The Deuterium Isotope Effect and Migratory Aptitudes in the Clemmensen Reduction of 1-Indanones

SUZANNE A. GALTON*[1] AND RANA ABBAS

College of Pharmaceutical Sciences, Columbia University, New York, New York 10023

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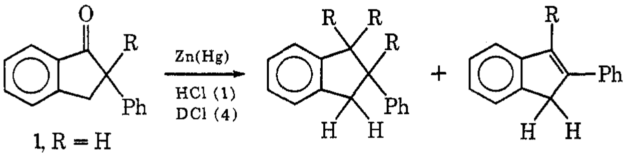
2-Phenyl-1-indanone-*2*-*d* (4) was reduced to 2-phenylindan-*1,1,2*-d_3 (5) and 2-phenylindene-*3*-d_1 (6), while 2-phenyl-1-indanone (1) under identical conditions gave 2-phenylindan (2) and 2-phenylindene (3), both in the ratio of 3:1. Kinetic measurements were carried out by following the increase in optical density for the formation of olefins. K_H/K_D was found to be 1.53. Reduction of 2-methyl-2-phenyl-1-indanone (10) gave 2-methyl-2-phenylindan (11) and 2-methyl-3-phenylindene (12), showing that the phenyl group migrated preferentially. 2,3,3-Triphenyl-1-indanone (7) under identical conditions gave 1,1,2-triphenylindan (8) and 1,1,2-triphenylindene (9). The formation of 3 and 6 shows that hydrogen migrates better than phenyl. The low isotope effect and the migratory aptitude of H > phenyl > methyl support the proposed mechanism.

In a previous paper on the reductive rearrangements of 1-indanones and 1,3-indandiones under Clemmensen conditions it was reported that rearranged indenes form sometimes as major products of the reduction along with unrearranged indans.[2] Davis and coworkers have proposed the formation of cyclopropanediol intermediates in the Clemmensen reduction of α,β-unsaturated ketones[3,4] and 1,3 diketones.[3-6] The formation of such intermediates, however, is excluded in the indan system on steric grounds. Indeed, no such intermediates, or rearranged ketonic products arising from them, have been observed. A mechanism for saturated and unsaturated hydrocarbon formation was proposed, where rearranged olefin formation occurs with hydride or phenyl migration from the 2 to the 1 position of an intermediate cation on the surface of zinc.[2] It was the purpose of this study to establish a 1,2-hydride shift in rearranged olefin formation and to study the migratory aptitudes of hydrogen, phenyl, and methyl in this system in order to gain further support for the proposed mechanism.[2] For simplicity 1-indanones were chosen for the deuterium studies, as the deuterated indene 6 uniquely arises from such a mechanism (Scheme I). Zn* denotes the zinc surface.

Results and Discussion

Clemmensen Reduction of 2-Phenyl-1-indanone (1) and 2-Phenyl-1-indanone-*2*-d_1 (4).—Deuteration of 2-phenyl-1-indanone (1) was carried out by exchange in DCl–D_2O and toluene to give 4. That the exchange was complete was confirmed by its nmr, which showed only two types of protons, methylene and phenyl protons, in the ratio of 2:9. In addition, the spectrum showed a geminal coupling constant for the C-3 protons $J_{AB} = -17.5$ Hz, $\delta_{H_B} = 214.86$ Hz, and $\delta_{H_A} = 191.14$ Hz. These results are similar to the reported nmr spectrum[7] of 2-methyl-1-indanone-*2*-d_1, which showed for the methylene protons in this AB type system a coupling constant $J_{AB} = -17.6$ Hz, $\delta_{H_B} = 152$ Hz, and $\delta_{H_A} = 192$ Hz.

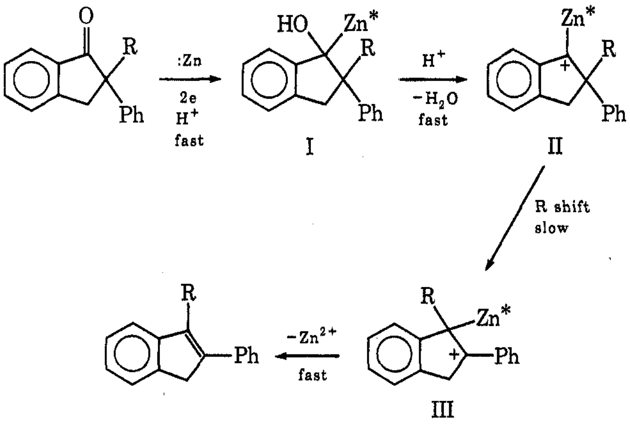


1, R = H
4, R = D

2, R = H
5, R = D

3, R = H
6, R = D

SCHEME I



Clemmensen reduction of 1 and 4 under identical conditions gave saturated hydrocarbons 2 and 5, and also olefins 3 and 6 in the ratio of 3:1, as determined by vapor phase chromatography.

The structures of 2 and 3 have already been established,[8,9] while the structures of 5 and 6 were determined by their nmr spectra. 2-Phenylindan-*1,1,2*-d_3 (5) showed a geminal coupling constant $J_{AB} = -16$ Hz, $\delta_{H_B} = 195.53$ Hz, and $\delta_{H_A} = 180.47$ Hz for the C-3 protons, while 2-phenylindene-*3*-d_1 (6) showed a 2 H singlet at δ 3.78 for the C-1 protons. Both compounds 5 and 6 showed phenyl protons at δ 7.00–7.72.

To detect any possible exchange of hydrogens in the product 2-phenylindene-*3*-d_1 (6), particularly that of the benzylic C-1 hydrogens, compound 3 (the undeuterated olefin) was subjected to Clemmensen reduction conditions in DCl–D_2O. Compound 3 was recovered unchanged as determined by its nmr.

Since according to the proposed mechanism[2] olefin formation involves a 1,2-hydride shift, the deuterium isotope effect for this reaction was determined. Rate of olefin formation was followed by ultraviolet spectroscopy. The ratio of the first-order rate constant (*i.e.*, the isotope effect) calculated (see Experimental Section) was 1.53. The deuterium isotope effect for

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[1] To whom all inquiries should be addressed.

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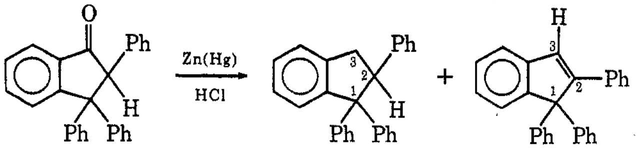
the abstraction of a proton (ionic reaction) is found to be higher, about four to ten.[10,11] It was reported by Hawthorne and Lewis[12a] that the isotope effect K_H/K_D in the hydrolysis of pyridine diphenylborane was 1.53, while Wiberg[10] in his study of the Cannizzaro reaction reported an isotope effect of 1.8. These authors have stated that as a rule small isotope effects are observed for hydride transfer reactions. In the proposed scheme for olefin formation, the rate-determining step involves a C–H bond breakage only in going from II to III. The isotope effect can be attributed only to this step. Thus the low isotope effect found in this study indicates that a hydride transfer is involved in rearranged olefin formation and is in accord with the proposed mechanism.

Reduction of 2,3,3-Triphenyl-1-indanone (7).—The reduction of this compound was undertaken to further demonstrate that the 3 position of 1-indanones is not involved in the reduction to saturated hydrocarbon as well as to rearranged olefins. Clemmensen reduction of 7 gave two components.

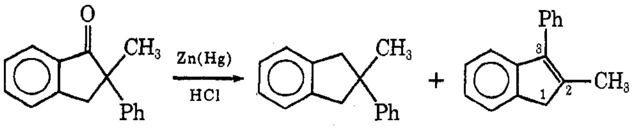


7 8 9

The first component was 1,1,2-triphenylindan (**8**) whose nmr spectrum showed a 2 H doublet at δ 3.12 for the C-1 proton (J = 8.5 Hz), a 1 H triplet at δ 4.70 for the C-2 protons (J = 8.5 Hz), and a 19 H multiplet for the phenyl protons centered at δ 6.97 (6.11–7.83). Elemental analysis was in accord with this structure.

The second component of this reduction was an indene, to which, based on spectral data, the structure of 1,1,2-triphenylindene (**9**) was assigned. This compound has not been reported in the literature. The nmr spectrum of compound **9** showed a complex multiplet at δ 7.03 (6.50–7.53) for the phenyl protons, which includes the vinylic C-3 proton.

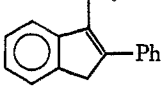
Reduction of 2-Methyl-2-phenyl-1-indanone (10).—From the reduction of 2-methyl-2-phenyl-1-indanone (**10**) the compounds 2-methyl-2-phenylindan (**11**) and 2-methyl-3-phenylindene (**12**) were obtained in the ratio of 3:1, as determined by vapor phase chromatography, along with some unchanged starting material. Separation of the first component **11** was achieved by column chromatography, followed by distillation of the petroleum ether (bp 30–60°) fraction. The nmr spectrum (in CCl_4) showed a geminal coupling constant $J_{AB} = -15$ Hz, $\delta_{H_B} = 198.82$ Hz, and $\delta_{H_A} = 180.58$ Hz (C-1 protons); $J_{AB} = -15$ Hz, $\delta_{H_B} = 198.82$ Hz, and $\delta_{H_A} = 180.58$ Hz (C-3 protons), indicating that the protons on C-1 and C-3 are equivalent; a 3 H singlet for C-2 methyl protons at δ 1.31 and a 9 H multiplet at δ 7.10 (6.83–7.41) for the phenyl protons. Elemental analysis further confirmed this compound to be **11**.



10 11 12

The second component, believed to be 2-methyl-3-phenylindene (**12**), could not be isolated from the reduction mixture as a pure compound. It distilled off together with the indan **11** from which it could not be separated. It has already been reported that 2-phenyl-3-methylindene (**13**) is a solid (lit.[13] mp 75–77°) and that 2-methyl-3-phenylindene (**12**) is an oil [lit.[14] bp 149–150° (0.5 mm).

The ultraviolet spectrum indicated the presence of olefin **12**, showing a λ_{max} at 267 nm. This was different from the uv spectrum observed for 2-phenyl-3-methylindene (**13**), which showed λ_{max} at 293 nm (reported[14] for **13** λ_{max} 293 nm and for **12** λ_{max} 263 nm).



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In addition it was shown by vapor phase chromatography that the olefin **12** obtained in this reduction mixture was not identical with 2-phenyl-3-methylindene (**13**), which was prepared independently,[15] as shown by their different retention times. Thus, it is believed that the olefin obtained in this reduction mixture was 2-methyl-3-phenylindene (**12**), as predicted by the proposed mechanism.[2] Migration of both groups from the C-2 carbon have not been observed in previous reductions and seem unlikely.

Relative migratory aptitudes to a carbonium ion in the pinacol system have been described to be in the order of hydrogen > aryl > alkyl group.[16] That a phenyl group migrated preferentially to an alkyl group was also shown in the acid-catalyzed dehydration of indanols.[14] Thus, where C-2 is disubstituted, there is a competition between an aromatic substituent and an alkyl substituent to migrate to C-3. Generally, the migration of the aromatic radical is observed.[14] This is the case noted in the dienone–phenol[17] rearrangement, in the dehydration of pinacols,[18] and in solvolysis.[19]

That hydrogen migrates preferentially to phenyl was shown by the formation of 2-phenylindene (**3**)[2] as the only olefin formed from the reduction of 2-phenyl-1-indanone (**1**). It was further found in this study that phenyl migrated rather than methyl in the formation of 2-methyl-3-phenylindene (**12**) from 2-methyl-2-phenyl-1-indanone (**10**). Thus, it was shown that under Clemmensen conditions phenyl migrated better than methyl and hydrogen migrated better than phenyl, indicating that hydrogen migration occurs with a pair of electrons (hydride shift). The possibility exists of these rearrangements occurring in a nonlinear activated complex where the C–H bending rather than the

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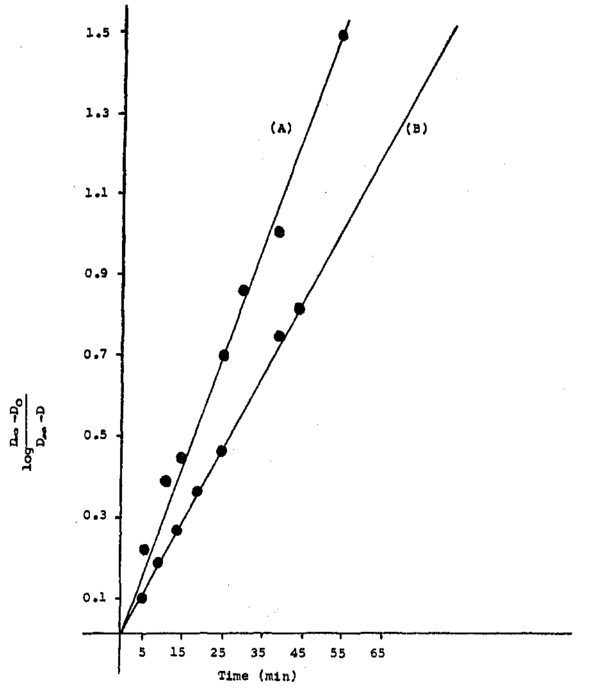

Figure 1.—Rate of olefin formation in the Clemmensen reduction of 2-phenyl-1-indanone (curve A) and 2-phenyl-1-indanone-*2*-d_1 (curve B).

stretching frequencies are dominant.[12] Such complexes would give rise to low K_H/K_D values. The above migratory aptitudes, however, support a hydride transfer mechanism.

Alcohols as intermediates have not been rigorously excluded from the proposed mechanism for reduction of above ketones. However, the preliminary vpc studies following the course of reaction from beginning to end do not show the appearance of any such intermediates. Further, more detailed studies on the nature of other possible intermediates are now being conducted.

Experimental Section

Infrared spectra were determined on a Perkin-Elmer 421 spectrophotometer. Ultraviolet spectra were run on a Perkin-Elmer 202 spectrophotometer. Nmr spectra were run on a A-60 spectrometer. Vapor phase chromatographic analyses were obtained on a F & M gas chromatograph. Melting points were determined on a Thomas-Hoover melting point apparatus. For kinetic measurements a Beckman D. U. spectrophotometer was used. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Starting Materials.—2-Phenyl-1,3-indandione and 2,3-diphenyl-1-indenone (for the preparation of 7) were purchased from Aldrich Chemical Co., Milwaukee, Wis. 1,2,2-Trichloropropane was obtained from K & K Laboratories, Plainview, N. Y. Deuterium chloride (38% in D_2O) and deuterium oxide (99.8% D) were purchased from Mallinckrodt Chemical Works, St. Louis, Mo.

2-Phenyl-1-indanone (1)[20] was prepared by the $AlCl_3$-catalyzed cyclization of 2,3-diphenylpropanoyl chloride,[21] mp 74–76° (lit.[22] mp 76–78°), and was purified by recrystallization from methanol.

2-Phenylindene (3) and 2-phenylindan (2) were prepared by the Clemmensen reduction of 2-phenyl-1,3-indandione.[2]

2,3,3-Triphenyl-1-indanone (7) was prepared by the procedure of Koelsch,[23] nmr ($CDCl_3$) δ 5.13 (1 H, singlet, C-2 protons) and 7.17 (6.30–8.05) (19 H, multiplet, phenyl protons).

2-Methyl-2-phenyl-1-indanone (10) was prepared according to Bruson and Plant,[15] nmr (CCl_4) J_{AB} = −17.5 Hz, δ_{H_B} = 212.78 Hz, and δ_{H_A} = 193.22 Hz (C-3 protons), δ 7.34 (6.86–7.83) (9 H, multiplet, phenyl protons), 1.54 (3 H, singlet, methyl protons).

2-Phenyl-3-methylindene (13) was prepared in accord with the procedure of Blum-Bergman,[13] nmr (CCl_4) δ 1.80 (3 H, triplet, methyl protons, J = 2 Hz), 3.16 (2 H, quartet, C-1 protons, J = 2 Hz), 6.92 (6.54–7.30) (9 H, multiplet, phenyl protons). Similar methyl triplets at 2.2–2.5 ppm and methylene quartets at 3.6–3.8 ppm (J = 2 Hz) have been reported for other methyl indenes.[20,24]

Preparation of 2-Phenyl-1-indanone-*2*-d_1 (4).—To a solution of 15 g (72 mmol) of 2-phenyl-1-indanone (1) in 60 ml of toluene was added 21 ml of D_2O (99.8% D) and 45 ml of DCl (38% in D_2O) with constant stirring at room temperature. The reaction mixture was refluxed overnight (24 hr). The organic phase was washed twice with D_2O and evaporated, thus leaving a cream-colored solid (14.8 g, 70 mmole, 97.2%) of 4, mp 74–76°.

Clemmensen Reductions. 2-Phenyl-1-indanone-*2*-d_1 (4).—A solution of 1 g of mercuric chloride in 15 ml of D_2O (99.8% D) was acidified with 0.5 ml of DCl (38% in D_2O). To this solution was added 10 g of granular zinc. After 15 min of stirring, the liquid was decanted and the residual amalgamated zinc was washed with D_2O. To this zinc amalgam was added a solution of 5 g (23 mmol) of 2-phenyl-1-indanone-*2*-d_1 (4) in 40 ml of toluene, 7 ml of D_2O, and 45 ml of DCl. The reaction mixture was refluxed overnight. The pale yellow toluene phase was then separated. Vapor-phase chromatography of this toluene phase of the reduction mixture on a polyethylene ether column (programming from 100 to 230° at 8°/min temperature rise) showed two peaks in the ratio of 3:1.

After the toluene was removed under reduced pressure, separation of the two components was achieved by column chromatography using Florisil (550 g, 100–200 mesh). In the petroleum ether fraction, after evaporation of the solvent, shiny white flakes were observed suspended in an oily medium. On addition of 5 ml of cold petroleum ether, shiny white flakes crystallized out and the colorless oil, after evaporation of the solvent, was distilled *in vacuo* (2 mm, 147–157°) [3.75 g (19 mmol), 75%, calculation based on vpc ratio]. Vpc retention time proved this compound to correspond to the first peak, which was identified as 2-phenylindan-*1,1,2*-d_3 (5), nmr (CCl_4) J_{AB} = 16 Hz, δ_{H_B} = 195.53 Hz, and δ_{H_A} = 180.47 Hz (C-3 protons), δ 7.13 (7.00–7.26) (9 H multiplet, phenyl protons).

Anal. Calcd for $C_{15}H_{11}D_3$: C, 91.31; H, 5.62. Found: C, 91.25; H,5.98.

The second component (shiny white flakes) was recrystallized from 20 ml of benzene, mp 165–166°. This compound had identical retention time with that of the second peak of the reaction mixture, and was identified as 2-phenylindene-*3*-d_1 (6) [1.25 g (6 mmol), 25%, calculations based on vpc ratio], nmr (CCl_4) δ 3.78 (2 H, singlet, C-1 protons), 7.35 (9 H, multiplet, phenyl protons).

Anal. Calcd for $C_{15}H_{11}D$: C, 93.21; H, 5.74. Found: C, 90.99, 92.77, 92.45; H, 5.93, 5.75, 6.71.

2-Phenylindene (3) in D_2O and DCl.—This reaction was run under the same conditions as described above. After 24-hr reaction the organic layer was separated. Analyses of the yellow toluene phase by vpc gave one peak with the same retention time as that of the starting material, mp 166–168° (lit.[9] mp 167.5°). The infrared and nmr spectra were identical with that of the unchanged starting 2-phenylindene (3).

2,3,3-Triphenyl-1-indanone (7).—The same reduction procedure was followed as described above, using H_2O–HCl instead of D_2O–DCl.

Thin layer chromatography of the toluene phase (MN silica gel S-HR, UV_{254} plates) showed two components in the reaction mixture which were separated by column chromatography using Florisil (550 g, 100–200 mesh). The petroleum ether fraction gave 1.3 g (3 mmol, 26%) of a white solid, identified as 1,1,2-triphenylindan (8), mp 134–135°.

Anal. Calcd for $C_{27}H_{22}$: C, 93.59; H, 6.40. Found: C, 93.47; H, 6.60.

The second component, 2,3,3-triphenylindene (9), was present in the petroleum ether–benzene (1:1) eluate. The light green solid was crystallized from 30 ml of benzene to give 0.2 g (0.5 mmol, 4%) of 2,3,3-triphenylindene (9).

2-Methyl-2-phenyl-1-indanone 10.—The same procedure for

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reduction was followed as described above. The toluene phase of the reduction mixture was found to be composed of three components in the ratio of 3:1:2.7 as detected by vpc on a polyethylene glycol column (programmed from 100 to 230° at 8°/min temperature rise). Chromatography on Florisil gave in the petroleum ether fraction two components, whose vpc retention time corresponded to that of the first two peaks of the reduction mixture, compounds **11** and **12**. The infrared spectrum of this mixture showed only hydrocarbon peaks. The ultraviolet spectrum indicated the presence of an olefin showing λ_{max} at 267 nm.

After removal of the solvent, 2-methyl-2-phenylindan (**11**) was obtained as a colorless oil [3.3 g (15 mmol), 44.7%, calculation based on vpc ratio] and was distilled *in vacuo* (0.5 mm, 90°). Vpc retention time proved this compound to be the first peak.

Anal. Calcd for $C_{16}H_{16}$: C, 92.30; H, 7.69. Found: C, 92.28; H, 7.77.

Various methods were employed to effect the isolation of the second component, 2-methyl-3-phenylindene (**12**). Among these were fractional distillation as well as separation by vpc on an Apiezon L preparative column, all of which proved fruitless.

It was shown, however, by vapor phase chromatography that the olefin **12** obtained in this reduction mixture was not identical with 2-phenyl-3-methylindene (**13**) which was prepared independently, as shown by their different retention times. Thus, it is concluded that the olefin obtained in this reduction mixture is the other isomer, 2-methyl-3-phenylindene (**12**), as predicted by the proposed mechanism.[2]

The third component was obtained from the petroleum ether-benzene (1:1) eluate, and was identified as starting ketone 2-methyl-2-phenyl-1-indanone (**10**) [3.0 g (13 mmol), 40%, calculation based on vpc ratios].

Kinetic Studies in the Clemmensen Reduction of 2-Phenyl-1-indanone-*2*-*d*₁ (4) and 2-Phenyl-1-indanone (1).—The two reactions below were run under identical Clemmensen conditions.

To a solution of 0.5 g of mercuric chloride in 7.5 ml of D_2O (99.8% D) and 0.25 ml of DCl (38% in D_2O) there was added 5 g of granular zinc. After 15 min of stirring, the liquid was decanted and the amalgamated zinc was washed twice with D_2O. To this zinc amalgam there was added a solution of 2.5 g (11 mmol) of 2-phenyl-1-indanone-*2*-d_1 (**4**) in 20 ml of toluene, 3.5 ml of D_2O, and 22.5 ml of DCl.

The undeuterated ketone (**1**) was subjected to identical Clemmensen conditions at the same time.

Kinetic measurements were carried out by following the increase of the uv absorption of 2-phenylindene-**3**-d_1 (**6**) and 2-phenylindene (**4**), respectively, at 315 nm. Aliquots of 0.100 ml were taken from the reaction mixture at different times and diluted with methanol to obtain an optical density reading of 0.3–0.8; these readings were then converted to a common volume (50 ml).

The change of optical density (*D*) with time was measured. The first-order rate constants were calculated from the following equation.

$$K = \frac{1}{t} \ln \frac{D_\infty - D_0}{D_\infty - D}$$

$$K_H = 6.490 \times 10^{-2}\ \text{sec}^{-1};\ K_D = 4.146 \times 10^{-2}\ \text{sec}^{-1}$$

A graph of log $(D_\infty - D_0)/(D_\infty - D)$ *vs.* time (see Figure 1) gave a straight line, indicating that the reaction is first order under these conditions. From the slopes of the lines K_H and K_D were obtained. K_H/K_D was found to be 1.53. This represents the average of four runs.

Registry No.—**4**, 39253-52-6; **5**, 39253-53-7; **6**, 39253-54-8; **7**, 39253-55-9; **8**, 39253-56-0; **10**, 10474-32-5; **11**, 39253-58-2.

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Modified Birch Reductions. Lithium in *n*-Alkylamines

HAROLD KWART* AND RICHARD A. CONLEY

Department of Chemistry, University of Delaware, Newark, Delaware 19711

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p-Methoxyanisole, *p*-methylanisole, *p*-*tert*-butylanisole, *N*,*N*-dimethyl-*p*-toluidine, and *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine were reduced using lithium–*n*-propylamine–*tert*-butyl alcohol reagent. The anisoles gave results equivalent to the Birch (liquid ammonia) reductions while the anilines gave mainly the tetrahydro derivatives. In the reduction of *p*-di-*tert*-butylbenzene and *p*-dicyclohexylbenzene using lithium–ethylamine–ethyl alcohol the principal respective products were 1,4-di-*tert*-butyl-1,4-cyclohexadiene and 1,4-dicyclohexyl-1,4-cyclohexadiene. This procedure may provide a general approach for preparing many cyclohexadiene derivatives in good yield and purity, which have not been accessible by any simple methods described hitherto. Upon reduction of 2,3-dimethylnaphthalene with lithium–ethylamine–ethyl alcohol the tetrahydro derivative 2,3-dimethyl-1,4,5,8-tetrahydronaphthalene was formed as the major product. The reduction of *p*-di-*tert*-butylbenzene with lithium–ethylamine provided an improved synthesis of 1,4-di-*tert*-butylcyclohexene, while reduction of *p*-diisopropylbenzene afforded 1,4-diisopropylcyclohexene; 1,4-dicyclohexylcyclohexene and 1,4-dimethylcyclohexene were also prepared using lithium–ethylamine.

The Birch reduction of aromatic compounds to the corresponding dihydro compounds by use of alkali metals and alcohols in liquid ammonia is a very useful synthetic procedure. In laboratories where Birch reductions are not frequently run, the use of an alkylamine, such as ethyl- or *n*-propylamine, as the solvent would be safer and more convenient than liquid ammonia. Benkeser[1] has previously reported that the reduction of ethylbenzene, cumene, *tert*-butylbenzene, and anisole using lithium–methylamine–alcohol combinations gave yields comparable with those of the Birch reductions. The purpose of this work was to investigate the synthetic scope and limitations of reductions of para-substituted aromatics with lithium–alkylamine–alcohol combinations and lithium–alkylamine combinations.

Reduction of Para-Substituted Anisoles.—The results obtained on reduction of *p*-methoxyanisole (**1**), *p*-methylanisole (**3**), and *p*-*tert*-butylanisole (**5**) to the corresponding 1-methoxy-4-substituted 1,4-cyclohexadienes using lithium–*n*-propylamine–*tert*-butyl alcohol are summarized in Table I. Preliminary experiments on the reduction of **1** indicated that the concentration of lithium and the presence of alcohol were the most

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(1) R. A. Benkeser, *et al.*, *J. Org. Chem.*, **28**, 1094 (1963). For a comprehensive treatment of Birch reductions and metal–amine reductions, several reviews on both theoretical and synthetic aspects exist in the literature: R. L. Augustine, "Reduction: Techniques and Applications in Organic Synthesis," Marcel Dekker, New York, N. Y., 1968; A. J. Birch, *Quart. Rev.* (*London*), **4**, 69 (1950); A. J. Birch and H. Smith, *ibid.*, **12**, 17 (1958); H. Smith, "Organic Reactions in Liquid Ammonia," Vol. 1, part 2, Wiley, New York, N. Y., 1963; R. G. Harvey, *Synthesis* **4**, 161 (1970); A. J. Birch and G. Subba Rao, *Advan. Org. Chem.*, **8**, 1 (1971); E. M. Kaiser, *Synthesis*, **8**, 391 (1972).