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

Condensation of the Tertiary Heptyl Alcohols with Phenol in the Presence of Aluminum Chloride

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A previous paper from this Laboratory[2] described the condensation of *t*-butyl, *t*-amyl, and the three *t*-hexyl alcohols with phenol in the presence of anhydrous aluminum chloride. To study further the scope of the reaction the following tertiary heptyl alcohols, *viz.*, *n*-butyldimethyl,[3] isobutyldimethyl,[4] *s*-butyldimethyl,[4] *t*-butyldimethyl,[4,5] *n*-propylmethylethyl,[5] isopropylmethylethyl,[6] and triethyl[7] carbinols were prepared and condensed with phenol. A yield of from 25 to 65% of a *p*-*t*-alkyl-phenol was obtained and no other isomers could be isolated. The benzoyl and *o*-chlorobenzoyl esters, and the α-naphthylurethans were prepared.

The structure of the alkylphenols was established by synthesis. In an unpublished paper[8] Huston and Binder condensed all the *t*-heptyl alcohols with benzene and identified the alkylbenzenes by molecular refraction, parachor, density and molecular volume determinations. 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.[9] The position was established by oxidation of the *p*-nitro-*t*-alkylbenzene by the Carius method to *p*-nitrobenzoic acid which was identified by its melting point and mixed melting point.[2]

More evidence in support of the structure is borne out in the physical properties. By observing the properties listed in Tables I, II, III, and IV, it is obvious that the seven phenols are all different. It is known also that the heaping of eurogens on adjacent carbon atoms of a compound causes an increase in the melting point of the compound. This fact is in support of the structure of the phenols for as the heaping increases there is a decided increase in the melting point.

All of the *t*-heptyl alcohols are found in the literature.[3–7]

Good yields were obtained in every case with the exception of isopropylmethylethyl- and *t*-butyldimethylcarbinols. For these new syntheses were employed. The first was made by condensing methyl isopropyl ketone and ethylmagnesium bromide; and the latter by condensing pinacolone with methylmagnesium iodide.

Experimental

Isopropylmethylethylcarbinol.—Thirty-six grams (1.5 moles) of magnesium and 200 cc. of anhydrous ether were placed in a one liter three-necked flask equipped with a mercury-sealed stirrer, a reflux condenser and a dropping funnel. To this 153.5 g. (1.5 moles) of dry, redistilled ethyl bromide was added with stirring through the dropping funnel at a rate fast enough to keep the mixture refluxing gently. After the addition was complete, the stirring was continued for one hour at room temperature. Then 130 g. (1.5 moles) of isopropyl methyl ketone[10] in 200 cc. of anhydrous ether was added dropwise.

After the ketone was all added stirring was continued at room temperature for two hours, then the mixture was decomposed. The usual methods for decomposition were employed. Eighty-seven grams of the alcohol, boiling at 50–52° (20 mm.), n^{20}_{D} 1.4283 was obtained which was 50% of the theoretical yield based on the ketone.

***t*-Butyldimethylcarbinol.**—The same procedure and the same proportional quantities as in the above were employed. Thus 128 g. (0.9 mole) of pinacolone yielded 75 g. of the alcohol which boiled at 48–51° (20 mm.) (71% of the theoretical yield). This consisted of a mixture of colorless crystals (m. p. 80°) and a liquid which solidified when cooled in ice. This corresponds to the carbinol described by Whitmore.[5] The alcohol was used without further purification for the condensation with phenol.

Condensations.—Inasmuch as all the condensations were carried out in a similar manner only a typical run is described here. Twenty-nine grams (0.25 mole) of *n*-butyldimethylcarbinol and 28 g. (0.30 mole) of phenol dissolved in 100 cc. of petroleum ether was added dropwise with stirring over a period of two hours to 17 g. of anhydrous aluminum chloride (0.125 mole) suspended in 150 cc. of petroleum ether. The addition was carried out at room temperature (20–30°)[11] during a period of four to

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[1] From a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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

[3] Whitmore and Church, *ibid.*, **55**, 1119 (1933).

[4] Edgar, *ibid.*, **51**, 1483 (1929).

[5] Whitmore and Badertscher, *ibid.*, **55**, 1559 (1933).

[6] Whitmore and Evers, *ibid.*, **55**, 812 (1933).

[7] "Organic Syntheses," **13**, 20 (1933).

[8] Huston and Binder, Masters Thesis, Michigan State College, 1933.

[9] No urethan of the *t*-butyl derivative was prepared. The phenol itself was identified.

[10] "Organic Syntheses," **13**, 68 (1933).

[11] Isopropylmethylethylcarbinol and *s*- and *t*-butyldimethylcarbinols were added to the suspension kept at 0–10°.

TABLE I

CONDENSATION OF *t*-HEPTYL ALCOHOLS WITH PHENOL

Product, *p*-hydroxyphenylmethanes	Yield, %	M. p., °C.	Boiling points				Anal. of $C_{13}H_{20}O$	
			°C.	Mm.	°C.	Mm.	Carbon, % Calcd. 81.18	Hydrogen, % Calcd. 10.49
n-Propylmethylethyl-[12]	30.7	.....	124.6	4	278.5	748.5	80.75	10.49
n-Butyldimethyl-	64.6	16–17	123.5	4	277	749.5	80.58	10.39
Isobutyldimethyl-	44.4	31–32	115–117	4	273	748.5	80.88	10.47
Isopropylmethylethyl-	40.6	42–43	125–127	4	272	748.5	80.66	10.24
s-Butyldimethyl-	27.3	49–50.5	117–119	4	281	748.5	80.81	10.44
Triethyl-	30.0	75.5–76.5	120–122	4	275	749.5	81.11	10.49
t-Butyldimethyl-	25.8	133–134			287	748.5	80.82	10.34

six hours. The mixture was allowed to stand overnight, then decomposed with ice and hydrochloric acid. The phenol was isolated by fractionation. Table I includes a summary of the results.

For further purification the phenols were pressed between filter paper and then recrystallized using 50% alcohol–petroleum ether solution.

The benzoyl and *o*-chlorobenzoyl esters were prepared by the method described by Shriner and Fuson.[13] After isolation the esters were distilled under reduced pressure, recrystallized first from an 85% alcohol solution and then an 85–90% acetic acid–water solution. The results are collected in Tables II and III.

TABLE II

BENZOYL ESTERS OF *p*-*t*-HEPTYLPHENOLS

Compound *p*-hydroxyphenylmethanes	M. p., °C.	Analyses of $C_{19}H_{24}O_2$	
		Carbon, % Calcd. 81.03	Hydrogen, % Calcd. 8.16
n-Propylmethylethyl-	38–39	80.40	8.16
n-Butyldimethyl-	36–37	80.91	8.10
Isobutyldimethyl-	71–72	80.42	8.12
Isopropylmethylethyl-	40–41	80.61	8.28
s-Butyldimethyl-	44–45	80.39	8.00
Triethyl-	74–75	81.09	8.19
t-Butyldimethyl-	84–84.5	81.01	8.15

The α-naphthylurethans were prepared by the method of Shriner and Fuson[13] (p. 63). The urethan of the *t*-butyl derivative could not be purified due to its extreme insolubility. The results are listed in Table IV.

TABLE III

o-CHLOROBENZOYL ESTERS OF *p*-*t*-HEPTYLPHENOLS

Compound *p*-hydroxyphenylmethanes	M. p., °C.	B. p. (2 mm.) °C.	Analyses of $C_{19}H_{23}O_2Cl$ Chlorine, % Calcd. 10.73
n-Propylmethylethyl-	25–26	...	10.68
n-Butyldimethyl-	...	177–179	10.71
Isobutyldimethyl-	51–52	...	10.63
Isopropylmethylethyl-	42–43	...	10.59
s-Butyldimethyl-	...	175–178	10.64
Triethyl-	67–68	...	10.81
t-Butyldimethyl-	83–85	...	10.62

TABLE IV

α-NAPHTHYLURETHANS OF *p*-*t*-HEPTYLPHENOLS

p-Hydroxyphenylmethanes	M. p., °C.	% N in $C_{24}H_{27}O_2N_2$ Calcd. 3.87
n-Propylmethylethyl-	82.3	3.84
n-Butyldimethyl-	110–11	3.87
Isobutyldimethyl-	114–115	3.78
Isopropylmethylethyl-	112–113	3.92
s-Butyldimethyl-	122–23	3.79
Triethyl-	133–35	3.91
t-Butyldimethyl-	...	..

Proof of Structure of the *t*-Heptylphenols.—The method employed was the same as that used by Huston and Hsieh[2] with two exceptions. In nitrating the alkylbenzenes, after the initial reaction had subsided, the acid mixture was warmed to 90° for two hours on the steam-bath, and the procedure for reducing was the same except that eight to ten hours was employed instead of two hours. The *p*-*t*-heptylphenylamines and nitro compounds and their properties are listed in Tables V and VI.

TABLE V

p-NITRO *t*-HEPTYLPHENOLS

p-Nitrophenylmethanes	M. or b. p., °C. (741 mm.)		% Nitrogen in $C_{13}H_{19}O_3N$ Calcd. 6.32
n-Propylmethylethyl-	B	292	6.31
n-Butyldimethyl-	B	291	6.31
Isobutyldimethyl-	B	284	6.25
Isopropylmethylethyl-	B	285	6.24
s-Butyldimethyl-	B	277	6.29
Triethyl-	B	282	6.30
t-Butyldimethyl- (solid)	M	108	6.33

TABLE VI

p-AMINO-*t*-HEPTYLPHENOLS

p-Aminophenylmethanes	M. p. or b. p.	°C.	mm.	% Nitrogen in $C_{13}H_{21}N$ Calcd. 7.17
n-Propylmethylethyl-	B	117–8	5	6.98
n-Butyldimethyl-	B	145–6	10	7.22
Isobutyldimethyl-	B	124–5	5	7.06
Isopropylmethylethyl-	B	146–8	11	7.01
s-Butyldimethyl-	B	120–1	5	6.87
Triethyl-	B	128–31	5	7.21
t-Butyldimethyl- (solid)	M	55–56	..	6.90

Summary

1. The aliphatic tertiary heptyl alcohols condense with phenol in the presence of aluminum chloride to give *p*-*t*-heptylphenols.

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(12) McGreal and Niederl, THIS JOURNAL, **57**, 2625 (1935).

(13) Shriner and Fuson, "The Systematic Identification of Organic Compounds," Edwards Brothers, Ann Arbor, Mich., 1933, p. 62.

2. The benzoyl and *o*-chlorobenzoyl esters and the α-naphthylurethans of the seven phenols were prepared.

3. The structure of each of the seven phenols was established by synthesis.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WORCESTER POLYTECHNIC INSTITUTE]

Quantitative Acetylation of Amines by Means of Acetyl Chloride and Pyridine

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In the case of organic hydroxy compounds, Smith and Bryant[3] recently have developed a rapid and precise method for the quantitative determination of primary and secondary hydroxyl groups. Their method consists essentially in modifying the usual acetic anhydride–pyridine acetylation mixture by the substitution of acetyl chloride for the anhydride, the acetyl chloride being a more reactive acetylating agent.

The above mentioned authors found that primary and secondary amines as well as mercaptans reacted with the acetylating medium to an extent not determined by them and they suggested that these types of compounds might be estimated by their method.

In the present work the applicability of the Smith–Bryant reagent as a quantitative acetylating agent was tested on a wide variety of amines as well as on a limited number of amine derivatives such as hydroxyamines, amine hydrochlorides, amides, anilides, etc., and on thiophenol. It was found that for some compounds practically quantitative results could be obtained, while in the case of other compounds various factors such as insolubility in the acetylating medium, low rate of reactivity due to the presence of certain substituents, decomposition of the amine during acetylation etc., materially decreased the yield of the acetylated compound and indicated the general inapplicability of the Smith–Bryant method.

An increase in the relative amount of pyridine in the acetylating reagent resulted in immaterial changes in the determined acetyl values.

Variation of the acetylating reagent solvent disclosed the fact that substituting di-*n*-butyl ether for toluene and increasing the temperature of the acetylation from 60 to 70° led to materially increased yields for many of the compounds investigated. Only those compounds which were found to be very unreactive using the original Smith–Bryant method or were particularly sensitive to the action of light and heat yielded acetyl values less than 90% of the theoretical.

The results secured using acetyl chloride and pyridine dissolved in di-*n*-butyl ether as an acetylating medium indicate that in addition to serving as a quantitative method for estimating certain amines and amine derivatives, this procedure may serve as a convenient simple method for preparing small amounts of the diacetyl derivatives.

Experimental

Reagents.—The original acetylating mixture was the same as that used by Smith and Bryant. Acetyl chloride (E. K. C. Practical) was dissolved in Mallinckrodt "Analytical Reagent" toluene which previously had been dried over sodium. In the modified reagent, the toluene was substituted by di-*n*-butyl ether (Commercial Solvents Corporation) which had been rendered peroxide free by the method of Brandt.[4] The boiling point of this reagent was 141°. Pyridine used in conjunction with the above reagents was made anhydrous by the method of Zerewitinoff.[5]

Compounds Acetylated.—A few of the compounds investigated were obtained from the Eastman Kodak Co., and the Mallinckrodt Chemical Co. The greater portion were prepared by the authors and were repeatedly recrystallized or distilled until they were at least 99% pure. All materials employed were desiccated for at least twenty-four hours before use.

Analytical Procedure and Apparatus.—The analytical procedure and apparatus, except for the modifications described below, were the same as those used by Smith and Bryant.[3]

In place of the 250-cc. g. s. volumetric flasks, 300-cc. long-necked, round-bottomed Pyrex flasks were used.

As a means of dispensing the acetylating reagent, a 10-cc. calibrated pipet was used. A rubber syringe bulb was attached to the end of this pipet by means of a rubber tube bearing a spring pinchcock.

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[1] Abstracted from a thesis by Verner R. Olson, submitted to the Faculty of Worcester Polytechnic Institute in partial fulfilment of the requirements for the Degree of Master of Science, June, 1937.

[2] Present address: E. I. du Pont de Nemours & Co. Inc., Finishes Division, Philadelphia, Penna.

[3] D. M. Smith and W. M. D. Bryant, THIS JOURNAL, **57**, 61 (1935).

[4] Brandt, *Chem.-Ztg.*, **51**, 981 (1927).

[5] Zerewitinoff, *Z. anal. Chem.*, **50**, 683 (1911).