TABLE II (*Concluded*)

	Formula	Sp. gr.	n_D	Carbon, %		Hydrogen, %	
				Calcd.	Found	Calcd.	Found
1	$CH_2{=}C(HOC_6H_4)CH_2C_6H_5$	0.953 (25°)	1.5027 (25°)	85.71	85.37	6.66	6.43
2	$C_{15}H_{14}O$	1.061 (25°)	1.5760 (25°)	85.71	85.46	6.66	6.46
3	$CH_2{=}C(HOC_6H_3CH_3)CH_2C_6H_5$	1.000 (27°)	1.5314 (27°)	85.71	85.40	7.14	7.36
4	$C_{16}H_{16}O$	1.047 (26°)	1.5778 (26°)	85.71	86.03	7.14	7.53
5	$C_7H_4OBr_4$			19.81	20.32	0.94	0.98
6	$C_{16}H_{16}O$	1.080 (29°)	1.5671 (29°)				
7	$C_{16}H_{11}OBr_5$			31.02	31.39	1.77	1.52
8	$CH_2{=}C(HOC_6H_3CH_3)CH_2C_6H_5$	1.033 (24°)	1.5299 (24°)	85.71	85.75	7.14	7.15
9	$C_{16}H_{16}O$	1.080 (24°)	1.5836 (24°)	85.71	85.38	7.14	7.08
10	$CH_2{=}C(HOC_6H_3CH_3)CH_2C_6H_5$	0.993 (21°)	1.5352 (21°)	85.71	85.56	7.14	7.54
11	$C_{16}H_{16}O$	1.047 (21°)	1.5860 (21°)	85.71	85.40	7.14	7.15

[a] This compound was prepared by P. F. Geller and M. Rothstein in conjunction with research work for the Master of Science degree at New York University.

Summary

1. Further studies in the addition reaction of phenols to unsaturated alcohols (allyl alcohol in the aliphatic and cinnamyl alcohol in the aromatic series) have shown that by altering experimental conditions, coumaranes can be obtained.

2. Under the new conditions (elevated temperature and solvent), the chief products were shown to be methylated coumaranes (with allyl alcohol), benzyl and methylbenzyl substituted coumaranes (with cinnamyl alcohol). This affords a new and convenient method for the synthesis of alkyl and aryl substituted benzodihydrofurans.

3. Further work is now in progress extending these studies to polyhydroxy phenols and other unsaturated alcohols (crotyl-, oleyl alcohols) under various reaction conditions.

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

Preparation and Reactions of 4,4-Dimethylpentene-1 (Neopentylethylene)

BY FRANK C. WHITMORE AND AUGUST H. HOMEYER[1]

The peculiar effects of the presence of a neopentyl system on the nature of a variety of compounds have been studied extensively in this Laboratory.[2] 4,4-Dimethylpentene-1 was synthesized from *tert*-butylmagnesium chloride and allyl bromide. Addition of hydrogen bromide gave only the primary bromide, 1-bromo-4,4-dimethylpentane. This appears to be the first case in which complete reversal of Markownikoff's Rule[3] has been observed in an aliphatic olefinic hydrocarbon. This anomalous behavior is

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(1) Mallinckrodt Research Fellow.

(2) Whitmore and co-workers, THIS JOURNAL, 1932–1933.

(3) Markownikoff, *Ann.*, **153**, 256 (1870).

doubtless attributable to the nature of the neopentyl group and recalls the action of benzylethylene[4] and acrylic acid to yield primary halides by addition. 4,4-Dimethylpentene-1 failed to react with dry hydrogen iodide at 0–5°.[5] Reaction with acetic acid in the presence of sulfuric acid gave the acetate of 4,4-dimethylpentanol-2 and a mixture of olefins. 4,4-Dimethylpentene-1 forms a dibromide from which the original olefin can be regenerated without rearrangement.

1-Bromo-4,4-dimethylpentane was converted to the corresponding alcohol by treatment of the Grignard reagent with oxygen.

Several of the preparations have been checked by W. R. Trent of this Laboratory.

Experimental

4,4-Dimethylpentene-1.—Five moles (605 g.) of allyl bromide, b. p. 68.8–69.3° (738 mm.), diluted with 500 cc. of dry ether was placed in a 5-liter 3-necked flask fitted with a mercury-sealed stirrer, a thermometer and a graduated separatory funnel of 1-liter capacity. The flask was cooled in a large bath of ice and salt at about −10° while 5.2 moles (2400 cc.) of carefully filtered *tert*-butylmagnesium chloride solution was added from the funnel during sixteen hours with the temperature of the reaction mixture below 5°. The coupling reaction took place with the evolution of heat and the separation of white magnesium halide. After stirring for several hours at room temperature the presence of excess Grignard reagent was verified by the color test of Gilman and Schulze[6] using a 5-cc. sample. The product was poured on ice. The voluminous solid magnesium halide etherate was broken up and decomposed with ice and ammonium sulfate. The ether layer was separated. The aqueous layer was steam distilled and the upper layer of the distillate was added to the main portion. The ether solution was washed with ammoniacal ammonium sulfate solution to remove magnesium salts, dried over 100 g. of calcium chloride and fractionated through an 85 × 2.1 cm. packed column of the total condensation, adjustable take-off type.[7] An efficient spiral condenser was used and the receiver was cooled in ice. After removing the ether, intermediate fractions were collected amounting to 159 g., b. p. 36–70.7°. Then 315 g. of 4,4-dimethylpentene-1 distilled at 70.7–71.2° (724 mm.), n^{20}_{D} 1.3918. The intermediate fractions were refractionated, yielding 105 g. more of the olefin.

Fraction	B. p., °C.	(Mm.)	n^{20}_{D}	Wt., g.
1–2	36–46	(724)	1.3528–1.3571	32
3–4	46–68		1.3810–1.3876	11
5–7	68–70.8		1.3902–1.3920	105
8–9	70.7–71.2		1.3918	315
10	Residue		Black oil	37

The yield (fractions 5–9) was 420 g. or 85% of the theoretical based on allyl bromide. The various fractions gave a slight Beilstein test for halogen and the index of

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(4) Kharasch and Darkis, *Chem. Rev.*, **5**, 571 (1928). Since this paper was completed interesting work by Kharasch and co-workers on the effect of peroxide on addition to olefins has appeared [THIS JOURNAL, **55**, 2468, 2521 (1933)]. The effect of peroxides and antioxidants on addition reactions of neopentylethylene is being studied in this Laboratory. Also Sherrill and co-workers have found that pentene-1 and heptene-1 with gaseous hydrogen bromide give exclusively the primary bromide (Organic Division, American Chemical Society Meeting, Chicago, September, 1933).

(5) Unpublished results by W. R. Trent of this Laboratory.

(6) Gilman and Schulze, *Bull. soc. chim.*, [4] **41**, 1479 (1927); THIS JOURNAL, **47**, 2002 (1925).

(7) Whitmore and Lux, *ibid.*, **54**, 3451 (1932).

refraction was a little higher than for the olefin purified through the dibromide. The low index of fractions 3–4 shows the absence of diallyl,[8] b. p. 59.6° (760 mm.), n^{20}_{D} 1.4044.

In a preliminary experiment it was found that the addition of allyl bromide diluted with ether to the *tert*-butylmagnesium chloride solution at 2° resulted in a four-fold increase in the high-boiling residue. Fractionation of the residue (160 g.) from a 5-mole run showed it to consist of polymers, and 23.5 g. of solid hexamethylethane, b. p. 101–109°, was isolated. In this case, and also when the Grignard reagent was added to the diluted allyl bromide without cooling, diallyl was isolated from the fore-runs as the tetrabromide, m. p. 52°, after crystallizing from alcohol and then from a mixture of ether and petroleum ether.

1,2-Dibromo-4,4-dimethylpentane.—The dibromide was prepared by adding dry bromine to a dilute ether solution of the olefin at −5°. The yield was 85%; b. p. 77–78° (9 mm.), n^{20}_{D} 1.4970, d^{20}_{4} 1.5129; MR found 49.89, calcd. 50.05.

4,4-Dimethylpentene-1 from its Dibromide.—Sixty-five grams of zinc dust and 260 cc. of 95% alcohol were placed in a 1-liter 3-necked flask fitted with a reflux condenser, mercury-sealed stirrer and dropping funnel. To the boiling mixture was added 192 g. of 1,2-dibromo-4,4-dimethylpentane from the dropping funnel during one and one-half hours. The product was distilled through a 91 × 1.4 cm. packed column. One hundred fifty cc. of distillate was collected at 59–78°. This was diluted with 400 cc. of water; the olefin layer was separated, washed with 250-cc. and 100-cc. portions of water, dried over 3 g. of calcium chloride and fractionated through a 91 × 1.4 cm. packed column. Forty-five grams (91%) of 4,4-dimethylpentene-1 distilled at 71.8° (730 mm.). There were no by-products and the product was free from halogen. 4,4-Dimethylpentene-1 has the following properties: b. p. 72.35° (760 mm.) (Cottrell); n^{20}_{D} 1.3911; d^{20}_{4} 0.6827; d^{0}_{0} 0.7007; MR found 34.15 (Lorentz–Lorenz), calcd. 34.06 (Eisenlohr).

Ozonolysis.—Several 0.5-mole quantities of 4,4-dimethylpentene-1 were ozonized.[9] The yield of ozonide was 85–91%. Decomposition gave both *tert*-butylacetaldehyde (40–45%) and *tert*-butylacetic acid (40%). Formaldehyde was identified by the resorcinol–sulfuric acid test. *tert*-Butylacetic acid was identified as the amide,[10] m. p. 132°.

tert-Butylacetaldehyde distilled at 102–104° (730 mm.); 2,4-dinitrophenylhydrazone, m. p. 146–147°. A mixture with acetaldehyde-2,4-dinitrophenylhydrazone, m. p. 147°, melted at 127–130°. *tert*-Butylacetaldehyde condensed with dimethyldihydroresorcinol[11] in alcoholic solution yielding a product melting at 167° after recrystallization from 70% alcohol.

3,3-Dimethylbutanol-1 was obtained by reduction of *tert*-butylacetaldehyde with an Adams catalyst. It distilled at 139–140° (727 mm.); Delacre[12] gives 142.6–143.6°. Its α-naphthyl urethan melts at 83°.

1-Bromo-4,4-dimethylpentane.—Fifty grams of 4,4-dimethylpentene-1 was saturated with dry hydrogen bromide at 0°. After keeping at 5° for eighteen hours, the bromide was refluxed under a 70 × 1 cm. indented column at 50 mm. to remove excess hydrogen bromide. A little anhydrous potassium carbonate was added and the bromide was fractionated. Seven fractions were collected; all had identical physical properties: b. p. 70–71° (35 mm.), 154° (730 mm.); n^{20}_{D} 1.4484; d^{20}_{4} 1.1343; MR found, 42.29, calcd. 42.29. The yield was 78 g. or 88%.

No hydrolysis could be detected after shaking a sample with water for thirty minutes. Shaking for three hours with 0.1 N silver nitrate gave 4.4% hydrolysis. It

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(8) Cortese, THIS JOURNAL, **51**, 2266 (1929).

(9) Whitmore and Church, *ibid.*, **54**, 3710 (1932).

(10) Homeyer, Whitmore and Wallingford, *ibid.*, **55**, 4211 (1933).

(11) Weinberger, *Ind. Eng. Chem., Anal. Ed.*, **3**, 365 (1931).

(12) Delacre, *Bull. sci. acad. roy. Belg.*, 7-41 (1906); *Chem. Zentr.*, I, 1233 (1906).

forms a Grignard reagent which reacts with mercuric bromide[13] to give 1-bromomercuri-4,4-dimethylpentane, m. p. 101°, after crystallization from 95% alcohol.

After passing dry hydrogen iodide through 0.5 mole of 4,4-dimethylpentene-1 for twenty-four hours at 0–5° there was no gain in weight. The olefin was recovered unchanged.[5]

4,4-Dimethylpentanol-1.—1-Bromo-4,4-dimethylpentane was converted to the Grignard reagent in the usual manner; yield 82% in a 0.5-mole run.

A solution of 0.14 mole of the Grignard reagent was cooled and treated with dry oxygen. The product was poured over ice and ammonium chloride; the ether layer was separated and the aqueous layer was extracted with 100 cc. of ether, the extract being added to the main portion. After drying over potassium carbonate the product was fractionated through a 55 × 1.2 cm. indented column. Fifteen grams (90% yield based on the Grignard reagent) of 4,4-dimethylpentanol-1 was obtained: b. p. 96° (62 mm.), 158° (737 mm.); n^{20}_{D} 1.4202; d^{20}_{4} 0.815; MR found 36.07, calcd. 36.17.

The α-naphthyl urethan of 4,4-dimethylpentanol-1 melts at 80.5–81° after crystallizing from petroleum ether. 4,4-Dimethylpentanol-2[14] boils at 137.5° (736 mm.) and its α-naphthyl urethan melts at 86.5–87°. A mixture melted at 60–65°.

The structure of 4,4-dimethylpentanol-1 was further established by oxidation with chromic acid yielding neopentylacetic acid, b. p. 198–208°; amide m. p. 141–142° after crystallization from water. Moureu and Delange[15] give 140–141°.

Addition of Acetic Acid to 4,4-Dimethylpentene-1.—Five cc. of 100% sulfuric acid (m. p. 8°), 150 cc. of glacial acetic acid (m. p. 16.6°) and 50 g. of 4,4-dimethylpentene-1 were heated on the steam-bath for two days. The solution became dark. The product was poured over ice and diluted with twice its volume of water. The dark upper layer was separated, washed with dilute sodium bicarbonate solution and dried over potassium carbonate. It weighed 46 g. Fractionation through a 70 × 1 cm. indented column gave 13 fractions. Fractions 1–6, 18 g. (36%), b. p. 72–82° (740 mm.), n^{20}_{D} 1.3960–1.4000. This mixture of heptenes was not investigated further.

Fractions 7–13, 26 g. (33%): b. p. 92° (90 mm.), 154° (735 mm.); n^{20}_{D} 1.4080; d^{20}_{4} 0.858. These properties agree with the properties of a known sample of the acetate of 4,4-dimethylpentanol-2:[14] b. p. 92–93° (90 mm.); n^{20}_{D} 1.4071; d^{20}_{4} 0.8563.

Twenty grams of the ester (fractions 8–12) was hydrolyzed by warming for two days with 15 g. of potassium hydroxide dissolved in 85 cc. of 80% alcohol. The product was diluted with three times its volume of water; the upper layer was separated, washed with water, dried over copper sulfate and fractionated through a 70 × 1 cm. indented column. Four fractions were obtained weighing 14 g.: b. p. 136–137° (741 mm.); n^{20}_{D} 1.4185–1.4190; d^{20}_{4} 0.812. These properties agree with those of a known sample of 4,4-dimethylpentanol-2: b. p. 137–137.5° (736 mm.); n^{20}_{D} 1.4188; d^{20}_{4} 0.8115. Its α-naphthyl urethan melted at 85–85.5°. The α-naphthyl urethan of a known sample of 4,4-dimethylpentanol-2 melted at 86.5–87° and a mixture melted at 85.8–86.4°.

Action of Sulfuric Acid on 4,4-Dimethylpentene-1.—Fifty grams of 4,4-dimethylpentene-1 was added with shaking to 156 g. of 85% sulfuric acid cooled to 5°. The temperature rose to 20°. The product was poured over ice; the upper layer was separated, washed with sodium bicarbonate solution, dried over potassium carbonate and fractionated through a 70 × 1 cm. indented column. The product was a mixture of polymers weighing 45 g.: b. p. 59° (13 mm.) to 122° (11 mm.), n^{20}_{D} 1.4309–1.4502.

Refluxing samples of 4,4-dimethylpentene-1 with 5% by volume of 100% sulfuric acid or small amounts of dilute sulfuric acid for one hour caused no appreciable change in the boiling point or index of refraction of the olefin. The strong acid caused some charring.

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[13] Marvel, Gauerke and Hill, THIS JOURNAL, **47**, 3009 (1925).

[14] Whitmore and Homeyer, *ibid.*, **55**, 4195 (1933).

[15] Moureu and Delange, *Bull. soc. chim.*, [3] **29**, 665 (1903).

Summary

4,4-Dimethylpentene-1 has been prepared from allyl bromide and *tert*-butylmagnesium chloride, and purified through its dibromide. Addition of hydrogen bromide takes place contrary to Markownikoff's rule, giving 1-bromo-4,4-dimethylpentane exclusively. The latter has been converted to 4,4-dimethylpentanol-1 through the Grignard reaction. 4,4-Dimethylpentene-1 does not add dry hydrogen iodide at 0–5°; it reacts with acetic acid in the presence of sulfuric acid yielding the acetate of 4,4-dimethylpentanol-2 and a mixture of olefins.

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[COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

Hydrogenolysis of Sugars

BY WALTER H. ZARTMAN AND HOMER ADKINS

Since certain types of glycols undergo cleavage at carbon to oxygen or carbon to carbon linkages when submitted to the action of hydrogen over a suitable catalyst, it seemed of interest to ascertain the facts with regard to the behavior of the sugars under these conditions. The experimental results of this study of the hydrogenolysis of the more common sugars may, perhaps, be most concisely and clearly presented by first giving a description of the experimental procedure and observations with respect to sucrose.

A rapid reaction ensued when 171 g. (0.5 mole) of sucrose in 175 ml. of dry ethanol with 20 g. of copper–chromium oxide at 250° was subjected to the action of hydrogen under a pressure of about 300 atmospheres.[1] During the course of two or three hours about 4.7 moles of hydrogen was absorbed, whereupon the reaction apparently stopped. After centrifuging out the catalyst the perfectly colorless reaction mixture was fractionated through an electrically heated Widmer column, having a spiral 20 cm. in length. Alcohol and water were distilled at atmospheric pressure. Fractionation of the remainder at 7 mm. resulted in a distillation curve similar to that marked "A" in Fig. 1. There was apparently a large amount of a compound boiling at about 80° (7 mm.), a very small amount at about 138° (7 mm.), a larger fraction at about 175° (7 mm.), with 22 g. of higher boiling material.

The fraction collected at atmospheric pressure was obviously largely composed of the ethanol originally used as the solvent. Analysis of it by the method of Wright showed that it contained about 4 g. of methanol.[2]

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[1] The catalyst and apparatus has been described by Connor, Folkers and Adkins, THIS JOURNAL, **54**, 1140 (1932), and Adkins, *Ind. Eng. Chem.*, *Anal. Ed.*, **4**, 342 (1932); see also Connor and Adkins, THIS JOURNAL, **54**, 4678 (1932), on hydrogenolysis of glycols.

[2] Wright, *Ind. Eng. Chem.*, **19**, 750 (1927).