THE PREPARATION AND REACTIONS OF THE 1,3-DIMETHYL-4-AMYLBENZENES

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In a previous paper (1) it was shown that the s- and t-butyl radicals in the 1,3-dimethyl-4-butylbenzenes reacted with decahydronaphthalene in the presence of aluminum chloride to form butanes in 24% and 41% yields respectively, and that the corresponding n-butyl and isobutyl hydrocarbons did not yield any paraffin.

To study further the effect of the branching of the chain on the yield of paraffin in this reaction, the eight 1,3-dimethyl-4-amylbenzenes were prepared and heated with decahydronaphthalene according to the directions of Ipatieff and Pines (2).

The effect of the branching of the pentane chain is striking. The 4-*n*amyl and 4-isoamyl hydrocarbons did not yield any paraffin, but the 4neopentyl isomer yielded some isopentane. The formation of a paraffin from this latter hydrocarbon was somewhat unexpected since no paraffin had been obtained previously from an alkyl group attached to the benzene ring through a primary carbon, and neopentyl derivatives are usually very stable. The formation of isopentane rather than neopentane is not surprising in view of the fact that neopentyl chloride and benzene in the presence of aluminum chloride yields only 2-methyl-3-phenylbutane (3). The paraffin did not react with a dilute solution of potassium permanganate or with bromine in carbon tetrachloride, indicating the absence of olefins such as isopropylethylene.

Of the three s-amyl radicals, (I) $CH_3CHC_3H_7$, (II) $C_2H_5CHC_2H_5$, and (III) $CH_3CHCH(CH_3)CH_3$, the one with the branched chain, III, gave a better yield of paraffin than the straight-chain radicals, I and II, and in less than half the time (Table III). The paraffins are mostly mixtures of *n*-pentane and isopentane, with the latter as the principal product from the highly branched radicals.

The best yield of paraffin was obtained from 1,3-dimethyl-5-t-amylbenzene. Since it is not certain that the 1,3-dimethyl-4-t-amylbenzene

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² Presented in part before the Organic Division of the American Chemical Society, St. Louis, Missouri, April 10, 1941. was entirely pure, any definite conclusions as to the relative ease of cleavage of the amyl radical in the 5 position as compared with the 4 position are not justified. The *t*-amyl radical and the *t*-butyl radical are both cleaved to the same extent from the 5 position.

These data definitely confirm the observations of Ipatieff and Pines (2) that the more highly branched the chain in an alkylbenzene, the more readily the radical is cleaved by aluminum chloride.

No effort was made to study the effect of aluminum chloride on the 1,3-dimethyl-4-amylbenzenes due in part to the probable formation of complicated mixtures through the extensive isomerization possible with the various amyl radicals. Even *n*-amyl chloride and benzene in the presence of aluminum chloride did not yield pure 2-phenylpentane. Furthermore, the necessary 1,3-dimethyl-5-amylbenzenes are not readily available for reference compounds.

It should be possible to synthesize some of the 1,3-dimethyl-5-amylbenzenes through the reaction of 3,5-dimethylbenzyl-potassium or -sodium with the butyl halides (4), but this method was practical only with *n*-butyl chloride. With the other butyl halides, reactions other than the expected coupling must have occurred for the small trialkyl fraction boiled over a range, and relatively large amounts of high-boiling products were formed. The effect of the structure of the butyl chloride on the yield of crude trialkyl fraction was apparent. The primary halides gave better yields than either the secondary or tertiary halides. The 3,5-dimethylbenzylsodium gave a better yield of alkylbenzene than did 3,5-dimethylbenzylpotassium.

The reaction between m-xylene and t-amyl alcohol in the presence of 85% sulfuric acid (5) at temperatures below 20° led to a product which contains some other hydrocarbon along with the expected 1,3-dimethyl-4-t-amylbenzene. The reaction product boils over a wide range and analyses for carbon and hydrogen of the fraction which should be the 4-t-amyl hydrocarbon did not agree with the theoretical values even after the hydrocarbon had been fractionated repeatedly and carefully. A pure diacetamino derivative could not be obtained from this fraction, but analyses of the dibenzamino derivative corresponded to that of a dimethylamylbenzene.

The reaction between the 2,4-dimethyl-6-amylbenzyl chlorides and acetamide at around 200° forms the corresponding acetyl benzylamine:



This reaction appeared promising for the preparation of derivatives of these hydrocarbons, but mixtures of isomers did not show a very large depression

of their melting points and some of the acetylated amines could not readily be obtained pure.

All of the hydrocarbons in this series other than the 1,3-dimethyl-4t-amylbenzene and 1,3-dimethyl-5-t-amylbenzene were prepared from ketones, either through the Clemmensen reduction, or by the addition of the appropriate Grignard reagent to a ketone followed by dehydration of the resulting carbinol and hydrogenation of the olefin at pressures up to 3300 pounds (225 atm.) with Raney nickel as the catalyst. The use of platinum at low pressures was unsatisfactory, probably due to traces of sulfur from the carbon disulfide used as a solvent for the preparation of the ketones. It was desirable to distill the olefin from Raney nickel before hydrogenation to ensure smooth reduction.

In the Grignard reactions, the effect of the branching of the chain in either the Grignard reagent or the ketone is clearly shown in the yield of hydrocarbon from 2,4-dimethylacetophenone and isopropylmagnesium bromide (32%) as compared with 2,4-dimethylisobutyrophenone and methylmagnesium iodide (64%), and 2,4-dimethyl-*n*-butyrophenone and methylmagnesium iodide (72%). These yields correspond to those obtained by Conant and Blatt (6) in their study of the effect of the branching of the chain in aliphatic ketones and Grignard reagents on the yield of tertiary carbinol.

In spite of the fact that products other than saturated hydrocarbons are formed during the reduction of alkyl aryl ketones by the Clemmensen method, this procedure was more satisfactory than high-pressure reduction of the ketones with hydrogen and Raney nickel. Prolonged refluxing was necessary to secure good yields. The formation of bimolecular reduction products lowered the yield of hydrocarbon.

Trimethylacetyl chloride and *m*-xylene formed not only some of the desired ketone but also a pale yellow solid, m.p. 165°, the identity of which has not yet been established. On the basis of Boeseken's observation that this acid chloride decomposes in the presence of aluminum chloride to form carbon monoxide, hydrogen chloride, isobutene, and a polymer of isobutene (7), a polybutylxylene might be formed, but analyses do not correspond to any of the polybutylxylenes. A methyl group from the radical of the acid chloride does not alkylate the nucleus as in the case of diamylacetyl chloride (8) for the yellow compound is not a ketone. Mesitylene and trimethylacetyl chloride also yielded the expected ketone and a solid by-product, while benzene formed a high-boiling liquid but no ketone. The structure and properties of these products are under investigation.

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EXPERIMENTAL³

All fractionations were carried out with columns packed with single turn glass helices. The physical constants and analyses of the hydrocarbons have been summarized in Table I.

1,3-Dimethyl-5-t-amylbenzene was obtained from 53 g. of m-xylene, 15 g. of aluminum chloride, and 26 g. of t-amyl chloride at room temperature by the usual Friedel-Crafts procedure. The yield was 30 g. (64%), b.p. $102-103^{\circ}$ (14 mm.). DeCapeller (9) states that he prepared this hydrocarbon from these reagents but mentions no physical constants.

| ALKYL BENZENE | D.B. °C 22 | | 220_ | ANALYSES ^b | | |
|---|------------|----------|--------|-----------------------|-----------|--|
| | D.F. | 0. | ·· B | Found % C | Found % H | |
| 1,3-Dimethyl- | | | | | | |
| 5- <i>t</i> -amyl | 102-103 (1 | l4 mm.) | 1.4982 | 88.43 | 11.37 | |
| 4- <i>t</i> -amyl | 93-95 (1 | l4 mm.) | | 87.93 | 11.37 | |
| 4- <i>n</i> -amyl | 123-124 (1 | l6 mm.) | 1.4972 | 88.50 | 11.57 | |
| 4-isoamyl | 116-117 (1 | 15 mm.) | 1.4966 | 88.42 | 11.40 | |
| 4-neopentyl | 97-98 (1 | l0 mm.) | 1.5081 | 88.66 | 11.03 | |
| 4-CH ₃ CHCH ₂ CH ₂ CH ₃ | 102-103 (1 | l1 mm.) | 1.4959 | 88.48 | 11.56 | |
| $4-CH_3C=CHCH_2CH_3$ | 104 (1 | l3 mm.) | | | | |
| 4-CH ₃ CHCH(CH ₃)CH ₃ | 100-102 (1 | l3 mm.) | 1.5022 | 88.48 | 11.17 | |
| $4-CH_3C=C(CH_3)CH_3$ | 106-110 (1 | l6 mm.) | | | | |
| $4-C_2H_5CHC_2H_5$ | 105-106 (1 | l3 mm.) | 1.4973 | 88.40 | 11.49 | |
| $4-C_2H_5C=CHCH_3$ | 103-105 (1 | l6 mm.) | | | | |
| $4-CH_2CH(CH_3)C_2H_5$ | 108–111 (1 | l3 mm.) | 1.4942 | 88.35 | 11.67 | |
| $4\text{-}CH = C(CH_3)C_2H_5$ | 107 (1 | l0 mm.) | | | | |

TABLE I

ALKYL BENZENES^a

^a The position of the double bond in the olefin was not determined and the olefins were not analyzed.

^b Calc'd for C₁₃H₂₀: C, 88.63; H, 11.37.

1,3-Dimethyl-4-t-amylbenzene. The procedure of Kirrmann and Graves (5) was adapted for the preparation of this hydrocarbon. The t-amyl alcohol (63 cc.) and m-xylene (375 cc.) were placed in a 2-liter round-bottom flask fitted with a mechanical stirrer and cooled with ice. A mixture of concentrated sulfuric acid (525 cc.) and water (110 cc.) was added over a period of one hour. Stirring was continued for an additional five hours. The acid layer was separated, the hydrocarbon washed repeatedly, dried, and fractionated. The following fractions were obtained at 16 mm.

⁸ Most of the semimicro analyses are by O. G. Shanholtzer. The remainder are by D. R. Smith and E. Milberger in the micro laboratory at the University of Missouri.

after removal of excess *m*-xylene: (I) 19 g. up to 93° ; (II) 4.5 g. $93-98^{\circ}$; (III) 22 g. $98-103^{\circ}$; (IV) 9.5 g. $103-104^{\circ}$; (V) 28 g. $85-94^{\circ}$ (5 mm.).

The trialkyl fractions (III) from several runs were combined and carefully refractionated. The hydrocarbon boiled at $93-95^{\circ}$ (14 mm.).

Preparation of 1,3-dimethyl-4-amylbenzenes from ketones. The ketones other than 2,4-dimethylisovalerophenone and 2,4-dimethylpivalophenone are already described in the literature.

The 2,4-dimethylisovalerophenone was prepared by the usual Friedel-Crafts procedure from *m*-xylene (54 g.), isovaleryl chloride (50 g.) and aluminum chloride (67 g.) with carbon disulfide (200 cc.) as the solvent; yield, 67 g. (85%), b.p. 131-132° (12 mm.); $n_{\rm D}^{20}$ 1.5113.

Anal. Calc'd for C₁₈H₁₈O: C, 82.11; H, 9.47.

Found: C, 82.21; H, 9.51.

The semicarbazone of this ketone, prepared by the usual procedure, melted at 196°. Anal. Calc'd for $C_{14}H_{21}N_3O$: C, 68.02; H, 8.50.

Found: C, 67.83; H, 8.50.

The 2,4-dimethylpivalophenone was prepared in the same manner from *m*-xylene (124 cc.), aluminum chloride (134 g.), and trimethylacetyl chloride (102 g.). The yield of ketone was 62 g. (38%), b.p. 107-109° (6 mm.); $n_{\rm D}^{\infty}$ 1.5058. This ketone did not form a semicarbazone.

Anal. Calc'd for C₁₃H₁₈O: C, 82.11; H, 9.47.

Found: C, 82.09; H, 9.28.

The pale yellow crystalline solid, m.p. 165°, isolated from the residue analyzed C, 91.14%, H, 7.94%.

The preparation of 2-(2, 4-dimethylphenyl)pentane is typical of the hydrocarbons prepared through the Grignard reaction and is described in detail. Quantities are listed in Table II. 1,3-Dimethyl-4-n-butyrylbenzene (66 g.) was added to the Grignard reagent prepared from methyl iodide (71 g.) and magnesium (12 g.). The product was decomposed, washed, and dried in the usual manner. The crude carbinol was added to acetic anhydride (100 cc.) and sulfuric acid (4 drops). The acetic anhydride was distilled from the mixture at 65 mm., and the residue distilled at 14 mm. Two fractions were obtained: (I) 5 g. up to 107°; (II) 55 g. 107-109°; residue 4 g.

Fraction II was redistilled, washed and dried, distilled from sodium, and finally from Raney nickel. The olefin was reduced in methyl alcohol solution with Raney nickel at a pressure range of 2200 to 3300 pounds per square inch (150-225 atm.) over a temperature range of 25° to 210°. After removal of the solvent, the hydrocarbon was washed, dried, and heated with sodium to remove impurities formed from the solvent, and fractionated from sodium; yield 48 g. (78%), b.p. 102-103° (11 mm.).

The three valeryl ketones were reduced by the method of Clemmensen (10). The best yields were obtained when the solution was refluxed eighty to ninety hours. The hydrocarbon was heated with sodium and finally distilled from sodium to remove impurities.

After long standing, 10–15 g. of white crystalline solids separated from the highboiling residues from these reductions. Analyses corresponded to the expected pinacols.

The solid from the 4-n-valeryl ketone melted at 146°.

Anal. Calc'd for C₂₆H₃₈O₂: C, 81.61; H, 10.02.

Found: C, 81.57; H, 10.46.

The solid from the 4-isovaleryl ketone melted at $139-140^{\circ}$.

Anal. Cale'd for $C_{28}H_{38}O_2$: C, 81.61; H, 10.02. Found: C, 81.84; H, 10.02.

Reactions of the hydrocarbons with decahydronaphthalene. The procedure was that of Ipatieff and Pines (2). The paraffin was collected in a receiver immersed in liquid air. The same amounts of reagents were used in all the reactions: 11.5 g. of hydrocarbon, 8 g. of aluminum chloride, and 25 g. of decahydronaphthalene. The data

| PREPARATION · | ог 1 | .3-DIMETHYL | 4-AMYLBENZENES | FROM | KETONES |
|---------------|------|-------------|----------------|------|---------|
|---------------|------|-------------|----------------|------|---------|

| ACYL GROUP | KETONE, HALIDE G. | | G. | ALKYL BENZENE, G. | YIELD % | |
|--|----------------------|--------------------------------------|------|-------------------------|-----------|--|
| CH ₃ C=0 | 106 | iso-C ₃ H ₇ Br | 100 | 40 | 32 | |
| $C_2H_5C=0$ | 48 | C_2H_5Br | 30 | 30 | 56.5 | |
| <i>n</i> -C ₃ H ₇ C=0 | 66 | CH3I | 71 | 48 | 72 | |
| <i>i</i> -C ₃ H ₇ C=O | 101 | CH3I | 99.4 | 65 | 64 | |
| $CH_{3}C-C_{2}H_{5}$ | 31.6 | 2,4-Dimethyl- benzylchloride | 70 | 35 | 41 | |
| <i>n</i> -C ₄ H ₉ C==O | 67 | reduceª | | 40 | 64 | |
| <i>i</i> -C ₄ H ₉ C=O | 40 | reduce ^a | | 18 | 47 | |
| <i>t</i> -C ₄ H ₉ C=O | 102 | reduceª | | 62 | 38 | |

^a Reduced by method of Clemmensen.

TABLE III

FORMATION OF PARAFFINS FROM DECAHYDRONAPHTHALENE^a

| ALKYLBENZENE | TIME, HRS. | TEMP., °C. | PARAFFIN | G. | % |
|---|---------------|------------|-----------------------------|-----|----|
| 1,3-Dimethyl- | | | | | |
| 4- <i>n</i> -amyl | 1.25 | 60-75 | Trace | | |
| 4-isoamyl | 1.5 | 59-79 | Trace | | |
| $4-CH_2CH(CH)_3C_2H_5$ | 1.5 | 60-80 | Trace | | |
| 4-neopentyl | 3.5 | 62-80 | Isopentane | 1 | 20 |
| 4- <i>t</i> -amyl | 2.0 | 60-76 | Mixture | 2.7 | |
| 5- <i>t</i> -amyl | 1.5 | 63-80 | Isopentane | 2.7 | 80 |
| 4-CH ₃ CHCH(CH ₃) ₂ | 1.5 | 65-71 | Isopentane | 2.2 | 48 |
| $4-C_2H_5CHC_2H_5$ | 4.0 | 60-80 | Isopentane and pen- tane | 1.7 | 37 |
| 4-CH ₃ CHC ₃ H ₇ | 1.5 | 6080 | Trace | 0.2 | |
| 4-CH ₃ CHC ₃ H ₇ | 4.0 | 75 | Isopentane and pen- tane | 1.9 | 41 |
| 5- <i>t</i> -butyl | 1.5 | 65-75 | Isobutane | 3.5 | 81 |

^a 11.5 g. of hydrocarbon, 8 g. of aluminum chloride, 25 g. decalin.

are summarized in Table III. The reactants were heated to $60-65^{\circ}$ initially. If no paraffin distilled, the temperature was increased until liquid appeared in the trap, and held approximately constant until no more paraffin distilled. Prolonged heating did not increase the yield.

Chloromethylations. Preparation of 2,4-dimethylbenzyl chloride. m-Xylene (52.6 g.) was chloromethylated with formalin (40 g.), concentrated hydrochloric acid (200 g.), and gaseous hydrogen chloride according to the procedure of v. Braun and Nelles (11). The yield of 2,4-dimethylbenzyl chloride was 51 g. (66%), b.p. 92-94° (8 mm.). When zinc chloride (20 g.) was added to the above reagents, the yield was reduced to 30%.

The chloromethylation of 1,3-dimethyl-5-t-amylbenzene (30 g.) was carried out in the same manner with 29 g. of formalin and 150 g. of concentrated hydrochloric acid at 70° for eight hours; yield, 16.5 g., b.p. $120-128^{\circ}$ (3 mm.).

The 4-t-amyl hydrocarbon was chloromethylated under the same conditions; yield, 13.5 g., b.p. 115-123° (4 mm.).

The 4-n-amyl hydrocarbon (30 g.) yielded 14.5 g. of chloromethyl derivative, b.p. 125-135° (3 mm.).

Reaction of chloromethyl compounds with acetamide. A sample (3.5 g.) of each of the above chloromethyl compounds was heated with excess acetamide at $190-220^{\circ}$ for one and one-half to two hours. The reaction product was poured into hot water to dissolve excess acetamide. The solid was recrystallized from petroleum ether. Yields were about 1.2 g. Their melting points and analyses are listed in Table IV.

| | TABLE IV | |
|-------------|-------------|-------------|
| Substituted | BENZYLAMINE | Derivatives |

| ALKYL BENZENE | N D . | ANALYSES- | % NITROGEN | |
|-------------------|----------|-----------|------------|--|
| | м.г., с. | Calc'd Fo | | |
| 1,3-Dimethyl- | | | | |
| benzene | 109ª | | | |
| 4-n-amyl | 105 | 5.66 | 5.88 | |
| 5- <i>t</i> -amyl | 150 | 5.66 | 5.63 | |

^a Anal. Calc'd for C₁₁H₁₅NO: C, 74.58; H, 8.48. Found: C, 74.52; H, 8.61.

Preparation of 1,3-dimethyl-5-n-amyl benzene. 3,5-Dimethylbenzylsodium was prepared by the method of Morton and Fallwell (4). Sodium sand (18 g.) and benzene (70 cc.) were placed in a flask fitted with a sealed stirrer, separatory funnel, and a reflux condenser. To this was added a mixture of benzene (37.5 cc.) and *n*-amyl chloride (37.5 cc.) over a period of two and one-half hours at $15-20^{\circ}$. The mixture was stirred for an additional one and one-half hours. Mesitylene (37.5 cc.) was added and the temperature raised to 75° . Stirring was continued for four and onehalf hours.

A mixture of *n*-butyl chloride (23 g.) and benzene (23 g.) was added to the 3,5dimethylbenzylsodium over a period of thirty minutes. The mixture was stirred an additional ten minutes, then decomposed with water, washed, dried, and distilled; yield, 10 g. (15%) b.p. $105-106^{\circ}$ (10 mm.).

Anal. Calc'd for C13H20: C, 88.63; H, 11.37.

Found: C, 88.25; H, 11.43.

From s-butyl chloride and 3,5-dimethylbenzylsodium, the yield of trialkyl fraction b.p. 105-111° (15 mm.) was 3 g., and from isobutyl chloride 7 g., b.p. 105-110° (15 mm.). These trialkyl fractions were not purified or analyzed.

3,5-Dimethylbenzylpotassium was prepared according to the directions of Gilman,

Pacevitz, and Baine (12), from 100 cc. of mesitylene and 8.5 g. of potassium. The mixture was cooled to $80-90^{\circ}$ and 12 cc. of *n*-butyl chloride added during twenty minutes. The mixture was refluxed for five minutes. The product was decomposed with alcohol, washed, dried, and distilled. The trialkyl fraction distilled at $85-105^{\circ}$ (4 mm.); yield 4.5 g.

t-Butyl chloride (15 cc.) was added to the same amount of 3,5-dimethylbenzylpotassium. The trialkyl fraction distilled at 85-105° (4 mm.); yield 2.2 g.

Diacetamino and dibenzamino derivatives. These derivatives were prepared by an adaptation of the procedure of Ipatieff and Schmerling (13).

The nitrating mixture (10 cc. of concentrated sulfuric acid and 5 cc. of concentrated nitric acid) was stirred mechanically in a test tube at -10° to -15° . The low temperature is essential. The hydrocarbon (3 cc.) was added dropwise during five to fifteen minutes. The stirring was continued for an additional five minutes. The solution was allowed to come to room temperature, poured on ice, and the nitro compound extracted with ether. The ether solution was washed repeatedly with

| | DIACE | TAMINO | DIBEN | ZAMINO |
|---|-----------|----------------------------------|-----------|----------------------------------|
| ALKYL BENZENE | M.p. °C. | % Nitrogen ^a found | М.р. °С. | % Nitrogen ^b found |
| I, 3-Dimethyl- | | | , | |
| 4- <i>n</i> -amyl | 234 | 9.41 | 220 | 6.74 |
| 4-isoamyl | | _ | 208 | 6.52 |
| 4- <i>t</i> -amyl | | | 308 | 6.94 |
| 5- <i>t</i> -amyl | 304 | 9.57 | 302 | 6.49 |
| 4-CH ₃ CHCH(CH ₃)CH ₃ | 264 | 9.55 | 234 - 235 | 6.85 |
| $4-C_2H_5CHC_2H_5$ | 279 - 280 | 9.49 | 252 - 253 | 6.73 |
| 4-CH ₃ CHC ₃ H ₇ | 234 | 9.88 | 241 | 6.65 |

TABLE V DIACETAMINO AND DIBENZAMINO DERIVATIVES

^a Calc'd. for C₁₇H₂₆N₂O₂: N, 9.65.

^b Calc'd. for C₂₇H₃₀N₂O₂: N, 6.76.

5% sodium bicarbonate solution and with water. The ether was removed and the nitro compound dissolved in alcohol. Tin (15 g.) and concentrated hydrochloric acid (15 cc.) were added to the alcohol solution. The reaction was usually vigorous, and cooling was sometimes necessary. The mixture was stirred mechanically for one hour.

The acid solution was diluted with water to 100 cc. and extracted twice with 20-cc. portions of ether. This ether extract was discarded. The water layer was made strongly basic and extracted twice with 35-cc. portions of ether. These ether extracts of the basic solution were combined, washed repeatedly with water, and divided into two equal portions.

(a) Acetic anhydride (5 cc.) was added directly to one portion and the flask stoppered tightly. After some time (from a few minutes to several hours) the diacetamino derivative separated in fairly pure form. The solid was washed repeatedly with ether and recrystallized from dilute alcohol (an excess of alcohol should be avoided) or from pyridine.

(b) The ether was evaporated from the second portion and the amine benzoylated

by the usual Schotten-Baumann method. The dibenzamino derivatives were washed with ether and recrystallized from dilute alcohol or pyridine.

It was not possible to obtain derivatives of all the hydrocarbons in pure form. The melting points and analytical data are summarized in Table V.

SUMMARY

Seven of the eight 1,3-dimethyl-4-amylbenzenes have been synthesized by methods which leave no doubt as to the structure and position of the amyl radical.

The reaction between 3,5-dimethylbenzyl-sodium or -potassium leads mainly to products other than the desired 1,3-dimethyl-5-amylbenzenes.

In the reaction between decahydronaphthalene, 1,3-dimethyl-4-neopentylbenzene and aluminum chloride the neopentyl radical is cleaved to form isopentane in 20% yield. This is the first primary alkyl radical to react in this manner. The branched s-amyl radical gives a larger yield of mixed pentanes in this reaction than do the two straight-chain s-amyl radicals. The 1,3-dimethyl-5-t-amylbenzene gives the highest yield of isopentane.

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