the internal standard, was determined and the appropriate correction factor was applied. This correction factor (same for both polyols) was assumed to be applicable to the unidentified peaks in the glpc trace. The 2,4- and 2,6-diols eluted simultaneously by the chromatographic technique used in this study.

Registry No.—**3**, 2613-61-8; 2,4,6-trimethyl-2,4-heptanediol, 33070-42-7; 2,4,6-trimethyl-2,6-heptanediol, 33070-43-8; 2,4,6-trimethyl-2,4,6-heptanetriol, 33070-44-9.

Lithium–Ammonia Reduction of Benzaldehydes to Toluenes

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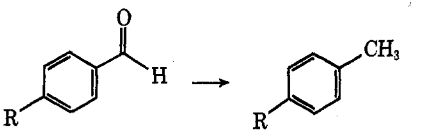
Two methods are reported for the reduction of benzaldehydes to toluenes in lithium–ammonia solutions. By these methods *p-tert*-butylbenzaldehyde, *p*-isopropylbenzaldehyde, *p*-methylbenzaldehyde, and benzaldehyde were reduced to *p-tert*-butyltoluene, *p*-cymene, *p*-xylene, and toluene, respectively. Both methods take advantage of good proton sources to minimize a serious competitive reaction which leads to dimers. Mechanistic implications are discussed.

The only reported reduction of an aldehyde in metal–ammonia solutions is that of vanillin to vanillyl alcohol plus a dimer in potassium–ammonia.[2] Presumably the reduction of aldehydes in liquid ammonia has been avoided because aldehydes readily condense with ammonia.[3] We have found that aromatic aldehydes are amenable to metal–ammonia conditions and wish to describe two useful methods for their reduction to toluenes.



R = *tert*-C_4H_9, *iso*-C_3H_7, CH_3, H

Recently we reported conditions for the reduction of aromatic ketones to aromatic hydrocarbons in lithium–ammonia (THF) solutions.[4] Extensions of this work to aromatic aldehydes[5] led to the following observations: (1) the aromatic aldehydes were reduced substantially faster than aromatic ketones; (2) trace amounts of cobalt had no noticeable reduction rate enhancement effect as was observed with aromatic ketones; and (3) aromatic aldehydes dimerize much more readily than aromatic ketones.[6]

The formation of dimers made the method inutile for our purposes as a synthetic reaction and consequently a modified method was sought which would minimize their formation. Since dimers had not been observed in the reduction of benzyl alcohols when subjected to these conditions,[7] thus excluding the possibility of dimer formation from the benzyl radical **5**, we assumed the ketyl radical **2a** to be the source of dimers.[8,9] It was reasoned that if the ketyl radical **2b** would be formed in the presence of a good proton source, such as *tert*-butyl alcohol or ammonium chloride, it might be quickly protonated forming the alkoxy radical **3**, which in turn would be rapidly reduced to the benzyl alkoxide **4**. The net effect should be a substantial decrease in the amount of dimer formed. Following this presupposition, two useful methods were developed and are described. The product toluene normally represented more than 90% of the chromatographable material and was usually isolated pure in at least 80% yield using either method.

Method A involves the addition of a solution of the benzaldehyde and *tert*-butyl alcohol in THF to a refluxing lithium–ammonia solution, followed by an ammonium chloride quench. Substituting sodium benzoate[10] for the ammonium chloride yielded mainly the toluene along with lesser amounts of the benzyl alcohol and aldehyde (*ca.* 5:1.5:1) indicating that the ammonium chloride quench is necessary to complete the reduction.

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[1] National Science Foundation Undergraduate Research Participant, summer 1971.

[2] K. Freudenberg, W. Lautsch, and G. Piazolo, *Chem. Ber.*, **74**, 1879 (1941).

[3] (a) R. L. Augustine, Ed., "Reduction," Marcel Dekker, New York, N. Y., 1968, p 116; (b) H. Smith, "Organic Reactions in Liquid Ammonia. Chemistry in Nonaqueous Ionizing Solvents," Vol. I, Part 2, Wiley, New York, N. Y., 1963, pp 123 and 216.

[4] S. S. Hall, S. D. Lipsky, F. J. McEnroe, and A. P. Bartels, *J. Org. Chem.*, **36**, 2588 (1971).

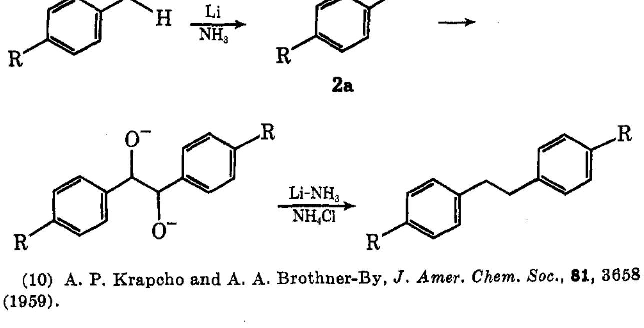
[5] The benzaldehyde in THF was added slowly (*ca.* 20 min) to a lithium–ammonia (THF) solution. After 20 min at reflux the mixture was cautiously quenched with excess ammonium chloride.

[6] The following interesting toluene/aromatic hydrocarbon dimer (2) ratio was observed for *p-tert*-butylbenzaldehyde, *p*-isopropylbenzaldehyde, *p*-methylbenzaldehyde, and benzaldehyde, respectively: 82/18, 77/23, 60/40, and 56/44. After analysis by glc the monomer–dimer aromatic hydrocarbon mixture was eluted from an alumina column with petroleum ether (bp 38–58°) and then distilled apart at reduced pressures. Spectral data (ir, nmr, and mass spectra) indicated the major dimer to be a 1,2-diarylethane. Perhaps the most revealing were the mass spectra. For example, 1,2-*p*,*p*′-dicumylethane from *p*-isopropylbenzaldehyde, *m/e* (rel intensity) 133 (100), 266 (8, M^+). In addition, the major dimer from the reduction of benzaldehyde was compared with an authentic sample of 1,2-diphenylethane.

[7] (a) S. S. Hall, S. D. Lipsky, and G. H. Small, *Tetrahedron Lett.*, 1853 (1971); (b) G. H. Small, unpublished results.

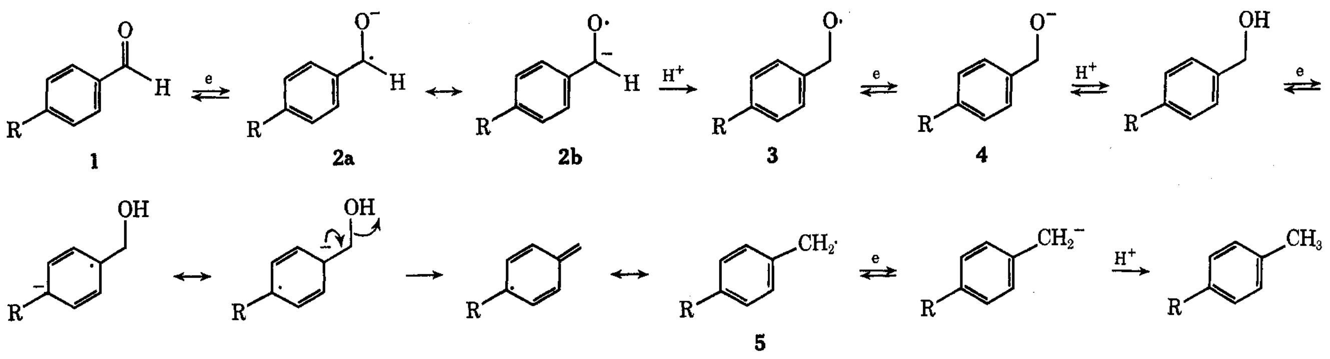
[8] (a) W. E. Bachmann, *J. Amer. Chem. Soc.*, **55**, 1179 (1933); (b) C. B. Wooster, *ibid.*, **59**, 377 (1937).

[9] We assumed the major dimer to be formed according to the following general scheme *via* a bimolecular reduction.

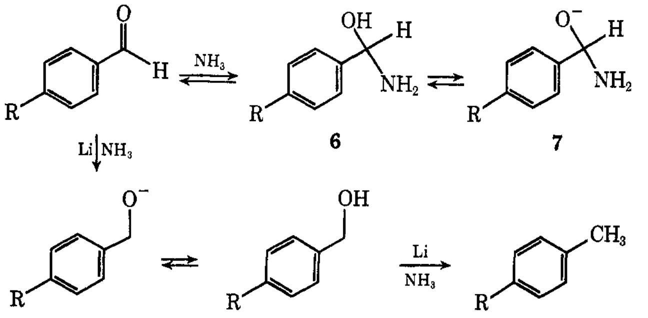


[10] A. P. Krapcho and A. A. Brothner-By, *J. Amer. Chem. Soc.*, **81**, 3658 (1959).

SCHEME I



Method B was designed to take advantage of the condensation reaction between the aldehyde and ammonia to form a hydrobenzamide.[3] The general procedure is to allow the aldehyde to react with the ammonia, then add lithium and quench the mixture with ammonium chloride. When sodium benzoate[10] was used as the quenching agent a 1:1 mixture of the toluene and the benzaldehyde was formed.[11] This result suggests that in liquid ammonia there is an equilibrium between the free aldehyde and hydrobenzamide **6**. When the lithium is added the free aldehyde is quickly reduced to the alkoxide, protonated by the hydrobenzamide **6**, and then is reduced further to the aromatic hydrocarbon. The resulting anion **7** of the hydrobenzamide probably resists reduction until the ammonium chloride is added regenerating the aldehyde, which is then rapidly reduced to a toluene before all the lithium is destroyed. In contrast, quenching with sodium benzoate would destroy the excess reducing agent and then during normal work-up the benzaldehyde would be regenerated.



Although both methods are satisfactory, we tend to favor method A for the reduction of benzaldehyde and alkylbenzaldehydes since less high molecular weight material seems to be formed (see Experimental Section).

Our suggestions for the mechanism of the reduction are outlined in Scheme I. The mechanism incorporates the reduction of a carbonyl group to an alcohol[12] and a benzyl alcohol to a toluene[13] and is analogous to that proposed for the reduction of aromatic ketones to aromatic hydrocarbons.[4]

Experimental Section[14]

Lithium–Ammonia Reduction.—Precautions for the exclusion of impurities (moisture, air, peroxides, contaminate metals, or metal salts) were scrupulously observed. All reductions were carried out under a static nitrogen (prepurified) atmosphere and anhydrous ammonia was distilled into the reaction vessel. Tetrahydrofuran (THF) was filtered through an alumina column, and then refluxed and distilled from LiAlH_4 just prior to use. Lithium wire (0.01% Na, Ventron Corp.) was wiped free of oil and washed with petroleum ether (bp 38–58°) immediately before use. All product toluenes gave satisfactory spectral and analytical data; and in the reductions of benzaldehyde, *p*-methylbenzaldehyde, and *p*-isopropylbenzaldehyde, the products were also compared with authentic samples of toluene, *p*-xylene, and *p*-cymene, respectively. The reduction of *p*-isopropylbenzaldehyde and *p-tert*-butylbenzaldehyde are described to illustrate each method.

Method A. *p*-Cymene.—To a mixture containing 20 ml of ammonia, 10 ml of THF, and 175 mg (25 mg-atoms, 10 pieces) of lithium was added dropwise (*ca.* 20 min)[15] a solution of 0.79 g (5 mmol) of *p*-isopropylbenzaldehyde and 0.46 g (6.25 mmol) of *tert*-butyl alcohol in 10 ml of THF. Almost immediately the excess lithium was consumed by the rather rapid addition (*ca.* 5 min) of excess ammonium chloride (*ca.* 5 g)[16] and the ammonia was allowed to evaporate. After the residue had been partitioned between aqueous NaCl and Et_2O, the organic layer was dried and concentrated. Analysis by glc indicated a 98% yield of *p*-cymene and a 2% yield of dimers (2). After chromatography (alumina, petroleum ether) a pale yellow liquid (0.60 g, 90%) was isolated which was identical with an authentic sample of *p*-cymene.

Method B. *p-tert*-Butyltoluene.—To a solution containing 20 ml of ammonia and 10 ml of THF was added a solution of 0.81 g (5 mmol) of *p-tert*-butylbenzaldehyde in 10 ml of THF. After 30 min 210 mg (30 mg-atoms, 12 pieces) of lithium was added. Once the dark blue solution was established,[17] excess ammonium chloride (*ca.* 4.5 g) was rather rapidly added (*ca.* 5 min)[16] and the ammonia was allowed to evaporate. After the residue had been partitioned between aqueous NaCl and Et_2O, the organic layer was dried and concentrated. Analysis by glc indicated a 94% yield of *p-tert*-butyltoluene along with a 2% yield of dimers (2) and a 4% yield of unknown high molecular weight material (1 major and 2 minor peaks). After chromatography (alumina, petroleum ether) a pale yellow liquid (0.66 g,

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[11] Prolonged equilibration of the aldehyde in liquid ammonia before the addition of lithium did not alter this result.

[12] See ref 3a, pp 97–98.

[13] H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, pp 74–75.

[14] Spectral measurements were determined with the following instruments: ir, Beckman Model IR-10; nmr, Varian Associates Model A-60; mass spectra, Perkin-Elmer Model 270 with a Varian Associates Model 620/i computer attachment. Gas chromatographic analyses (glc) were performed on a Hewlett-Packard Model 5750 research chromatograph (flame detector) using a 6 ft × $^1/_8$ in. 10% silicon gum rubber UCC-W-982 (methylvinyl) on 80–100 Chromosorb W. Separations and purifications were attained on absorption alumina (80–200 mesh) columns. Further purification, for analytical purposes, was accomplished by flash distilling the samples at reduced pressure.

[15] The rate of addition should be slow enough to maintain a dark blue solution.

[16] For a convenient method of adding the quenching agent see ref 4.

[17] We normally waited for *ca.* 20 min, although this length of time does not seem to be necessary.

89%) was isolated: nmr τ 8.71 (s, 9 H), 7.71 (s, 3 H), 2.98 (d, 2 H, J = 8 Hz), 2.77 (d, 2 H, J = 8 Hz); mass spectrum m/e (rel intensity) 39 (21), 40 (21), 41 (42), 77 (16), 91 (26), 93 (26), 105 (50), 133 (100), 148 (20, M$^+$).

Anal. (flash distilled, 14 mm). Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.26; H, 10.86.

Registry No.—Lithium, 7439-93-2; ammonia, 7664-41-7; *p*-isopropylbenzaldehyde, 122-03-2; *p*-cymene, 99-87-6; *p-tert*-butyltoluene, 98-51-1; *p-tert*-butyl benzaldehyde, 939-97-9.

Acknowledgments.—The authors are grateful to Miss Rose Marie Luethy and Mr. Paul P. Vallon, Givaudan Corp., Clifton, N. J., for the mass spectra, and to Dr. Franz J. Scheidl, Hoffmann-La Roche Inc., Nutley, N. J., for the microanalyses.

The Origin of the Paramagnetic Species in Lignin Solutions. Autoreduction of 2,6-Dimethoxybenzoquinone and Related Quinones to Radical Anions in Alkaline Solution

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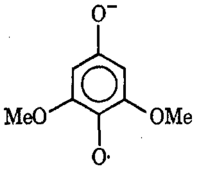
The lignin model compound, 2,6-dimethoxybenzoquinone (**3**), is spontaneously reduced to stable semiquinone radical anions by alkaline solutions of water or alcohol. This behavior parallels that of hardwood lignins. Rapid replacement of the methoxyl groups by alkoxide ion occurs in alkanolic solvents; steric factors play an important role in this exchange. The primary reaction intermediate appears to be a cyclohexadienone adduct of quinone and nucleophile; its concentration is rate determining. A mechanism for the reaction is proposed.

Lignin, the ubiquitous component of terrestrial plants, has been shown to be paramagnetic.[2-5] The paramagnetism of lignin preparations increases with extent of chemical and enzymatic degradation.[5] Hardwood lignins, which contain a high proportion of 3,5-dimethoxy-4-hydroxyphenyl elements, have a higher spin content than analogous softwood lignins (whose chief structural elements are 4-hydroxy-3-methoxyphenyl groups). Alkali lignins show the highest radical content of all preparations.

When hardwood lignin preparations are dissolved in dilute aqueous base, a paramagnetic species is formed. This has been identified as 2,6-dimethoxy-*p*-benzosemiquinone (**1**).[6] In strong base, a second radical (**2**) appears.[6] All commercial hardwood lignins, such as kraft and Meadol, yield **1** and **2**. Brauns native and Bjorkman hardwood lignins yield low concentrations of **1**, as does Indulin (predominantly a softwood product).

We have found that hot water extracts of commercial alkali lignins contain appreciable amounts of 2,6-dimethoxyquinone (**3**) and small quantities of vanillin, syringaldehyde, and polymeric material. No 2-methoxybenzoquinone (**4**) was found. Native hardwood lignins do not yield any of the above with hot water. However, when refluxed with 1.0 M NaOH in air, they form vanillin, syringaldehyde, and traces of **3**. Since **3** appears to be the sole structural precursor of the paramagnetic species (apparently formed during a Dakin-type cleavage of native lignin during the pulping process),[7] we decided to investigate its behavior in a variety of basic solvents. The behavior of **3** may have relevance for other systems. Redox reactions of **3** have been implicated in plant resistance to fungal attack;[8a] its formation in plants may have arisen by a Dakin cleavage of lignin during attack by oxidases and peroxide.[8b]



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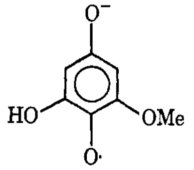

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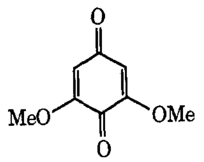

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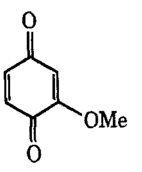

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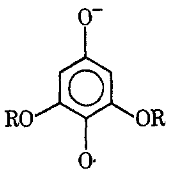

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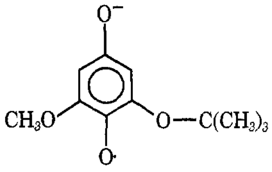

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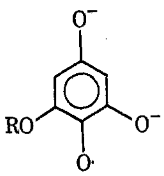

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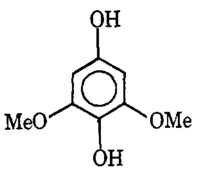

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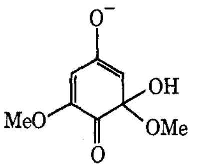

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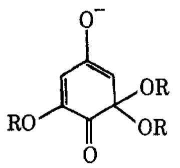

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Results

Reduction of Quinone 3 in Alkanolic Solvents.—When 10^{-3} M solutions of **3** were mixed with anhydrous alkanols and sodium ethoxide, strong esr signals were observed for 2,6-dialkoxybenzosemiquinones (**5**). Sec-

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[1] Presented at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 29, 1971.

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