

esting to study some related alcohols and hydrocarbons in the same way.

Summary

The relative densities of solutions of methyl alcohol and toluene have been measured over the entire concentration range at -21.1 , 0.0 , 25.0 and 49.7° .

The volume changes attending mutual solution of the two liquids have been calculated from these

densities and the volume changes at a temperature near the boiling point have been estimated by extrapolation.

Suggestions have been offered as to the nature of the association, dissociation and solvation effects which may be responsible for the observed behavior.

NORTH TEXAS AGRICULTURAL COLLEGE
ARLINGTON, TEXAS

NEBRASKA STATE TEACHERS COLLEGE

CHADRON, NEBRASKA

RECEIVED OCTOBER 3, 1938

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

Condensation of Tertiary Aliphatic Alcohols with Aromatic Compounds in the Presence of Aluminum Chloride. IV. Tertiary Dimethyl Amyl Carbinols with Phenol

BY R. C. HUSTON AND R. L. GUILÉ¹

Previous papers from this Laboratory^{2,3} have described the condensations of *t*-butyl, *t*-amyl, the *t*-hexyl, and the *t*-heptyl alcohols with phenol in the presence of aluminum chloride. To extend the scope of this investigation the following tertiary dimethyl amyl carbinols, *viz.*: 2-methylheptanol-2,⁴ 2,3-dimethylhexanol-2,⁵ 2,4-dimethylhexanol-2,^{6,7} 2,5-dimethylhexanol-2,⁸ 2-methyl-3-ethylpentanol-2,⁹ 2,3,3-trimethylpentanol-2,¹⁰ 2,3,4-trimethylpentanol-2, and 2,4,4-trimethylpentanol-2,¹¹ were prepared and condensed with phenol. Yields of from 2.1 to 69.5% of a *p*-*t*-alkylphenol were obtained with no isolation of other isomers. The benzoyl esters and α -naphthylurethan derivatives of these phenols excepting 2,3,3-trimethyl-2-*p*-hydroxyphenylpentane were prepared.

The structure of six of these *p*-*t*-alkylphenols was established by synthesis. Thus, in an unpublished paper Huston and Sculati¹² isolated and identified from condensations between benzene and tertiary dimethyl amyl carbinols, 2-methyl-2-phenylheptane, and the 2,3-dimethyl-, 2,4-dimethyl-, and 2,5-dimethyl-2-phenylhexanes. In

a similar fashion Huston and Guile¹ prepared 2,4,4-trimethyl-2-phenylpentane and 2-methyl-3-ethyl-2-phenylpentane. These alkylbenzenes were nitrated, reduced, diazotized, and hydrolyzed to the phenols. The melting points and mixed melting point determinations of the α -naphthylurethans of the phenols thus prepared indicated that they were the same as those prepared in the condensations. The position of the entering group was established through oxidation¹³ of the *p*-nitro-*t*-alkylbenzene by heating a portion with 6 *N* nitric acid in a sealed Carius tube at 103° . In each case the product obtained was *p*-nitrobenzoic acid, which was identified by melting point and mixed melting point.

More evidence in support of the structure of 2,4,4-trimethyl-2-*p*-hydroxyphenylpentane was obtained by synthesizing it by the method of Natelson.¹⁴ This compound was identical with that obtained from the condensation of 2,4,4-trimethylpentanol-2 and phenol under the action of aluminum chloride.

The first four of the above alcohols were prepared by treatment of the Grignard reagent of an amyl halide with acetone. Although the yields in some cases were small by this method, the amyl alcohols could be obtained in sufficient quantities to offset this difficulty. For the preparation of 2,4,4-trimethylpentanol-2 a method outlined by Butlerow¹¹ was used. Syntheses of 2,3,3-trimethylpentanol-2 and 2,3,4-trimethylpentanol-2, the latter not previously reported in

(1) From a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) R. C. Huston and T. Y. Hsieh, *THIS JOURNAL*, **58**, 439 (1936).

(3) R. C. Huston and G. W. Hedrick, *ibid.*, **59**, 2001 (1937).

(4) F. C. Whitmore and F. E. Williams, *ibid.*, **55**, 408 (1933).

(5) L. Clark, *ibid.*, **33**, 529 (1911).

(6) L. Clark, *ibid.*, **30**, 1150 (1908).

(7) P. A. Levene and R. E. Marker, *J. Biol. Chem.*, **91**, 416 (1931).

(8) V. Grignard, *Chem. Zentr.*, **72**, II, 623 (1901).

(9) L. Clark, *THIS JOURNAL*, **39**, 574 (1917).

(10) F. H. Norton and H. B. Hass, *ibid.*, **58**, 2148 (1936).

(11) A. Butlerow, *Ann.*, **189**, 53 (1877).

(12) R. C. Huston and Sculati, Master's Thesis, Michigan State College, 1936.

(13) Malherbe, *Ber.*, **52**, 319 (1919).

(14) S. Natelson, *THIS JOURNAL*, **56**, 1583 (1934).

TABLE I
 CONDENSATION OF *t*-OCTYL ALCOHOLS WITH PHENOL

Product	Yield, %	M. p., °C.	B. p., °C. 2 mm., 741 mm.	Sp. gr. 20/20	n_D^{20}	γ^{25} , dynes	Analyses of $C_{14}H_{22}O$		
							Carbon, % Calcd. 81.48	Hydrogen, % Calcd. 10.75	
2-Methyl-2- <i>p</i> -hydroxyphenylheptane	69.5	...	114-117	293.5	0.95053	1.5102	32.31	81.16	10.74
2,3-Dimethyl-2- <i>p</i> -hydroxyphenylhexane	35.5	...	111-114	293	.96836	1.5191	33.74	80.94	10.59
2,4-Dimethyl-2- <i>p</i> -hydroxyphenylhexane	58.5	...	113-116	290.5	.95427	1.5121	32.00	81.00	10.48
2,5-Dimethyl-2- <i>p</i> -hydroxyphenylhexane	64.6	...	105-107	288	.95183	1.5110	31.69	80.79	10.59
2-Methyl-3-ethyl-2- <i>p</i> -hydroxyphenylpentane	28.3	...	109-111	293	.96845	1.5190	33.80	80.90	10.65
2,4,4-Trimethyl-2- <i>p</i> -hydroxyphenylpentane	64.6	83	289	80.95	10.48
2,3,4-Trimethyl-2- <i>p</i> -hydroxyphenylpentane	23.1	74	80.81	10.62
2,3,3-Trimethyl-2- <i>p</i> -hydroxyphenylpentane	2.1	160	325 dec.	80.98	10.68

 TABLE II
 BENZOYL ESTERS AND α -NAPHTHYLURETHANS OF *p*-*t*-OCTYLPHENOLS

Parent compound	M. p., °C.	Benzoyl esters— Analyses of $C_{20}H_{28}O_2$ Hydrogen,		α -Naphthylurethans— Anal. of $C_{25}H_{29}O_2N$	
		Carbon, % Calcd. 81.23	% Calcd. 8.45	M. p., °C.	Nitrogen, % Calcd. 3.73
2-Methyl-2- <i>p</i> -hydroxyphenylheptane	27-23	80.55	8.27	120-121	3.69
2,3-Dimethyl-2- <i>p</i> -hydroxyphenylhexane	54.2-55.2	81.22	8.33	105-105.5	3.75
2,4-Dimethyl-2- <i>p</i> -hydroxyphenylhexane	37-38	81.28	8.41	119.5-120.5	3.72
2,5-Dimethyl-2- <i>p</i> -hydroxyphenylhexane	46-47	81.18	8.26	132.5-133.5	3.70
2-Methyl-3-ethyl-2- <i>p</i> -hydroxyphenylpentane	69-70	81.19	8.39	109.5-110.5	3.70
2,4,4-Trimethyl-2- <i>p</i> -hydroxyphenylpentane	73-74	80.66	8.22	102-103	3.69
2,3,4-Trimethyl-2- <i>p</i> -hydroxyphenylpentane	47-48	80.45	8.18	114.5-115.5	3.68

the literature, were accomplished by a modification of the Whitmore-Badertscher procedure.^{15,16}

Experimental

Synthesis of 2,3,4-Trimethylpentanol-2.—In a 3-liter three-necked round-bottomed flask equipped with a mercury sealed stirrer, a reflux condenser and dropping funnel was placed 122 g. (9.5 moles) of magnesium and a few crystals of iodine. The iodine vaporized by the application of heat after which the flask and contents were cooled to room temperature. To this was then added directly 30 cc. of a 1:1 mixture of anhydrous ether and 2-methyl-3-bromobutane followed by 200 cc. of anhydrous ether after the reaction had started. The reaction was then continued by adding 755 g. (5 moles) of dry 2-methyl-3-bromobutane in 800 cc. of anhydrous ether at the rate of a drop a second. Titration of a hydrolyzed aliquot of the resulting solution¹⁷ showed 412 g. (45% yield) of Grignard reagent.

This Grignard reagent was added to 308 g. (3.95 moles) of acetyl chloride in 700 cc. of anhydrous ether contained in a 5-liter three-necked round-bottomed flask fitted with reflux condenser, separatory funnel, and mechanical stirrer. The rate of addition was such that the ether refluxed gently. After standing overnight the mixture was decomposed by pouring on ice. From the ether layer and ether extracts of the resulting solution was obtained a crude ketonic fraction. This was purified by steam distillation over aqueous potassium carbonate. Salted out from the distillate with sodium chloride it was separated, dried over anhydrous sodium sulfate, and fractionally distilled. Fifty-five grams (9.3%) of 3,4-dimethylpentanone-2 boiling at 135-140° (744 mm.) was obtained.

(15) F. C. Whitmore and D. E. Badertscher, *THIS JOURNAL*, **55**, 1561-1562 (1933).

(16) F. C. Whitmore and D. E. Badertscher, *ibid.*, **55**, 1564-1565 (1933).

(17) H. Gilman and others, *ibid.*, **45**, 153 (1923).

To a solution of methylmagnesium iodide prepared from 0.6 mole of methyl iodide and 0.7 mole of metallic magnesium in a 1-liter three-necked round-bottomed flask with reflux condenser, stirrer, and dropping funnel was added at the rate of a drop a second the 55 g. of the ketone obtained above in an equal volume of anhydrous ether. The reaction mixture was allowed to stand overnight and decomposed by the usual methods. Thirty-six grams of the alcohol was obtained boiling at 47-50° (13 mm.), 58.1% based on the ketone. The following physical constants were determined for the 2,3,4-trimethylpentanol-2: b. p. 155-157° at 752 mm.; n_D^{20} 1.4400; sp. gr.²⁰ 0.8095; γ^{20} 27.48 dynes.

Condensations.—Since all the condensations were carried out in a similar manner, a typical run is described. Thirty-two grams of the octyl alcohol and 28 g. (0.3 mole) of phenol dissolved in 100 cc. of petroleum ether was added dropwise with stirring over a period of two hours to 17 g. (0.125 mole) of aluminum chloride suspended in 150 cc. of petroleum ether in a 500-cc. three-necked, round-bottomed flask equipped with condenser, dropping funnel, and mercury-sealed stirrer. The addition was carried out at 25-30° and the temperature kept constant by use of a water-bath, when necessary for cooling purposes. After standing overnight the mixture was decomposed by pouring on ice and hydrochloric acid and non-aqueous material extracted out with ether. From this ether extract the phenols were isolated by fractionation.

Solid phenols were freed of oily impurities by use of porous plates and recrystallized from petroleum ether solution.

The benzoyl esters were prepared by the method of Shriner and Fuson.¹⁸ Distillation under reduced pressure was used when necessary to obtain a product pure enough for crystallization. Once crystallized the esters were recrystallized from 75% alcohol.

(18) Shriner and Fuson, "Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, 1935, p. 62.

TABLE III
p-NITRO-*t*-OCTYL BENZENES AND *p*-AMINO-*t*-OCTYL BENZENES

Benzene derivatives	<i>p</i> -Nitro			Nitrogen, % in C ₁₄ H ₂₁ O ₂ N Calcd., 5.95	<i>p</i> -Amino			Nitrogen, % in C ₁₄ H ₂₁ N Calcd., 6.82
	°C.	B. p.,	Mm.		°C.	B. p.,	Mm.	
2-Methyl-2- <i>p</i> -()-phenylheptane	148-150		2	6.01	108-111		2	6.77
2,3-Dimethyl-2- <i>p</i> -()-phenylhexane	133-135		2	5.99	115-119		4	6.58
2,4-Dimethyl-2- <i>p</i> -()-phenylhexane	135-137		2	5.98	99-101		2	6.87
2,5-Dimethyl-2- <i>p</i> -()-phenylhexane	129-131		2	6.09	99-102		2	6.92
2-Methyl-3-ethyl-2- <i>p</i> -()-phenylpentane	127-130		4	6.09	103-106		2	6.86
2,4,4-Trimethyl-2- <i>p</i> -()-phenylpentane	108-110		4	6.05	112-115		5	6.73

The α -naphthylurethans were prepared by the method of French and Wirtel.¹⁹ Their purification was accomplished from hot ligroin.

Proof of Structure of *t*-Octylphenols.—The method employed was identical with that used by Huston and Hsieh² and by Huston and Hedrick.³ The longer heating both for nitration and reduction, as outlined by the latter workers, was found to be necessary for the octyl derivatives.

The 2,4,4-trimethyl-2-*p*-hydroxyphenylpentane obtained in condensation was found to check with this compound as prepared and reported in the literature.¹⁴

(19) H. E. French and A. F. Wirtel, *THIS JOURNAL*, **48**, 1736 (1926).

Summary

1. The isomeric amyldimethylcarbinols condense with phenol in the presence of aluminum chloride to give *p-t*-octylphenols.
2. The benzoyl esters and α -naphthylurethans of seven of these phenols have been prepared.
3. The structures of six of them have been established by synthesis.
4. A new tertiary dimethyl amyl alcohol, 2,3,4-trimethylpentanol-2, has been prepared and some of its physical constants determined.

EAST LANSING, MICH.

RECEIVED OCTOBER 13, 1938

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Reaction of Thiol Compounds with Aliphatic Olefins

BY V. N. IPATIEFF AND B. S. FRIEDMAN

It has been shown previously^{1,2} that the addition of thiophenol to an olefinic double bond proceeds contrary to the course suggested by Markownikoff's rule. The present paper deals with the addition of other thiol compounds to aliphatic olefins.

Several patents³ have been granted on the preparation of mercaptans and thioethers by treating hydrogen sulfide and mercaptans with olefins. Except in a few isolated instances, however, no proof has been given of the structure of the products formed. Barr and Keyes⁴ showed that *n*- and isopropyl mercaptans were produced in the ratio of approximately 2:1 by passing hydrogen sulfide and propene over a nickel sulfide catalyst at 250–300°. Kharasch, Read, and Mayo^{4b} found that the addition of thioglycolic acid to iso-

butylene and styrene proceeded abnormally from the standpoint of the Markownikoff rule.

In the present work the addition of hydrogen sulfide, aliphatic mercaptans, and thioacetic acid to aliphatic olefins was carried out under varying conditions of temperature, pressure and contact time. No catalyst was added, but, in those reactions run in a bomb, the materials (stainless steel) of the vessel, especially the sulfides, might have played the part of a catalyst. The data obtained from these experiments are tabulated in Table I.

From these data⁵ and those previously given² it is evident that aliphatic mercaptans and thioacetic acid add to the ethylenic group contrary to Markownikoff's rule, paralleling thiophenol in this respect, whereas hydrogen sulfide adds in accordance with the rule.^{5a} In all instances the

(1) Posner, *Ber.*, **38**, 646 (1905).

(2) Ipatieff, Pines and Friedman, *THIS JOURNAL*, **60**, 2731 (1938).

(3) (a) Lee, U. S. Patent 2,020,421; *C. A.*, **30**, 489 (1936); (b) Williams and Allen, U. S. Patent 2,052,268; *C. A.*, **30**, 7122 (1936); (c) Allen, U. S. Patent 2,051,807; *C. A.*, **30**, 6760 (1936); (d) I. G. Farbenind. A.-G., French Patent 797,606; *C. A.*, **30**, 8244 (1936).

(4) (a) Barr and Keyes, *Ind. Eng. Chem.*, **26**, 1111 (1934); (b) Kharasch, Read and Mayo, *Chem. and Industry*, **57**, 752 (1938).

(5) No attempt was made to free the reagents from peroxides or to run the reactions in the absence of air. Professor M. S. Kharasch has informed us that he is investigating the peroxide effect in connection with the reaction of thiols with olefins. Cf. Reference 4b.

(5a) Cf. the paper (which appeared just after this manuscript was submitted for publication) by Jones and Reid, *THIS JOURNAL*, **60**, 2452 (1938), on the addition of sulfur, hydrogen sulfide and mercaptans to unsaturated hydrocarbons.