

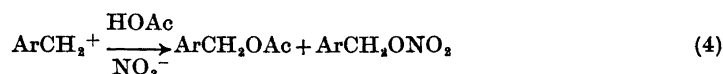
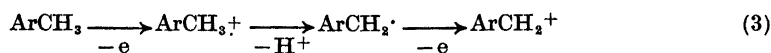
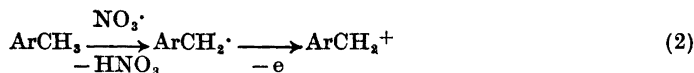
Some New Anode Reactions Involving Nitrate Ions and Aromatic Compounds

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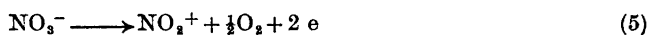
The anodic oxidation of some aromatic compounds in acetonitrile and nitromethane in the presence of nitrate ions has been investigated. Electrolysis of mesitylene at a platinum anode produces mainly 3,5-dimethylbenzaldehyde and 3,5-dimethylbenzyl nitrate, whereas at a carbon anode the major product is 2,4,6-trimethylphenol. In nitromethane at a carbon anode another major product is 2-nitromesitylene. The anodic nitration is assumed to occur by oxidation of nitrate ions to nitronium ions followed by electrophilic reaction with mesitylene. The possibility that 2,4,6-trimethylphenyl nitrate is a precursor for the phenol is discussed. Oxidation of naphthalene at a carbon anode produces 1-nitronaphthalene and 1,4-naphthoquinone in low yield. Electrolysis of *t*-butylbenzene at a platinum anode produces, among other products, *t*-butyl-*o*-nitrophenols probably arising by rearrangement of *t*-butylphenyl nitrate.

The mechanism of anodic substitution reactions has been studied in great detail in the last decade and it has been shown that for most substitution reactions the primary electrode process involves oxidation of the organic compound followed by reaction with nucleophiles in the electrolysis solution.^{1,2} However, there are cases where it is difficult to determine which species undergoes the primary anode reaction. This is especially true for the anodic oxidation of aromatic compounds in the presence of nitrate ions. Ross and coworkers found that electrolysis of toluene or mesitylene in acetic acid containing nitrate ions gave products resulting from substitution in the side-chain only.³ It was proposed that these products resulted from initial discharge of nitrate ion, giving the nitrate radical which abstracted a hydrogen atom from the benzylic position (eqns. 1 and 2). This proposal was modified after a study of the anodic oxidation of toluene in the presence of nitrate or tosylate ions. It was then proposed that oxidation of toluene (eqns. 3 and 4) could occur simultaneously with oxidation of nitrate ion.⁴ Nyberg came to the same conclusion after investigating the electrolysis of mesitylene in acetic acid containing nitrate ion.⁵ It was therefore suggested that two anode reactions took place and both could account for the formation of products.



From voltammetric studies it was shown that reactions (1) and (3) could take place simultaneously. The formation of bibenzyl products is evidence for intermediate benzyl radicals and thus nitrate radicals might abstract hydrogen atoms according to eqn. 2. Although the major products were benzyl acetates and benzyl nitrates (eqn. 4), unexpected large amounts of benzaldehydes were also formed. Their presence can be explained by assuming that hydrolysis of benzyl nitrates occurs during electrolysis or that benzyl cations react with water in the medium to form benzyl alcohols that are further oxidized to the aldehydes.

From electroanalytical studies of the anodic oxidation of nitrate ion in nitromethane containing perchlorate ions it was proposed that oxidation of nitrate ion gives nitronium ion.⁶

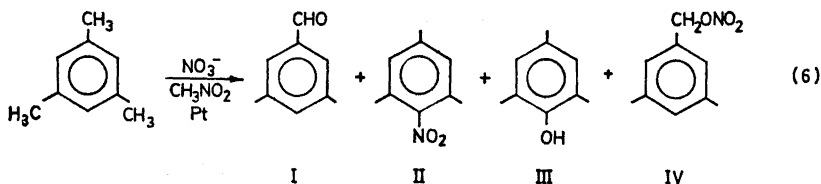


Mann and coworkers have studied the oxidation of nitrate ion in acetonitrile and propose that nitrate radical is formed and reacts with the solvent.⁷ Oxidation of nitrate ion in the presence of perchlorate ion gave some reaction with perchlorate ion at anode potentials low enough to preclude oxidation of perchlorate ion. The oxidation of nitrate ion took place at a voltammetric peak potential of 1.76 V.

In order to avoid reactions between organic intermediates and the solvent, as found with acetic acid, the present study is concerned with electrolysis of some aromatic compounds in nitromethane or acetonitrile containing tetrabutylammonium nitrate. The electrolyses were carried out using either a platinum or a carbon anode and it is demonstrated that anode material has a great effect on product distribution. The aromatic substrate for most electrolyses was mesitylene, since it is oxidized in the same potential region as nitrate ion.

RESULTS

Electrolysis of mesitylene in $\text{CH}_3\text{NO}_2/\text{Bu}_4\text{NNO}_3$ using a platinum anode produced at least four compounds, product distribution depending on the reaction conditions. The compounds were 3,5-dimethylbenzaldehyde (I), 2-nitromesitylene (II), 2,4,6-trimethylphenol (III), and 3,5-dimethylbenzyl nitrate (IV) (eqn. 6). Small amounts of higher molecular weight compounds were also formed, but attempts to identify them by their mass spectra were



not successful. It was shown that bimesityl, a product resulting from direct oxidation of mesitylene in $\text{CH}_3\text{NO}_2/\text{Bu}_4\text{NBF}_4$ ⁸ or $\text{CH}_3\text{CN}/\text{Bu}_4\text{NBF}_4$ ⁹ was not present. The results from three experiments are given in Table 1. In all electrolyses products I and IV are the major components and thus the experiments

Table 1. Electrolysis of mesitylene in $\text{CH}_3\text{NO}_2/\text{Bu}_4\text{NNO}_3$. Product distribution and current yield.

Mesitylene conc. (M)	Bu_4NNO_3 conc. (M)	Anode material	Anode pot. (V)	Relative distribution				Current yield %
				I	II	III	IV	
0.2	0.2	Pt	2.4	46	—	4	50	8 ^a
0.2	0.6	Pt	2.1	41	4	6	49	15 ^b
1.0	0.2	Pt	2.1	8	—	—	92	41 ^c
0.2	0.2	C	1.4	5	5	67	23	11 ^a
1.0	0.2	C	1.5	5	39	56	—	6 ^d

^a 0.2 F/mol was passed.

^b 0.5 F/mol of mesitylene was passed.

^c 0.5 F/mol of Bu_4NNO_3 was passed.

^d 1 F/mol of Bu_4NNO_3 was passed.

resemble the electrolysis of mesitylene in acetic acid containing nitrate ion, where side-chain substituted products predominate.

The electrolysis of mesitylene in $\text{CH}_3\text{NO}_2/\text{Bu}_4\text{NNO}_3$ was then carried out using a carbon anode and the results are given in Table 1. Products I–IV are also formed in these experiments but the relative amounts changed remarkably. The major product at the carbon anode is 2,4,6-trimethylphenol. It can be seen from the last entry in the table that a large amount of 2-nitromesitylene is formed when an excess of mesitylene relative to Bu_4NNO_3 is used.

Current-potential curves were recorded for the electrolysis of Bu_4NNO_3 in CH_3NO_2 , with and without added mesitylene. Fig. 1. shows that the addition of mesitylene resulted in a shift to slightly lower anode potentials at the carbon anode. At the platinum anode the effect of added mesitylene is quite different and the rise in current did not take place until rather high anode potentials were employed.

The results obtained from the electrolysis of mesitylene in $\text{CH}_3\text{CN}/\text{Bu}_4\text{NNO}_3$ using a platinum anode are given in Table 2. The major products were the

Table 2. Electrolysis of mesitylene in $\text{CH}_3\text{CN}/\text{Bu}_4\text{NNO}_3$. Product distribution and current yield.

Mesitylene con. (M)	Bu_4NNO_3 conc. (M)	Anode material	Anode pot. (V)	Relative distribution				Current yield % ^a
				I	II	III	IV	
0.2	0.2	Pt	2.1	79	1	20	33	
0.2	0.2	C	1.5	1	99	—	12	
1.0	1.0	C	1.5	—	97	3	10	
1.0	0.2	C	1.3	—	100	—	6	

^a 0.2 F/mol of Bu_4NNO_3 was passed in all experiments.

benzaldehyde (I) and the benzyl nitrate (IV) similar to the results in nitromethane. Whereas the benzyl nitrate was the major product in nitromethane, the benzaldehyde was the major product in acetonitrile.

Using a carbon instead of a platinum anode had a similar effect to that observed with nitromethane. The results in Table 2 show that 2,4,6-trimethylphenol was the predominant product and only traces of the benzaldehyde and benzyl nitrate were formed. An exhaustive electrolysis of mesitylene (1.0 M) was carried out in $\text{CH}_3\text{CN}/\text{Bu}_4\text{NNO}_3$ (1.0 M) and it was found that the current yield of III dropped sharply, indicating further reaction of the product. The effect of added water on the electrolysis of mesitylene using a carbon anode was also examined. In this experiment the relative amount of III decreased slightly at the expense of a new compound. The mass spectrum of

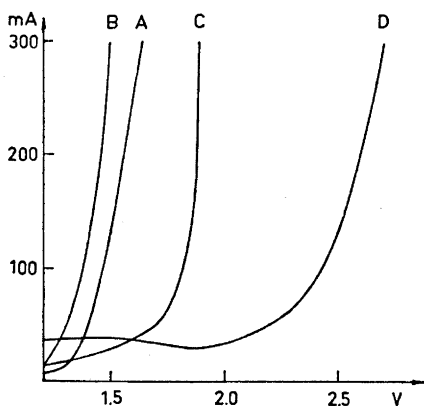


Fig. 1. Current-voltage curves. A, electrolysis of nitromethane containing 0.2 M Bu_4NNO_3 at a carbon anode. B, with added 0.2 M mesitylene. C, electrolysis of nitromethane containing 0.2 M Bu_4NNO_3 at a platinum anode. D, with added 0.2 M mesitylene.

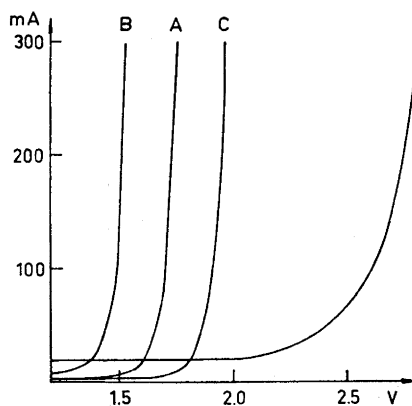


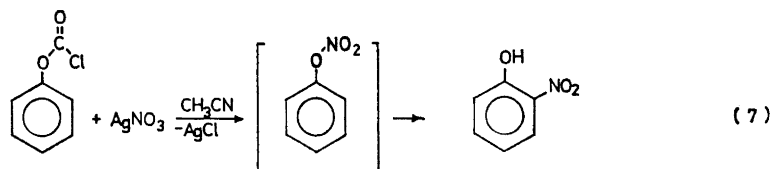
Fig. 2. Current-voltage curves. A, electrolysis of acetonitrile containing 0.2 M Bu_4NNO_3 at a carbon anode. B, with added 0.2 M mesitylene. C, electrolysis of acetonitrile containing 0.2 M Bu_4NNO_3 at a platinum anode. D, with added 0.2 M mesitylene.

this (V) showed that two hydroxyl groups had been incorporated in mesitylene. The current yield of III was 13 %.

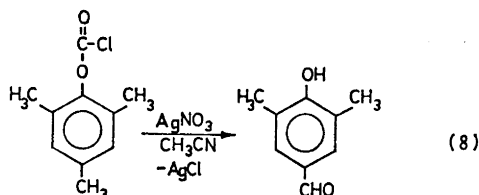
Current-potential curves were recorded for the electrolysis of mesitylene Bu_4NNO_3 in acetonitrile at a platinum and at a carbon anode (Fig. 2). The results are similar to those shown in Fig. 1. Addition of mesitylene results a shift towards lower anode potentials at a carbon anode, whereas a shift towards higher anode potentials occurs at the platinum anode.

Electrolysis of nitrate ion in the presence of naphthalene was also carried out. Naphthalene was chosen for two reasons. It is oxidized in the same potential region as nitrate ion, and it does not carry any methyl groups, thus avoiding side-chain substitution. Electrolysis of naphthalene (1.0 M) in acetonitrile containing Bu_4NNO_3 (0.2 M) was carried out using a carbon anode (anode potential 1.3 V) until 0.2 F/mol of Bu_4NNO_3 had passed. Traces of 1-nitronaphthalene were detected in the electrolysis solution, but the only other product was 1,4-naphthoquinone (current yield 3 %). When the electrolysis was repeated at a platinum anode, no naphthalene derivative was detected. Electrolysis of naphthalene in nitromethane containing Bu_4NNO_3 was carried out using the same concentrations at a carbon anode (anode potential 1.2 V) until 0.2 F/mol of Bu_4NNO_3 had passed. 1,4-Naphthoquinone was again formed (2 % current yield) but the major product was 1-nitronaphthalene (4 % current yield). When the electrolysis was conducted at a platinum anode, no naphthalene derivative was detected.

The formation of 2,4,6-trimethylphenol during the oxidation of mesitylene is very interesting from a mechanistic point of view. It is possibly formed by hydrolysis of 2,4,6-trimethylphenyl nitrate, since this compound is probably very unstable. No nuclear substituted aryl nitrate appears to have been isolated previously. An attempt to synthesize phenyl nitrate has been described.¹⁰ The reaction between silver nitrate and phenyl chloroformate in acetonitrile produces *o*-nitrophenol in high yield. It was suggested that the product was formed by rearrangement of phenyl nitrate as shown in eqn. 7.



If it is assumed that this reaction actually proceeds through an intermediate phenyl nitrate, it is of course of interest to carry out a similar reaction with 2,4,6-trimethylphenyl chloroformate. This was done under the same conditions as those used for phenyl chloroformate (stirring at room temperature) but required longer time for completion (three days as compared to 1 h for the phenyl compound). In one experiment a single major product was detected by GLC. After isolation by column chromatography this product was identified as 3,5-dimethyl-4-hydroxybenzaldehyde (eqn. 8). Small amounts of 2,6-



dimethylbenzoquinone and 2,4-dimethyl-6-nitrophenol were detected by GLC in combination with mass spectrometry. In two other experiments low yields of aldehyde were obtained and other unidentified products were formed. Further work on this reaction will be reported later. At present it is sufficient to note that the reaction does not yield the same products as the electrochemical experiments with mesitylene and nitrate ion.

Finally, some reactions were carried out using *t*-butylbenzene as the aromatic compound. Electrolysis of *t*-butylbenzene (1.0 M) in nitromethane containing Bu_4NNO_3 (0.2 M) was carried out at a platinum anode (anode potential 2.0 V) until 0.5 F/mol of Bu_4NNO_3 had passed. Several products were formed, but no nitro-*t*-butylbenzene nor any *t*-butylphenol was detected. By comparison with authentic specimen at least three isomeric *t*-butyl-*o*-nitrophenols were found to be present. Repeating the reaction in acetonitrile showed the presence of at least two similar products. The current yields were less than 5%. When the electrolyses were carried out at a carbon anode no products were detected by GLC. The authentic *t*-butyl-*o*-nitrophenols were prepared by reaction between silver nitrate and *t*-butylphenyl chloroformates in acetonitrile.

DISCUSSION

In the earlier work on the electrolysis of mesitylene and toluene in acetic acid containing nitrate ions the major products were benzyl acetates and benzyl nitrates.³⁻⁵ The present work shows that three other types of substitution may take place depending on the choice of solvent and anode material: hydroxylation, nitration and nitrohydroxylation.

Hydroxylation of mesitylene takes preferentially place at the carbon anode in both nitromethane and acetonitrile. Different reaction paths leading to the phenol could be envisaged. Oxidation of mesitylene to a cation radical, followed by reaction with residual water would give the phenol. The absence of bimesityl even at high mesitylene concentrations makes this path seem unlikely, since it has been shown that oxidation of mesitylene in $\text{CH}_3\text{CN}/\text{Bu}_4\text{NBF}_4$ produces bimesityl both at a platinum and a carbon anode.⁹ If oxidation of mesitylene does take place at the carbon anode, it is perhaps better to assume that nitrate ion reacts with the cation radical to form mesityl nitrate, which is hydrolyzed to the phenol. On the other hand, oxidation of nitrate ion to nitrate radical could lead to the same product, if the nitrate radical attacks the ring in mesitylene. The current-potential curves recorded at the carbon anode show that addition of mesitylene causes a slight decrease in anode potentials at constant current. The formation of 2-nitromesitylene

from the electrolysis of mesitylene in $\text{CH}_3\text{NO}_2/\text{Bu}_4\text{NNO}_3$ must certainly involve the oxidation of nitrate ion to nitronium ion (eqn. 5). However, this does not mean that oxidation of nitrate ion is the only anode reaction. The possibility that oxidation of mesitylene does take place simultaneously with oxidation of nitrate ion must be taken into account.

The reaction between silver nitrate and 2,4,6-trimethylphenyl chloroformate did not produce 2,4,6-trimethylphenol. Whether the reaction proceeds through 2,4,6-trimethylphenyl nitrate or not cannot be determined at present. It is interesting to note that 3,5-dimethyl-4-hydroxybenzaldehyde as well as the corresponding benzyl alcohol and 2,6-dimethylbenzoquinone have been found from oxidation of 2,4,6-trimethylphenol with different reagents, e.g. hydrogen peroxide in the presence of peroxidase,¹¹ silver thiosulphate,¹² potassium nitrosulphonate.¹³

The electrolysis of naphthalene in the presence of nitrate ion produced 1-nitronaphthalene at the carbon anode in nitromethane, whereas the major product in acetonitrile was 1,4-naphthoquinone. The nitro derivative is certainly an indication of the oxidation of nitrate ion to nitronium ion (eqn. 5). The mode of formation of the quinone is less obvious, although 1-naphthol could be the precursor.

The formation of *o*-nitrophenols from the electrolysis of *t*-butylbenzene in the presence of nitrate ion at the platinum anode is probably due to the rearrangement of initially formed *t*-butylphenyl nitrate. Such a nitrate could undergo rearrangement, since at least one *ortho* position is unsubstituted. It is somewhat surprising that no products were detected when the electrolysis was carried out at the carbon anode.

Extensive formation of side-chain products occurred during the oxidation of mesitylene at the platinum anode, as observed during the electrolysis of mesitylene in acetic acid containing nitrate ion. Whereas electrolysis of mesitylene in acetonitrile or in nitromethane at the carbon anode changed the product distribution completely, no change was observed when electrolysis of mesitylene was carried out in acetic acid at a carbon anode.

The current-voltage curves recorded at the platinum anode showed a remarkable shift towards high anode potentials on addition of mesitylene to the electrolyte. This could be due to passivation of the electrode by mesitylene, preventing the nitrate ions from being oxidized at lower anode potentials. Whether this means that mesitylene is not oxidized at all or that a high anode potential is required for its oxidation at platinum is not clear.

It is evident from the results that it is not possible to invoke one single anode reaction mechanism to explain the formation of the products from the anodic oxidation of aromatic compounds in the presence of nitrate ion. The results show that oxidation of nitrate ion to nitronium ion takes place. Oxidation of nitrate ion to nitrate radical might explain some of the results alternatively oxidation of the aromatic compounds might also take place. The anode reactions involving nitrate ion are no doubt complex and further speculation about the reaction mechanism (or mechanisms) should await further studies.

EXPERIMENTAL

Controlled potential electrolysis was carried out in a 60 ml water-jacketed cell equipped with a platinum anode (surface area 50 cm²) or with a carbon anode (surface area 15 cm²) and with a platinum cathode (surface area 12 cm²) using the saturated calomel electrode as reference electrode. The anode potential was controlled by means of an Amel Model 557 Potentiostat in connection with an Amel Model 558 Integrator. Gas chromatographic analysis was done with a Perkin-Elmer Model 880 instrument, equipped with a Perkin-Elmer D 26 Integrator, on a 4 m × 0.3 cm 5 % NPGS on Chromosorb W column. Mass spectrometric analysis was obtained with an LKB Model 9000 instrument connected to a gas-liquid chromatograph.

Materials. Acetonitrile, nitromethane, mesitylene, *t*-butylbenzene, and naphthalene were of high commercial quality. Tetrabutylammonium nitrate was prepared by mixing equivalent amounts of sodium nitrate and tetrabutylammonium hydrogensulphate in water. The solution was extracted twice with methylene chloride and the combined extracts were dried over molecular sieves. After removal of the solvent the white crystalline residue was washed several times with ether and finally dried to give tetrabutylammonium nitrate, m.p. 118–120°, yield 90 %. 3,5-Dimethylbenzaldehyde was prepared by oxidation of 3,5-dimethylbenzyl alcohol with Ce(NH₄)₂(NO₃)₆, 3,5-dimethylbenzyl nitrate³ was prepared by reaction between silver nitrate and 3,5-dimethylbenzyl bromide in acetonitrile. Nitromesitylene, 2,4,6-trimethylphenol, 1-nitrophenalene and 1,4-naphthoquinone were commercial samples.

Electrolysis. Controlled potential oxidation was carried out with 50 ml solutions containing the appropriate concentration of reagents that has already been specified in the text of the tables. At the end of an electrolysis the solvent was removed by evaporation *in vacuo*, and ether was added to the residue in order to precipitate the salt. After filtration, the ether solution was concentrated and analyzed by GLC. The current yields and product distribution were calculated after calibration of the authentic compounds against a standard substance. The results have been given in the text or the tables. Compound V obtained in the electrolysis of mesitylene in acetonitrile at a carbon anode gave the following major fragments in the mass spectrum, *m/e* = 152 (50 % abundance), 137 (100 %), 136 (15 %), 135 (21 %), 124 (23 %), 121 (15 %), 109 (65 %) and also fragments at 91, 81, 43, 41, and 39.

Silver nitrate reaction with 2,4,6-trimethylphenyl chloroformate. In a typical experiment 5 g (0.025 mol) 2,4,6-trimethylphenyl chloroformate in 10 ml acetonitrile was added dropwise to a solution of 5.9 g (0.035 mol) silver nitrate in 50 ml acetonitrile under stirring. After three days at room temperature all the ester had reacted and silver chloride was filtered off. Acetonitrile was removed by evaporation *in vacuo* and to the residue was added methylene chloride and sodium chloride in water. Silver chloride was again filtered off and the methylene chloride phase separated. After drying over sodium sulphate the solvent was removed and the residue analyzed by GLC, IR, NMR, and mass spectrometry. In one run the major GLC peak was 3,5-dimethyl-4-hydroxybenzaldehyde. This compound was isolated after column chromatography on neutral alumina, m.p. 113–115° (lit.¹⁰ 114.5–115°). The mass spectrum of this compound showed two large fragments at *m/e* = 150 (70 %) and 149 (100 %) in addition to several minor fragments. The NMR spectrum (in CDCl₃) showed three signals at δ = 2.27 ppm (6 protons), 7.48 ppm (2 protons), and 9.72 ppm (1 proton). In another run the aldehyde peak in the GLC analysis had diminished in relation to the other peaks. The NMR spectrum of the crude product showed in addition to the three peaks another three signals at δ = 2.23, 5.28, and 7.05 ppm in the integrated area ratio of 3:1:1. The crude product was reduced with LiAlH₄ in ether and the NMR spectrum of the new product was recorded. The aldehyde signals had disappeared and the only other change in the NMR spectrum was the change of the 5.28 ppm signal to 4.48 ppm. It is quite possible that this corresponds to 3,5-dimethyl-4-hydroxybenzyl alcohol, since the IR spectrum showed the presence of hydroxyl absorption but no carbonyl absorption. In a third run the aldehyde was almost absent according to GLC and NMR. However, it was not possible to isolate any pure material.

Silver nitrate reaction with *t*-butylphenyl chloroformates. The appropriate *t*-butylphenyl chloroformate (0.05 mol) in 15 ml acetonitrile was added dropwise to silver nitrate (12 g) in 50 ml acetonitrile under stirring. After 3 h silver chloride was filtered off and acetonitrile was removed. From the *para* compound 4-hydroxy-3-nitro-*t*-butylbenzene was isolated

after distillation at 87–90°/0.4 mm in 63 % yield. From the *meta* compound a mixture of three products was obtained in 40 % yield after steam distillation. The major product (92 % of the mixture) was identified as 3-hydroxy-4-nitro-*t*-butylbenzene on basis of the NMR and mass spectra. Three products were similarly obtained from the *ortho* compound in 37 % yield and the major component (80 % of the mixture) was identified as 2-hydroxy-3-nitro-*t*-butylbenzene on basis of the NMR and mass spectra.

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