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Reduction of Aromatic Compounds with Alkali Metals in Neat Ammonia

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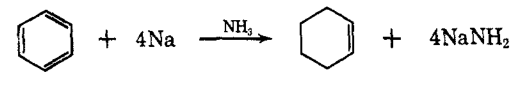
Benzene is reduced exclusively to cyclohexene by elemental sodium or potassium in neat, liquid ammonia at ~60–130° without the added acids (water, alcohols, etc.) required for the Birch reduction of benzene to cyclohexadiene. Lithium reduces benzene in neat ammonia predominantly to cyclohexadiene. Metal amides are the inorganic products obtained in high yield. Part of the metal reacts directly with the ammonia to form hydrogen and a metal amide. This side reaction is catalyzed by sodium amide and to a lesser degree by hydrogen. Alkyl-substituted benzenes also are reduced to the corresponding cyclohexenes by sodium in neat ammonia. The following orders of ease of reduction are indicated: benzene > toluene > ethylbenzene > *t*-butylbenzene and *p*-xylene > *m*-xylene > *o*-xylene. Biphenyl is reduced mainly to phenylcyclohexane. *p*-Terphenyl is reduced to 1,4-dicyclohexylbenzene and 1-phenyl-4-cyclohexylcyclohexane.

In 1937 Wooster discovered that monocyclic aromatic compounds are reduced mainly to cyclohexadienes by alkali and alkaline earth metals in refluxing ammonia (~−34°) containing a substance more acidic than the solvent.[1] Subsequently, Birch extended the scope of this reaction which now bears his name.[2-4] Birch reductions supposedly do not occur in the absence of the added acid (H_2O, ROH, NH_4Cl etc.). We would like to report the results of our investigation wherein metal reductions of aromatic hydrocarbons have been carried out at elevated temperatures (~60–130°) in neat, liquid ammonia without added acids. During the course of this investigation, a patent appeared which disclosed that benzene and toluene are reduced to cyclohexenes by alkali and alkaline earth metals in liquid ammonia containing less than a stoichiometric amount of or no added protic material.[5] Temperatures >0° were employed.

Results and Discussion

An efficiently stirred, stainless steel, Magnadrive autoclave was employed for all experiments. In contrast to the Birch reaction which produces mainly dienes, sodium in excess neat ammonia reduces benzene at ~60–130° exclusively to cyclohexene (eq 1). Cyclohexane, cyclohexadienes, or dimeric products could not be detected by glpc even when the reaction times were short and the conversions of benzene low. Upon distillation of the liquid products, high yields of white, powdery sodium amide were obtained as residues. The time required for complete consumption of 4 moles of sodium per mole of benzene in 28 moles of ammonia follows: >>24 hr at 60°, 4–8 hr at 100°, 1–3 hr at 125°, and ~0.8 hr at ~130°. Conversions of benzene as high as 43–45% were obtained. The ultimate conversion of benzene for a given quantity of sodium was not affected significantly by increasing the temperature from 100 to 130°.



(1)

Part of the metal reacted directly with the ammonia to produce hydrogen (eq 2). The hydrogen producing side reaction was found to be autocatalytic. Most of the cyclohexene formation occurs during the early stages of the reaction whereas the sodium–ammonia reaction (eq 2) is dominant thereafter. There are two obvious possibilities which might account for the autocatalytic effect. Sodium amide is known to promote its own formation from sodium and ammonia.[6] Also, the captive hydrogen being produced may unite with unconverted sodium metal to form sodium hydride which, in turn, would react readily with ammonia to form sodium amide and additional hydrogen (eq 3–5). As would be expected, the addition of either extraneous sodium amide or hydrogen to the autoclave at the start of the reaction decreased the conversion of benzene to cyclohexene by promoting the side reaction of sodium with ammonia. The catalytic effect of sodium amide was more pronounced than that of hydrogen.

$$2Na + 2NH_3 \longrightarrow 2NaNH_2 + H_2 \qquad (2)$$

$$2Na + H_2 \longrightarrow 2NaH \qquad (3)$$

$$2NaH + 2NH_3 \longrightarrow 2NaNH_2 + 2H_2 \qquad (4)$$

$$\text{net reaction:}\quad 2Na + 2NH_3 \longrightarrow 2NaNH_2 + H_2 \qquad (5)$$

Relative reagent concentrations are important. With a given quantity of sodium, variations in the ammonia–benzene molar ratio from 28:1 to ~1:1 result in marked changes in the yield[7] of cyclohexene (Table I).

At 100°, if stirring is not applied, the time required for complete consumption of sodium varies erratically from 2 to 24 hr and the conversion of benzene varies from 13 to 60%. These observations indicate that the system may not be homogeneous.

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(1) C. B. Wooster and K. L. Godfrey, *J. Am. Chem. Soc.*, **59**, 596 (1937); C. B. Wooster, U. S. Patent 2,182,242 (1939).

(2) A. J. Birch, *Quart. Rev.* (London), **4**, 69 (1950).

(3) A. J. Birch, *ibid.*, **12**, 17 (1958).

(4) H. Smith, "Organic Reactions in Liquid Ammonia," Vol. 1, Part 2, Interscience Publishers, Inc., New York, N. Y., 1963.

(5) M. Amagasa and T. Yamaguchi, French Patent 1,363,841 (May 4, 1964).

(6) R. Levin and W. C. Fernelius, *Chem. Rev.*, **54**, 449 (1959).

(7) Based on metal reacted, assuming the stoichiometry of eq 1.

TABLE I

EFFECT OF REAGENT CONCENTRATIONS

(temp = 100°; time = 12 hr; sodium = 0.40 mole)

Benzene, moles	Ammonia, moles	Cyclohexene[a] yield,[b] %
0.1	2.8	30.8
0.2	2.6	34.6
0.5	2.3	34.1
0.7	2.0	19.1
1.2	1.1	5.6

[a] Cyclohexene was the only product of reduction. Material balances ranged from 86 to 100%. [b] Reference 7.

Like sodium, potassium in excess, neat ammonia reduces benzene to cyclohexene exclusively. Compared to sodium, the rate of potassium consumption is estimated to be ~25 times greater at 100°. However, under comparable conditions, the yield of cyclohexene[7] (27 *vs.* ~35%) is lower owing to the greater reactivity of potassium with ammonia to form hydrogen and potassium amide.

The cyclohexene yields at 75–125° are lower, *i.e.*, 11–18%, for sodium–potassium alloys than for either potassium or sodium metal alone. Only a small quantity of potassium, ~10% *M*, in sodium is sufficient to decrease markedly the metal utilization for the reduction of benzene.

Whereas sodium and potassium produce only cyclohexene, lithium in excess, neat ammonia reduces benzene to cyclohexadiene as well as cyclohexene. In the best experiment for diene formation (expt 2), the reduced product consisted of 91.1% 1,4-cyclohexadiene and 8.9% cyclohexene with 58.4% of the benzene converted. Cyclohexene formation is more important at higher temperatures or with prolonged reaction times. Calcium in neat ammonia at 60° reduced benzene to 79.3% cyclohexene and 20.7% cyclohexadienes (expt 5, Table II).

TABLE II

REDUCTION OF BENZENE (0.1 MOLE) BY LITHIUM AND CALCIUM IN NEAT AMMONIA (2.5 MOLES)

Expt	Metal, moles	Temp	Time, hr	% convn of benzene	Product composition,[a] %: Cyclohexene	Product composition,[a] %: 1,4-Cyclohexadiene
1	Li, 0.4	25	12	44.5	9.9	89.0
2	Li, 0.4	60	2	58.4	8.9	91.1
3	Li, 0.4	100	0.5	54.1	35.3	64.3
4	Li, 0.4	120	0.16	69.7	82.8	17.2
5	Ca, 0.20	60	2	26.9	79.3	3.4[b]

[a] Cyclohexane formation was ~1 and 0.4% in expt 1 and 3, respectively. [b] Plus 17.3% 1,3-cyclohexadiene.

To ascertain further the scope of these reactions, we have studied the sodium reduction of substituted benzenes in neat ammonia. Many substituents other than alkyl groups are not stable under the reaction conditions. Anisole at 20–100° was reduced quantitatively to sodium phenolate and methane. N,N-Dimethylbenzamide at 100° was converted in low yield to benzaldehyde and benzyl alcohol. Chlorobenzene was converted to mainly benzene and a trace of cyclohexene and aniline.

Alkyl-substituted benzenes are more difficult to reduce than benzene (Table III). Substituted cyclohexenes were the only products formed. Based upon the relative conversions obtained for a given quantity of metal consumed, the following orders of ease of reduction by sodium in ammonia are indicated: benzene > toluene > ethylbenzene > *t*-butylbenzene; *p*-xylene > *m*-xylene > *o*-xylene. The first of these orders is consistent with the extent of inductive electron donation by alkyl groups to the benzene ring: *t*-butyl > ethyl > methyl. That is, the intermediate anion radicals, produced by interaction of the metal with the aromatic hydrocarbon (*vide infra*), would form less easily as the electron donation of the alkyl group to the ring increases.

TABLE III

REDUCTION OF AROMATIC HYDROCARBONS

(aromatic hydrocarbon = 0.1 mole; ammonia = ~2.7 moles; metal = 0.4 mole)

Aromatic hydrocarbon	Metal[a]	Temp, °C	Time, hr	% convn to cyclic monoolefin
Benzene	Na	125	1.5	45.6
Toluene	Na	125	2.5	19.7[b]
Ethylbenzene	Na	125	3.5	8.7[c]
Toluene	K	60	1.3	1.2[d]
t-Butylbenzene	Na	125	3.8	1.2[d]
p-Xylene	Na	125	2.8	7[e]
m-Xylene	Na	125	2.8	2.1[d]
o-Xylene	Na	125	3	0.7[d]

[a] All of the metal was converted to the metal amide. [b] Isomer distribution: 75% 1-methylcyclohexene and 25% combined 3- and 4-methylcyclohexene. [c] Isomer distribution: ~65% 1-ethylcyclohexene and ~35% combined 3- and 4-ethylcyclohexene. [d] Isomer distribution not determined. [e] Main isomer is 1,4-dimethylcyclohexene.

Biphenyl is rapidly reduced by sodium in neat, liquid ammonia at 120° to a mixture containing 86% phenylcyclohexane and 11% dimer. At 25° with either lithium or sodium, the monomeric product consisted of 65–80% phenylcyclohexane and 35–20% phenylcyclohexene. Biphenyl is converted under conditions of the Birch reaction ($Na/NH_3/CH_3CH_2OH$) into either 1,1′,4,4′-tetrahydrobiphenyl or 1,4,2′,5′-tetrahydrobiphenyl.[8] With the addition of ammonium chloride to a red ammonia solution of biphenyl and sodium, 1,4-dihydrobiphenyl was the product.[8] Also, 1-phenylcyclohexene and 3,4-dihydrobiphenyl reportedly are products obtained at −75° in liquid ammonia.

p-Terphenyl is very rapidly reduced by sodium in neat ammonia at ≤125° to a mixture consisting of 71% 1,4-dicyclohexylbenzene (I) and 29% 1-phenyl-4-cyclohexylcyclohexane (II). It is surprising that some 1,4-diphenylcyclohexane (III) was not obtained. Once formed, III should not further reduce extensively since alkyl-substituted benzenes react slowly under these conditions (*vide supra*). Since III apparently was not formed, the initial reduction of *p*-terphenyl must have occurred at a terminal ring to give 4-cyclohexylbiphenyl (IV) which was subsequently reduced to a mixture of I and II. The center ring of IV is somewhat deactivated by the cyclohexyl group; therefore, a higher relative yield of I compared with II would be expected since the terminal ring of IV should reduce more easily. By way of comparison, the partial

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[8] Reference 4, p 275.

hydrogenation of *p*-terphenyl at 200–275° (1500–2500 psi) over copper chromite or nickel gives a mixture of products which indicates that the initial hydrogenation proceeds randomly with a slight preference for an outer ring.[9]

A kinetic study of the Birch reduction of benzene has shown that over a limited range of concentration the rate of reduction is governed by the law $-d(\mathrm{ArH})/dt = k(\mathrm{ArH})(\mathrm{M})(\mathrm{ROH})$.[10] The metal dissolved in ammonia reversibly donates an electron to the aromatic compound to form a steady-state concentration of anion-radicals. These subsequently are protonated in the rate-determining step to form uncharged free radicals which are rapidly further reduced to the cyclohexadienyl anion. The anion may either form 1,4-cyclohexadiene or 1,3-cyclohexadiene upon protonation. 1,4-Cyclohexadiene is the major product of the Birch reaction. The alkali metal reduction of aromatic compounds in excess, neat ammonia probably proceeds in the same manner as the Birch reaction. Ammonia is a much weaker acid than the protic materials added for the Birch reaction; therefore, it is understandable that the rate-determining proton abstraction reaction would not occur at a significant rate in neat, refluxing (−34°) ammonia. Only by employing higher temperatures of $\geq 60°$ are observable rates obtained. If in ammonia, as in THF,[11] the steady-state concentration of aromatic anion radicals decreases with increasing temperature, then our results imply the reasonable conclusion that the activation energy for proton removal from ammonia by these anion radicals is greater than, and opposite in sign to, the enthalpy of formation of the anion radicals.

Experimental Section

General Procedure.—A 300-ml, stainless steel Magnadrive autoclave was loaded inside a nitrogen-flushed drybox with the reactant metal and aromatic compound to be reduced. Outside of the drybox, ammonia was distilled before being introduced into the autoclave from a weighed stainless steel vessel of ~250-cc capacity.

The autoclave was then heated to the desired temperature and stirred with a paddle speed of ~1000 rpm. After reaction was complete, the autoclave was cooled to room temperature and the excess ammonia allowed to evaporate through a solvent (*e.g.*, toluene when benzene was reduced) scrubber. A vacuum was applied through the scrubber to the autoclave and the organic product distilled into the cooled solvent. This distillation procedure worked well for substrates such as benzene, toluene, xylene, and *t*-butylbenzene. However, for biphenyl and other high boiling materials, the organic product was separated by filtration and solvent washing of the resultant metal amide in the drybox.

The weights of the resultant metal amides were usually 90–100% of theory. The following is a typical analysis of the white, powdery sodium amides collected.

Anal. Calcd for $NaNH_2$: Na, 58.9; N, 35.9; H, 5.2. Found: Na, 60; N, 35.0; H, 5.1.

Products from the Reduction of Benzene.—The products were analyzed quantitatively by glpc for cyclohexene, 1,3-cyclohexadiene, and 1,4-cyclohexadiene. A 20-ft polyphenyl ether column at 100° was employed. The products, isolated by preparative glpc, had infrared spectra and mass spectrometric fragmentation patterns identical with those of authentic materials. A careful search was made for dimeric products, but, apparently, none was formed.

Products from Reduction of Ethylbenzene and Toluene.—The ethylcyclohexene product (Table III) was trapped using a Wilkins Autoprep glpc instrument with a neopentyl glycol succinate/firebrick column (NPGS) and analyzed by infrared and mass spectrometry. The mass spectrum indicated the material to be mainly 1-ethylcyclohexene with minor amounts of the 3- and 4-ethylcyclohexenes present. No diene was present. The infrared spectrum indicated the material to be ~65% 1-ethylcyclohexene.

The isomeric composition of the product obtained from toluene (Table III) was ascertained by a combination of glpc, infrared, and mass spectrometric techniques. 1-Methylcyclohexene was resolved quantitatively from 3- and 4-methylcyclohexenes with a NPGS glpc column.

Products from Reduction of *t*-Butylbenzene.—The reduced product (Table III) was shown by mass spectrometry to be *t*-butylcyclohexene. The isomer distribution was not determined. Dienes were not formed.

Products from Reduction of *o*-, *m*- and *p*-Xylene.—The products of reduction of *o*- and *m*-xylene (Table III) were identified by mass spectrometry as dimethylcyclohexenes. The isomer distribution was not determined. No dienes were formed.

The product of reduction of *p*-xylene (Table III) was identified by mass spectrometry as dimethylcyclohexene. No dienes were present. An nmr analysis (Varian Associates Model A-60) of the isolated product indicated that it was mainly 1,4-dimethylcyclohexene. That is, the absorption centered at $\delta = 5.3$ ppm from tetramethylsilane indicated that only one vinylic (olefinic) hydrogen was present.

Products from Reduction of Biphenyl.—By the general procedure described above, biphenyl (15.4 g, 0.1 mole) was reduced by sodium (0.6 g-atom) in ammonia (2.8 moles) at ~120–125° for 0.5 hr. Ninety-two percent of the biphenyl was reduced. The reduced product composition, as determined by mass spectrometry, was approximately 86% $C_{12}H_{16}$, the fragmentation pattern of which was identical with that of phenylcyclohexane. Also present were 11% of C_{24} compounds and 1% each of $C_{12}H_{12}$ and $C_{12}H_{14}$ compounds.

When the reaction was carried out at 25° for 4.5 hr, 54% of the biphenyl was converted and the reduced product was analyzed: 2.2% $C_{12}H_{12}$, 23.5% $C_{12}H_{14}$ (phenylcyclohexene), 65.0% $C_{12}H_{16}$ (phenylcyclohexane), and 9.2% C_{24} compounds.

Products from Reduction of *p*-Terphenyl.—*p*-Terphenyl (0.05 mole) was reduced by sodium (0.7 g-atom) in ammonia (3.2 moles) at 125° for 0.75 hr. The solid remaining after the ammonia was removed by evaporation was placed in a Soxhlet extractor and extracted with benzene. A glpc analysis (5-ft DC-710 at 300°) showed that all of the *p*-terphenyl had been converted. The solvent was removed under vacuum leaving a white solid with mp 96–100°. A mass spectrometric analysis of this material indicated that it was predominantly $C_{18}H_{26}$ corresponding to either 1,4-dicyclohexylbenzene (I) or 1-phenyl-4-cyclohexylcyclohexane (II). Infrared analysis (KBr plate) showed, by comparison of the spectrum with that of an authentic compound, that the major component was I. A monosubstituted benzene, probably II, also was indicated.

An nmr analysis (Varian Associates Model A-60) in $DCCl_3$ indicated that the product was ~71% I and ~29% II. The calculation of relative yields was made by comparing the areas for the aromatic hydrogens ($\delta = 7.1$ ppm from tetramethylsilane) and the total cyclohexyl hydrogens ($\delta = 1$–2.8 ppm).

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