obtained. The density of the distillate was 0.759 at 25° and its boiling point 121° at 760 mm.

Anal. Calcd. for $C_8H_{18}O$: C, 73.84; H, 13.84; mol. wt. 130. Found: C, 73.86; H, 13.84; mol. wt. 126.

From the analytical data and the fact that (B) did not react with sodium, it seemed likely that (B) was a dibutyl ether.

Conversion of (B) to *s*-Butyl Bromide.—Forty grams of (B) was saturated with hydrogen bromide and heated under reflux for three hours. The product was washed with water and saturated sodium bicarbonate solution, dried and distilled; 68.5 g. of a bromide with the following physical properties was obtained (81.2%): b. p. 90–91° at 757 mm.; n^{25}_{D} 1.4341; d^{25} 1.250. From these physical constants[8] it is apparent that the bromide formed is probably *s*-butyl bromide.[8]

This conclusion is strengthened by a comparison of densities and boiling points of the three known di-butyl ethers with those of (B).[9]

Preparation of the 3,5-Dinitrobenzoate of *s*-Butyl Alcohol from (B).—One milliliter of (B) was mixed with 0.5 g. of 3,5-dinitrobenzoyl chloride and 0.15 g. of anhydrous zinc chloride and refluxed for one hour. After purification 0.1 g. of ester melting at 75.5° was obtained. This dinitrobenzoate was shown by the method of mixed melting points to be identical with the ester obtained directly from *s*-butyl alcohol and 3,5-dinitrobenzoyl chloride.

Discussion

The theory of the mechanism of the polymerization of olefins by acid catalysts suggested by Whitmore[10] would predict the formation of 3,4-dimethylhexene-2 and 3,4-dimethylhexene-1 from *s*-butyl alcohol under the conditions studied, with the latter olefin present in smaller quantity than the former. We have been unable to detect the presence of formaldehyde after ozonization of any of the fractions of the reaction product, and must conclude that 3,4-dimethylhexene-1 is not formed under the condition studied.

The theory of the mechanism of polymerization of olefins suggested by Kline[11] would likewise lead to the prediction of two products only one of which was found. In this case, however, the product expected in greatest abundance, *viz.*, 4,5-dimethylhexene-2 is not the one actually produced.

Summary

1. The formation of 3,4-dimethylhexene-2 and di-*s*-butyl ether by the action of 75% sulfuric acid on *s*-butyl alcohol at 80° under pressure has been demonstrated.

2. The theory of the mechanism of polymerization by acids suggested by Whitmore explains the observed facts better than that of Kline.

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[8] "Int. Crit. Tables," Vol. I, pp. 188, 276, 277.

[9] "Int. Crit. Tables," Vol. I, p. 204.

[10] Whitmore, *Ind. Eng. Chem.*, **26**, 94 (1934).

[11] Kline and Drake, *Bur. Standards J. Research*, **13**, 705 (1934).

COLLEGE PARK, MD.

RECEIVED SEPTEMBER 27, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF ST. JOHN'S UNIVERSITY AND WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

Studies in the Synthesis of Certain Alkyl and Aryl Cryptophenols[1]

BY MARTIN E. MCGREAL AND JOSEPH B. NIEDERL

Introduction

Since *p*-*t*-octylphenol (*p*-(2,2,4,4-tetramethyl)-butylphenol)[2] has a rather high phenol coefficient (150), it was one of the objects of this investigation to prepare and study the yet unreported *p*-*t*-hexyl and *p*-*t*-heptylphenols. These phenols were prepared by condensing dimethylisopropylcarbinol (I) (b. p. 116–120°) and dimethyl-*n*-butylcarbinol (II) (b. p. 130–130.5°) with phenol in the presence of zinc chloride, utilizing the method of Liebmann, Fischer and Gruetzner.[3]

The condensation of diisobutyl alcohol (2,2,4-trimethylpentanol-4) (b. p. 145–149°) with phenol under identical reaction conditions, however, did not yield the expected *p*-*t*-octylphenol, but *p*-*t*-butylphenol as the main reaction product.[4]

The second object was to investigate the applicability of these condensations to primary, secondary and tertiary aromatic alcohols, and the following carbinols were therefore studied: phenyl (VI), phenylmethyl (VII), benzyl (VII), phenylmethylethyl (VIII) and phenylmethylisopropyl (IX). The last was prepared by the action of isopropylmagnesium bromide on acetophenone.[5]

The condensation products with phenol (VIII

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[1] Presented before the Division of Organic Chemistry at the New York meeting of the American Chemical Society, April, 1935.

[2] J. B. Niederl, U. S. Patent 2,008,337 (1935); British Patent 431,487 (1935); Niederl, Natelson and Beekman, THIS JOURNAL, **55**, 2571 (1933).

[3] (a) A. Liebmann, *Ber.*, **14**, 1842 (1881); (b) Fischer and Gruetzner, *ibid.*, **26**, 1646 (1893).

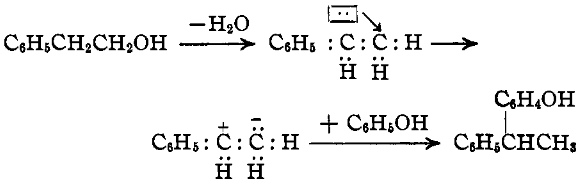
[4] P. W. Hodges, M.Sc. Thesis, New York University, 1935.

[5] B. Gutchin, M.Sc. Thesis, New York University, 1935.

and IX) of the last two compounds were also prepared by the addition of phenol to β-phenyl-β-butylene and phenyl-β-amylene[5,6] using the method of Niederl and co-workers.[7]

In the condensation of β-phenylethyl alcohol (benzylcarbinol) with phenol, apparently simultaneous rearrangement took place as the end-product does not appear to be the expected 4-hydroxydibenzyl but the *p*-(α-phenylethyl) phenol (VII).

Interpretation of this rearrangement phenomenon seems to involve the electronic postulations of Whitmore, Kline and Drake and others[8] and would indicate that dehydration of the β-phenylethyl alcohol precedes the addition of the phenol. The dehydration would activate the alpha carbon of the intermediary styrene as follows.



$$C_6H_5CH_2CH_2OH \xrightarrow{-H_2O} C_6H_5:\underset{\ddot{H}}{C}:\overset{\boxed{..}\searrow}{\underset{\ddot{H}}{C}}:H \longrightarrow$$

$$C_6H_5:\underset{\ddot{H}}{\overset{+}{C}}:\underset{\ddot{H}}{\overset{\bar{\ddot{}}}{C}}:H \xrightarrow{+\ C_6H_5OH} C_6H_5\overset{C_6H_4OH}{\overset{|}{C}}HCH_3$$

1-phenyl-1-(4-hydroxy)-phenylethane

Under the influence of the cationoid condensing agent it can be assumed that on account of incipient ionization of the phenol, or the phenol-condensing agent addition compound, the positive *p*-hydrogen ion would have to add on to the negative primary carbon atom, consequently addition of the negatively charged phenol ion would then have to take place at the secondary carbon atom with the incomplete electron octet thus yielding the above 1-phenyl-1-(4-hydroxy)-phenylethane. The repeatedly observed rearrangements in the butyl series to *t*-butyl compounds may be interpreted in an analogous manner.[3a,9]

The third object in these studies was to extend these condensations to the alkylated cyclohexanol series. Here positive condensations were observed in all the cases investigated. The condensation system of the three isomeric methylcyclohexanols, the hydrogenation products of the three cresols (1-methylcyclohexanol-2 (III), 1-methylcyclohexanol-3 (IV), 1-methylcyclohexanol-4 (V)) proved to be positive in all instances and the corresponding (methylcyclohexyl)-phenols (III, IV and V) were obtained, with the para substituted phenol forming the major reaction product.

An exception again was the condensation of the 4-*t*-octylcyclohexanol-1 (prepared by catalytic hydrogenation of *p*-*t*-octylphenol). In this case, not the expected *p*-(4-*t*-octyl)-cyclohexylphenol, but *p*-*t*-butylphenol again appeared to be the main reaction product, an observation which is entirely in harmony with the experimental findings of Gilman and Burtner[9c] who observed the formation of the *t*-butyl group in their alkylation reactions in the furan series not only involving a butyl, but also an amyl, a hexyl and even an octadecyl radical.

Experimental Part

The molar mixture of the alcohol and of phenol was first warmed to about 150° and to this preheated mixture 1.5 moles of finely powdered, anhydrous zinc chloride was added and the whole refluxed for several hours at 180° (two to ten hours depending upon the reactivity of the alcohol). The reaction mixture, while still warm, was then poured into warm water (80°) acidified with hydrochloric acid. Slowly the phenolic condensation products separated and were then dissolved in toluene following the procedure of Behaghel and Freiensehner.[10] This toluene extract was shaken out first with acidified water and then repeatedly with Claisen solution (50% aqueous potassium hydroxide solution mixed with an equal volume of methyl alcohol).[11] The combined Claisen solution extracts, containing the phenolic condensation products, were washed once with toluene and then acidified with dilute hydrochloric acid (10%). The phenolic condensation products thus separated were then dissolved in ether. This ether extract was dried over calcium chloride and allowed to stand until a clear solution resulted. After removal of the ether by distillation, the residue was repeatedly fractionated under diminished pressure. The solid condensation products were recrystallized from diisobutylene; yield 40–80%.

The above phenol coefficients are the average of four to five determinations employing the standard phenol coefficient technique (30% alcoholic

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(6) Ch. Zimmerman, M.Sc. Thesis, New York University, 1935.

(7) Niederl and Riley, THIS JOURNAL, **56**, 2412 (1934).

(8) Whitmore, *Ind. Eng. Chem.*, **26**, 94 (1934); Kline and Drake, *Bur. Standards J. Research*, **13**, 705 (1934); Kharasch and Sher, *J. Phys. Chem.*, **29**, 625 (1925); Kharasch and Darkis, *Chem. Rev.*, **5**, 571 (1928); G. N. Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York City, 1923.

(9) (a) Reilly and Hickinbottom, *J. Chem. Soc.*, **117**, 103 (1920); (b) Effront, *Ber.*, **17**, 2324 (1884); (c) Gilman and Burtner, THIS JOURNAL, **57**, 909 (1935); (d) Read and Miller, *ibid.*, **54**, 1195 (1932).

(10) Behaghel and Freiensehner, *Ber.*, **67**, 1368 (1934).

(11) Claisen, *Ann.*, **418**, 96 (1919).

Compound	M. p., °C.	B. p., °C.	Phenol coefficient	Analyses, % Calcd. C	Calcd. H	Found C	Found H
t-alkyl phenols							
I *p*-(2,2,3-Trimethyl)propylphenol $(CH_3)_2CHC(CH_3)_2C_6H_4OH$	105		45	80.85	10.16	80.72	10.02
II *p*-*t*-Heptylphenol $(CH_3)_2(C_4H_9)CC_6H_4OH$		280 (760 mm.)		81.18	10.49	81.35	10.70
Cycloalkyl phenols							
III *p*-(2-Methyl)-cyclohexylphenol $CH_3C_6H_{10}C_6H_4OH(2)$	107		50	82.04	9.54	82.37	9.71
IV *p*-(3-Methyl)-cyclohexylphenol $CH_3C_6H_{10}C_6H_4OH(3)$	101		105	82.04	9.54	82.22	9.60
V *p*-(4-Methyl)-cyclohexylphenol[a] $CH_3C_6H_{10}C_6H_4OH(4)$	108		70				
Alkyl-aryl phenols							
VI *p*-Benzylphenol[b] $C_6H_5CH_2C_6H_4OH$	82						
VII *p*-(α-Phenylethyl)phenol $C_6H_5CH(CH_3)C_6H_4OH$	64		40				
VIII 2-Phenyl-2-(4-hydroxy)[c]phenylbutane $C_6H_5C(CH_3)(C_2H_5)C_6H_4OH$[6]		145–148 (2.5 mm.)	33	84.90	8.02	85.00	8.22
IX 2-Methyl-3-phenyl-3-(4-hydroxy)phenylbutane $C_6H_5C(CH_3)(CH(CH_3)_2)C_6H_4OH$[5]		157–160 (3 mm.)		84.94	8.39	85.12	8.51

[a] Meyer and Bernhauser, *Monatsh.*, **54**, 721 (1929). [b] Paternò, *Gazz. chim. ital.*, **2**, 1 (1872); Fileti, *ibid.*, **3**, 121 (1873); *Ber.*, **6**, 757 (1873); Rennie, *J. Chem. Soc.*, **41**, 34 (1882); Zincke and Walter, *Ann.*, **334**, 373 (1904); Perkin and Hodgkinson, *J. Chem. Soc.*, **37**, 725 (1880). [c] Pickard and Littlebury, *ibid.*, **89**, 469 (1906); Stoermer and Kippe, *Ber.*, **36**, 4012 (1903); Koenigs and Carl, *ibid.*, **24**, 3894 (1891).

solutions at 37°) using *Staphylococcus aureus*. The authors desire to thank Dr. Wm. A. Feirer of Sharp and Dohme, Philadelphia, for performing these determinations.

Summary

1. The Liebmann method of condensing alcohols with phenols in the presence of zinc chloride has been extended to include *t*-hexyl, *t*-heptyl and *t*-octyl alcohols, giving in the first two cases the corresponding substituted phenols, while *p*-*t*-butylphenol was obtained from 2,2,4-trimethylpentanol-4.

2. Application of the same method to aromatic alcohols led to positive results in all cases, encountering a rearrangement in the case of β-phenylethyl alcohol.

3. Methylcyclohexanols also could be condensed with phenols by this method, with the *t*-octylcyclohexanol again giving *p*-*t*-butylphenol, instead of the expected *t*-octylcyclohexylphenol.

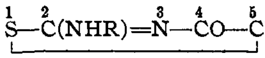
NEW YORK, N. Y. RECEIVED JULY 1, 1935

[CONTRIBUTION FROM THE UNIVERSITY OF KANSAS]

Some Alkyl Derivatives of Certain Aryl Substituted Thiazolidones[1]

BY JOHN A. DAVIS AND F. B. DAINS

In a recent paper by Eberly and Dains[2] it was shown that the alkylation of the mono-aryl thiazolidones,



$\underbrace{\overset{1}{S}—\overset{2}{C}(NHR)=\overset{3}{N}—\overset{4}{C}O—\overset{5}{C}H_2}$, gave two isomeric products, one of the 2-aryl-2-alkylthiazolidone and the other the 2-aryl-3-alkylthiazolidone; results not in harmony with the structure assigned by Beckurts and Frerich,[3] *viz.*, 2-alkyl-3-arylthiazolidone. This paper is a further study of nine aryl substituted thiazolidones in order to determine the structure of the alkylation products and to determine the effect both of the aryl groups and of different alkyl halides on the amount of the two possible isomers.

A. Two methods were used in preparing the thiazolidones.

(1) **From $RNHCOCH_2Cl$ and KSCN.**—Equal molecular quantities of the two were dissolved in alcohol and refluxed for one to five hours. In certain cases this method gave a tarry product and a poor yield.

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[1] From a thesis presented to the Graduate School of the University of Kansas by John A. Davis in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Eberly and Dains, THIS JOURNAL, **55**, 3859 (1933).

[3] Beckurts and Frerich, *Arch. Pharm.*, **253**, 233–265 (1915).