denser fitted with a calcium chloride tube. The cyclohexene previously had been refluxed over potassium and distilled through a 30-cm. Vigreux column; b.p. 82.1°, $n^{25}\mathrm{D}$ 1.4440. After 24 hr. under reflux in a nitrogen atmosphere, the solution was concentrated by distillation at 60 mm. The residue was dissolved in ether, extracted with four 25-ml. portions of 5% aqueous sodium hydroxide, washed with three 25-ml. portions of water, dried, and concentrated. The residue (34.5 g.) was fractionally distilled *in vacuo*, giving 17.75 g. of a fraction, b.p. 92–110° at 0.6 mm., which was redistilled to give 16.45 g. of the mixture of cyclohexyl and cyclohexenyl benzoate, b.p. 108.5–114.3° at 0.8 mm. Duplicate analyses of this sample indicated 1.36 and 1.35% ^{18}O calculated for one oxygen atom.

The second run carried out under the same conditions with 20.0 g. of labeled peroxide and 64.9 g. of cyclohexene afforded 12.72 g. of a mixture of cyclohexyl and cyclohexenyl benzoate, b.p. 114.0–119.0° at 1.0 mm. containing 1.39 and 1.36% ^{18}O in duplicate analyses.

Reduction of the Mixture of Cyclohexyl and Cyclohexenyl Benzoate-^{18}O with Lithium Aluminum Hydride.—A mixture of 9.5 g. of lithium aluminum hydride in a 2-l., three-necked flask equipped with a reflux condenser, a drying tube, a dropping funnel and a magnetic stirrer and 640 ml. of anhydrous ether was stirred for 2 hr. under a nitrogen atmosphere and treated with 14.5 g. of the mixture of cyclohexyl and cyclohexenyl benzoate-^{18}O in 200 ml. of dry ether over a period of 10 min. After stirring for 5 hours and allowing to stand overnight, the mixture was treated with 20 ml. of water, added over a period of 1 hour. The precipitated material was filtered and washed with 300 ml. of ether, and the combined ether solution was concentrated. The residue (17.0 g.) was distilled under reduced pressure to give 5.15 g. of a mixture of cyclohexanol and cyclohexenol, b.p. 75–90° at 25 mm., and 6.05 g. of a fraction, b.p. 90–106° at 25 mm., consisting mainly of benzyl alcohol. Redistillation of this fraction gave 4.30 g. of benzyl alcohol, b.p. 105.0–106.5° at 25 mm., $n^{25}\mathrm{D}$ 1.5378, containing 0.724 and 0.734% ^{18}O in duplicate analyses.

Anal. Calcd. for C_7H_8O: C, 77.8; H, 7.5. Found: C, 77.9; H, 7.4.

A fraction of b.p. 75–79° at 27.0 mm. obtained by redistillation of the mixture of cyclohexanol and cyclohexenol was separated by gas–liquid partition chromatography on a 2.5-m. column (6 mm. i.d.) packed with 40–60 mesh firebrick supporting one-quarter its weight of monohydroxyethyltrihydroxypropylethylenediamine (Visco Products, Inc., Houston, Tex.). Samples of 0.13–0.15 ml. were diluted with one-half their volume of *n*-pentane and separated in the column at 110° and 20 p.s.i. Thirty-six runs (4.1 g. of the mixture) gave 295 mg. of material with retention times of 80–84 min. (mainly cyclohexenol) and 3.80 g. of cyclohexanol with retention times of 60–70 min. The cyclohexenol fractions were refractionated twice under the same conditions to give 77 mg. of pure cyclohexanol, $n^{25}\mathrm{D}$ 1.4832, 0.420 and 0.405% ^{18}O.

Anal. Calcd. for $C_6H_{10}O$: C, 73.4; H, 10.3. Found: C, 73.3; H, 10.3.

A portion of the combined cyclohexanol fractions was refractionated under the same conditions to give pure cyclohexanol, $n^{25}\mathrm{D}$ 1.4632, 0.615 and 0.635% ^{18}O.

Anal. Calcd. for $C_6H_{12}O$: C, 71.9; H, 12.2. Found: C, 72.2; H, 12.2.

The mixture of cyclohexyl and cyclohexenyl benzoate-^{18}O (12.0 g.) obtained in the second experiment gave benzyl alcohol containing 0.658 and 0.654% ^{18}O, cyclohexenol, 0.392 and 0.400% ^{18}O and cyclohexanol, 0.647 and 0.622% ^{18}O.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

"1,3-Shifts" in Rearrangements of 3,4,4-Trimethyl-2-pentyl Derivatives[1]

BY WILLIAM H. SAUNDERS, JR., AND GERARD L. CARGES

RECEIVED OCTOBER 24, 1959

The dehydration of 3,4,4-trimethyl-2-pentanol (I) has been studied under a variety of conditions. Product identification was accomplished by gas chromatography and infrared spectra, using independently-prepared olefins as reference samples. Under conditions where the dehydration of I is irreversible, nearly all of the product has the same carbon skeleton as I. Significant amounts of product having the 2,3,4-trimethylpentane skeleton result only under conditions strenuous enough to cause isomerization of the first-formed products. Thus the apparent "1,3-shift" is most probably a succession of 1,2-shifts rather than a direct process.

All but a handful of the many examples of carbonium-ion rearrangements are simple 1,2-shifts or combinations of 1,2-shifts. Among the few apparent exceptions to this rule have been the 1,3-shifts of methyl groups reported in certain highly-branched systems.[2,3,4] Schneider and Kennedy[5] have argued that most of these examples can be explained as successive 1,2-shifts. Mosher and Cox,[6] however, examined a system in which the distinction could be made and reported results consistent only with a direct 1,3-shift.

Our aim in the present work was to define more clearly the conditions for 1,3-shifts. In addition, more positive separation and identification of products is possible through the use of gas chromatography. We could thus eliminate the possibility that observed rearrangements might be artifacts of the degradative procedures used by earlier workers.

The simplest system which gives apparent 1,3-shift is 3,4,4-trimethyl-2-pentyl.[7] The corresponding alcohol, 3,4,4-trimethyl-2-pentanol (I) was therefore chosen for our work so as to minimize the task of separating and identifying the products. This substance resulted from the lithium aluminum hydride reduction of 3,4,4-trimethyl-2-pentanone, which in turn was obtained by the action of dimethylcadmium on the acid chloride of the known[8] methyl-*t*-butylacetic acid. Further details of the synthesis of I will be found under Experimental.

Since I has two asymmetric carbons (C_2 and C_3) it should be capable of existing in two diastereomeric

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[1] This work was supported in part by the Office of Ordnance Research, U. S. Army. G. L. C. received a stipend from the has. Pfizer and Co. grant during part of the period of this work.

[2] F. C. Whitmore, K. C. Laughlin, J. F. Matuszeski and J. D. Surmatis, THIS JOURNAL, **63**, 756 (1941).

[3] F. C. Whitmore and W. A. Mosher, *ibid.*, **68**, 281 (1946).

[4] N. L. Drake, G. M. Kline and W. G. Rose, *ibid.*, **56**, 2076 (1934).

[5] A. Schneider and R. M. Kennedy, *ibid.*, **73**, 5017, 5024 (1951).

[6] W. A. Mosher and J. C. Cox, Jr., *ibid.*, **72**, 3701 (1950).

[7] The 3,4,4-trimethyl-2-pentyl carbonium ion was undoubtedly an intermediate in the acid-catalyzed copolymerization of *sec*-butyl and *t*-butyl alcohols,[2] in which 2,3,4-trimethyl-2-pentene, the result of a 1,3-shift, was a major product.

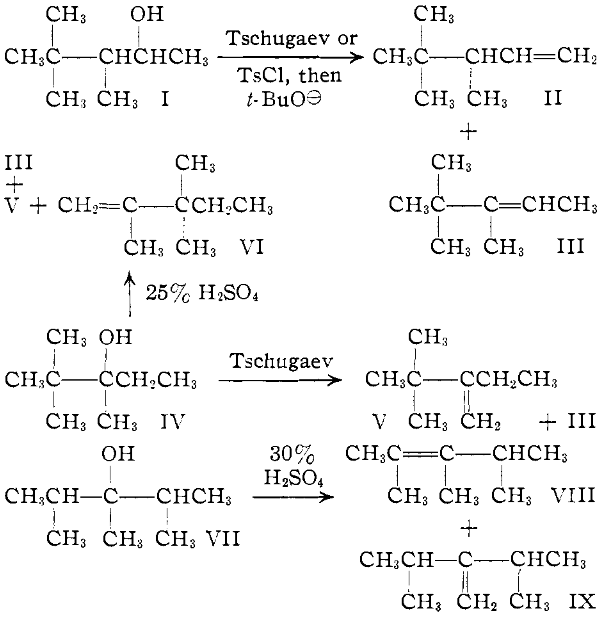
[8] C. G. Overberger and M. B. Berenbaum, THIS JOURNAL, **74**, 3293 (1952).

forms. A gas chromatogram of I showed two peaks in a ratio of about 3:2. Each of these peaks was collected and the infrared spectra taken. These spectra showed the same functional-group absorption, differing only in the $7–11\ \mu$ region. The ketone from which compound I was obtained gave only one peak. The I used in the dehydration experiments was the mixture of diastereomers.

Identification of the dehydration products required reference samples of the expected olefins. Attention therefore was directed to preparation of the isomeric trimethylpentenes. The methods employed are outlined in Chart I. None of the syntheses gave a single pure product, but the olefins could be separated from each other by gas chromatography and the peaks in the chromatograms identified. For example, the common product in dehydrations of I and IV must be III. The predominant (*ca.* 80%) product from dehydration of VII was assumed to be VIII. No unequivocal synthesis of VI was undertaken, but it did not correspond to any other reasonable possibility and has been found in dehydration of IV under other conditions.[9,10] Another possible product is 2,3,4-trimethyl-1-pentene, but this should reduce (see below) to XII, which was not obtained in appreciable amounts from the olefinic products from I or IV.

CHART I

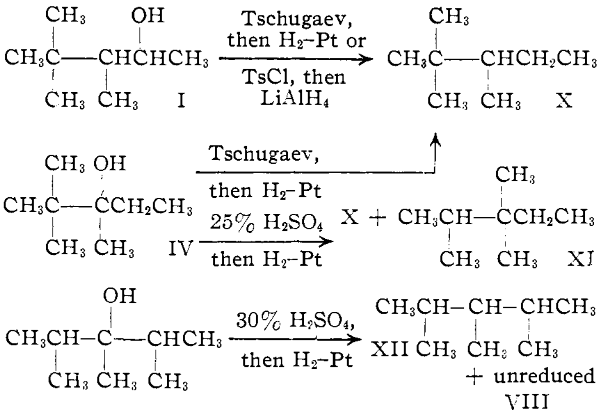
PREPARATIONS OF REFERENCE OLEFINS



As a further check on the carbon skeletons of some of the products from acid-promoted dehydration of I, the olefins were reduced to saturated hydrocarbons and these compared on the gas chromatograph with independently-prepared reference samples. Chart II shows the syntheses of these reference samples. Infrared spectra were also compared in some cases.

CHART II

PREPARATION OF SATURATED HYDROCARBONS



Compositions of products obtained in preparation of the reference olefins and in the dehydration experiments on I and related compounds are recorded in Table I. Table II gives the compositions of the saturated hydrocarbon mixtures obtained by reduction of selected olefin mixtures. In general the results in Table II confirm those in Table I, though incomplete reduction makes some of the comparisons only semi-quantitative. Details on reaction conditions and methods of analysis are given under Experimental.

Relatively mild conditions, such as distillation of I from naphthalenesulfonic acid (run 1) or acetolysis of I-tosylate (Ia, runs 6 and 7) give olefin mixtures having the same carbon skeleton (> 95%) as I. Yields in these reactions were 80% or better. Thus *irreversible* carbonium-ion processes seem to give little or no 1,3-shift product.

As conditions become more strenuous, the proportion of rearranged material increases (runs 2–4). A similar phenomenon is observed with IV (runs 15–18), where increasing acid concentrations or longer contact times lead to more VIII. The increase in rearranged olefin is largely at the expense of III and under the stronger conditions small amounts of di-isobutylenes (2,4,4-trimethylpentenes) are formed as well.

The data so far cited suggest strongly that rearranged products result only when the first-formed olefins can revert repeatedly to carbonium ions. Efforts to provide further confirmation by isomerizing known olefin mixtures gave inconclusive results (runs 5, 9–12). In two runs (9 and 12) isomerization did occur, but in others it did not. Even when it did, it obviously was slower than the formation of rearranged products in the dehydrations. Possibly the dehydration of the alcohol gives small amounts of by-products which increase the mutual solubility of olefin and acid and thereby facilitate the isomerization.

We also repeated the original example of the 1,3-shift of methyl in the copolymerization of *s*-butyl and *t*-butyl alcohols.[2] This presumably involves addition of *t*-butyl carbonium ion to 2-butene to give the 3,4,4-trimethyl-2-pentyl carbonium ion, followed by direct proton loss or rearrangement and proton loss. The results (run 21) compare remarkably well with those reported by Whitmore[2] (run 22). Although there are some differences on minor products, the two major products agree within experimental error.

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(9) F. C. Whitmore and K. C. Laughlin, THIS JOURNAL, **54**, 4011 (1932).

(10) A. L. Henne and A. H. Matuszak, *ibid.*, **66**, 1649 (1944).

TABLE I

COMPOSITION OF OLEFIN MIXTURES

Run	Starting material	Conditions[a]	Product composition, %[m] II	III	V	VI	VIII
1	I	N	8	75	13	Tr.	3
2	I	25% S, 2 hr.	3	66	7	16	8
3	I	25% S, 9 hr.	3	65	.. (21)[b]	.	11
4	I	25% S, 18 hr.	6[c]	39	19[d]	11	25
5	[e]	25% S, 20 hr.	3	69	.. (21)[b]	..	7
6	Ia[f]	A	5	80	10	3	2
7	Ia	A	5	82	8	3	2
8	Ia	B	55	45	.		
9	[g]	20% S, 20 hr.	3	72	.. (16)[b]	.	9
10	[g]	20% S, 18 hr.	5	77	.. (16)[b]	..	2
11	[g]	30% S, 20 hr.	7[c]	75	.. (16)[b]	.	2
12	[g]	40% S, 20 hr.	8[c]	64	.. (18)[b]	.	9
13	I	T	47	48	..	.	5[h]
14	IV	T	..	51	49	..	
15	IV	25% S, 2 hr.	..	76	5	19	..
16	IV	20% S, 18 hr.	Tr.	77	4	16	3
17	IV	40% S, 18 hr.	Tr.	68	7[d]	19	5
18	IV	75% S, 2 hr.	5[c]	37	16[d]	11	30
19	VII	30% S, 2 hr.	..	..	..	..	83[i]
20	VII	30% S, 18 hr.	..	..	..	..	80[i]
21	[j]	75% S	14[k]	39	8	..	37
22	[l]	75% S	25[k]	40	..	..	37

[a] The entries in this column refer to the following code: A = acetolysis, B = potassium *t*-butoxide in *t*-butyl alcohol, S = sulfuric acid, T = Tschugaev reaction, N = 2-naphthalenesulfonic acid. [b] Resolution on the gas chromatogram insufficient for separate measurement of V and VI. [c] This value represents a mixture of II and the diisobutylenes; resolution was insufficient for separate measurement. [d] This value represents a mixture of V and IX. [e] Product of run 2. [f] Ia = *p*-toluenesulfonate of I. [g] In runs 9, 10, 11, 12 the starting materials are the products of runs 6, 7, 10, 11, respectively. [h] Identity uncertain, VIII does not show in infrared spectrum and is an unlikely product in this reaction. [i] The other product was assumed to be IX. [j] Copolymerization of *s*-butyl and *t*-butyl alcohols by directions of Whitmore (ref. 2). [k] This figure represents mainly or entirely diisobutylenes; hydrogenation gave a product containing isoöctane in a proportion about the same as this peak in the olefin mixture. [l] Whitmore's figures (ref. 2) for the copolymerization of *s*-butyl and *t*-butyl alcohols; data are based on fractionation and ozonolysis of the fractions. [m] These sometimes do not add up to exactly 100%, since some mixtures contained minor (< 2%) unidentified components; "tr." means "trace."

TABLE II

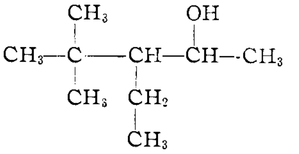
COMPOSITIONS OF SATURATED HYDROCARBON MIXTURES

Olefin mixture no.[a]	Product composition, % X	XI	XII	XIII[d]
1	97	..	3[c]	..
2[b]	70	15	..	..
4[b]	50	10	Tr.	5
13	95	..	5[c]	..
14	99	..	..	..
15	80	20	..	..
19[b]	..	..	15	..

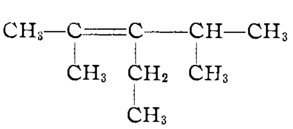
[a] "Olefin mixture no." refers to numbers of runs in Table I. [b] Incomplete hydrogenation; tetrasubstituted olefin (*cf.* Table I) accounts for all of the remainder in run 19 and most in runs 2 and 4. [c] This peak actually corresponds to unreduced VIII. [d] XIII is 2,2,4-trimethylpentane.

The system we have used does not permit an unequivocal distinction between a 1,3-shift and two successive 1,2-shifts, since the same product would result from either. The absence of "1,3-shift" in a number of irreversible carbonium-ion reactions does show that formation of the "1,3-shift" product is slow compared to loss or migration of hydrogen. Again, IV behaves in a manner similar to I and obviously VIII must be formed from IV *via* a succession of shifts. This sequence could, of course, include a 1,3-shift, but the general pattern of results makes this improbable. The isomerization experiments at least demonstrate the possibility of isomerizing III under conditions similar to those of the dehydrations. We therefore conclude that the apparent 1,3-shifts are most probably a succession of 1,2-shifts that require reversible conditions to occur to any important extent.[11]

In disagreement with this conclusion there remains the work of Mosher and Cox,[6] who dehydrated 3-ethyl-4,4-dimethyl-2-pentanol (XIV) and reported that about half of the product was XV,



XIV



XV

the result of a direct 1,3-shift (the remainder had the same skeleton as XIV). Recently, however, doubt has been cast on the structure of XIV since two efforts to repeat the scheme leading to it gave different products.[12,13,14] We have learned that the work of Mosher and Cox is being repeated.[15] Until these results are in, it seems wise to reserve judgment on the reality of the 1,3-shift in open-chain systems.

Experimental[16]

Methyl neopentyl ketone was prepared as described by Mosher and Cox[6] in yields of 20–40%, b.p. 123.5–125°, n^{25}_D 1.4020 (lit.[6] b.p. 124–125°, n^{25}_D 1.4018).

4,4-Dimethyl-3-bromo-2-pentanone was prepared by the method of Aston.[17] The product composition was about 15–25% unreacted ketone, 20–30% high-boiling material (dibromoketone?) and 45–55% monobromoketone, b.p. 57–59° (12 mm.), n^{25}_D 1.4597 (lit.[8] b.p. 83–87° (20 mm.), n^{25}_D 1.4602). The nuclear magnetic resonance spectrum (at 60 mc.) showed three peaks with areas in a ratio of 1:3:9, demonstrating that bromination had occurred at the methylene carbon.

Methyl Ester of Methyl-*t*-butylacetic Acid.—Treatment of 4,4-dimethyl-3-bromo-2-pentanone with sodium methoxide[17] gave a 70% yield of the desired ester, b.p. 86–87° (20 mm.), n^{25}_D 1.4100 (lit.[8] b.p. 143–144°, n^{25}_D 1.4090).

Methyl-*t*-butylacetic acid was obtained by saponifying the methyl ester with potassium hydroxide in diethylene glycol.[8] The product was distilled to give 80% of material, b.p. 112–114° (18 mm.), m.p. 53–55° (lit.[17] m.p. 53.5°).

Methyl-*t*-butylacetyl Chloride.—A mixture of 1.0 mole of benzoyl chloride and 0.4 mole of methyl-*t*-butylacetic acid

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(11) Another apparent 1,3-shift of methyl is found in the enzymatic cyclization of squalene and has recently been shown to occur *via* two 1,2-shifts: R. K. Maudgal, T. T. Tchen and K. Bloch, THIS JOURNAL, **80**, 2589 (1958); J. W. Cornforth, R. H. Cornforth, A. Pelter, M. G. Horning and G. Popjak, *Tetrahedron*, **5**, 311 (1959). We are indebted to a referee for calling these papers to our attention.

(12) M. F. Ansell, M. A. Davis, J. W. Hancock and W. J. Hickinbottom, *Chemistry & Industry*, 1483 (1955).

(13) M. F. Ansell, J. W. Hancock and W. J. Hickinbottom, *J. Chem. Soc.*, 911 (1956).

(14) R. Luft, *Bull. soc. chim. France*, **24**, 181 (1957).

(15) Professor W. A. Mosher, private communication.

(16) Melting points and boiling points are uncorrected. Analyses by Miss A. Smith.

(17) J. G. Aston, J. T. Clark, K. A. Burgess and R. B. Greenberg, THIS JOURNAL, **64**, 300 (1942).

was refluxed for one hour and distilled to give 83% of the desired acid chloride, b.p. 155–157°, $n^{25}\mathrm{D}$ 1.4374. *Anal.* Calcd. for $C_7H_{13}OCl$: C, 56.56; H, 8.81. Found: C, 56.51; H, 8.89.

3,4,4-Trimethyl-2-pentanone.—A Grignard reagent was prepared from 2.6 moles each of methyl bromide and magnesium in 600 ml. of dry ether and then treated with 1.4 moles of anhydrous cadmium chloride in small portions at 0°. The mixture was refluxed until a negative Gilman test[18] was obtained. There was then added dropwise at room temperature 0.37 mole of methyl-*t*-butylacetyl chloride. The mixture was refluxed for 2 hours and left stirring overnight. It was poured onto ice and the inorganic solids dissolved with dilute sulfuric acid. The ether layer was washed with water, dilute acid, sodium bicarbonate, and again with water. The ether solution was dried over magnesium sulfate and the ether removed to give 72% of 3,4,4-trimethyl-2-pentanone, b.p. 78–79.5° (77 mm.), $n^{25}\mathrm{D}$ 1.4161.

The dinitrophenylhydrazone had m.p. 112.5–113.0°. *Anal.* Calcd. for $C_{14}H_{20}O_4N_4$: C, 54.53; H, 6.54. Found: C, 54.55; H, 6.68. The semicarbazone had m.p. 151.5–152.0°. *Anal.* Calcd. for $C_9H_{19}ON_3$: C, 58.34; H, 10.34. Found: C, 58.20; H, 10.24

3,4,4-Trimethyl-2-pentanol.—The reduction of 3,4,4-trimethyl-2-pentanone with lithium aluminum hydride afforded 87% of 3,4,4-trimethyl-2-pentanol, b.p. 93–95° (67 mm.), $n^{25}\mathrm{D}$ 1.4332 (lit.[12] b.p. 159–160°, $n^{20}\mathrm{D}$ 1.4355).

The phenylurethan had m.p. 79–80°. *Anal.* Calcd. for $C_{15}H_{23}O_2N$: C, 72.25; H, 9.30. Found: C, 72.32; H, 9.44. The 3,5-dinitrobenzoate had m.p. 75.9–76.5° (lit.[12] m.p. 72–72.5°).

Anal. Calcd. for $C_{15}H_{20}N_6O_2$: C, 55.55; H, 6.18; N, 8.64. Found: C, 55.40; H, 6.08; N, 8.57.

3,4,4-Trimethyl-2-pentyl *p*-toluenesulfonate was prepared by the method of Tipson.[19] Recrystallization of the crude product from petroleum ether (30–60°) afforded material of m.p. 51–52°. This product decomposes on standing overnight at room temperature.

2,2,3-Trimethyl-3-pentanol.—The reaction of ethylmagnesium bromide with pinacolone gave 55% of the desired alcohol, b.p. 66–69° (34 mm.), $n^{25}\mathrm{D}$ 1.4319 (lit.[10] b.p. 76° (40 mm.), $n^{20}\mathrm{D}$ 1.4353).

2,3,4-Trimethyl-3-pentanol.—The reaction of methylmagnesium iodide with diisopropyl ketone gave 65% of the desired alcohol, b.p. 50–53° (16 mm.), $n^{25}\mathrm{D}$ 1.4310 (lit.[20] b.p. 75–77° (40 mm.), $n^{20}\mathrm{D}$ 1.4343).

Dehydration of 3,4,4-Trimethyl-2-pentanol with β-Naphthalenesulfonic Acid.—A mixture of 10.0 g. of 3,4,4-trimethyl-2-pentanol and 0.1 g. of β-naphthalenesulfonic acid was heated to boiling and the olefin–water mixture distilled as it formed. The olefin mixture was separated, dried and distilled to give 8.5 g. (98%) of material boiling 103–110°, $n^{25}\mathrm{D}$ 1.4181.

Dehydrations with Sulfuric Acid.—One part by weight of the alcohol and 1–2 parts by weight of sulfuric acid of the indicated concentration were heated under reflux for the indicated time. The olefin–water mixture then was distilled and the olefin separated and dried over magnesium sulfate. Conditions and results are recorded in Table I.

Tschugaev Eliminations.—A mixture of 0.04 mole of 3,4,4-trimethyl-2-pentanol and 0.04 mole of sodium chips in 25 g. of toluene was refluxed for 6 hours. The mixture was cooled, 0.1 mole of carbon disulfide was added slowly and the mixture heated for 2 hours. There was then added 0.07 mole of methyl iodide and heating was continued for 2 hours. The mixture was stirred overnight, filtered, and the solid washed with toluene. The toluene solution was washed with water and the toluene then removed under reduced pressure. The residual oil was heated to 120° and the distillate collected in a cold trap. The distillate was examined directly by gas chromatography, since separation of the residual toluene could not be accomplished readily by fractionation. (It was shown that the toluene used as solvent was free of impurities.)

Essentially the same procedure was applied to 2,2,3-trimethyl-3-pentanol. Yields were lower but adequate for our purposes.

Reaction of 3,4,4-Trimethyl-2-pentyl Tosylate with Potassium *t*-Butoxide.—In 50 ml. of dry *t*-butyl alcohol was dissolved 2.0 g. of potassium chips. To this was added 11.0 g. of 3,4,4-trimethyl-2-pentyl tosylate and the solution maintained at 70° for two hours. The mixture was poured into 175 ml. of cold water and the aqueous mixture extracted with ether. The ethereal solution was dried and examined directly by gas chromatography.

Acetolysis of 3,4,4-Trimethyl-2-pentyl Tosylate.—A mixture of 75 ml. of glacial acetic acid, 3.1 g. of potassium acetate and 2.0 g. of acetic anhydride was refluxed for 3 hours and then cooled. There was added 5.0 g. of 3,4,4-trimethyl-2-pentyl tosylate and the solution heated for 3 hours. Olefinic material was collected in a cold trap as it formed. The distillate, which contained an almost quantitative yield of olefin plus traces of acetic acid, was examined directly by gas chromatography (Table I).

Condensation of *s*-Butyl and *t*-Butyl Alcohols with Sulfuric Acid.—The procedure was essentially that of Whitmore,[3] except on a 1-mole rather than a 10-mole scale. The time of addition of the *t*-butyl alcohol was reduced to 2.5 hours. Material boiling 110–116° was examined by gas chromatography. Results are given in Table I.

Isomerization Experiments on Olefin Mixtures.—Portions of the products from the dehydration experiments were refluxed with sulfuric acid of the indicated concentration for 20 hr. each and the olefin mixture distilled and dried. Recovery from 20 and 30% sulfuric acid was nearly quantitative and about 75% was recovered from 40% sulfuric acid. Product compositions are recorded in Table I.

Reduction of 3,4,4-Trimethyl-2-pentyl Tosylate.—One gram of the tosylate in 15 ml. of anhydrous ether was added to 0.2 g. of lithium aluminum hydride in 25 ml. of anhydrous ether and the mixture stirred for 12 hours. The mixture was worked up by the method of Amundsen and Nelson[21] and the dried ethereal extract examined directly by gas chromatography. The product was 2,2,3-trimethylpentane plus a little olefinic material shown to be 3,4,4-trimethylpentene-1 and -2.

Hydrogenation of Olefin Mixtures.—Solvents used were ether, toluene or cymene. Each solvent was examined by gas chromatography to make sure it contained nothing that would contaminate the hydrocarbon mixture. To 10–15 ml. of solvent was added 0.5 g. of platinum oxide and the catalyst prereduced. The olefin mixture (1–2 g.) was added, the reduction carried out at atmospheric pressure, and the mixture filtered to remove catalyst. With cymene solutions the olefin could be distilled from the cymene. With toluene or ether solutions it was found preferable to examine the solution directly by gas chromatography. Product compositions are recorded in Table II.

Gas chromatographic studies were carried out on an Aerograph model A-110-C (Wilkins Instrument and Research, Inc.). Two 0.25-in. diameter columns were used in most of the work: di-*n*-decyl phthalate on Chromosorb (Johns-Manville, Inc.), 25 ft. and tri-*m*-cresyl phosphate on Chromosorb, 10 ft. Approximate operating conditions were, for the decyl phthalate column, 90–100°, 150–200 ml. of helium/min.; for the tricresyl phosphate column, 60–70°, 100–150 ml./min. The two columns were similar in their ability to resolve the olefin and hydrocarbon mixtures. There was overlapping of peaks for some of the mixtures, but in most cases complete or nearly complete resolution was obtained. Results are given in Tables I and II. In nearly all cases figures were reproducible to better than ±5%.

ROCHESTER 20, N. Y.

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