

#### THE PREPARATION AND IDENTIFICATION OF THE ACETAMINO DERIVATIVES OF TERTIARY ALKYL BENZENES

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# THE PREPARATION AND IDENTIFICATION OF THE ACETAMINO DERIVATIVES OF TERTIARY ALKYL DENZENES

by

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#### A THESIS

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#### Introduction

In the course of a study of aromatic hydrocarbons Ipatieff (1) found need of a simple method of the identification of alkylbenzenes. Boiling points and other physical constants would have been satisfactory for distinguishing between homologous compounds but inadequate in the case of isomers, oxidation could have been used to distinguish between mono- and dialkylbenzenes, but of course, would have failed to determine the configuration of the alkyl groupings.

Ipatieff and Schmerling (2) in an attempt to establish a suitable means of identification of several alkyl benzenes, studied the mono- and di-acetamino derivatives. No previous study of the nitration, reduction, and acylation of a series of alkylbenzenes under a single set of conditions had been attempted.

A procedure for the quick and easy identification of mono-alkyl benzenes was developed. Under the prescribed conditions pure 4-nitroalkylbenzenes may be obtained by use of a nitrating mixture of equal volumes of concentrated sulfuric and nitric acids. Ortho isomers are present in only small amounts and do not interfere; and the dinitro derivatives which may be present may be readily separated by an ether extraction of the solution obtained on reducing with tin and hydrochloric acid. The mono-amino complex forms an ether soluble salt with tin chloride in the presence of acid; the diamino salt is ether-insoluble.

Ipatieff and Schmerling prepared both mono- and di-

acetamino derivatives of toluene, ethyl benzene, the propyl benzenes, the butyl benzenes and the amyl benzenes. All were white crystals, possessed sharp melting points, and were easily identified.

In this laboratory since 1934 higher alkyl benzenes have been prepared by condensation of tertiary alcohols with benzene in the presence of aluminum chloride. A fairly satisfactory method of identification of these hydrocarbons has been effected in the preparation of the corresponding alkyl phenols (and subsequent preparation of urethane derivatives) by nitration, reduction, diazotization, and hydrolysis. However, the method is long, and not entirely gratifying with small amounts.

Since it was necessary, for a complete study of the mechanics of condensation reactions, to establish the identification of mixed fractions and split alkyl benzene products, and since the acetamino derivatives of some alkyl benzenes had been prepared, the preparation and identification of the mono-acetamino derivatives of all the condensation products (tertiary alkyl benzenes) was highly desirable.

#### History

Huston and Fox (3) in 1934 successfully condensed tertiary butyl alcohol, tertiary anyl alcohol, dimethyl n-propyl carbinol, and dimethyl iso-propyl carbinol with benzene to give the expected products, tertiary tutyl benzene, tertiary amyl benzene, dimethyl n- ropyl phenyl methane, and dimethyl iso-propyl methane, is good yields.

Huston and Einder (4) in 1935 condensed dimethyl nbutyl carbinol, dimethyl iso-butyl carbinol, dimethyl secbutyl carbinol, methyl ethyl n-propyl carbinol, methyl ethyl iso-propyl carbinol, and trimethyl carbinol to obtain in good yields the products, dimethyl n-butyl phenyl methane, dimethyl iso-butyl phenyl methane, dimethyl sec-butyl phenyl methane, methyl ethyl n-propyl phenyl methane, methyl ethyl iso-propyl phenyl methane, and triethyl phenyl methane. A condensation with dimethyl tertiary butyl carbinol gave a product in the expected range, but it was not identified with certainty.

Huston and Sculati (5) in 1936 condensed dimethyl amyl carbinols (n-amyl, active amyl, iso-amyl, sec-amyl) with benzene to form the alkyl benzenes dimethyl n-amyl phenyl methane, dimethyl active amyl phenyl methano, di-methyl isoamyl phenyl methane, and dimethyl sec-amyl phenyl methane in yields which decreased with the approach of the branching to the carbinol grouping.

Huston and Freining (6) in 1938 by condensation with benzene prepared diethyl n-propyl phenyl methane and di-

ethyl iso-propyl phenyl methane in approximately 25% yields from diethyl n-propyl carbinol and diethyl iso-propyl carbinol respectively.

Huston and Cline (7) in 1939 were able to isclate methyl di-n-propyl phenyl methane and methyl n-propyl-iso-propyl phenyl methane in 37% and 18% yields respectively; and also small emounts (7%) of methyl di-iso-propyl phenyl methane from the respective carbinols.

Huston and Synder (8) in 1939 in their proof of structure were successful in isolating and identifying the normal products of condensation of n-butyl methyl ethyl carbinol, secbutyl methyl ethyl carbinol, and iso-butyl methyl ethyl carbinol, with benzene.

Huston and Masson (9) in 1940 by reactions of 2,4,4-trimethyl pentanol-2, 2,3,3-trimethyl pentanol-2, and 2-methyl-3-ethyl-pentanol-2 with benzene, prepared the corresponding alkyl benzenes, 2,4,4-trimethyl-2-phenyl-pentane, 2,3,3-trimethyl-2-phenyl-pentane, and 2-methyl-3-ethyl-2-phenyl-pentane (the later which Huston and Guile (10) had earlier reported) although in small yields.

#### Experimental

Materials

1. N-amyl, sec-amyl, iso-amyl, active amyl, n-propyl, iso-propyl, and n-butyl bromides were prepared from the corresponding alcohols (Eastman technical) by the action of sulfuric acid and hydrobromic acid (11).

2. Tertiary anyl bromide was prepared by shaking the alcohol with 48% hydrobromic acid in the cold and salting out with calcium chloride (12). Two degree ranges were taken on all bromides.

3. Benzene was thiophene free, C. P. and was dried over sodium before use.

4. Diethyl ether was C. P. anhydrous, and was dried over sodium before use. During the last of the work it was necessary to use U. S. P. ether which was first washed with water to remove the alcohol, chloroform, etc., dried over calcium chloride, distilled from sodium, and dried over sodium.

Petroleum ether was dried over sodium (B.F.30-65°).
 Acetone was C.P. and was first dried over sodium sulfate.

7. Magnesium turnings especially prepared for Grignard reactions were used after being dried in an oven at 50°.

8. Aluminum chloride was Baker's Analyzed, special for condensations.

9. Acetic anhydride was Eastman.

10. Iso-butyryl chloride was prepared for use by the action of phosphorous trichloride on iso-butyric acid.
B.P. 90-91°at atmospheric pressure. (13)
11. Dimethyl iso-butyl carbinol was prepared by Binder. (4)
12. Dimethyl sec-butyl carbinol was prepared by Binder. (4)
13. Triethyl carbinol was prepared by Binder. (4)
14. Diethyl n-propyl carbinol was prepared by Langdon. (14)
15. Methyl di-iso-propyl carbinol was prepared by Meloy. (15)
16. 2,4,4-trimethyl-pentanol-2 was prepared by Guile.

(10)

Carbinols

1. Dimethyl iso-propyl carbinol

This was prepared by the action of acetone on the Grignard reagent, iso-propyl magnesium bromide. Yield-35%.

2. Dimethyl n-butyl carbinol

This alcohol was prepared from n-butyl magnesium bromide and acetone (16). Yield - 57%.

3. Methyl ethyl iso-propyl carbinol

Prepared from methyl iso-propyl ketone and an ethyl Grignard reagent. Yield - 63%.

4. Methyl ethyl n-propyl carbinol

This was prepared by the method of Whitmore and Badertscher, (17) from methyl ethyl ketone and n-propyl magnesium bromide. Yield - 60%.

5. Dimethyl n-amyl carbinol

Frepared from n-amyl bromide and acetone. Grignard's reaction (18). Yield - 40%.

6. Dimethyl sec-amyl carbinol

This was prepared by the above method, substituting sec-amyl bromide. Yield - 12%.

7. Dimethyl iso-amyl carbinol

This alcohol was also prepared by the same method using iso-amyl bromide. Yield - 41%.

8. Dimethyl active-amyl carbinol

This was prepared from active-amyl bromide and acetone by the above method. Yield - 13%.

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9. Dimethyl tert-anyl carbinol

2,3,3-trimethyl-pentanol-2 was prepared from directions given by Whitmore and Badertscher (18), and consisted of the preparation of the ketone, 3,3dimethyl-pentanone-2 and reacting this with methyl magnesium iodide. Yield - 12/2.

10. Diethyl iso-propyl carbinol

This was prepared from the interaction of one mole of iso-butyryl chloride and two moles of ethyl magnesium bromide. B. P. 64-66° at 20mm. Yield - 25%. Condensations

1. Dimethyl iso-propyl phenyl methane

Run in an ice water bath, by the method of Fox

(3). Yield - 20%.

2. Dimethyl n-butyl phenyl methane

Run according to that method used by Binder (4). Yield - 40%.

3. Dimethyl iso-butyl phenyl methane

Run by Binder's technique (4). Yield - 195.

4. Dimethyl sec-butyl phenyl methane

From benzene and dimethyl sec-butyl carbinol (4). Yield - 285.

5. Methyl ethyl n-propyl phenyl methane

From methyl ethyl n-propyl carbinol by condensation with benzene (AlCl<sub>3</sub>) (4). Yield - 34%.

6. Methyl ethyl iso-propyl phenyl methane

Run by the Shaker method, the aluminum chloride being slowly added to the stirred mixture of carbinol and benzene. The reaction mixture was cooled in a salt-ice bath, which was allowed to warm to room temperature upon completion of the addition. Yield -23%. (4)

7. Triethyl phenyl methane

From triethyl carbinol by the method of Binder (4). Yield - 50%.

8. Dimethyl n-amyl phenyl methane

Run in a cold water bath by the Shaker method, using dimethyl n-amyl carbinol and benzene in the presence of AlCl<sub>3</sub> (5). Yield - 23%.

9. Dimethyl iso-amyl phenyl methane

Run by Sculati's technique (5). Yield - 24%.

10. Dimethyl sec-amyl phenyl methane

Run as above (5). Yield -  $\delta_{\bullet}4$ 

11. Dimethyl act-anyl phenyl methane

From dimethyl active-amyl carbinol using the method of Sculati (5). Yield - 14%.

12. Diethyl n-propyl phenyl methane

Run according to the technique of Breining (6). Yield - 19%.

13. Diethyl iso-propyl phenyl methane

Run as above (6). Yield - 20%.

14. Methyl di-iso-propyl phenyl methane

This was prepared using a slightly modified technique. Cline (8) prepared this product in small amounts by first suspending the benzene and aluminum chloride in petroleum ether, cooling to a minus 30° and slowly adding the carbinol. In this condensation, the suspended benzene, aluminum chloride, and petroleum ether, were stirred for twenty-four hours at room temperature, cooled over-night in a refrigerator, and then cooled to about a minus 24°. The carbinol was then slowly added so that there was no appreciable change in temperature. This treatment gave a higher yield of the desired product. Yield - 5%. 15. 2,3,3-trimethyl-2-phenyl pentane

From 2, 3, 3-trimethyl pentanol-2 by the technique

evolved by Wasson (9). Yield - 6.25. 16. 2,4,4-trimethyl-2-phenyl pentane

Run by the Shaker method, the aluminum chloride being slowly added to a stirred mixture of benzene, petroleum ether, and carbinol, which was cooled in a salt-ice bath. Yield - 7.45.

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### Preparation of derivatives

In the technique evolved by Ipatieff and Schmerling (2) either the mono- or the di-acetamino derivatives may be prepared as the worker desires. By varying the nitrating mixture either one may be successfully isolated as the principal product, or both may be obtained from the same small amount of starting material required. The derivatives chosen here are the mono-acetamino alkyl benzenes.

The directions given are as follows:

"Procedure-- A mixture of 0.5 to 1.0 c.c. of the aromatic hydrocarbon and 5 c.c. of a nitrating mixture was shaken for three to five minutes. The nitrating mixture consisted of equal volumes of sulfuric acid (d-1.84) and nitric acid (d-1.42), when the mononitro compound was desired as the chief product, or of two volumes of the sulfuric acid to one of the nitric acid when it was the disubstituted derivative which was to be obtained. No attempt was made to cool the reaction mixture. When the evolution of heat had ceased, the mixture was poured upon a small amount of cracked ice, the oily nitro layer was taken up in ether, washed twice with water, and the ether was evaporated on a water-bath. To the residue was added five grams of granulated tin, 5 c.c. of concentrated hydrochloric acid, and sufficient ethyl alcohol to bring all of nearly all of the nitro compound into solution. The mixture was shaken until reduction was complete as was shown by the absence of marked turbidity on pouring a test portion into water. This usually required less than ten minutes. In those cases in which the reduction took place more slowly, the reaction was hastened by heating the mixture on the water-bath; usually, however, the reduction was very exothermic and did not require the application of external heat. When reduction was complete, the aqueous alcoholic solution was decanted from the excess tin into about 20 c.c. of water. The solution was extracted with ether and sufficient concentrated alkali was added to the aqueous solution to discolve most of the precipitate of tin hydroxide which formed at first. The amino compound was extracted with ether, washed with water, dried by shaking for a few minutes with potassium carbonate, and the ether removed by evaporation. To the residue was added one c.c. of acetic anhydride. The derivative usually crystallized almost immediately. The material was warmed with 5 c.c. of water to hydrolyze the excess anhydride. Since some of the acetamino derivatives are quite soluble in dilute acetic acid it was occasionally necessary to evaporate almost to dryness the solution containing the hydrolyzed acetic anhydride. The crude derivative was filtered and then recrystallized from hot water or dilute alcohol, yield 40-70%."

This was found in general to be satisfactory, but a few modifications were made. As the mono-derivatives were the only ones desired, the nitrating mixture consisted of equal parts of sulfuric and nitric acids. The ether extract of the reduced product was evaporated, the complex broken by neutralization with sodium hydroxide, the pure amine extracted with ether, and the ether evaporated. It was also found necessary with most of the amines, to reflux them with

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acetic anhydride for five or ten minutes. The resultant solution was then cooled, hydrolyzed with 25 c.c. of water, and then carefully neutralized with 10% sodium hydroxide. The oily liquid was freed of water by filtration and washed with water several times.

With the exception of the octyl derivatives, recrystallization from dilute alcohol was convenient. Hexane and isopropyl alcohol diluted with water also worked very well.

Those derivatives which the author was unable to crystallize as indicated in Table A refused to come down from a great variety of solvents. All the common solvents known water, alcohols, hexane, Skellysolve, acids, dioxane, nitrobenzene, benzene and others, were tried with no success.

Some of the derivatives crystallized from the oils on long standing (a year), but attempts to recrystallize them from any solvents were of no avail.

Farent Hydrooarbon	-	Derivative	-	Melting Point	: Crystalline Form
<b>Tertiary</b> butyl benzene		(p) -tert-butyl* acetanilide	<b>64 74</b>	<b>169-1</b> 70°*	: plates*
Tertiary amyl b <b>e</b> nzene	•••	(p) tertiary amyl acetanilide**	•• ••	1420**	s plates*
2-methy1-2-pheny1 pentane	•• •• ••	2-methyl-2- (p)- acetyl amino phenyl pentane	•• •• ••	84 <b>•5-</b> 85 <b>•50</b>	: plates
2,3 dimethyl-2-phenyl butane	(V Q)	2,3-dimethyl-2 (p- acetyl amino) phenyl butane		0611	: small plates :
3-methy1-3-pheny1 pentane	•• ••	3-methy1-3 (p-acety1 umino) phenyl pentane	•• ••	000 <b>1-</b> 066	s small plates
2-methyl-2-phenyl hexàne	·· ·· ··	2-methyl-2 (p- acetyl amino) phenyl hexane	** ** **	78.5-79.50	s small plates
2,4-dimethy1-2 pheny1 pentane	•• •• ••	2,4-dimethyl-2 (p- icetyl amino) phenyl pentane	** ** **	<b>1</b> 06 <sup>0</sup>	: plates
* Shoesmith and Mackie ** Ipatieff and Schmerl	C anti	19) 3			

TABLE A

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Parent Hydrocarbon f	Derivative	-	Melting Point	: Crystalline Form
2,3 dimethyl-2-phenyl ; pentane ;	2,3 dimethyl-2 (p- acetyl amino) phenyl pentane	** ** **	85-86 <sup>0</sup>	: plates
2,3,3-trimethy1-2-pheny1: butane :	2,3,3-trimethy1-2 (p- acetyl amino) phenyl butane	•• •• ••	142-1430	: small plates
3-methyl-3-phenyl : pentane :	3-methyl-3 (p-acetyl amino) phenyl pentane	•• ••	71-720	; plates
2.3-dinethyl-3-phenyl : butane :	2,3-dimethy1-3 (p-acetyl amino) phenyl butane	** ** **	67 <del>~</del> 67	: small plates :
3-ethy1-3-pheny1 : pentane :	3-ethy1-3 (p-acetyl amino) phenyl pentane	•• ••	1260	: small plates
2-methy1-2-phenv1 heptane	2-methyl-2 (p-acetyl amino) phenyl heptane	** **	68 <b>-5-</b> 690	: small plates ;
2,5 dimethy1-2-pheny1 : hexane	2,5-dimethy1-2- (p- acetyl amino) phenyl hexane	54 +4 +4		red oil

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TABLE A



Parent Hydrooarbon	Derivative ;	Melting Point	: Crystalline Form
2,4-dimethy1-2-pheny1 ; hexane	2,4-dimethy1-2(p-acety1; amino) pheny1 hexane ;		t red oil t
2,3-dimethy1-2-phenyl : hexane	2,3-dimethyl-2(p-acetyl: amino) phenyl hexane :		: yellow oil ;
2,3,3-trimethy1-2- : phenyl pentane :	2,3,3-trimethy1-2(p- : acety1 amino) pheny1 : pentane :	920	: plates
3-ethy1-3-phenyl hexane	3-ethyl-3(p-acetyl : amino) phenyl hexane :		: yellow oil ;
3-ethyl-4-methyl-3- : phenyl pentane :	3-ethyl-4-methyl-3- ; p(acetyl amino) phenyl ; pentane ;	83 <b>•5</b> 0	r plates
4-methyl-4-phenyl : heptane :	<pre>4-methyl-4(p-acetyl : amino) phenyl heptane ;</pre>		: dark orange oil :
2,3-dimethy1-3-pheny1 : hexane :	2,3-dimethyl-3(p- acetyl amino) phenyl : hexane :		: dark red oil :
2, 3, 4-trimethy1-3-pheny1: pentane :	2,3,4-trimethy1-3(p- : acetyl amino) phenyl : pentane :		: dark red oil :

TABLE A

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Parent Hydrocarbon 1	Derivatives		Melting Point	; Grystall	ine Form
2,4,4 trimethyl-2-phenyl: pentane	2,4,4-trimethy1-2(p- acety1 amino) phenyl pentane			t : yello :	w oil
2-methyl-3-ethyl-2- 3 phenyl pentane 3	<pre>2-methyl-3-ethyl-2(p- acetyl amino) phenyl pentane</pre>			: F Bello	w oil
2,4 dimethyl-4-phenyl : hexane :	2,4-dimethyl-4(p- acetyl amino) phenyl hexane	•• ••		i dark r	ed o <b>11</b>
3-methy1-3-pheny1 ; heptane ;	3-methy1-3(p-acety1 amino) phenyl heptane	** **		ark r	ed o <b>il</b>
3,4-d1methy1-4-pheny1 : hexane :	3,4-dimethy1-4(p-acety1 amino) phenyl hexane	•• ••		red	oil
3,4,4-trimethy1-3-pheny1; pentane	3,4,4 trimethyl-3(p- acetyl amino phenyl pentane	<b>44 *</b> • ••		: ; ; ; ; ; ; ; ; ; ; ; ; ; ; ; ; ; ; ;	w oil

TABLE A

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TABLE B

RELATIVE SOLUBILITIES In 1 c.c. Solvent

Solvent		Hot	••	Cold 1	-	Solvent	••	Hot	••	Colđ
water		Insoluble		insoluble:		lsopropy1 alcohol		soluble		soluble
95% alcohol	** **	readily soluble	•• ••	readlly : soluble :		buty1 alcohol	** **	soluble	** **	solub <b>le</b>
50% alcohol	48 <del>78</del>	read11y soluble	** **	insoluble:	•• ••	methyl alcohol	** **	soluble	<b>** **</b>	soluble
ether	•• ••	readily soluble		reaŭily : solubie :	8	setic acid (glaofal)	** **	soluble	•• ••	soluble
petroleum ether	<b>**</b> **	readily soluble	<b>**</b> **	readily : soluble ;	ba 64	dioxane	** **	<b>soluble</b>	** **	soluble
3kellysolve	** **	<b>readily</b> soluble	** **	fairly : soluble ;	•• ••	1010 •	** **	soluble	** **	soluble
legroin	**	soluble	••	solub <b>le ;</b>	••	hloroform	**	soluble	**	soluble
acetone	<b>68 +4</b>	soluble	** **	soluble : 1	re te	oarbon trachloride	** **	soluble	** **	soluble
benzene	-	soluble	••	soluble :	••	hexane	**	soluble	••	insoluble

#### Discussion

The general procedure for the preparation of the acetamino derivatives of the alkyl benzenes described in this work consisted of nitration by means of a mixture of equal parts of concentrated sulfuric and nitric acids; reduction of the product with tin and hydrochloric acid; and acylation of the pure mono-amine with acetic anhydride.



In a few cases, pure anines (para), which had been previously prepared in the laboratory, were acylated. Electing points of these derivatives checked with those made by the above method.

Fairly good yields resulted with all the products, averaging about 40%.

Evidently those derivatives which the author was unable to crystallize possess a latent lattice formation which makes recrystallization impossible. This is the only method of explaining the resultant crystallization from the oils on long standing. The forces necessary to form the lattice work are not sufficiently strong to permit latticing in solvents.

No generalizations on the melting points can be made aside from the fact that lengthening the chain lowers the melting point, and branching (heaping of eurogens) raises it to a certain extent.

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1. Some tertiary alcohols were synthesized and condensed with bergene in the presence of aluminum chloride to form the alkyl bengenes.

2. Identification of tertiary alkyl benzenes has been made through the preparation of the mono-acetanino derivatives. The technique consists of nitration, reduction, and acylation, and may be applied quickly to small amounts of the hydrocarbon.

3. Fifteen of these derivatives have been successfully recrystallized. Melting points and crystal forms have been recorded.

4. Various solvents, scratching, seeding, cooling, and other accepted methods of inducing crystallization (20) were utilized on the remaining derivatives which were those of the tertiary octyl benzenes. These were not successful.
5. Some of these on long standing crystallized from the oils. However, attempts to recrystallize from solvents failed.

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