

TABLE IV  
CHARACTERISTICS OF TRIALKYL PHOSPHITES PREPARED BY THE REACTION OF  
PHOSPHORUS TRICHLORIDE WITH CORRESPONDING ALCOHOLS

(RO) <sub>3</sub> P, R =	Base	Yield, %	Bp, °C (mm)	<i>n</i> <sub>D</sub> (deg)
C <sub>2</sub> H <sub>5</sub>	Diethylaniline	60	54 (17)	1.4104 (25)
<i>i</i> -C <sub>3</sub> H <sub>7</sub>		70	57 (9)	1.4049 (25)
<i>sec</i> -C <sub>4</sub> H <sub>9</sub>		70	77-78 (3.5-4)	1.4294 (25)
CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub>		80	99 (1.5)	1.4365 (25)
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	Pyridine	73	89 (10)	1.4239 (24)
<i>n</i> -C <sub>4</sub> H <sub>9</sub>		65	100-101 (4)	1.4307 (25)
<i>n</i> -C <sub>5</sub> H <sub>11</sub>		64	94-99 (1-1.5)	1.4369 (25)
<i>n</i> -C <sub>8</sub> H <sub>17</sub>		67	189-195 (1)	1.4468 (25)

TABLE V

UV SPECTRA OF DIOXAPHOSPHOLES (3) IN *n*-HEXANE

R =	Registry no.	$\lambda_{\max}$ , m $\mu$	$\epsilon_{\max}$ $\times 10^{-4}$
CH <sub>3</sub>	4850-55-9	319	1.14
C <sub>2</sub> H <sub>5</sub>	6509-75-7	323	1.18
<i>i</i> -C <sub>3</sub> H <sub>7</sub>	4850-57-1	322	1.12
<i>sec</i> -C <sub>4</sub> H <sub>9</sub>	30415-15-7	319	1.23
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	30415-16-8	321	1.28
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	30415-17-9	321	1.21
<i>n</i> -C <sub>5</sub> H <sub>11</sub>	30415-18-0	321	1.19
<i>n</i> -C <sub>8</sub> H <sub>17</sub>	30415-19-1	322	1.19
CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub>	30477-09-9	316	1.15

### Experimental Section

**Materials.**—Trialkyl phosphites were prepared by the reaction of phosphorus trichloride with corresponding alcohols in the presence of base below 15°<sup>21</sup> and purified by repeated distillations with metallic sodium under reduced pressure with nitrogen atmosphere. The characteristics of prepared trialkyl phosphites were listed in Table IV. Benzil was prepared as mentioned in our previous paper.<sup>1</sup>

(21) A. H. Ford-Moore and B. J. Perry, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 955.

2,2,2-Trialkoxy-4,5-diphenyl-1,3,2-dioxaphospholes (3) were prepared by the reaction of benzil with excess trialkyl phosphite without solvent or in anhydrous dioxane under nitrogen atmosphere at 25.0° for 3-12 hr. The structure of 3 (R = Me) was confirmed by ir, nmr, and uv spectra.<sup>1</sup> The uv spectra of 3 were measured in anhydrous *n*-hexane and listed in Table V.

The hydrolysis product of 3 (R = Me) showed new peaks in ir and uv spectra: ir 3350 (OH, broad) and 1230 cm<sup>-1</sup> (P=O, broad); uv  $\lambda_{\max}$  285 m $\mu$  but not 313 m $\mu$  (in dioxane). Solvents were purified and dried before use.

**Kinetic Procedure.**—The kinetic experiments for the reaction of trialkyl phosphite with benzil were carried out in anhydrous dioxane. The rate measurements were done by means of the procedure as mentioned previously.<sup>1-3</sup> An isosbestic point was observed during the reaction of 1 (R = Me) at 287 m $\mu$  in dioxane.

The <sup>31</sup>P nmr chemical shifts were measured by a JNM-C60-HL model of Japan Electron Optics Laboratory Co., Ltd., at 24 MHz with proton decoupling at room temperature. The data were shown in Table III.<sup>19a,22-24</sup>

**Registry No.**—1, 134-81-6.

**Acknowledgments.**—The authors are thankful to Japan Electron Optics Laboratory Co., Ltd., for their kind measurement of the <sup>31</sup>P nmr chemical shift of trialkyl phosphites.

(22) J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, *J. Amer. Chem. Soc.*, **78**, 5715 (1956).

(23) K. Moedritzer, *J. Inorg. Nucl. Chem.*, **22**, 19 (1961).

(24) W. McFarlane and R. F. M. White, *Chem. Commun.*, 744 (1969).

## Lithium-Ammonia Reduction of Aromatic Ketones to Aromatic Hydrocarbons<sup>1</sup>

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Aromatic ketones are reduced, almost quantitatively, to aromatic hydrocarbons by lithium-ammonia solutions followed by an ammonium chloride quench. Lithium is more effective than sodium as the dissolving metal; in addition, the reduction is apparently catalyzed by trace amounts of metals such as cobalt or aluminum. The series of aromatic ketones which were reduced to aromatic hydrocarbons includes 1-tetralone to tetralin, 7-*tert*-butyl-1-tetralone to 6-*tert*-butyltetralin, 1-indanone to indan, 3,3-dimethyl-1-indanone to 1,1-dimethylindan, 2,2,3,3-tetramethyl-1-indanone to 1,1,2,2-tetramethylindan, 5-chloro-3,3-dimethyl-1-indanone to 1,1-dimethylindan, 3,3,4,5,6,7-hexamethyl-1-indanone to 1,1,4,5,6,7-hexamethylindan, benzophenone to diphenylmethane, xanthenone to xanthene, and dibenzoylmethane to 1,3-diphenylpropane. This study reveals various reduction rate relationships which are interpreted as due to steric effects, relief of strain, or stable ketyl radical formation. A mechanism is proposed for the catalyzed and uncatalyzed reduction.

Hitherto, it has been assumed that aromatic ketones are reduced, as are alkyl ketones, to alcohols in metal-ammonia reductions.<sup>3</sup> This presumption is apparently

based on work involving the reduction of benzophenone to diphenylmethanol with sodium in liquid ammonia.<sup>4</sup>

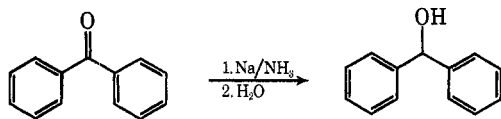
(1) This research was supported by The Research Council, Rutgers University.

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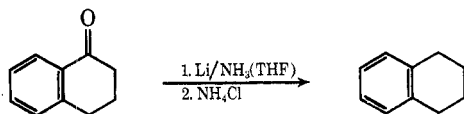
(3) For general discussions and leading references, see (a) A. J. Birch, *Quart. Rev., Chem. Soc.*, **4**, 69 (1950); (b) A. J. Birch and H. Smith, *ibid.*, **12**, 17 (1958); (c) G. W. Watt, *Chem. Rev.*, **46**, 317 (1950); (d) C. Djerassi, Ed., "Steroid Reactions," Holden-Day, San Francisco, Calif., 1963, pp

267-288, 299-325; (e) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, pp 50-77; (f) H. Smith, "Organic Reactions in Liquid Ammonia. Chemistry in Nonaqueous Ionizing Solvents," Vol. I, part 2, Wiley, New York, N. Y., 1963, pp 216-219; (g) R. L. Augustine, Ed., "Reduction," Marcel Dekker, New York, N. Y., 1968, pp 116-117.

(4) (a) H. Schulbach, *Chem. Ber.*, **48**, 12 (1915); (b) W. E. Bachmann, *J. Amer. Chem. Soc.*, **55**, 1179 (1933); (c) C. B. Wooster, *ibid.*, **59**, 377 (1937).



We have found that aromatic ketones are reduced, almost quantitatively in most cases, to aromatic hydrocarbons in lithium-ammonia (THF) solutions followed by an ammonium chloride quench. This incongruity, it turns out, is quite rational. First of all, lithium was found to be much more effective than sodium as the dissolving metal; second, the reduction of diaromatic ketones, *e.g.*, benzophenone, is sluggish compared to monoaromatic ketones, *e.g.*, 1-tetralone; and last, it is important that the reaction be quenched with ammonium chloride.



The reduction is also apparently catalyzed by trace metals such as cobalt and aluminum. For example, the rate of reduction of 1-tetralone was *ca.* doubled and that of benzophenone at least quintupled when trace amounts of cobalt powder were added. This observation is unusual since certain transition metals are known to catalyze the reaction of the alkali metal with ammonia forming sodium or lithium amide and hydrogen. The net result is the loss of reducing agent and therefore precautions are normally taken to avoid contamination by trace metals.<sup>5</sup>

In Table I is listed a selection of aromatic ketones reduced to aromatic hydrocarbons when subjected to these conditions. All products gave satisfactory spectral and analytical data and, in addition, were compared with authentic samples. Some of the reactions listed in Table I yielded minor products. Small amounts of alcohol and ketone generally indicated that the reduction had been stopped prematurely. Some ketones, especially the less sterically hindered indanones, formed dimers.<sup>6</sup>

The results of some of the reductions listed in Table I merit comment. Earlier in the discussion we indicated that lithium was more effective than sodium. An example of this is given by comparing the reduction of 1-indanone with lithium/cobalt and with sodium/cobalt. That diaromatic ketones are reduced significantly slower than monoaromatic ketones in the absence of trace metals is demonstrated by comparing the reduction of benzophenone with 1-tetralone. The slower rate of reduction of diaromatic ketones is undoubtedly

due to the formation of stable ketyl radicals.<sup>7</sup> Thus, it is interesting that the trace metal has a more decided effect on the rate of reduction of benzophenone than on 1-tetralone. This will be taken up again later in this discussion.

Other ketones also revealed some interesting reduction rate relationships. For example, 1-indanone is reduced considerably faster than 1-tetralone, which perhaps reflects the relief of strain in the indanone system, and 3,3-dimethyl-1-indanone is reduced faster than 5-chloro-3,3-dimethyl-1-indanone. When the reduction of the latter ketone was stopped prematurely, none of the isolated products (aromatic hydrocarbon, alcohol, and ketone) contained chlorine.

In addition, the reduction is apparently sensitive to steric effects, since 2,2,3,3-tetramethyl-1-indanone is reduced much more slowly than 3,3-dimethyl-1-indanone; the latter more slowly than 1-indanone; and 7-*tert*-butyl-1-tetralone more slowly than 1-tetralone.

Substantial information about the mechanism of this reaction was obtained when sodium benzoate,<sup>8</sup> instead of ammonium chloride, was used to destroy the excess lithium prior to reaction work-up. Rather than the expected aromatic hydrocarbon, the only product formed was a benzyl alcohol. Since sodium benzoate destroys the excess lithium in the absence of an added proton source, the reduction of aromatic ketones to aromatic hydrocarbons is clearly a two-sequence process. The first, which is slow, is the conversion of the aromatic ketone to a benzyl alkoxide in lithium-ammonia. The second sequence, which must be rapid, is initiated by the added proton source (NH<sub>4</sub>Cl) generating the benzyl alcohol, which in turn is reduced to the aromatic hydrocarbon before all the excess lithium is destroyed.<sup>9</sup>

Scheme I outlines our suggestions for the mechanism of the reduction, which incorporates the accepted mechanisms of reduction of ketones to alcohols<sup>10</sup> and benzyl alcohols to aromatic hydrocarbons.<sup>11</sup>

The catalytic effect of the trace metal, on the other hand, is enigmatic. At this time we wish to suggest that a hydrogen radical, generated at the surface of the metal,<sup>5</sup> is transferred to the ketyl radical intermediate **1**, generating the alkoxide **3**. The result would be to disrupt the initial equilibrium between ketone and ketyl radical **1** and force the reaction irreversibly to the alkoxide **3**. This would explain the more pronounced effect the trace metal has on the rate of reduction of the diaromatic ketones, since one would not expect the stable ketyl radical to be quickly protonated by ammonia but would expect it to react rather rapidly with a hydrogen radical.

Perhaps as important as the mechanistic implications of the results with sodium benzoate is the fact that by the simple choice of quenching agent one can selectively reduce aromatic ketones to benzyl alcohols or aromatic hydrocarbons.

(5) (a) H. L. Dryden, G. M. Webber, R. R. Burtner, and J. A. Cella, *J. Org. Chem.*, **26**, 3237 (1961); (b) W. Huckel, B. Graf, and D. Munker, *Justus Liebigs Ann. Chem.*, **614**, 47 (1958). The catalytic effect of the trace metals was accidentally discovered in this laboratory when we used a glass-coated magnetic stirring bar which contained a capillary flaw. Since the magnetic alloy was Alnico V, trace amounts of granular aluminum (20 mesh and finer), nickel powder, cobalt powder, copper powder, and iron filings (40 mesh) were tested. The most effective was cobalt, followed by aluminum, and then nickel in studies with 1-tetralone. The influence of iron and copper seemed to be negligible. We wish to thank a referee who has suggested that perhaps the catalytic effect of the trace metals might be greatly enhanced if the metal were present in a nearly colloidal state of subdivision. We are presently exploring this possibility.

(6) The dimers, normally in the ratio of *ca.* 2/1, have been tentatively assigned, using the reduction of 1-indanone as an example, as *meso*- and *dl*-1,1'-diindan based upon mass spectra and infrared and nmr data.

(7) (a) C. B. Wooster, *J. Amer. Chem. Soc.*, **50**, 1388 (1928); (b) C. B. Wooster, *ibid.*, **57**, 112 (1935); (c) C. B. Wooster, *ibid.*, **59**, 377 (1937).

(8) A. P. Krapcho and A. A. Bothner-By, *ibid.*, **81**, 3658 (1959).

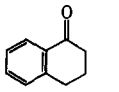

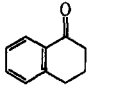

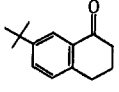
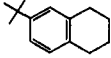
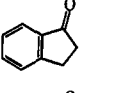

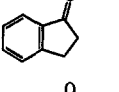

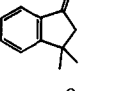
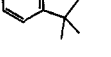
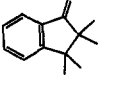
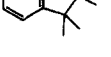
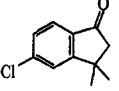
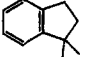
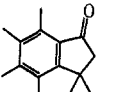
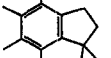
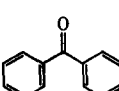
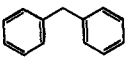
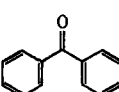
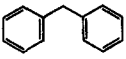
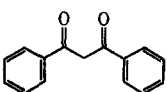
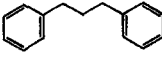
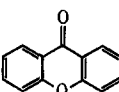
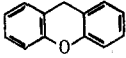
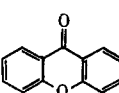
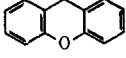
(9) It is important that the reduction be carried out as a two-sequence process in order to avoid overreduction. When 1-indanone, in the presence of an added proton source (EtOH), was subjected to these conditions, *ca.* equal amounts of indan, 4,7-dihydroindan and unreacted ketone were isolated.

(10) See ref 3g, pp 97-98.

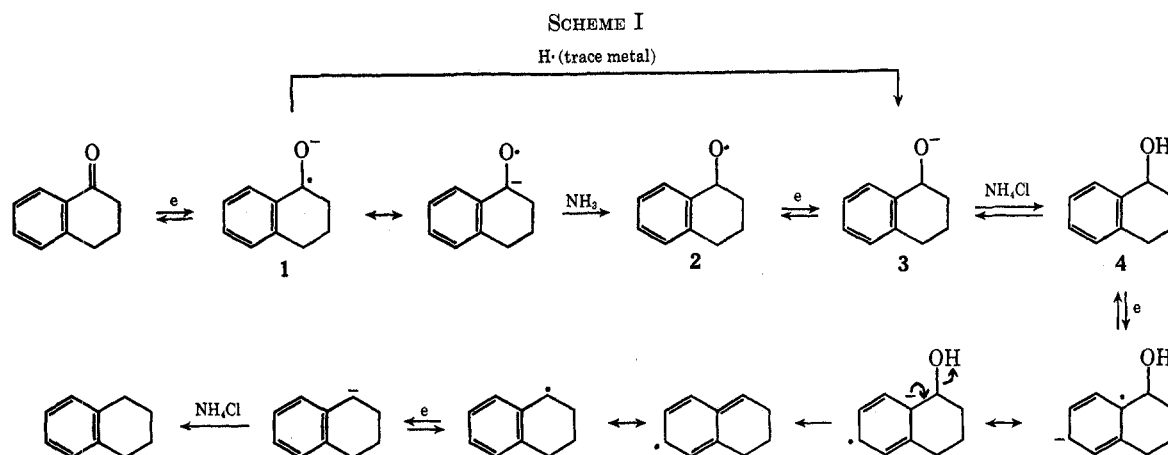
(11) See ref 3e, pp 74-75.

TABLE I<sup>a</sup>

## LITHIUM-AMMONIA REDUCTION OF AROMATIC KETONES TO AROMATIC HYDROCARBONS

Ketone	Registry no.	Dissolving metal/ trace metal	Product	% yield		Time, <sup>d</sup> hr	Minor product(s)	Comments
				Analytical <sup>b</sup>	Isolated <sup>c</sup>			
	529-34-0	Li/none		99	96	2	0.5% alcohol 0.5% dimers (2)	
		Li/Co		98	95	1	1.5% alcohol 0.5% dimers (2)	<i>e</i>
	22583-68-2	Li/Co		95	92	2	5% alcohol	<i>e</i>
	83-33-0	Li/Co		93	91	0.33	7% dimers (2)	
		Na/Co		86	84	3	9% alcohol 5% dimers (3)	<i>e</i>
	26465-81-6	Li/Al		90	79	1	10% dimers (2)	
	10474-33-6	Li/Al		95		4	5% alcohol	<i>f</i>
	30428-23-0	Li/Al		92	73	2	8% dimers (2)	<i>g</i>
	30427-98-6	Li/Al		96	75	1	4% unknowns (2)	<i>h</i>
	119-61-9	Li/none		86		4	14% alcohol	
		Li/Co		97	87	1	3% alcohol	<i>i</i>
	120-46-7	Li/Co		100	77	1		<i>j</i>
	90-47-1	Li/none		98		4	2% unknowns (2)	<i>k</i>
		Li/Co		98	77	1	2% unknowns (2)	<i>k</i>

<sup>a</sup> Reaction conditions are those discussed in the Experimental Section, unless noted otherwise. <sup>b</sup> Analyzed by glc using a 6 ft × 1/8 in. 10% silicon gum rubber UCC-W-982 (methyl vinyl) on a flame detector instrument at a 40-ml/min flow rate. All samples were injected at a reasonable temperature, followed by a 10-min post injection interval, and then programmed 10°/min to 290° and held at limit 1–2 hr. <sup>c</sup> Isolated pure from an aluminum oxide column by eluting with petroleum ether, bp 38–58°. <sup>d</sup> Time of reflux after ketone had been added to reaction mixture. <sup>e</sup> Similar results were observed with aluminum trace metal. <sup>f</sup> Analytical yield estimated from a 1-hr reaction mixture consisting of 54% aromatic hydrocarbon and 46% alcohol. <sup>g</sup> In this experiment 3.3 mmol of ketone was used. <sup>h</sup> The unknowns have physical properties characteristic of compounds which have been overreduced. When no trace metal was present, the reduction of the ketone took ca. twice as long and in the process substantial overreduction occurred. <sup>i</sup> Aluminum was less effective as a trace metal catalyst for this ketone. <sup>j</sup> In this experiment 2.5 mmol of ketone was used. <sup>k</sup> Because of the insolubility of the ketone in 10 ml of THF, a solution of the ketone in 20 ml of THF was added to the Li or Li/Co in 20 ml of ammonia. The unknowns have physical properties characteristic of compounds which have been overreduced.



### Experimental Section

**General Comments.**—The nmr spectra were determined at 60 MHz with a Varian Model A-60 nmr spectrometer in  $\text{CCl}_4$  or  $\text{CDCl}_3$  solutions containing tetramethylsilane. The ultraviolet spectra were determined with a Cary spectrophotometer, Model 14. The infrared spectra were determined with a Beckman Model IR-10 infrared spectrophotometer. The mass spectra were obtained with a Perkin-Elmer Model 270 mass spectrometer, equipped with a Varian Model 620/i computer attachment. Gas chromatographic analyses were performed on a Hewlett-Packard Model 5750 research chromatograph. Separations and purifications were attained on adsorption alumina (80–200 mesh) columns. Further purification, for analytical purposes, was attained by gas-liquid partition chromatography (glc). The spectral data, analytical data, and physical characteristics of all aromatic hydrocarbons were in agreement with that of authentic samples.

**Lithium-Ammonia Reduction.**—Precautions for the exclusion of impurities (moisture, air, peroxides, contaminant metals, or metal salts) were scrupulously observed. All reductions were carried out under a static nitrogen (prepurified) atmosphere. Tetrahydrofuran (THF) was filtered through an alumina column and then refluxed and distilled from  $\text{LiAlH}_4$  just prior to use. Anhydrous ammonia was distilled into the reaction vessel. Lithium wire (0.01% Na, Alpha Inorganics, Inc.) was wiped free of oil and washed with petroleum ether, bp 38–58°, immediately before use.

All reactions employed the conditions described for the reduction of 1-tetralone, except for variations in reaction time or other minor changes noted in Table I.<sup>12</sup>

(12) See ref 3g, pp 98–105, for a useful general discussion of metal-ammonia experimental techniques.

**Tetralin.**—To a mixture containing 20 ml of ammonia, 10 ml of THF, and 2.95 mg (0.05 mg-atom) of cobalt powder was added 175 mg (25 mg-atoms, 8 pieces) of Li, followed almost immediately by the dropwise addition (15 min) of a solution of 0.731 g (5 mmol) of 1-tetralone in 10 ml of THF. After the mixture had been stirred under reflux for 1 hr, the excess Li was consumed by the rather rapid addition (~4 min) of excess  $\text{NH}_4\text{Cl}$  (~4 g)<sup>13</sup> and the ammonia was allowed to evaporate. After the residue had been partitioned between aqueous NaCl and  $\text{Et}_2\text{O}$ , the organic layer was dried, concentrated, and analyzed by glc. The crude product was purified by column chromatography, yielding 0.626 g (95%) of a liquid which was identical with tetralin.

**Registry No.**—Ammonia, 7664-41-7; lithium, 7439-93-2.

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(13) The addition should be smooth, relatively rapid, and continuous in order to avoid any overreduction of the product. This can be accomplished by attaching a piece of Tygon tubing, connected to a glass tube (sealed at one end) filled with ammonium chloride, to a side arm of the reaction vessel near the end of the reaction. When the ammonium chloride is needed, the tube is elevated and tapped gently to introduce the salt.