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Synthesis and Dediazoniation of 2-Butyl- and 2,5-Dibutylbenzenediazonium Ions

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2-Butylbenzenediazonium ion (*1a*) and 2,5-dibutylbenzenediazonium ion (*1b*) have been thermally decomposed in aqueous acid solution. In addition to the major product, the corresponding phenol, 5- and 6-membered ring products are formed (in a ratio of *ca.* 7:1) as well as products of elimination and substitution in the *o*-butyl group. The formation of the non-phenolic products is explained in terms of competing reactions of the initially formed aryl cations: cyclization by electrophilic attack on the *o*-butyl group and 1,5-hydride ion transfer from the *o*-butyl group with concomitant elimination or reaction with the medium.

Decomposition of *1a* in the presence of copper(I) oxide, believed to generate aryl radicals, does not yield any measurable quantities of cyclized products, however.

It has been reported that *ortho*-alkylbenzenediazonium ions with a three-carbon alkyl chain yield indan derivatives as a result of an internal cyclization reaction[1,2] on thermal decomposition in aqueous solution. The study of this reaction has now been extended to *ortho*-butylbenzenediazonium ions.

SYNTHESES

ortho-Alkylanilines have usually been made by nitration of the appropriate alkylbenzene with subsequent separation of isomers and reduction of the nitro group. In this way *o*-butylaniline has been prepared in a rather low yield.[3] An alternative method involves nitration of butyrophenone, separation of the nitro isomers and reduction of the *o* derivative first to *o*-aminobutyrophenone[4] and then to *o*-butylaniline.

To avoid the problem of the separation of isomers, two more specific routes to *o*-alkylanilines were investigated. The first method is a reaction between an alkylmagnesium halide and *o*-(methoxymethyl)aniline.[5] The limitation of this method is, in our experience, the increased formation of by-products as the alkyl halide becomes more branched. The second method is based on an observation by Grammaticakis[6] that *o*-aminobenzonitrile reacts with a seven- to ninefold excess of an alkylmagnesium halide to yield, after hydrolysis, the corresponding *o*-acylaniline. This method, to which has been paid relatively little attention,[7-9] gives rather high yields of products and has the advantage of starting with the commercially available *o*-aminobenzonitrile. Since *o*-acylanilines can easily be reduced it was to us the method of choice for the synthesis of *o*-alkylanilines. Reaction with a sevenfold excess of propylmagnesium chloride gave an overall crude yield of 72 % of *o*-butylaniline, based on *o*-aminobenzonitrile. This two-step sequence is a simple and inexpensive way to *o*-alkylanilines.*

Another way of obtaining a similar compound and still avoiding the isolation of the *ortho* isomer in a nitration product mixture is to start with the

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* Two other methods of specific *o*-alkylation[10] and *o*-acylation[11] of substituted anilines have been reported and seem interesting, especially when ring-substituted products are needed.

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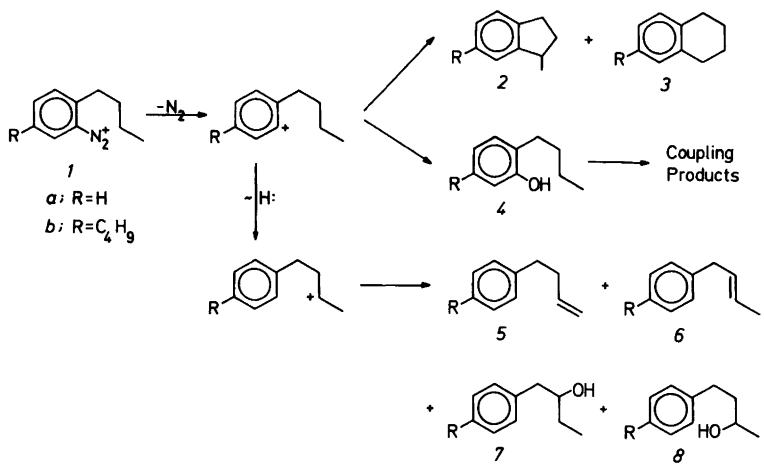

Scheme 1.

para disubstituted alkylbenzene which is often relatively easily available. Thus 2-amino-1,4-dibutylbenzene was made by nitration of 1,4-dibutylbenzene and subsequent reduction according to standard procedures.

RESULTS

Diazotization of *o*-butylaniline and 2-amino-1,4-dibutylbenzene was performed [2] in 3 M sulfuric acid with sodium nitrite, and the resulting solutions of *o*-butylbenzenediazonium ion (*1a*) and 2,5-dibutylbenzenediazonium ion (*1b*) were carefully decomposed in boiling 1.5 M sulfuric acid. GLC analysis of the crude material showed that thermal decomposition of *1a* gave a more complex product mixture (see Scheme 1) than might be expected from previous work on *o*-alkylbenzenediazonium ions with a three-carbon alkyl chain.[1,2] The product composition is shown in Table 1. Structure identification of the various components was obtained by GLC-MS analyses. Comparison was made with authentic samples or with published mass spectra of the compounds (see Experimental).

The expected 1-methylindan (*2a*) and *o*-butylphenol (*4a*) were identified as decomposition products from *1a*. Cyclization at the δ-carbon in the butyl side-chain to yield tetralin (*3a*) also occurred. The formation of two isomeric olefins, 4-phenyl-1-butene (*5a*) and 1-phenyl-2-butene (*6a*) in a ratio of 1:2 and of two isomeric alcohols, 1-phenyl-2-butanol (*7a*) and 4-phenyl-2-butanol (*8a*) in a ratio of 1:4 was observed. In addition, four higher boiling compounds were always present in the reaction mixture, three of which had a nominal mass of 282, compatible with hydroxybiaryls and diaryl ethers and a fourth compound which had a nominal mass of 362, compatible with a diaryl sulfate structure. These four compounds are collectively termed as coupling products in Table 1. Similar results were obtained from the decomposition of *1b*.

When *1a* was decomposed in 9 M sulfuric acid, the product composition was very similar except for a decrease in the phenol content (62 %) and an increase in the content of coupling products (26 %).

Table 1. Thermal decomposition of 2-butylbenzenediazonium ion (*1a*) and 2,5-dibutylbenzenediazonium ion (*1b*) in 1.5 M sulfuric acid.

Substrate	Product composition (%)[a] *5+6*	*2*	*3*	*7+8*	*4*	Coupling products	Total product yield (%)
1a	1.5	6.0	1.0	2.5	87	2.0	93
1b	1.0	7.0	1.0	2.0	86	3.0	90

[a] Normalized peak area values.

Redistilled water was used in all reactions during diazotization and decomposition of *1a*.

It is known that diazonium salts are influenced by traces of metal ions. Especially copper(I) ions are known to induce decomposition in a radical fashion to yield some reduction products.[12] To investigate whether the ring closure reaction takes place during homolytic conditions,[12,13] a solution of *1a* was diluted with ice-cold, redistilled water and split into three equal parts. Decomposition was then performed in three different ways: A. decomposition in 1.5 M sulfuric acid as described above, B. decomposition at 0 °C by the addition of copper(I) oxide[12] and C. decomposition at room temperature by the addition of copper(I) oxide and copper(II) nitrate.[13] The product mixture from A is given in Table 1. In the radical decompositions B and C, butylbenzene, *4a*, *5a*, *6a* and *8a* were identified. In addition two compounds compatible with a biaryl structure ($m/e=266$) and an azobenzene structure ($m/e=294$) were also formed. No cyclization products could be detected in the reaction mixtures. However, the phenylbutenes and 1-methylindan have the same m/e value and similar patterns of mass fragmentation. To prove the absence of 1-methylindan and tetralin in the radical decompositions, the crude products of A, B and C were all subjected to catalytic hydrogenation and then analysed. From A butylbenzene was found together with unaffected 1-methylindane and tetralin, and from B and C butylbenzene was the only hydrocarbon found.

In one experiment diazotization of 3-amino-1-phenylbutane was performed in an acetic acid–water mixture and the resulting solution poured into boiling 1.5 M sulfuric acid. The crude product was a mixture of the two olefins *5a* and *6a* together with the alcohol *8a* and benzylacetone. Again, to confirm that no cyclized products were formed, the hydrocarbon part was fractionally distilled off and then hydrogenated. The single product obtained was shown by GLC-MS to be butylbenzene.

DISCUSSION

o-Alkylsubstituted benzenediazonium ions with a three-carbon alkyl chain have been shown to undergo intramolecular cyclizations in thermally induced dediazoniations.[1,2] A direct attack by the initial phenyl cation on the alkyl side-chain to yield indan derivatives was suggested. In the present investigation, intramolecular cyclization occurs to give both indan and tetralin derivatives in a ratio of about 7:1 for *1a* and *1b*. This high ratio is in accordance with the common predominance of formation of 5-membered rings in comparison with 6-membered ones.[14] In intramolecular Friedel-Crafts alkylation reactions, however, 6-membered rings are usually the predominant products.[15]

We suggest that the olefins *5a* and *6a* and the alcohols *7a* and *8a* are formed *via* 1,5-hydride ion transfer within the cation. The sum of the products from the intramolecular electrophilic reactions of the *o*-butyl system in *1a* (11 %, see Table 1) is in good agreement with the *o*-propyl system[2] (13 % indan). Thus the steric bulk of the propyl and butyl groups are approximately the same in this reaction and they affect the phenol formation to a very similar degree. There is, however, some uncertainty in such a comparison due to the formation of coupling products. As can be seen from Table 1, similar results are obtained for *1b*. Such 1,5-hydride ion transfers, which are known to occur in certain diazonium ion decompositions[12,16] (to give intermediate carbocations stabilized by a nearby nitrogen atom), are absent in the *o*-propyl system (where a primary alkyl cation would result) but seem to be operative in the *o*-butyl system (to form a secondary cation).

In this context it can be pointed out that when a diazonium salt solution of methyl 6(5)-amino-5(6)-butyl-2-benzimidazolecarbamate was thermally decomposed in aqueous sulfuric acid[17] the corresponding phenol was found together with the reduced material and methyl 5(6)-(3-oxobutyl)-2-benzimidazolecarbamate. The latter product was claimed to be formed by a 1,5-hydride ion transfer to yield the γ-alcohol by reaction with water. This alcohol would then be oxidized to the ketone by a diazonium ion. Although no alcohol was found, some of the crude product was reported to contain material giving a molecular ion in GLC-MS compatible with the cyclized indan derivative.

The possibility that the secondary alkyl cation from a 1,5-hydride ion shift might undergo an intramolecular electrophilic aromatic substitution to produce the 5-membered ring can *a priori* not be excluded, though it seems more difficult to explain the formation of the 6-membered ring by such a route. There is no *a priori* support for the rearrangement to the necessary primary cation. The absence of cyclized products both in the decomposition of the diazonium ion derived from 3-amino-1-phenyl-

butane as well as in the Friedel-Crafts reactions of 3-chloro-1-phenylbutane, 4-phenyl-2-butanol and 4-phenyl-1-butene [15] strengthens the argument that ring formation in the thermal decomposition of *o*-butylbenzenediazonium ions occurs from a direct attack by the initial phenyl cation on the alkyl side-chain.

A radical mechanism for the formation of the cyclized products can be excluded as *1a* did not yield any 1-methylindan or tetralin when decomposed in the presence of copper salts, which are known to generate aryl radicals.[12,13] Phenol formation and reduction are known reactions in radical decompositions of arenediazonium ions [13] and biaryls and azoarenes are frequent by-products in such reactions.[18,19] Elimination and substitution in the butyl side-chain of *1a* can be rationalized by a 1,5-hydrogen atom transfer process [12,20] between the initially formed phenyl radical and the γ position in the butyl group. This alkyl radical can then undergo an electron transfer by reaction with a copper(II) complex to the corresponding cation which in turn forms the products of elimination and substitution.[21]

In the radical decompositions of *1a* the formation of the terminal alkene, 4-phenyl-1-butene, is favoured over 1-phenyl-2-butene (approximate ratio 2:1) in contrast to the thermal decomposition of *1a* (approximate ratio 1:2). It has been observed that in some *ortho*-substituted benzenediazonium salts both 1,5- and 1,6-hydrogen atom transfers take place in copper(I) promoted dediazoniations.[22] In one particular case the preference for 1,6-abstraction over 1,5-abstraction was estimated to about 4:1. Furthermore it is known [21] that secondary butyl radicals show a rather random loss of β-hydrogens in oxidative eliminations whereas primary butyl radicals give the terminal alkene exclusively with no rearrangement. Thus the preference for 4-phenyl-1-butene in the radical decomposition of *1a* may at least partly be due to a 1,6-hydrogen abstraction.

EXPERIMENTAL

Materials. *o*-Aminobenzonitrile (Fluka AG) was recrystallized from aqueous ethanol. 1-Methylindan was obtained by catalytic hydrogenation of 3-methylindene. Butylbenzene, tetralin, 1-phenyl-2-butanol and 4-phenyl-2-butanol were purchased from EGA-CHEMIE and purified by distillation. Sulfuric acid (Merck, analytical grade) was diluted with water which had been distilled twice in a Heraeus-Schott all-glass apparatus. All other chemicals were of the reagent grade and were used without further purification unless otherwise stated.

Measurements. GLC analyses were performed with a Perkin-Elmer 3920 gas chromatograph equipped with flame ionization detectors and 2 m packed columns. All analyses were performed with three different (3 % SE-30, 3 % Carbowax 20M and 3 % OV-17) stationary phases. Percentage composition refers to relative areas as measured by a Hewlett-Packard 3380 A integrating recorder. Mass spectra were recorded at 70 eV with an LKB 9000 instrument (at the Department of Medical Chemistry, University of Göteborg) fitted with a gas chromatograph using an SE-30 stationary phase. The ^{1}H NMR spectra were recorded on a Bruker WH 270 instrument operating at 270 MHz.

Syntheses

2-Butylaniline. 1. From *o*-aminobenzonitrile.A solution of 23.6 g (0.2 mol) of *o*-aminobenzonitrile in 200 ml of dry ether was added rapidly, under vigorous stirring, to a Grignard reagent prepared from 172 g (1.4 mol) of 1-bromopropane in 200 ml of ether. The immediately formed precipitate dissolved by refluxing the mixture under constant stirring for 3.5 h. The reaction mixture was then cooled and decomposed by careful addition of 500 ml of 6 M hydrochloric acid. The whole mixture was heated for 4 h, during which time the ether was distilled off. The homogeneous solution was cooled and treated with solid sodium carbonate until basic and then extracted twice with ether. The combined ether extracts were washed with aqueous sodium chloride and then dried. Evaporation of the ether yielded the crude *o*-aminobutyrophenone (28 g, 86 %) that was sufficiently pure (96 %, GLC) to be used directly in the next step. This ketone was reduced to the hydrocarbon by a Wolff-Kishner reduction.[23] The reaction was performed in a solution of 44.8 g (0.8 mol) of potassium hydroxide and 30 ml of hydrazine hydrate (95 %) in 200 ml of triethylene glycol. A crude yield of 21.5 g (85 %) of *o*-butylaniline was obtained. Distillation afforded the pure (>99 %, GLC) product. It was identified by MS and NMR and had physical properties in accordance with those previously reported.[5]

2. From *o*-(methoxymethyl)aniline. *o*-Nitrotoluene was brominated with NBS and benzoyl peroxide to *o*-nitrobenzyl bromide which was in turn transformed to methyl *o*-nitrobenzyl ether by reaction with sodium methoxide in methanol. Reduction of the nitro group with hydrazine hydrate and palladium gave *o*-(methoxymethyl)aniline in an overall yield of 29 %. By following a literature

procedure[5] *o*-butylaniline was obtained in 58 % yield when an ethereal solution of *o*-(methoxymethyl)aniline was reacted with a Grignard reagent, prepared from 1-bromopropane.

3. From butyrophenone. *o*-Aminobutyrophenone was made from butyrophenone according to a literature method.[4] Reduction of this ketone was performed as mentioned previously. An overall yield of 18 % of *o*-butylaniline was obtained after distillation. A small amount of the *m*-isomer (~2 %) was still present.

2-Amino-1,4-dibutylbenzene. 1,4-Dibutylbenzene[24] was prepared by a Friedel-Crafts acylation of butylbenzene with butyryl chloride followed by reduction[23] of the carbonyl group. Nitration in nitric acid ($d=1.52$) with subsequent reduction of the nitro group yielded the crude amine. Purification was achieved *via* the amine hydrochloride, yielding, after hydrolysis, 2-amino-1,4-dibutylbenzene, 99 % pure according to GLC. It was identified by MS and NMR and had physical properties in accordance with those previously reported.[24]

3-Amino-1-phenylbutane. Benzylacetone (48 g, 0.32 mol) and formamide (114 g, 2.53 mol) were stirred at 160 °C for 20 h. Small portions of formic acid (~5 ml) were added through an attached reflux condenser whenever there appeared some clogging of ammonium carbonate in the condenser. A total of 35 ml of formic acid was sufficient. The reaction mixture was then cooled and 200 ml of 30 % sodium hydroxide solution was added. After refluxing for 24 h the mixture was cooled again and the aqueous phase decanted off and discarded. The oily residue was dissolved in 150 ml concentrated hydrochloric acid and refluxed for 1 h. The cooled, aqueous solution was made alkaline with 30 % sodium hydroxide solution and steam distilled. Ether extraction of the distillate yielded, after drying and evaporation of the ether, 24.8 g (52 %) of pure 3-amino-1-phenylbutane. NMR: δ 1.05 (3H, d, $J=6.1$ Hz, methyl), 1.21 (2H, s, amino), 1.59 (2H, m, methylene), 2.59 (2H, m, methylene), 2.84 (1H, m, methine), 7.21 (5H, m, aromatic).

Reactions

Diazotizations. Diazotization of 2-butylaniline and 2-amino-1,4-dibutylbenzene in 3 M sulfuric acid with sodium nitrite was performed as previously described.[2] In all experiments 0.01 mol of substrate in about 30 ml of 3 M sulfuric acid was used unless otherwise stated and the resulting solutions were then treated in different ways.

Decomposition of 1a *in 1.5 M sulfuric acid.* Small portions of the solution of *1a* were added to 200 ml of boiling 1.5 M sulfuric acid and the products steam distilled before the next addition. The sulfuric acid solution was then cooled and combined with the distillate. After the usual work-up procedure,[2] the crude material was subjected to GLC and GLC-MS analyses. Yield and product composition are shown in Table 1. The following compounds were identified by GLC-MS [*m/e*; (rel. int.)]: 4-Phenyl-1-butene (*5a*), 132(19), 104(7), 91(100), 77(6), 65(12), 51(6), 39(8); 1-phenyl-2-butene (*6a*), 132(46), 117(100), 115(12), 104(6), 91(56), 78(8), 77(10), 65(14), 51(17), 39(21). The structures of *5a* and *6a* were confirmed by comparison with published spectra.[25] 1-Methylindan (*2a*), 132(31), 117(100); tetralin (*3a*), 132(63), 104(100); 1-phenyl-2-butanol (*7a*), 150(2), 92(100); 4-phenyl-2-butanol (*8a*), 150(10), 91(100). The structures of *2a*, *3a*, *7a* and *8a* were confirmed by comparison with GLC retention values (coinjection technique) and mass spectra of authentic samples. 2-Butylphenol (*4a*), 150(23), 107(100). The structure of *4a*, obtained from the crude material by preparative TLC on silica gel using hexane-EtOAc (20:1 v/v) as eluent, was confirmed by NMR (270 MHz, $CDCl_3$): δ 0.92 (3H, t, methyl), 1.37 (2H, m, methylene), 1.56 (2H, m, methylene), 2.60 (2H, m, methylene), 4.78 (1H, s, hydroxy), 6.83 (4H, m, aromatic).

Decomposition of 1a *in the presence of copper salts.* A solution of *1a* made from 0.03 mol of 2-butylaniline was diluted with ice-cold water to a total volume of 300 ml. This solution was split into three approximately equal parts and decomposed as follows. A. One part was thermally decomposed in 1.5 M sulfuric acid as described above. B. To one vigorously stirred part of the diazonium salt solution, held at 0 °C, 1.43 g (0.01 mol) of copper(I) oxide was added. The cooling-bath was then removed and the solution was stirred until no further gas evolution was noticed. C. A solution of 36.0 g (0.15 mol) of copper(II) nitrate trihydrate in 200 ml of water at room temperature was added to one part of the diazonium salt solution. Under vigorous stirring, 1.43 g (0.01 mol) of copper(I) oxide was added and the solution was stirred until no further gas evolution was noticed.

After the usual work-up procedure, the crude products from A, B and C were subjected to GLC and GLC-MS analyses. The product composition from A was identical with that observed before. From B and C butylbenzene was found to be a major component (17–24 %). In both reactions 4-phenyl-1-butene (*5a*) and 1-phenyl-2-butene (*6a*) were formed in an approximate ratio of 2:1. Formation of 2-butylphenol (*4a*) and 4-phenyl-2-butanol (*8a*) was also noticed as well as large amounts of two other compounds which had mass spectra compatible with a biaryl ($m/e=266$) and an azoarene ($m/e=294$).

The crude materials from A, B and C were all dissolved in methanol and subjected to catalytic

hydrogenation (10 % palladium on charcoal) in a Parr apparatus for 1 h. From A a new peak, according to GLC, had emerged in the hydrocarbon region while two peaks had disappeared and two remained unchanged. The new component was identified as butylbenzene by GLC-MS while the two unchanged components were identified as *2a* and *3a*, the latter two apparently stable under the reaction conditions. From B and C a single peak was observed in the hydrocarbon region, identified as butylbenzene.

Decomposition of 1a *in 9 M sulfuric acid.* When the solution of *1a* was decomposed in 9 M sulfuric acid at 90 °C without steam distillation of products, a GLC analysis of the crude material showed that the phenol content had decreased and the coupling products had increased, whereas the relative amounts of the different hydrocarbons and alcohols remained practically unchanged.

Decomposition of 1b *in 1.5 M sulfuric acid.* A solution of *1b* was decomposed in the same manner as described for *1a*. Yield and product composition is shown in Table 1. The following compounds were identified by GLC-MS [*m/e*; (rel.int.)]: 1-(4-Butylphenyl)-2-butene (*6b*), 188(56), 173(12), 145(100), 131(92), 117(28), 105(10), 91(36), 77(8), 41(11); 6-butyl-1-methylindan (*2b*), 188(48), 173(63), 146(22), 145(100), 131(59), 117(33), 115(19), 91(15), 57(15); 6-butyltetralin (*3b*), 188(29), 160(3), 146(25), 145(100), 131(8), 117(13), 115(10), 91(11); 1-(4-butylphenyl)-2-butanol (*7b*), 206(10), 188(5), 177(8), 163(22), 148(54), 147(17), 106(29), 105(100), 92(7), 91(54), 59(27), 29(12); 4-(4-butylphenyl)-2-butanol (*8b*), 206(28), 188(33), 173(11), 163(12), 147(32), 145(100), 131(56), 117(28), 105(44), 91(56), 77(39), 45(19), 43(21); 2,5-dibutylphenol (*4b*), 206(19), 164(23), 163(100), 121(18), 107(32), 93(8), 91(36), 77(25), 43(14). These mass spectra are all consistent with the suggested structures.

Preparative TLC on silica gel using hexane-EtOAc (20:1 v/v) as eluent yielded pure 2,5-dibutylphenol. NMR (270 MHz, $CDCl_3$): δ 0.90 (6H, m, methyl), 1.32 (4H, m, methylene), 1.54 (4H, m, methylene), 2.51 (4H, m, methylene), 5.38 (1H, s, hydroxy), 6.53 (1H, s, aromatic), 6.67 (1H, d, $J = 7.3$ Hz, aromatic), 6.99 (1H, d, $J = 7.3$ Hz, aromatic).

Diazotization of 3-amino-1-phenylbutane. 3-Amino-1-phenylbutane (10.4 g, 0.07 mol) was dissolved in a solution of 5 ml of acetic acid, 0.1 ml of concentrated sulfuric acid and 50 ml of redistilled water. To the stirred solution was added, at room temperature, 5.5 g (0.08 mol) of sodium nitrite in 15 ml of water in small portions. The reaction mixture was stirred at 90 °C for 30 min and then poured into 1.5 M sulfuric acid and refluxed for 15 min. After the usual work-up procedure the crude material (8.2 g) was subjected to GLC and GLC-MS analyses. 4-Phenyl-1-butene (*5a*) and 1-phenyl-2-butene (*6a*) were identified together with 4-phenyl-2-butanol (*8a*) and benzylacetone. Fractional distillation gave 3.5 g of the olefin mixture which was hydrogenated in the same way as described above. The obtained pure (GLC) compound was identified by MS and NMR as butylbenzene.

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