

propionyl chloride (3 mL, 35 mmol). An aliquot (1 mL) was pipetted out at an interval of 15 min, added to  $\text{CCl}_4$  (1 mL) and  $\text{CHCl}_3$  (0.1 mL), and analyzed by means of NMR. The yields were calculated by the NMR area ratio of the proton of  $\text{CHCl}_3$  and the  $\alpha$ -proton of the product.

The second-order rate constants were calculated by using the conversion curves and the rate equation shown in eq 5, where subscripts 0 and  $t$  mean initial and any times, respectively.

$$v = k([\text{CH}_3\text{CH}_2\text{CO}_2\text{H}]_0 - [\text{CH}_3\text{CHICO}_2\text{H}]_t)([\text{I}_2]_0 - [\text{I}_2]_t) \quad (5)$$

#### Kinetics of the Reaction of Propionyl Chloride with ICl

A typical kinetic procedure for  $\alpha$  iodination of propionyl chloride with ICl was as follows. An EDC solution of ca. 0.2 M ICl was heated under a reflux condenser in a thermostated flask, and propionyl chloride (1 or 2 mL) was added by pipet. An aliquot (1 mL) was taken out at appropriate intervals of time, poured into aqueous KI- $\text{H}_2\text{SO}_4$ , and titrated with 0.01 N  $\text{Na}_2\text{S}_2\text{O}_3$  to follow the consumption of ICl. The volume change on addition of propionyl chloride (sp gr 1.0646) was taken into account for the calculation of reactant concentrations.

**Acknowledgment.** We are grateful to Whei-Ing Woo for her helpful assistance in the kinetic experiments and preparation of manuscripts and also to Tsong Ueng for his pertinent advice in conducting experiments. Financial support from National Science Council, ROC, and the Japanese Ministry of Education is gratefully acknowledged.

**Registry No.**  $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$ , 79-09-4;  $\text{CH}_3\text{CH}_2\text{COCl}$ , 79-03-8; *trans*- $\text{PhCH}=\text{CHCO}_2\text{CH}_3$ , 1754-62-7;  $\text{SOCl}_2$ , 7719-09-7;  $\text{I}_2$ , 7553-56-2; ICl, 7790-99-0;  $\text{PhCHClCHICO}_2\text{CH}_3$ , 87207-03-2.

### Metal-Ammonia Reduction of 1-Acetylnaphthalenes

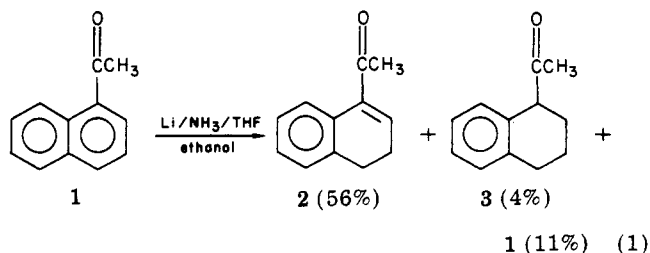
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Received March 15, 1983

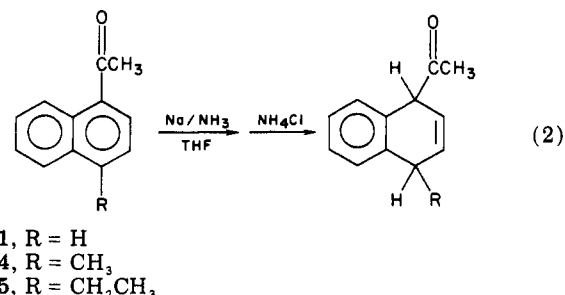
Although the reduction of aromatic rings by metal-ammonia solutions is a general method for the preparation of the corresponding dihydroaromatic structures, application to aryl ketones is often accompanied by partial or complete reduction of the carbonyl.<sup>1</sup> For example, acetophenone is reduced to ethylbenzene under normal reduction conditions even though the use of cation-exchange techniques facilitates reductive alkylation, providing 1-alkyl-1,4-dihydroacetophenones in fair to good yields.<sup>1</sup>

Some polynuclear ketones may be reduced without loss of the carbonyl group, and 1-acetylnaphthalene has recently received a considerable amount of attention.<sup>2-6</sup> In one report,<sup>2</sup> a detailed product analysis was given, and the 3,4-dihydro derivative **2** was indicated as the major product (56%, eq 1). The same conjugated product was also in-



dicated in a very recent report, and although other products were not mentioned, the yield of **2** was 75%. In any event, 1-acetyl-3,4-dihydronaphthalene appears to be generally accepted<sup>2-6</sup> as the usual reduction product of 1-acetylnaphthalene without mention of any detection of the expected<sup>7</sup> 1,4-dihydro product. This prompts us to report our results which indicate that rapid quenching techniques can, in fact, produce this latter 1,4-dihydro isomer exclusively.

We have found that the sodium-ammonia reductions of **1** and its 4-methyl (**4**) and 4-ethyl (**5**) derivatives provide the corresponding 1,4-dihydro products<sup>8</sup> in essentially quantitative yields<sup>9</sup> (eq 2). These products are quite



stable, and we have not noted any unusually facile conversion to the conjugated isomers such as **2**. These compounds can be purified by vacuum distillation or steam distillation, although the latter process does produce a little rearomatization. However, no trace of the conjugated isomers was detected by either process.

The marked contrast to previous results warrants some attempt at explanation, and a careful comparison of reaction conditions must be made. Although we obtained good results under all of the conditions which we employed, we did observe an improvement proceeding as follows from a to c: (a) rapid quenching with aqueous  $\text{NH}_4\text{Cl}$ , (b) inverse quenching into aqueous  $\text{NH}_4\text{Cl}$ ,<sup>10</sup> and (c) addition of 1.5 equiv of  $\text{H}_2\text{O}$  before the addition of the sodium.<sup>11</sup> The latter method ensures efficient conversion to the monoanion **6** (eq 3) which is resistant to side reactions sometimes observed with radical anions (e.g., dimerization). An inverse quench also quickly eliminates the presence of strong base which could cause subsequent isomerization.<sup>11</sup>

(7) (a) Birch, A. J. *Q. Rev., Chem. Soc.* 1950, 4, 69. (b) House, H. O. "Modern Synthetic Reactions", 2nd ed.; W. A. Benjamin: Los Angeles, 1972. (c) Harvey, R. G. *Synthesis* 1970, 4, 161. (d) Birch, A. J.; Subba Rao, G. "Advances in Organic Chemistry, Methods and Results"; Taylor, E. C., Ed.; Wiley-Interscience: New York, 1972.

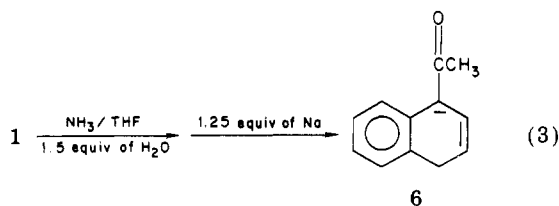
(8) Both *cis* and *trans* products are formed with **4** and **5**. The stereochemistry of reduction (as well as the conformational analysis of products) of a variety of naphthalene and anthracene ketones and esters is the subject of current research.

(9) NMR analysis of the crude reaction mixture shows no other products. However, some material is lost in isolation (see Experimental Section).

(10) We have previously reported on the importance of the quenching process and the general usefulness of an inverse quench: Rabideau, P. W.; Burkholder, E. G. *J. Org. Chem.* 1978, 43, 4283.

(11) The presence of water before the addition of metal has provided a method for the ring reduction of benzoate esters. Rabideau, P. W.; Huser, D. L.; Nyikos, S. J. *Tetrahedron Lett.* 1980, 21, 1401.

(1) Narisada, M.; Watanabe, F. *J. Org. Chem.* 1973, 38, 3887.  
(2) Mejer, S.; Pacut, R. *Pol. J. Chem.* 1978, 52, 529.  
(3) Mejer, S.; Marcinow, Z. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* 1976, 24, 175.  
(4) Subba Rao, G. S. R.; Shyama Sundar, N. *J. Chem. Soc., Perkin Trans. 1* 1982, 875.  
(5) Radhakrishna Murthy, A.; Shyama Sundar, N.; Subba Rao, G. S. R. *Tetrahedron* 1982, 38, 2831.  
(6) Shyama Sundar, N.; Subba Rao, G. S. R. *J. Chem. Soc., Perkin Trans. 1* 1982, 1381.



The results of ref 2 are easily explained since these workers used ethanol as a quenching agent. As we have previously pointed out,<sup>10</sup> ethanol should never be used as a quenching agent or cosolvent for metal-ammonia reductions unless it is required to shift the initial equilibrium<sup>7,10</sup> (i.e., benzene and its derivatives). Ethanol does not destroy excess metal fast enough, and it generates ethoxide which can cause isomerizations. Isomerization in the presence of the aforementioned excess metal also leads to overreduction in many cases.<sup>12</sup>

The results of ref 4 were initially more difficult to explain. These workers state that reductions were performed with lithium, sodium, or potassium in ammonia/THF (5:1) with ammonium chloride, sodium benzoate, or absolute ethanol as a quenching agent and that all of these reactions produced the 3,4-dihydro isomer, presumably due to unavoidable isomerization during workup. However, as we have noted, the 1,4-dihydro isomer has no tendency to isomerize during normal workup (ether partition). We carried out a reduction under one set of their conditions [Na, NH<sub>3</sub>/THF (5:1), 30 min at -33 °C, solid NH<sub>4</sub>Cl quench] and again obtained only the 1,4-dihydro isomer, although in somewhat lower yields. Unfortunately, they did not provide exact details of any single representative reaction, and a later, general comment in the Experimental Section leads us to believe that ethanol may also have been present as a cosolvent. This would, of course, explain the isomerization. We cannot emphasize too strongly that the presence of ethanol as a cosolvent (i.e., traditional Birch reduction) can cause substantial changes in the outcome of metal-ammonia reductions. In fact, when ethanol is used as a cosolvent with polynuclear systems, it serves as an internal quench, and the choice of the ultimate "quenching agent" is relatively unsequential.

### Experimental Section

NMR spectra were recorded on Varian EM-390 (90 MHz, proton) and CFT-20 (20 MHz, carbon-13) spectrophotometers. Microanalyses were performed by Galbraith Laboratories, Inc.

**Metal-Ammonia Reduction. General Procedure.** Ammonia was passed through a barium oxide drying chamber, condensed into a three-necked flask under a pressure of helium gas, and cooled with a dry ice/acetone bath.<sup>13</sup> The aromatic substrate

(12) These same problems were encountered with the metal-ammonia reduction of 1-naphthoic acid. See: Rabideau, P. W.; Burkholder, E. G.; Yates, M. J. *Synth. Commun.* 1980, 10, 627.

dissolved in THF (freshly distilled from sodium benzophenone ketyl) containing 1.5 equiv of H<sub>2</sub>O was then added followed by the metal (2.5 mmol/mmol of substrate) in pieces. After 30 min the reaction mixture was pumped into a large excess of aqueous NH<sub>4</sub>Cl. Products were isolated by ether extraction and vacuum distilled. In some cases, a small impurity (NMR, singlet ca.  $\delta$  2.2–2.7) was carried through the distillation. This may be a result of relatively little fractionation due to small sample size.<sup>14</sup> However, the impurity could be subsequently removed by column chromatography. It should also be noted that the yields reported were lowered due to unavoidable loss in distilling small samples<sup>14</sup> and that the overall conversions as indicated by the NMR spectrum of the crude reaction products appear to be 95–98%.

**1-Acetyl-1,4-dihydronaphthalene.** 1-Acetylnaphthalene (1.1 g) was reacted with sodium (1.2 equiv) in 25 mL of THF and 50 mL NH<sub>3</sub><sup>14b</sup> containing 1.5 equiv of H<sub>2</sub>O according to the general procedures to produce a colorless oil: 0.76 g (68% yield, after vacuum distillation); bp 115 °C (3 torr); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  206.4 (C=O), 132.4, 130.7, 127.8, 127.4, 126.9, 126.5, 125.6, 122.3, 55.5 (d in off resonance), 28.8 (t in off resonance), 25.0 (q in off resonance); <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  7.1 (m, 4 H), 5.9 (AB, 2 H), 4.2 (apparent q, 1 H), 3.4 (m, 2 H), 1.8 (s, 3 H). Anal. Calcd for C<sub>12</sub>H<sub>2</sub>O: C, 83.72; H, 6.98. Found: C, 83.98; H, 6.88.

**1-Acetyl-4-methyl-1,4-dihydronaphthalene.** 1-Acetyl-4-methylnaphthalene (1 g) was reduced with sodium (1.2 equiv) according to the general procedure in 25 mL of THF and 50 mL of NH<sub>3</sub> containing 1.5 equiv of H<sub>2</sub>O to afford a colorless oil: 60% yield (after distillation); bp 82 °C (5 torr); NMR (CCl<sub>4</sub>)  $\delta$  7.15 (m, 4 H, Ar), 5.9 (AB, 2 H, vinyl), 4.2 (m, 1 H), 3.5 (m, 1 H), 1.9 and 1.8 (acetyl singlets, total 3 H),<sup>15</sup> 1.2 (d, 3 H). Anal. Calcd for C<sub>13</sub>H<sub>14</sub>O: C, 83.83; H, 7.58. Found: C, 83.96; H, 8.05.

**1-Acetyl-4-ethyl-1,4-dihydronaphthalene.** 1-Acetyl-4-ethylnaphthalene (1 g) was reduced with sodium (1.2 equiv) according to the general procedure in 25 mL of THF and 50 mL of NH<sub>3</sub> containing 1.5 equiv of H<sub>2</sub>O to afford a colorless oil: 62% yield (after distillation); bp 110 °C (0.4 torr); NMR (CCl<sub>4</sub>)  $\delta$  7.1 (m, 4 H), 5.9 (m, 2 H), 4.2 (m, 1 H), 3.3 (m, 1 H), 1.6–2.6 (CH<sub>2</sub> resonances),<sup>16</sup> 1.75 and 1.93 (acetyl singlets),<sup>16</sup> 0.9 and 0.7 (methyl triplets).<sup>16</sup> Anal. Calcd for C<sub>14</sub>H<sub>16</sub>O: C, 83.96; H, 8.05. Found: C, 83.73; H, 8.13.

**Acknowledgment.** We thank the U.S. Department of Energy, Office of Basic Energy Science, for support of this work.

**Registry No.** 1, 941-98-0; 4, 28418-86-2; 5, 58149-62-5; 1-acetyl-1,4-dihydronaphthalene, 56282-10-1; 1-acetyl-4-methyl-1,4-dihydronaphthalene, 87191-34-2; 1-acetyl-4-ethyl-1,4-dihydronaphthalene, 87191-35-3.

(13) The reduction of 1 gave best results at reflux temperature (-33 °C), whereas little difference was noted for 4 and 5 at either -33 °C or -78 °C.

(14) (a) Relatively small samples were reduced due to lack or expense of starting materials. 4 and 5 were prepared by Friedel-Crafts acylation of the corresponding alkylnaphthalenes. (b) Running with very high dilution seems to avoid trace impurities which are sometimes found with normal dilution (25 mL THF/50 mL of NH<sub>3</sub>).

(15) These are the only signals for this cis/trans mixture which do not overlap (see ref 8).

(16) With this compound, CH<sub>3</sub>, CH<sub>2</sub>, and CH<sub>3</sub>CO show separated signals for each isomer. The CH<sub>2</sub> resonance is not clearly defined, however, due to serious overlap with CH<sub>3</sub>CO (see ref 8).