# CONDENSATION OF DIMETHYLAMYL CARBINOLS WITH BENZENE IN THE PRESENCE OF ALUMINUM CHLORIDE

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In continuation and extension of previous work from this laboratory (1), the following tertiary dimethylamyl carbinols, *viz*: 2-methylheptanol-2 (2), 2,3-dimethylhexanol-2 (3), 2,4-dimethylhexanol-2 (4, 5), 2,5-dimethylhexanol-2 (6), 2-methyl-3-ethylpentanol-2 (7), 2,3,3-trimethylpentanol-2 (8), 2,3,4-trimethylpentanol-2 (9), and 2,4,4-trimethylpentanol-2 (10) were prepared and condensed with benzene.

The resulting alkyl benzenes were separated from the reaction-mixtures by repeated fractionation under reduced pressure. Physical constants were determined. In cases where sufficient quantity of the alkylated product was available, it was nitrated, reduced, diazotized, and hydrolyzed to the corresponding phenol (9). In some cases, the monoacetamino derivative (11), was prepared.

The alcohols were prepared as reported in a previous communication (9) with these exceptions. Some of the 2-methyl-3-ethylpentanol-2 was prepared by a modification of the Whitmore (12) procedure, by reacting the Grignard reagent of 3-bromopentane with acetyl chloride, treating the ketone with methylmagnesium bromide and finally hydrolyzing to give the tertiary alcohol; yield, 11%. A part of the 2,4,4-trimethylpentanol-2 was prepared by oxidation of di-isobutylene (13) to 2,2-dimethylpentanone-4 and subsequent reaction of this ketone with methylmagnesium bromide. This method gave a 22% yield of the carbinol based on di-isobutylene. The method of Butlerow (10) gave a 46% yield based on di-isobutylene. The physical constants of the alcohols were carefully determined and are included in summary in Table I.

## CONDENSATIONS

In general, the following procedure with slight modifications was adopted. Two and one-half moles of benzene was placed in a 500 ml. three-necked round-bottom flask with a glycerine-sealed mechanical stirrer, a thermometer, calcium chloride tube, and dropping-funnel. To this was added one-quarter mole of anhydrous aluminum chloride (Baker's C. P.). The aluminum chloride was kept in suspension in the benzene by vigorous mechanical stirring while one-half mole of the carbinol

was added by dropping-funnel at the rate of approximately a drop a second. Temperature control was maintained when necessary by immersion of the reaction-flask in a suitable bath. To prevent freezing of the benzene at low temperatures, 125 ml. of petroleum ether per mole of benzene was added.

After addition of all the carbinol the reaction-mixture was stirred for at least four hours at the temperature used in the condensation and then allowed to stand overnight. It was then stirred for an hour and decomposed by ice and concentrated hydrochloric acid.

The organic layer was separated from the aqueous layer and the latter extracted three times with ether. The combined ether extracts were added to the organic layer and the whole was washed with dilute sodium carbonate and dried overnight with anhydrous sodium sulfate. The low-boiling solvents were removed by distillation on a water-bath and the remaining fraction was distilled under reduced pressure, using a twelve-inch Vigreux column.

Upon condensation several of the carbinols gave, in addition to the expected octylbenzenes, alkyl benzenes of lower molecular weight. Because this was apparently

	в.р., °С. 748 мм. міско	в.р. °С,	d <sup>20</sup>	$n_{ m D}^{20}$	γ <sup>20</sup>
2-Methylheptanol-2	161.2	77-80 at 30 mm.	0.8142	1.4250	26.75
2,3-Dimethylhexanol-2	159.6	68–69 at 15 mm.	.8365	1.4335	27.65
2,4-Dimethylhexanol-2	150.2	66-69 at 10 mm.	.8099	1.4232	26.50
2,5-Dimethylhexanol-2	151.6	73–75 at 20 mm.	.8158	1.4210	25.48
2-Methyl-3-ethylpentanol-2	157.2	46-50 at 5 mm.	.8382	1.4325	27.43
2,4,4-Trimethylpentanol-2	145.8	42–44 at 7 mm.	.8225	1.4284	26.23
2,3,3-Trimethylpentanol-2	156.6	45–47 at 6 mm.	.8517	1.4393	28.77
2,3,4-Trimethylpentanol-2	157.2	43–48 at 5 mm.	.8080	1.4365	27.48

TABLE I

PHYSICAL PROPERTIES OF ALCOHOLS

the result of fragmentation of the longer alkyl chains, methods to eliminate or decrease this splitting were sought. One modification already described was the lowering of reaction temperature. In the condensation of both 2,4,4-trimethylpentanol-2 and 2,3,3-trimethylpentanol-2, the result was a greater yield of octylbenzene.

The method used in condensation of phenol and tertiary alcohols (14), which was found to be less effective with benzene and secondary or tertiary alcohols of lower molecular weight, was reinvestigated in connection with these highly-branched tertiary alcohols and found to give condensation. An apparatus similar to the one already described was used except that a stopper replaced the dropping-funnel. The alcohol (one-half mole) and the benzene (two and one-half moles), with or without petroleum ether, depending on the temperature, was placed in the flask and anhydrous aluminum chloride was added to the mixture a little at a time (one-half gram per five minute interval) from an especially designed shaker. The shaker consisted of 10 cm. of a 14 mm. glass tube inserted in the cork of the aluminum chloride bottle. The whole shaker was kept sealed except when in use and then the powdered reagent was added to the flask through the shaker tube. The amount added was determined by weight difference.

Another method still under investigation and worthy of mention from a theoretical

standpoint is that in which aluminum chloride and benzene were heated together for several hours at the reflux temperature. The mixture was then cooled and the carbinol added. An extension of this procedure was the treatment of benzene with aluminum chloride and heat, and subsequent filtration of the yellow to orange, oily liquid to remove any solid aluminum chloride. When a carbinol was dropped into this filtrate, it was decolorized and a small volume of hydrochloric acid was liberated. Using 2,4,4-trimethylpentanol-2 as the carbinol, small yields of both tertiary butylbenzene and 2,4,4-trimethyl-2-phenylpentane were isolated.

ALCOHOL	TEMP. of cond., °C.	PET. Ether	NO. COND.	PRODUCTS	AV. YIELD,
2-Methylheptanol-2	25	0	4	2-methyl-2-phenylheptane	24.4
2,3-Dimethylhexanol-2	10 25	0 0	4 2	2,3-dimethyl-2-phenyl- hexane	$\begin{array}{c} 19.5\\ 6.3\end{array}$
2,4-Dimethylhexanol-2	25	0	4	2,4-dimethyl-2-phenyl- hexane	24.5
2,5-Dimethylhexanol-2	25	0	5	2,5-dimethyl-2-phenyl- hexane	22.7
2-Methyl-3-ethylpentanol-2	$10 \\ -15$	0 300 cc.	$\frac{3}{2}$	2-methyl-3-ethyl-2-phenyl- pentane	$17.5 \\ 12.5$
2,4,4-Trimethylpentanol-2	10 -10	0 300 cc.	2	2,4,4-trimethyl-2-phenyl- pentane tertiary butylbenzene 2,4,4-trimethyl-2- phenylpentane	9.4 42.0 22.0
2,3,3-Trimethylpentanol-2	-15	300 cc.	3	2,3,3-trimethyl-2-phenyl- pentane tertiary butylbenzene	17.5 3.5 9.

TABLE II Condensation of Alcohols

A summary of condensations, conditions, and yields is included in Table II. This summary is limited to condensations carried out by addition of carbinol to a benzene aluminum chloride suspension with or without petroleum ether.

## PHYSICAL CONSTANTS

The physical constants, *i.e.*, boiling point, refractive index, surface tension, molecular volume, molecular refraction, and parachors were determined by methods indicated in a previous paper (1). Molecular weights were determined by the cryoscopic method, using benzene as the solvent.

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#### DERIVATIVES

The *p*-nitro, *p*-amino, and *p*-hydroxy derivatives of six of the *tert*-octylbenzenes have been reported (9) along with their methods of preparation and analysis.

In the present investigation all but one of the possible amyldimethylphenylmethanes were converted into the *p*-hydroxy derivatives by nitration, reduction to the amine, and diazotization. These were proved, by mixed melting points of the  $\alpha$ -naphthylurethane, to be identical with the products formed by direct alkylation of phenol (9).

The melting point recorded (9) for 2,3,3-trimethyl-2-p-hydroxyphenylpentane is in error and is corrected to  $60-61^{\circ}$ . Condensations in which larger quantities of reactants were used gave this phenol in yields as high as forty per cent. The benzoyl derivative (m.p. 47-48°) and the  $\alpha$ -naphthylurethane (m.p. 118-119°) were prepared and analyzed.

Anal. Calc'd for C20H26O2: C, 81.23; H, 8.45.

Found: C, 81.39; H, 8.21.

Calc'd for C<sub>25</sub>H<sub>29</sub>NO<sub>2</sub>: N, 3.73. Found: N, 3.75.

Tert-butylbenzene was isolated in yields from 17 to 42% depending on conditions, from the condensation of 2,4,4-trimethylpentanol-2 and benzene.

Three to seven grams of *tert*-butylbenzene per quarter-mole of alcohol was also isolated as a by-product in the condensation of 2,3,3-trimethylpentanol-2 with benzene. This was recovered after repeated fractionation of a complex mixture which boiled between 100° and 190° (746 mm.). Identification was carried out by two methods.

(a) Nitration, reduction, and diazotization followed by hydrolysis to give *p-tert*butylphenol.

(b) Nitration, reduction, and acylation of the amine, by the method of Ipatieff and Schmerling (11) to give a monoacetamino derivative melting at 170°.

Attempts to condense 2,3,4-trimethylpentanol-2 with benzene at a temperature of  $-15^{\circ}$  resulted in a mixture of hydrocarbons which distilled over a wide range below the boiling points of the octylbenzenes. We were unable to isolate 2,3,4-trimethyl-2-phenylpentane.

## DISCUSSION

Confirming the generalizations drawn from the lower homologs, we have found a marked reduction in yield of octylbenzene from those alcohols in which there is an accumulation of alkyl groups on the carbon adjacent to the carbinol carbon.

Both 2,3,3-trimethylpentanol-2 and 2,4,4-trimethylpentanol-2 gave, in addition to the octylbenzene, hydrocarbons of lower molecular weight, the formation of which might be explained by dehydration of the alcohol with subsequent chain splitting and condensation of the unsaturated fragments with benzene. The isolation of *tert*-butylbenzene as a by-product in the condensation of 2,3,3-trimethylpentanol-2 was something of a surprise. It is suggested that fragmentation of the hydrocarbon chain, in this case, may take place through the intermediate formation of 2,3,3trimethylpentene-1. Splitting of bonds between the number three carbon and the three alkyl groups attached to it would give isobutene, and a complex mixture of other unsaturated hydrocarbons resulting from the splitting

# TABLE III

NO.	FORMULA	в.р., °С. ат <i>р</i> . мм.	MOLEC- ULAR WT. CALC'D	ANA CAL C, 8 H, 1	LYSIS .C'D 18.35 11.65	n <sup>20</sup> D	MR <sup>20</sup> CALC'D 63.25
			190.18	С	н		50.20
I	CH <sub>3</sub>   CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CC <sub>6</sub> H <sub>5</sub>   CH <sub>3</sub>	243 at 748 116-118 at 16	185.3	88.23	11.57	1.4951	63.36
II	$\begin{array}{c c} CH_3 & CH_3 \\   &   \\ CH_3(CH_2)_2C & CC_6H_5 \\   &   \\ H & CH_3 \end{array}$	236 at 748 105-107 at 14	187.2	88.26	11.53	1.4961	62.71
III	$CH_3 CH_3$ $  \\CH_3CH_2CCH_2CC_6H_6$ $  \\H CH_3$	238 at 748 112–115 at 17	190.9	88.30	11.67	1.4920	63.22
IV	$\begin{array}{c c} CH_3 & CH_3 \\   &   \\ CH_3C(CH_2)_2CC_6H_5 \\   &   \\ H & CH_3 \end{array}$	237 at 748 113-116 at 19	190.	88.24	11.56	1.4939	63.18
v	$\begin{array}{c c} H & CH_3 \\ &   &   \\ CH_3CH_2C - CC_6H_5 \\ &   &   \\ C_2H_5 & CH_3 \end{array}$	236 at 748 103–106 at 12	191.5	88.37	11.68	1.4942	62.98
VI	$\begin{array}{c} CH_3  CH_3 \\      \\ CH_3CH_2C - CC_6H_5 \\      \\ CH_3  CH_3 \end{array}$	235 at 748 110-113 at 17	191.1	88.28	11.53	1.5031	62.9
VII	$\begin{array}{c c} CH_3 & CH_3 \\   &   \\ CH_3CCH_2CC_6H_5 \\   &   \\ CH_3 & CH_3 \end{array}$	234.5 at 748 103-106 at 15	188.5	88.23	11.4	1.4938	62.89

Boiling Points, Molecular Weight, Analysis, Indices of Refraction, and Molecular Refraction

off of methylene and ethylene. Similar mechanisms may be involved in the catalytic breakdown of *tert*-amyl chloride to form *tert*-butyl chloride (15).

Assignment of structure to the *tert*-octylbenzenes is based upon considerations outlined in an earlier publication and upon their conversion to p-tert-octylphenols (9).

It is worthy of note that we were unable to obtain an octylbenzene from 2,3,4-trimethylpentanol-2 but were able to effect condensation of this alcohol with phenol (9).

Densities and molecular volumes are shown in Table IV. The difference between the observed and calculated molecular volume of 2-methyl-2-phenylheptane is somewhat greater than in the case of 2-methyl-2phenylhexane (1). This is in agreement with the stepwise differences of the lower homologs, and indicates a greater effect of the accumulation of

SUBSTANCE $d_4^{20}$	DENSITIES	MOLECULAR	or <sup>20</sup>	PARACHORS		
	220.76	,	Calc'd	Found		
I	0.8756	217.24	32.13	516.4	517.3	
II	.8861	214.64	32.99	513.4	514.4	
III	.8729	217.89	31.01	513.4	514.2	
IV	.8749	217.39	31.19	513.4	513.7	
v	.8782	216.23	31.17	513.4	511.0	
VI	.8939	212.77	32.51	510.4	508.1	
VII	.8803	216.06	31.05	510.4	510.0	

TABLE IV Physical Properties of Octylbenzenes

methyl groups on the carbon adjacent to the ring, with an increase in length of the normal chain.

The boiling points of both of these compounds (Table III) is higher than would be expected from their densities. 2-Methyl-2-phenylheptane boils higher than any of its isomers. These are of approximately the same or higher density. The maximum difference between calculated and observed molecular volumes of these octylbenzenes is found in 2,3,3-trimethyl-2phenylpentane, in which there is the greatest possible accumulation of methyl groups on adjacent carbon atoms. The molecular volume of 2,3dimethyl-2-phenylhexane, which has only one methyl group on the third carbon atom, is intermediate between that of 2,3,3-trimethyl-2-phenylpentane and 2-methyl-2-phenylheptane. The largest molecular volumes are found in 2,3-dimethyl-2-phenylhexane and 2,5-dimethyl-2-phenylhexane, where accumulation of methyl groups is on non-adjacent carbons. The molecular volume of 2,4,4-trimethyl-2-phenylpentane is smaller than theory would predict. Parachors (also shown in Table IV) were calculated using the constants of Mumford and Phillips, together with decrements for chain branching and for attachment of alkyl to the benzene ring. The greatest difference between calculated and observed values is found in 2,3,3-trimethyl-2phenylpentane. This difference is closely followed by that of 2-methyl-3ethyl-2-phenylpentane in which there is also branching on the third carbon.

The other isomer in which branching occurs on the third carbon atom, 2,3-dimethyl-2-phenylhexane, shows close agreement between calculated and observed parachors, indicating in this case complete compensation in the surface tension for the branching effect. In spite of the relatively high density of 2,4,4-trimethyl-2-phenylpentane, the observed parachor is in close agreement with the calculated.

Molecular refractions (Table III). The greatest deviations between calculated and observed values which may be attributed to chain branching are found in 2,3,3-trimethyl-2-phenylpentane, in 2,3-dimethyl-2-phenylhexane and in 2-methyl-3-ethyl-2-phenylpentane. The high density of 2,4,4-trimethyl-2-phenylpentane gives a small lowering of the molecular refraction. The highest molecular refraction is shown by 2-methyl-2phenylpentane which contains the longest carbon chain. The same relationship was found to hold in the heptylbenzenes (1). These high molecular refractions are coincident with relatively high boiling points and may be taken as indicating increased polarizability with lengthening of the chain.

#### SUMMARY

1. Several known isomeric dimethylamyl carbinols have been prepared in quantity and their physical constants determined.

2. The isomeric amyldimethyl carbinols condense with benzene in the presence of aluminum chloride to give, with one exception, *tert*-octyl-benzenes. In cases where the amyl radical was highly branched, alkyl benzenes of lower molecular weight were formed.

3. Physical constants of the alkyl benzenes have been determined and derivatives have been prepared.

4. Several new procedures for condensing benzene and tertiary alcohols in the presence of aluminum chloride have been suggested.

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