

chloride, and dried with  $MgSO_4$ . The methylene chloride was removed at reduced pressure and the residue washed with several portions of ether, leaving behind a white solid ( $Bu_4NI$ ). The ethereal solution upon evaporation afforded 0.36 g (97%) 3-methyl-1-phenyl-2,4-pentanedione.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  7.4-8.1 (m, 5 H, Ar), 4.5 (q, 1 H,  $CHCH_3$ ), 2.2 (s, 3 H,  $COCH_3$ ), 1.5 (d, 3 H,  $CHCH_3$ ).

Bis(siloxy) diene **3c** (0.035 mmol) in 0.5 mL of  $THF-d_8$  was treated first with  $Bu_4NF$  (0.035 mmol) at 20 °C followed by addition of complex **1** (0.035 mmol) at -78 °C. After warming to 20 °C over a period of 1 h the solution was homogeneous (orange), and its  $^1H$  NMR spectrum was identical with that obtained directly from **1** and **3c** (vide infra).

**In Situ NMR of 1 + 3c Reaction.** To a  $THF-d_8$  suspension (0.5 mL) of 0.035 mmol of (butadiene)tricarbonyl cobalt tetrafluoroborate was added an equimolar quantity of 1,3-bis(trimethylsiloxy)-1-phenyl-1,3-butadiene at -78 °C. The mixture was allowed to warm to 20 °C over a period of 3 h, at which time the solution was homogeneous.  $^1H$  NMR ( $THF-d_8$ )  $\delta$  8.0 (m), 7.51 (m), 6.32 (m), 5.17 (d,  $J = 16$  Hz), 5.05 (d,  $J = 9$  Hz), 2.04 (s), 1.94 (s), 1.28 (s), 0.90 (s), 0.20 (s), 0.18 (s), 0.11 (s), 0.06 (s), 0.02 (s), -0.095 (s), -0.15 (s). Irradiation at  $\delta$  6.32 caused collapse of the signals at  $\delta$  5.17 and 5.05 to singlets, suggesting the presence of an uncoordinated vinyl group.

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### Metal-Ammonia Reduction of $\alpha$ -Tetralone. Competition between Ring Reduction, Carbonyl Reduction, and Dimer Formation

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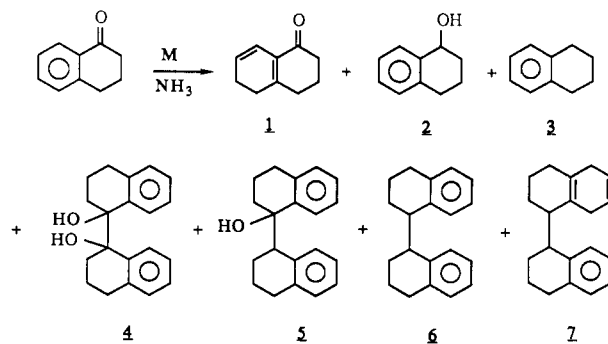
The metal-ammonia reduction of cyclic ketones has received considerable attention,<sup>1</sup> and the mechanistic aspects of this reaction have been somewhat controversial.<sup>1c,d</sup> The incorporation of additional unsaturation present in aryl ketones provides greater complexity since, in principle, reduction may occur either at the carbonyl group or in the aromatic ring. In fact the reduction of aryl ketones to alcohols and/or hydrocarbons has been known for some time, but nuclear reduction was first observed in 1973 by Narisada and Watanabe.<sup>2</sup> We now report our results with the metal-ammonia reduction of  $\alpha$ -tetralone that provide mechanistic insight into this complex process.

We have found that the reaction of  $\alpha$ -tetralone with alkali metal (especially lithium) in ammonia can produce as many as seven different products (1-7) including the previously unknown nuclear reduction product **1**.<sup>3</sup> Moreover, the reaction shows considerable sensitivity to conditions as illustrated in Table I.

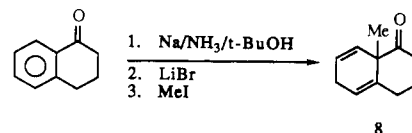
(1) For reviews, see: (a) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972. (b) Rautenstrauch, V.; Willhalm, B.; Thommen, W.; Burger, U. *Helv. Chim. Acta* 1981, 64, 2109. (c) Huffman, J. W. *Acc. Chem. Res.* 1983, 16, 399. (d) Pradhan, S. K. *Tetrahedron* 1986, 42, 6351.

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(3) Products were isolated by silica gel chromatography. New compounds (1, 3, and 5) were identified by GC/MS and NMR.



Previously, Hall et al.<sup>4</sup> reported the conversion of  $\alpha$ -tetralone to tetralin in high yield, while Narisada and Watanabe carried out the reductive methylation<sup>2</sup> affording the methyl dihydro product **8** in 60% yield. In neither case, however, was any significant amount of dimerization observed. As indicated in Table I, reduction with Li at



-78 °C provides dimeric products as the major outcome (54-84%), whereas higher temperatures (-33 °C) or the use of Na reduces dimer formation to a trace (0-2%). The method of addition was important (i.e.,  $\alpha$ -tetralone vs metal added last; methods A and B), especially at -78 °C where dimeric products increased ca. 25% when  $\alpha$ -tetralone was added last. The method of quench was also important, as noted by Hall et al.,<sup>4</sup> especially for Li at -33 °C where direct quench with  $NH_4Cl$  gives 98% tetralin and inverse quench into aqueous  $NH_4Cl$  affords the alcohol as the major product (70%).

We feel that Scheme I provides a plausible explanation for these results. The initially formed radical anion may form a dimeric ion pair of the type suggested by Huffman<sup>1c,5,6</sup> (or some other aggregate) or accept a second electron, resulting in a dianion. The presence of the aromatic ring is quite important here since the ketyl dimer should be less important (relative to aliphatic ketones) due to greater charge delocalization, and the dianion should be more stable.<sup>7</sup> Hence we suggest the ion pair dimer as the major route to dimeric products. This is consistent with the metal effect since such dimers are expected to be more important for Li than Na.<sup>5</sup> The effect of temperature may result from greater solvation of the ion dimer at lower temperature<sup>6</sup> making it more resistant to protonation.<sup>10,11</sup> Adding  $\alpha$ -tetralone last also leads to more dimer. Since at the early stage of the reaction this means excess metal, and presumably more dianions, perhaps path A of Scheme I represents the actual mode of ion dimer formation.

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(5) Hirota, N.; Weissman, S. I. *J. Am. Chem. Soc.* 1964, 86, 2538.

(6) Hirota, N. *J. Am. Chem. Soc.* 1967, 89, 32.

(7) The dianion is expected to be accessible under these conditions since the half-wave potentials for the formation of the monoanion/dianion from acetophenone, for example, are -1.99 V/-2.46 V (vs SCE),<sup>8</sup> and the reduction potentials in ammonia (at -50 °C) are -2.99 V for Li and -2.59 V for Na.<sup>9</sup>

(8) Meites, L. *Polarographic Techniques*, 2nd ed.; Wiley-Interscience: New York, 1965.

(9) Wilds, A. L.; Nelson, N. A. *J. Am. Chem. Soc.* 1953, 75, 5360.

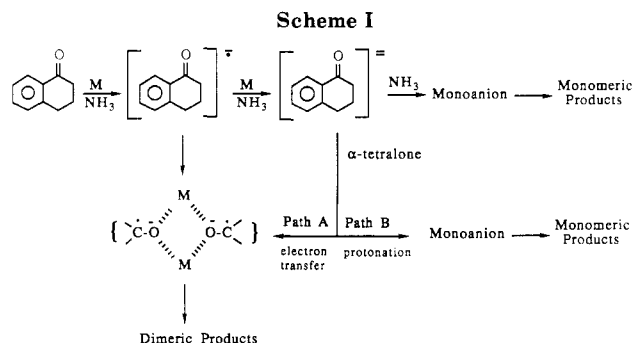
(10) *Ions and Ion Pairs in Organic Reactions*; Szwarc, M., Ed.; Wiley: New York, 1972; Vol. 1.

(11) A reviewer has suggested that dimerization might be more common at lower temperature since it is an entropically disfavored pathway.

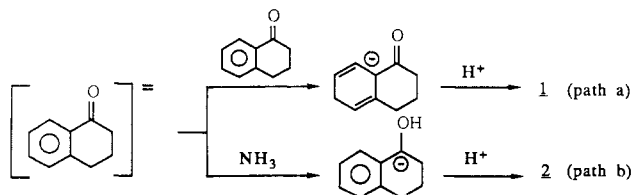
Table I. Metal-Ammonia Reduction of  $\alpha$ -Tetralone

entry	metal (amt) <sup>a</sup>	meth of addn <sup>b</sup>	temp, °C	time, h	meth of quench <sup>c</sup>	% product composition <sup>d</sup>							
						1	2	3	4	5	6	7	unreacted $\alpha$ -tetralone
1	Li (5)	A	-78	1	A			13	5	2	71	6	3
2	Li (5)	A	-78	1	B	7	8	~1	57	13	9		5
3	Li (5)	A	-33	1	A		~1	98					~1
4	Li (5)	A	-33	1	B	~1	70	13	~1				15
5	Li (5)	B	-78	1	A	8	~1	18	~1		54	2	16
6	Li (5)	B	-78	1	B	21	11	9	21	24	9		5
7	Li (5)	B	-33	1	A	11	5	70					14
8	Li (5)	B	-33	1	B	22	26	48	~2				2
9	Li (2.5)	B	-78	0.5	B	21	10	7	42	14			6
10	Na (2.5)	B	-78	0.5	B	30	56	4	~2				8
11	Na (2.5)	B	-33	0.5	B	31	49	12	~1				7

<sup>a</sup> Millimoles of metal per 1.0 mmol of  $\alpha$ -tetralone (2 mmol of metal is the minimum required for complete reduction: an overall two-electron process). <sup>b</sup> Method A:  $\alpha$ -tetralone added last. Method B: metal added last. <sup>c</sup> Method A: normal quench with solid ammonium chloride (in the several cases studied, comparable results were obtained with aqueous ammonium chloride solution). Method B: inverse quench into aqueous ammonium chloride solution. <sup>d</sup> By uncorrected GLPC with fid detector.

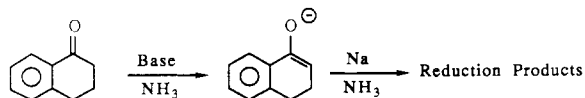


Lastly we note the competition between ring reduction and carbonyl reduction. Assuming that inverse quenching traps whatever species are present at the time, it would appear that adding metal last has the effect of increasing 1 over 2 (and 3). Since the metal is added slowly and in pieces, this procedure results in an excess of  $\alpha$ -tetralone throughout most of the reaction. Moreover, since  $\alpha$ -tetralone is by far the most acidic species present, it should be expected to protonate the dianion (path a). However,



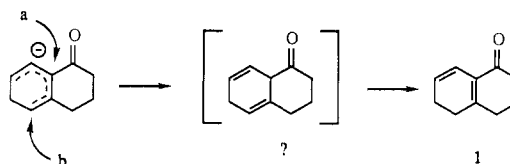
electron addition is a very rapid process, and so when  $\alpha$ -tetralone is added last (i.e., excess of metal), it is not expected to participate in the protonation process, leaving ammonia as the sole proton source (path b). Thus the interesting possibility arises that the softer acid ( $\alpha$ -tetralone) may be protonating at carbon whereas the harder acid (ammonia) may be protonating at oxygen. This would, as depicted in paths a and b, provide an explanation for the dependence of 1:2 on the order of addition.

If this is true, the process of adding ketone last would generate the enolate of  $\alpha$ -tetralone, and so *if it persisted*, one would expect substantial amounts of recovered  $\alpha$ -tetralone. Since we did not recover much starting material in these reactions, we generated the enolate separately and then reacted it with Na/NH<sub>3</sub>. This did lead to reduction



providing the alcohol as the major product (65%), some 1 (10%), and recovered  $\alpha$ -tetralone (20%). This experiment, however, does not discriminate between actual reduction of the enolate and reduction of  $\alpha$ -tetralone that may be in equilibrium with the enolate (i.e., reaction of  $\alpha$ -tetralone shifting the equilibrium). For our purposes, of course, it does not make any difference since either path consumes  $\alpha$ -tetralone and so the enolate, if formed, is not expected to survive under the reduction conditions.

We also note that the dihydro product 1 produced by reduction has a different regiochemistry from that formed by reductive methylation. It may be that protonation and methylation take place at different sites (b vs. a) or al-



ternatively, isomerization occurs after this protonation step (i.e., during quench or workup). The NMR spectrum of 1 excluded other isomers since the vinyls appeared as an AB quartet ( $J = 9.9$  Hz) with only the upfield doublet further split into triplets (i.e., adjacent to CH<sub>2</sub>). Moreover, the other vinyl is shifted downfield (6.5 ppm) as expected for its position relative to the carbonyl.

### Experimental Section

Proton NMR spectra were obtained on a 90-MHz Varian EM-390 spectrometer. Mass spectra were determined on a HP 5988A GC/MS spectrometer at an ionization potential of 30 eV. Gas chromatographic analyses (GLPC) were performed on a Tracor 500 (fid) instrument using 10% OV-101 column. The yields of metal-ammonia reductions entered in Table I were determined by GLPC and NMR. Microanalyses were performed by Galbraith Laboratories, Inc.

**General Procedure for Metal-Ammonia Reduction of  $\alpha$ -Tetralone.** All the reactions were carried out under slight pressure of dry argon. THF was distilled from sodium benzophenone ketyl immediately before use. Reactions were carried out in the following way. **Method A.**  $\alpha$ -Tetralone (5 mmol) in 10 mL of THF was added dropwise (10 min) to a solution of the metal (12.5–25 mmol; see Table I) in 20 mL of ammonia containing 10 mL of THF at reflux (-33 °C) or at dry ice bath temperature (ca. -78 °C). After the indicated reaction period, the reaction was quenched by adding solid NH<sub>4</sub>Cl followed by water (quench method A) or by pumping (or pouring) the reaction mixture into saturated ammonium chloride solution. **Method B.** The metal was added in pieces (over a few minutes) to a solution of  $\alpha$ -tetralone (5 mmol) in 20 mL of ammonia containing 10 mL of THF. After the reaction period, quenching was carried out as in method

A above. Products were isolated by ether extraction, and purification was accomplished by column chromatography on 230-400-mesh silica gel (Merck) with hexane/ethyl acetate (10:1) as solvent.

**3,4,5,6-Tetrahydro-1(2H)-naphthalenone (1):** oil (unstable; gradually rearomatizes, and so microanalysis was not possible); IR (CCl<sub>4</sub>) 1680 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>) δ 1.8-2.5 (m, 10 H), 5.75 (1 H, vinyl), 6.45 (1 H, vinyl); mass spectrum, *m/e* 148 (M<sup>+</sup>).

**1,1',2,2',3,3',4,4'-Octahydro-1,1'-binaphthyl-1,1'-diol (4):** mp 189-191 °C (lit.<sup>12</sup> mp 191 °C); NMR (CCl<sub>4</sub>) δ 1.0-1.8 (m, 8 H), 2.4-2.8 (m, 4 H), 3.1 (s, 2 H), 7.0-7.4 (m, 6 H), 8.0-8.35 (m, 2 H).

**1,1',2,2',3,3',4,4'-Octahydro-1,1'-binaphthyl-1-ol (5):** mp 92-94 °C (hexane); NMR (CCl<sub>4</sub>) δ 1.0-1.75 (m, 8 H), 1.8 (s, 1 H), 2.45-2.70 (m, 4 H), 3.65 (t, 1 H), 6.85-7.15 (m, 6 H), 7.35-7.60 (m, 1 H), 7.7-7.9 (m, 1 H); mass spectrum, *m/e* 278 (M<sup>+</sup>).

Anal. Calcd for C<sub>20</sub>H<sub>22</sub>O: C, 86.28; H, 7.96. Found: C, 86.13; H, 7.88.

**1,1',2,2',3,3',4,4'-Octahydro-1,1'-binaphthyl (6):** oil;<sup>13</sup> NMR (CCl<sub>4</sub>) δ 1.2-2.0 (m, 8 H), 2.6 (t, 4 H), 3.3 (m, 2 H), 6.7-7.0 (m, 8 H); mass spectrum, *m/e* 262 (M<sup>+</sup>).

**1,1',2,2',3,3',4,4',5,8-Decahydro-1,1'-binaphthyl (7):** colorless oil; NMR (CCl<sub>4</sub>) δ 1.15-2.05 (m, 10 H), 2.6 (m, 7 H), 3.1 (m, 1 H), 5.65 (br s, 2 H), 6.8-7.35 (m, 4 H); mass spectrum, *m/e* 264 (M<sup>+</sup>).

Anal. Calcd for C<sub>20</sub>H<sub>24</sub>: C, 90.85; H, 9.15. Found: C, 90.35; H, 9.07.

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**Registry No.** 1, 113668-50-1; 2, 529-33-9; 3, 119-64-2; 4, 3073-53-8; 5, 113668-51-2; 6, 1154-13-8; 7, 113668-52-3; α-tetralone, 529-34-0.

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## Diethyldithiocarbamic Acid S-Oxide: A New Class of Sulfine

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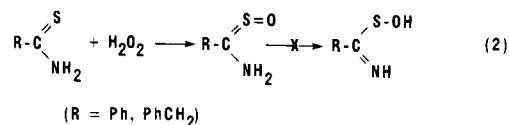
Received September 24, 1987

Sodium diethyldithiocarbamate (1a) has been widely used as a copper trapping reagent. Thus, the inhibition of an enzymatic reaction by 1a has been regarded as a proof of the participation of copper in the reaction.<sup>1</sup> However, we previously noted that the inhibitory effect of 1a on the oxygenase activity of L-tryptophan 2,3-dioxygenase was caused by its rapid reaction with hydrogen peroxide, the activator of the enzyme, instead of the chelation with copper.<sup>2</sup> While the oxidation product(s) of 1a with hydrogen peroxide has never been characterized, compounds bearing a dithiocarboxylic acid group are known as strong reducing reagents,<sup>3</sup> even sulfoxides are readily reduced to give the corresponding sulfides (eq 1).<sup>4</sup>



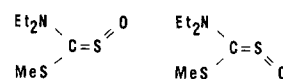
Since thiols and dithiocarboxylic acids show similar reactivity to give the corresponding disulfides in oxidation

reactions,<sup>5</sup> the dimeric form of 1a can be a candidate for the product in the reaction of 1a with hydrogen peroxide. On the other hand, the oxidation of thioamides by hydrogen peroxide is known to afford thioamide S-oxides (eq 2).<sup>6</sup> Accordingly, sodium diethyldithiocarbamate S-oxide



might be an alternative for the oxidation product. Despite many examples of sulfines<sup>7</sup> such as the S-oxides of thio-ketones,<sup>8</sup> thioaldehydes,<sup>9</sup> and dithiocarboxylic esters,<sup>10</sup> a dithiocarboxylic acid S-oxide has not been observed. In this paper, we report the first example of a new class of sulfine; i.e., a dithiocarbamic acid S-oxide formed in the oxidation of either 1a or the corresponding acid 1b by hydrogen peroxide.

The reaction of 1a and 1 equiv of hydrogen peroxide proceeded instantaneously in methanol at 0 °C to afford a sole product (2a). A time course of the UV spectral changes observed for the reaction was very similar to those observed in a phosphate buffer solution (pH 7.5).<sup>2</sup> When a mass spectroscopic measurement of 2a was made, nothing was detected. This suggested that 2a could still be a sodium salt, since 1a itself was silent in mass spectroscopy, whereas its acid form (1b) gave a good spectrum (*M* + 1 = 150 by CI method). This was also consistent with TLC (Al<sub>2</sub>O<sub>3</sub>) analysis of 2a (*R<sub>f</sub>* 0, by CHCl<sub>3</sub>). Therefore, the reaction mixture was washed with an ice-cold buffer (pH 3.3, 0.02 M) and then extracted with methylene chloride to yield 2b, the acid form of 2a. The mass spectrum of 2b indicated that it was a monooxide of 1b (Et<sub>2</sub>NCS<sub>2</sub>H + O: *M* + 1 = 166 by CI method). Oxidation of 1b by hydrogen peroxide directly produced 2b in good yield. Since 2b was not stable enough to give a high-resolution mass spectrum by the EI method, it was treated with methyl iodide, and the formation of a new compound (3) having *R<sub>f</sub>* 0.2 on TLC (Al<sub>2</sub>O<sub>3</sub>, Bz/CHCl<sub>3</sub> = 3) was observed. 3 was assigned as methyl diethyldithiocarbamate S-oxide on the basis of the following observations: (i) A high-resolution mass spectroscopic measurement of the derivative indicated the monooxide formula of methyl diethyldithiocarbamate. (ii) An IR spectrum of the derivative showed two strong bands at 960 and 1025 cm<sup>-1</sup> characteristic of a sulfine (C=S=O).<sup>11</sup> (iii) Two distinguishable methyl resonances (2.23 and 2.83 ppm, 0.63 Me: 0.37 Me) were observed in the <sup>1</sup>H NMR spectrum of 3 due to the *E* and *Z* sulfine isomers.<sup>10,12</sup> (iv) An independent



(E)-3

(Z)-3

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