glycol made from butylmagnesium bromide and ethyl α-hydroxyisobutyrate. In order to conserve the pinacolones, the methods of reducing ketones, of dehydrating secondary alcohols and of ozonizing

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[1] Presented in partial fulfilment of the requirements for the Ph.D. degree. Part of this work was done under a Grant-in-Aid from the National Research Council.

[2] Couturier, *Ann. chim. phys.*, [6] **26**, 433–501 (1892); Zelinsky and Zelikow, *Ber.*, **34**, 3250 (1901); Delacre, *Mem. acad. roy. Belg.*, 296 (1904); *Bull. soc. chim.*, [4] **1**, 575, 978 (1907); Nybergh, Hyllningsskrift tillagnad Ossian Aschan, 98–102 (1920); Van Risseghem, *Bull. soc. chim. Belg.*, **30**, 8 (1921); Fomin and Sochanski, *Ber.*, **46**, 244 (1913); H. S. Rothrock and P. L. Meunier, unpublished results from this Laboratory.

[3] Faworsky and Alexejewa, *J. Russ. Phys.-Chem. Soc.*, **50**, 557–70 (1918).

[4] Edgar, Calingaert and Marker, THIS JOURNAL, **51**, 1483 (1929).

[5] Whitmore and Houk, *ibid.*, **54**, 3714 (1932).

[6] Whitmore, *ibid.*, **54**, 3274 (1932).

[7] Meerwein, *Ann.*, **419**, 121–75 (1919).

olefins were studied with related compounds which were available in larger amounts.

By applying the principles which have been found to hold in related rearrangements,[6] the products which might be formed by dehydrating the pinacolyl alcohols may be predicted. 6,6-Dimethyldecanol-5 (I) might give (a) without rearrangement, 6,6-dimethyldecene-4 (III); (b) with rearrangement of methyl, 2-butyl-3-methylheptene-1 (IV), 5,6-dimethyldecene-4 (V) and 5,6-dimethyldecene-5 (VI); (c) with rearrangement of butyl, 2-methyl-3-butylheptene-1 (VII) and 2-methyl-3-butylheptene-2 (VIII). Similarly 3-methyl-3-butylheptanol-2 (II) might give (a) without rearrangement, 3-methyl-3-butylheptene-1 (IX); (b) with rearrangement of methyl, VIII and 2-methyl-3-butylheptene-3 (X); (c) with rearrangement of butyl, IV, V and VI. Both alcohols gave the same olefins, namely, 5,6-dimethyldecene-4 (V), 5,6-dimethyldecene-5 (VI), and 2-methyl-3-butylheptene-2 (VIII). Relatively more of V and VI were obtained from II than from I, indicating the greater mobility of the butyl group. No test for formaldehyde was obtained with any of the ozonolysis products, thus proving the absence of IV, VII and IX and indicating the difficulty in the loss of hydrogen from a methyl group when larger groups are available even though rearrangement is necessary to give an olefin without a terminal methylene group.[8] Butyldimethylacetaldehyde, the ozonolysis product characteristic of III, was carefully sought for Neither it nor the corresponding acid could be found. Thus neither alcohol gave a detectable amount of normal dehydration without rearrangement.

The only unsatisfactory part of the study is that involving the presence or absence of X. Although its characteristic ozonolysis product, 2-methylheptanone-3, could not be identified by a solid derivative, its properties are so nearly like those of its isomer, 3-methylheptanone-2 obtained from V that this failure is not necessarily significant. Moreover, the dehydration of the related substance 2-methyl-3-butylheptanol-3 gave VIII and X. The latter gave 2-methylheptanone-3 which was identified as the semicarbazone without trouble.

Experimental

Preparation of the Pinacolones.—*n*-Butyl bromide was prepared in 24-mole runs by slight modification of the sodium bromide method of Kamm and Marvel.[9] The mixture was refluxed for eight hours. Stirring was continued through the distillation of the bromide from the reaction mixture. The sulfuric acid washings on dilution with a large amount of water gave 440 g. of the bromide. The total yield of *n*-butyl bromide, b. p. 98–100° (735 mm.), was 2930 g. (89% of the theoretical amount).

n-Butylmagnesium bromide was prepared in 8-mole runs with yields of 90–92%.

Commercial ethyl α-hydroxyisobutyrate was dried with sodium sulfate and distilled through a 40 × 1.5 cm. packed, insulated, total condensation, adjustable take-off

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[8] This agrees with a large mass of unpublished data accumulated in this Laboratory.

[9] "Organic Syntheses," 1921, Vol. I, p. 6.

column,[10] using a 5:1 reflux ratio. The fraction of b. p. 144–145.5° (730 mm.) was used for the preparation of 2-methyl-3-butylheptandiol-2,3 according to the method of Meerwein.[7] The ester in 2-mole lots was added to the Grignard solution from 8 moles of *n*-butyl bromide using a total of 3 liters of ether per run. After removal of ether, the product was distilled at 2 mm. pressure and divided into fractions below and above 50°. The lower fraction was distilled through the 40 × 1.5 cm. column at 730 mm., giving fractions: (1) below 115°, 7 g.; (2) 115–122°, 15 g. (*n*-butyl alcohol, identified by the 3,5-dinitrobenzoate); (3) 122–140°, 9 g.; (4) 140–148°, 21 g. (unchanged α-hydroxyisobutyrate, identified by conversion to the solid acid); (5) 148–183°, 10 g.; (6) 183–188°, 10 g. (reacted instantly with bromine in carbon tetrachloride). The material boiling above 50° (2 mm.) could not be distilled through a packed column because of its high viscosity. It was distilled through a 40 × 2.4 cm. column without packing except a layer of beads at the bottom. Otherwise the arrangement of the column was as usual. A reflux ratio of over 5:1 and a pressure of 1 mm. were used. The fractions were: (1) 50–80°, 11 g.; (2) 80–85°, 29 g.; (3) 85–94°, 24 g.; (4) 94–99°, 7 g.; (5) 99–104°, 159 g. Fractions 2–4 contained mixtures of the desired glycol and the by-product identified by Meerwein as 2-methylheptanediol-2,3.[7] Fraction 5 solidified in long waxy needles, m. p. 31.5–32° (Meerwein 32°); yield 45%, based on the ester not recovered. A total of 1314 g. of the glycol-2-methyl-3-butylheptanediol-2,3 was prepared.

Meerwein's method of rearranging the glycol was slightly modified by lowering the temperature of the sulfuric acid by means of solid carbon dioxide (Dry Ice). The glycol and a mortar and pestle were cooled to 0°. At this temperature the glycol could be finely powdered. A half mole of the glycol was then added over half an hour to 1 kg. of concd. sulfuric acid kept at −20° by the addition of pieces of Dry Ice. Stirring was continued for two hours and then the orange colored reaction mixture was kept in the refrigerator for ten hours. The mixture (then at −2°) was poured on 1.5 kg. of finely cracked ice. The oil layer was separated and the acid layer was extracted with ether. The product was distilled under reduced pressure, b. p. 76–82° (4 mm.), 97–107° (15 mm.). The yield was 63 g. (69%). The other fractions were: (1) below 97° (15 mm.), 6 g.; (3) 107–140° (15 mm.), 3 g.; (4) residue 17 g. Using dilute sulfuric acid kept at −10° instead of ice for diluting the reaction mixture did not increase the yield. A total of 626 g. of the mixture of pinacolones was prepared.

The pinacolones were separated according to the procedure outlined by Meerwein, the details of which were worked out as indicated in the following typical run. To 184 g. (1 mole) of the pinacolone mixture, containing about 35% of the methyl ketone, were added a solution of 40 g. (0.36 mole) of semicarbazide hydrochloride in 100 cc. of water and a solution of 50 g. (0.36 mole) of sodium acetate crystals in 500 cc. of 95% alcohol. After cooling for twenty hours in the refrigerator, a considerable crop of crystals of the semicarbazone of the methyl ketone (3-methyl-3-butylheptanone-2) separated. After stirring and standing six hours more, the crystals were removed by filtration and the mother liquor was diluted to 2 liters with water to precipitate the unreacted ketone, mainly the butyl ketone (6,6-dimethyldecanone-5). On standing for twenty-four hours longer at 0°, more crystals of the semicarbazone of the methyl ketone separated and were removed. The unreacted pinacolone from six runs was treated with semicarbazide as before and allowed to stand a month. More of the crystalline semicarbazone of the methyl ketone separated. The entire process was repeated once more to give only a small amount of crystals.

The semicarbazone of 3-methyl-3-butylheptanone-2 after four crystallizations from 95% alcohol melted at 105–107°. It was better purified by two crystallizations from 60–80° ligroin. The m. p. was 107.2–107.7° (corr.) and was not raised by further crystallizations. A total of 299 g. of semicarbazone of this purity was obtained. The

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[10] Whitmore and Lux, THIS JOURNAL, **54**, 3451 (1932).

methyl ketone was regenerated by refluxing half mole portions of the semicarbazone with ten weights of 20% oxalic acid solution for four hours. The yield was 88 g. (96%). Distillation of the products from several runs through a 30 × 0.7 cm. indented column using a reflux ratio of 10:1 gave 206 g. of 3-methyl-3-butylheptanone-2 of b. p. 104.5–105.5° (14 mm.), 70–71° (2 mm.), n^{20}_{D} 1.4371. Meerwein gives b. p. 107.5–108.5° (14 mm.), and n^{20}_{D} 1.43667.

The butyl ketone was recovered from the mother liquors, which gave no further crystallization of the semicarbazone of the methyl ketone. Dilution of the solution with water, separation and drying of the oily layer gave 313 g. of material. Of this only 200 g. distilled. The residue was a tarry material of ammoniacal odor. This proved to be impure semicarbazone of the butyl ketone. Treatment with oxalic acid solution gave a 78% recovery of the butyl ketone from the tar. All the butyl ketone was distilled through the 30 × 0.7 cm. column giving 206 g. of 6,6-dimethyldecanone-5, b. p. 63.0–63.5° (1.5 mm.), 216–217° (735 mm.), n^{20}_{D} 1.4346. Meerwein gives b. p. 105.5–106.5° (14 mm.) and n^{20}_{D} 1.43420.

The 2-methylheptanediol-2,3 obtained as a by-product in the preparation of the main glycol was rearranged by concentrated sulfuric acid at −5°. From 284 g. of crude material boiling at 80–99° (1 mm.) was obtained 123 g. of 2-methylheptanone-3 boiling at 155–156° (728 mm.).

Reduction of the Pinacolones.—Preliminary experiments on various methods of reduction were tried with less expensive ketones.

Platinum oxide catalyst was prepared according to the method of Adams and Shriner and successfully tested in the reduction of maleic acid in a Burgess–Parr hydrogenation apparatus according to the method of Adams and Voorhees. Acetone was hydrogenated with this catalyst to give an 80% yield of isopropyl alcohol, b. p. 79–82° (732 mm.). All attempts to reduce the following ketones with this platinum oxide catalyst gave only unchanged material: methyl isopropyl ketone, methyl *n*-amyl ketone, 2-methylheptanone-3 and the pinacolone, 3-methyl-3-butylheptanone-2.

Reduction of the first three of these ketones by sodium and moist ether, moist benzene and various dilutions of ethyl alcohol with water gave yields of the carbinols up to 65%. When the best conditions were used with the pinacolones further refinements were introduced which increased the yields. A typical run follows.

To 46 g. (0.25 mole) of 6,6-dimethyldecanone-5 in a 500-cc. three-necked flask fitted with a special mercury-sealed stirrer and a reflux condenser were added 150 cc. of a solution of sodium carbonate saturated at room temperature and 150 cc. of benzene. The stirrer, of the propellor type with highly pitched blades, extended just below the surface of the benzene and was run at a rate slow enough to avoid much disturbance of the sodium carbonate solution. Over a period of thirty-six to forty-eight hours 30 g. (1.3 moles) of sodium was added in small portions in 1–2 mm. cubes. The pieces of sodium floated on the sodium carbonate layer. At the end of the time, 50 cc. of water was added to dissolve solid sodium carbonate which had separated and to react with the last of the sodium. The benzene layer was distilled through a 60 × 1.4 cm. packed adiabatic column using a reflux ratio of 1:1 until the boiling point reached 82° (733 mm.). The residue was distilled under reduced pressure through the same column using a reflux ratio of 5:1. The yield of 6,6-dimethyldecanol-5 of b. p. 112–113° (15 mm.) was 90%. The ketone was reduced in six runs, the fore-run from each distillation being added to the next reduction. A total of 174 g. of the alcohol was prepared. It had the following properties: n^{20}_{D} 1.4469; d^{20}_{4} 0.845.

Anal. Calcd. for $C_{12}H_{26}O$: C, 77.3; H, 14.1. Found: C, 77.4; H, 14.1.

In an exactly similar way 3-methyl-3-butylheptanone-2 was reduced to give 180 g. of 3-methyl-3-butylheptanol-2, b. p. 112.0–112.5° (14 mm.), n^{20}_{D} 1.4492, d^{20}_{4} 0.850.

Anal. Calcd. for $C_{12}H_{26}O$: C, 77.3; H, 14.1. Found: C, 77.6; H, 14.0.

Dehydration of the Pinacolyl Alcohols.—Again preliminary experiments were tried on less expensive carbinols. Since the literature is definitely lacking on the dehydration of alcohols these experiments will be given in some detail.

n-Butylisopropylcarbinol (24 g.), b. p. 159–164° (740 mm.), was heated with pure *p*-toluene sulfonic acid (0.5 g.) at 150° for two hours without the formation of any olefin. The addition of a trace of phenol and heating for two hours more gave no change. Finally the mixture was refluxed (162°) for two hours. The original carbinol was recovered unchanged. When 20 g. of the recovered carbinol was refluxed for two hours with a solution of 15 cc. of concd. sulfuric acid in 25 cc. of water, 8.5 g. of olefin, b. p. 125–140° (739 mm.), was obtained.

Capryl alcohol was treated with various concentrations of 100% sulfuric acid in glacial acetic acid at various temperatures. At lower temperatures there was no reaction. At higher temperatures small amounts of olefin and large amounts of capryl acetate were obtained.

Experiments with solutions of 100% sulfuric acid in diethyl ether were more successful, giving as high as 50% yields of olefin.

Finally nineteen runs were made with capryl alcohol and 100% sulfuric acid in varying amounts and under widely varied conditions.[11] The best run follows. To 130 g. of capryl alcohol (b. p. 177.2–177.4° (740 mm.), n^{20}_{D} 1.4260), in a 250-cc. flask connected to a 60 × 1.4 cm. packed adiabatic column set for vacuum distillation was added 5 cc. of 100% sulfuric acid. The mixture was heated to boiling and distilled at atmospheric pressure for eight minutes. The pressure was then gradually reduced to 50 mm. while the remainder distilled. The total time was twenty-five minutes and the highest temperature at the head of the column was 92°. A 90% yield of olefin of b. p. 122–128° (733 mm.) was obtained.

Similar experiments were made with dicapryl alcohol, 7-methylpentadecanol-9, (b. p. 130–132° (2 mm.), 102–104° (0.25 mm., McLeod gage), n^{20}_{D} 1.4478). With 25 and 50% solutions of 100% sulfuric acid in glacial acetic acid, 60% yields of olefins were obtained. Nine runs were made with dicapryl alcohol and small amounts of sulfuric acid. The best of these follows. To 54.3 g. of dicapryl alcohol in a flask attached to a 10 × 1 cm. packed column was added 1.3 cc. of 100% sulfuric acid. The mixture was heated for five minutes at a gradually decreased pressure of 500–100 mm. The few cc. of distillate was returned to the flask, the whole washed with sodium carbonate solution and water, dried by heating under reduced pressure and distilled through the 30 × 0.7 cm. column (McLeod gage). A yield of 45.7 g. of olefin of b. p. 106–111° (4 mm.) and n^{20}_{D} 1.4419 corresponding to 91% was obtained. This procedure was repeated with a yield of 90%.

6,6-Dimethyldecanol-5 was dehydrated in the same way as the dicapryl alcohol. This was done in five runs, each using 55 g. of the alcohol and 2 cc. of 100% sulfuric acid. The pressure was reduced to 400 mm. and the mixture was heated as rapidly as possible with a free flame. In seven minutes 4 cc. of water and 10 cc. of olefin distilled, the distillation temperature reaching 140°. The reaction mixture was cooled at once, mixed with the distillate, washed with 20 cc. of sodium carbonate solution saturated at 25°, separated, dried by warming under reduced pressure and distilled through the 30 × 0.7 cm. column without reflux. The yield was 46.6 g. of olefin of b. p. 78–83° (14 mm.), and n^{20}_{D} 1.4370, corresponding to 93%. A residue of 2.9 g. was added to the next run for dehydration. In this way 183 g. of the alcohol gave 135 g. of olefin representing a yield of 82%.

3-Methyl-3-butylheptanol-2 was dehydrated in an exactly similar way in three

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[11] *Cf.* Senderens. *Compt. rend.*, **154**, 777 (1913).

runs. In this way 167 g. of the alcohol gave 141 g. of olefin of b. p. 80–85° (15 mm.) and n^{20}_{D} 1.4374 corresponding to a 93% yield.

The Structure of the Olefins.—The technique of ozonolysis and identification of the resulting products was developed with the olefins from the dehydration of dicapryl alcohol and of 5-isopropylnonanol-5. The latter was prepared in 69% yield from ethyl isobutyrate and *n*-butylmagnesium bromide. Properties: b. p. 75.0–75.5° (2 mm.), 110–113° (16 mm.), n^{20}_{D} 1.4446, d^{20}_{4} 0.844.

Anal. Calcd. for $C_{12}H_{26}O$; C, 77.3; H, 14.1. Found: C, 77.4; H, 14.0.

The olefin mixture from dicapryl alcohol on ozonolysis[12] gave definite indications of hexaldehyde, heptaldehyde and 2-methyloctanal.[13]

The dehydration of 5-isopropylnonanol-5 with a trace of sulfuric acid or iodine gave 90% yields of olefins (b. p. 190–195° (732 mm.), n^{20}_{D} 1.4376). Ozonized oxygen was passed for thirty-two hours into a solution of 33.6 g. (0.2 mole) of these olefins in 200 cc. of petroleum ether (b. p. 5–30°).[14] The solvent was then removed at 35° and 25 mm. pressure; yield of crude ozonide 96%. This was decomposed with boiling water and zinc dust.[12] A trap containing alcohol kept below 0° was connected with the apparatus. When the first part of the aqueous distillate was redistilled and the first portion treated with benzaldehyde and alcoholic sodium hydroxide,[15] dibenzylidene acetone, m. p. 110–111°, was formed. Extraction of the reaction mixture with ether gave 29 g. of carbonyl compounds, a yield of 76%. Two distillations through the 30 × 0.7 cm. column using a reflux ratio of about 10:1 gave eight fractions of b. p. 48 to 200° and n^{20}_{D} 1.4119 to 1.4237. The 65–75° fraction gave the 2,4-dinitrophenylhydrazone of butyraldehyde, m. p. 122°. The 153–158° fraction gave the semicarbazone of 2-methylheptanone-3, m. p. 109°. The 183–188° fraction gave the semicarbazone of nonanone-5, m. p. 89–89.5°. These were all confirmed by mixed melting point determinations. No other products were identified. The dehydration of 5-isopropylnonanol-5 thus gives two olefins, 2-methyl-3-butylheptene-2 and 5-isopropylnonene-4, hydrogen being supplied by both the isopropyl and butyl groups. The amounts of the various carbonyl compounds obtained indicates that the former is formed in much the larger amounts.

The olefins from 6,6-dimethyldecanol-5 were ozonized in the same way giving yields of crude ozonides of 94–98%. These were decomposed by zinc and boiling water as before using the special apparatus devised by one of us (K.) for the rapid removal of the products to avoid their oxidation.[12] The ozonolysis products (65 g.) were twice distilled through a 60 × 1.4 cm. packed adiabatic column using a reflux ratio of over 20:1. Sixteen fractions and a residue of 7 g. were obtained. Fraction 1 gave dibenzylidene acetone, m. p. 110.5–111.5°; fraction 3, 6.5 g., b. p. 70–75° (741 mm.), n^{20}_{D} 1.3813, and fraction 5, 6.7 g., b. p. 123–127° (741 mm.), n^{20}_{D} 1.4009, gave the 2,4-dinitrophenylhydrazones of *n*-butyraldehyde, m. p. 121° and of hexanone-2, m. p. 106°. Mixed melting point determinations confirmed these substances. Fraction 8, 4.3 g., b. p. 150–155° (741 mm.), n^{20}_{D} 1.4124 gave no semicarbazone even on standing for seventeen days.

Repeated attempts to make a solid derivative from this fraction resulted in only a small amount of the semicarbazone of 3-methylheptanone-2, m. p. 87°,[16] which was obtained in larger amounts from fractions 9–11, 10.4 g., b. p. 155–161°, n^{20}_{D} 1.414; mixed m. p. 87–88°.

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[12] Whitmore and Church, This Journal, 54, 3712 (1932).

[13] This work is being continued by J. M. Herndon in this Laboratory.

[14] Supplied by The Viking Corporation, Charleston, W. Va.

[15] Straus and Caspari, *Ber.*, 40, 2698 (1907).

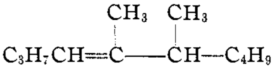
[16] Powell [This Journal, 46, 2517 (1924)] gives the melting point of this semicarbazone as 82°. This is evidently in error. 3-Methyl-heptanone-2 was synthesized from ethyl *n*-butylacetoacetate and methyl iodide in 45% yield. It had b. p. 157–161° (733 mm.) and n^{20}_{D} 1.414. Its semicarbazone was crystallized from absolute ethyl alcohol to constant m. p. 87–88°. *Anal.* Calcd. for $C_9H_{19}ON_3$: C, 58.3; H, 10.3. Found: C, 58.5; H, 10.5.

Fractions 14 to 16, 9.1 g., b. p. 178–200°, n^{20}_{D} 1.42, on distillation gave material of b. p. 187–192° and n^{20}_{D} 1.421, which formed the semicarbazone of nonanone-5, as shown by melting point and mixed melting point of 89°.

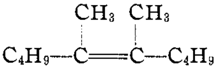
The material in the cold alcohol trap and the aqueous distillates were tested for formaldehyde using resorcinol and sulfuric acid. No formaldehyde was detected. The test as used gave positive results with known solutions of formaldehyde in the presence of acetone, butyraldehyde and a mixture of the two.

If the dehydration of 6,6-dimethyldecanol-5 had taken place without rearrangement, one of the ozonolysis products of the resulting olefin would be a C_8 aldehyde boiling in the range 130–150°. Fractions 7–9, b. p. 130–157°, were tested for aldehydes with Schiff's reagent with negative results.[17]

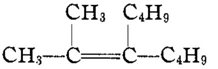
The identification of acetone, butyraldehyde, nonanone-5, hexanone-2 and 3-methylheptanone-2 in the ozonolysis products shows that the olefins from the dehydration of 6,6-dimethyldecanol-5 are

(a) 5,6-dimethyldecene-4, 

$$C_3H_7CH{=}\overset{CH_3}{\overset{|}{C}}{-}\overset{CH_3}{\overset{|}{C}}H{-}C_4H_9$$ (V)

(b) 5,6-dimethyldecene-5, 

$$C_4H_9{-}\overset{CH_3}{\overset{|}{C}}{=}\overset{CH_3}{\overset{|}{C}}{-}C_4H_9$$ (VI)

(c) 2-methyl-3-butylheptene-2, 

$$CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}\overset{C_4H_9}{\overset{|}{C}}{-}C_4H_9$$ (VIII)

The olefins from the dehydration of 3-methyl-3-butylheptanol-2 were ozonized in an exactly similar way. The yields of crude ozonide and crude carbonyl compounds were 96 and 80%, respectively. The careful fractionation of 71 g. of the carbonyl compounds through a 60 × 1.4 cm. column and then through a 60 × 0.7 cm. column of the usual type employed in these researches gave fifteen fractions and a residue of 6.3 g. The water layer from the steam distillation of the ozonolysis product contained acetone. Fraction 3, 3 g., 5–6, 13.5 g., contained butyraldehyde and hexanone-2. Fractions 8–9, 13 g., b. p. 153–158° (733 mm.), n^{20}_{D} 1.413, gave a semicarbazone which melted at 76° even after many crystallizations. The melting points of the semicarbazones of 2-methylheptanone-3 and 3-methylheptanone-2 are 110 and 88°, respectively, the boiling points of the ketones are 155–156° and 157–159° and their refractive indices are 1.412 and 1.414, respectively. Treatment of 16 g. from fractions 7–12 with sodium bisulfite solution failed to give any separation. The material which did not react with the bisulfite was fractionated giving 2 g. of material of b. p. 152–157° (738 mm.) and n^{20}_{D} 1.4120. This gave a small amount of a semicarbazone of m. p. 75°. Three crystallizations from absolute alcohol and three from 50–70° petroleum ether gave a constant melting point of 86–87°. A mixed melting point proved this to be the semicarbazone of 3-methylheptanone-2. Study of the mother liquors from this material failed to indicate the presence of any of the semicarbazone of the isomeric 2-methylheptanone-3.

Fractions 10–11, 9.1 g., b. p. 158–161° (735 mm.), n^{20}_{D} 1.414, also contained 3-methylheptanone-2. Fractions 14–15 on redistillation gave material of b. p. 186–190° (735 mm.) and n^{20}_{D} 1.424 which formed the semicarbazone of nonanone-5.

The water layers and the alcohol trap gave no test for formaldehyde, thus eliminating from consideration all olefins containing a terminal double bond, including the product which would be formed by a normal dehydration without rearrangement.

The identification of *n*-butyraldehyde and 3-methylheptanone-2 showed the presence of 5,6-dimethyldecene-4. Hexanone-2 indicated 5,6-dimethyldecene-5. These two olefins were formed by the shift of one of the two butyl groups. The formation

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[17] *Cf.* Conant and Bartlett, THIS JOURNAL, **54**, 2896 (1932).

of acetone and nonanone-5 showed the presence of 2-methyl-3-butylheptene-2, formed by the shift of the methyl group. If none of the isomeric substituted heptene-3 was formed (as indicated by the failure to identify any 2-methylheptanone-3), it indicates that the loss of a proton by the rearranged fragment took place exclusively from the tertiary hydrogen and not at all from the butyl group. This would be surprising in that the dehydration of 5-isopropylnonanol-5 gave dehydration involving both the tertiary hydrogen and the butyl group, although mainly the former. This possible inconsistency is being studied further.

Summary

1. Meerwein's preparation of 6,6-dimethyldecanone-5 and 3-methyl-3-butylheptanone-2 has been repeated and checked in every detail.

2. A method for reducing complex ketones has been developed and applied to these two pinacolones to give nearly quantitative yields of 6,6-dimethyldecanol-5 and 3-methyl-3-butylheptanol-2.

3. A method for dehydrating secondary alcohols with sulfuric acid has been developed with capryl alcohol and dicapryl alcohol and has been applied to the two pinacolyl alcohols in 2 to give over 90% yields of olefins.

4. The two pinacolyl alcohols in 2 underwent the reversed pinacolone rearrangement, giving mixtures of the same three olefins, 5,6-dimethyldecene-5 and -4 and 2-methyl-3-butylheptene-2. None of the expected 2-methyl-3-butylheptene-3 was detected in the olefins from 3-methyl-3-butylheptanol-2. The structure of the olefins was determined by ozonolysis by a technique developed in this Laboratory.

5. 5-Isopropylnonanol-5 was prepared and dehydrated to give the olefins, 2-methyl-3-butylheptene-2 and -3 as shown by their ozonolysis products.

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