trolyzed at 2.2 V (vs. SCE) constant potential and 20 mA cm^{-2} initial current density. The reaction mixture was worked up as previously described except that the organic layer was washed with 5% NaHCO$_3$. The crude product, analyzed by ^{1}H NMR, consisted of a mixture of starting material, 4-acetylbibenzyl (9), 1-(4-ethylphenyl)-2-phenylethyl acetate (6) and 1-(4-phenethyl)phenylethyl acetate (7).

Single Electron Transfer in the Meerwein–Ponndorf–Verley Reduction of Benzophenone by Lithium Alkoxides

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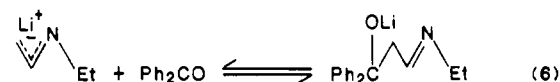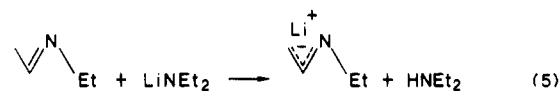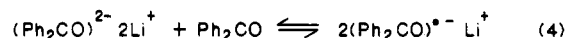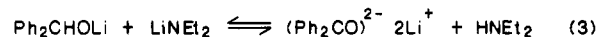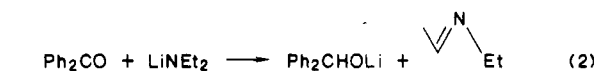
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The Meerwein–Ponndorf–Verley reduction of benzophenone by lithium alkoxides was determined to proceed via a radical intermediate. The radical intermediate was identified as the lithium ketyl of benzophenone and was found to be reduced to lithium benzhydrolate by abstracting a β-hydrogen atom from the lithium alkoxide. The major pathway to benzophenone ketyl appears to be the result of a one-electron transfer from the lithium alkoxide to benzophenone. The formation of benzophenone ketyl from the corresponding dianion, formed in low concentration by deprotonation of lithium benzhydrolate by the alkoxide, provides an alternate pathway to ketyl although it should be a minor one. On the other hand, aluminum isopropoxide gave no indication that it reduces benzophenone via a radical intermediate.

The Meerwein–Ponndorf–Verley reduction of ketones is generally believed to proceed via a polar mechanism[1] involving a cyclic transition state (eq 1).[2] Nevertheless,

(1)
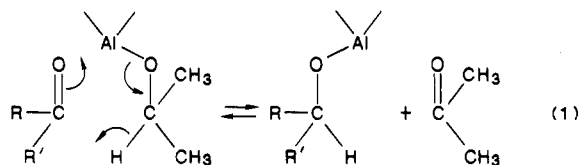
a single electron transfer (SET) pathway has been proposed for the reduction of benzophenone by lithium, sodium, and potassium alkoxides.[3,4] The basis of the proposed SET mechanism was the appearance of benzophenone ketyl (observed by ESR and visible spectroscopy) as well as the formation of benzophenone ketyl coupling products. In addition, stereochemical evidence for a single electron transfer pathway in the reduction of cyclic ketones with alkoxyaluminum dichlorides has been reported.[5]

The presence of benzophenone ketyl in the reactions of benzophenone with certain nucleophiles has recently been questioned by Newcomb[6] as indication of a SET process. In the reaction of benzophenone with lithium dialkylamides, he proposed an alternate scheme involving fast concerted β-hydride reduction of benzophenone to give lithium benzhydrolate (eq 2), the formation of dilithium benzophenone dianion from the deprotonation of lithium benzhydrolate by the lithium dialkylamide (eq 3), and fast electron transfer from benzophenone dianion to benzophenone to give two molecules of ketyl (eq 4). Benzophenone is provided throughout the reaction by retroaldolization of an aldol-like adduct formed early in the reaction (eq 5 and 6). In support of the pathway depicted in eq 2–6, Newcomb showed that 10% benzophenone dianion was formed when lithium benzhydrolate was treated with a fivefold excess of LDA (eq 3) for 22 h at 22 °C.

$$Ph_2CO + LiNEt_2 \longrightarrow Ph_2CHOLi + \text{(enamine)} \quad (2)$$

$$Ph_2CHOLi + LiNEt_2 \rightleftharpoons (Ph_2CO)^{2-} 2Li^+ + HNEt_2 \quad (3)$$

$$(Ph_2CO)^{2-} 2Li^+ + Ph_2CO \rightleftharpoons 2(Ph_2CO)^{\bullet-} Li^+ \quad (4)$$

$$\text{(enamine)} + LiNEt_2 \longrightarrow \text{(Li enamine)} + HNEt_2 \quad (5)$$

$$\text{(Li enamine)} + Ph_2CO \rightleftharpoons \text{(aldol adduct)} \quad (6)$$

Furthermore, the deprotonation of lithium benzhydrolate by LDA in THF at 22 °C occurred with an apparent second-order rate constant which was approximately equal to one-half of the apparent second-order rate constant for ketyl formation when benzophenone was treated with LDA under similar conditions. Lithium diisopropylamide was also found to rapidly reduce benzophenone to give approximately 55% lithium benzhydrolate (after the first few minutes no significant change in the yield of benzhydrol was detected during the next 24 h). Conversely, the ketyl formed slowly and reached a maximum after 30 h, hence indicating that it is not the intermediate in the formation of the reduction product. Based on these results, Newcomb suggested that a similar pathway might be in effect for the reduction of benzophenone by alkoxides.

With this background, a more detailed study of the reaction of lithium alkoxides with benzophenone was carried out in order to determine whether the Meerwein–

(1) Wilds, A. L. In *Organic Reactions*; Adams, R., Bachmann, W. E., Fieser, L. F., Johnson, J. R., Snyder, H. R., Ed.; Wiley: New York, 1944.
(2) Shiner, V. J.; Whittaker, D. *J. Am. Chem. Soc.* 1963, *85*, 2337.
(3) Screttas, C. G.; Cazianis, C. T. *Tetrahedron* 1978, *34*, 933.
(4) Ashby, E. C.; Goel, A. B.; Argyropoulos, J. N. *Tetrahedron Lett.* 1982, *23*, 2273.
(5) Nasipuri, D.; Gupta, M. D.; Banerjee, S. *Tetrahedron Lett.* 1984, *25*, 5551.
(6) (a) Newcomb, M.; Burchill, M. T. *J. Am. Chem. Soc.* 1984, *106*, 2450; (b) 8276.

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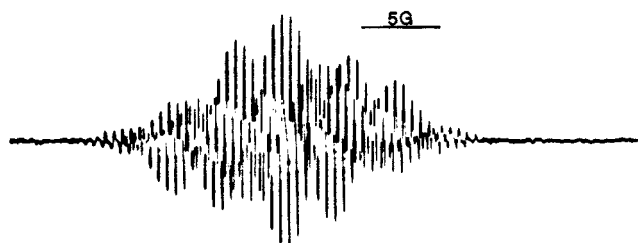
Figure 1. EPR spectrum of the paramagnetic intermediate formed in the reaction of benzophenone with lithium isopropoxide.
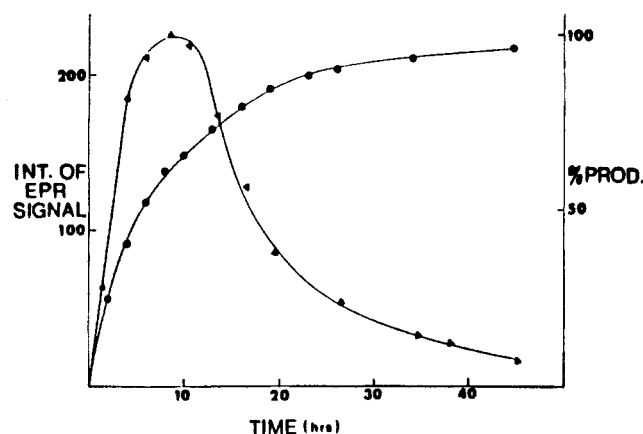

Figure 2. Reaction of benzophenone (0.076 M) with lithium isopropoxide in THF: (▲) intensity of EPR signal (mm) vs. time (h), where 1 mm = 0.01% radical; (●) reduction product (%) vs. time (h).

Ponndorf–Verley reduction proceeds via a radical intermediate, as we had earlier proposed, or by a polar process. In addition, the specific questions raised by Newcomb's study with LDA were addressed.

Results and Discussion

When a solution of freshly prepared lithium alkoxide (LiOR where R = n-butyl, neopentyl, isopropyl, benzhydryl, and $tert$-butyl) was allowed to react with benzophenone in THF at 22 °C, a blue solution developed in all cases. The colored solutions gave rise to well-resolved EPR spectra (Figure 1) as well as visible spectra (λ_{max} 632 nm) all of which were identical with the EPR and visible spectra recorded for an authentic sample of lithium benzophenone ketyl (prepared by the reaction of lithium metal with benzophenone in THF) (eq 7). Hence the possibility

$$Li \text{ or } LiOR + Ph_2C{=}O \rightarrow [Ph_2C{=}O]^{\cdot-} \text{ (blue solution)}$$
(7)
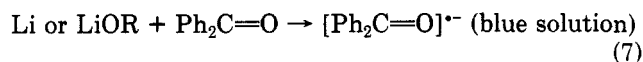
that the paramagnetic intermediate is the radical anion–radical cation pair[4] was ruled out in favor of the lithium ketyl of benzophenone.

In the reaction of lithium isopropoxide and benzophenone in a 20:1 molar ratio, respectively, in THF at 22 °C, a blue solution developed in a few hours. The paramagnetic intermediate reached a maximum at about 8 h (Figure 2) and then decreased in an apparent first-order fashion with k = 2.0 × 10^{-5} s^{-1}. The first-order rate constant was determined by plotting ln H vs. time, where H represents the height of the EPR signal (Figure 3). The product of the reaction, benzhydrol, was formed quantitatively after 2 days (Figure 2) in a pseudo-first-order fashion (Figure 4) with k = 2.5 × 10^{-5} s^{-1}.

The reaction of lithium n-butoxide with benzophenone in a 20:1 molar ratio, respectively, in THF at 24 °C also gave a blue solution in a few hours. The paramagnetic intermediate reached a maximum at 24 h and then de-
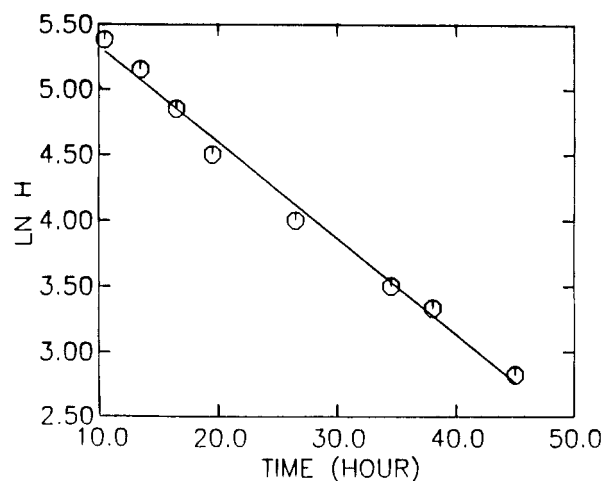

Figure 3. Plot of ln H vs. time for the first-order decay of radical intermediate in the reaction of benzophenone with lithium isopropoxide.

Figure 4. Plot of ln $(P_\infty - P_t)$ vs. time for the pseudo-first-order formation of benzhydrol in the reaction of benzophenone with lithium isopropoxide.

Figure 5. Plot of ln H vs. time for the first-order decay of radical intermediate in the reaction of benzophenone with lithium n-butoxide.

creased very slowly in an apparent first-order fashion (Figure 5) with k = 5.0 × 10^{-6} s^{-1}. Benzhydrol also formed slowly in a pseudo-first-order fashion (Figure 6) with k = 6.8 × 10^{-6} s^{-1}. The above kinetic analyses indicate that in each reaction a paramagnetic intermediate is formed which decays in a first-order fashion and that the rate constant for the disappearance of the ketyl intermediate is within
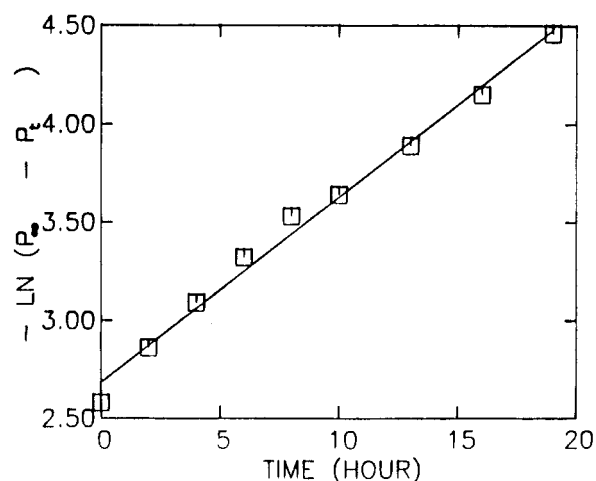
Figure 6. Plot of ln $(P_\infty - P_t)$ vs. time for the pseudo-first-order formation of benzhydrol in the reaction of benzophenone with lithium n-butoxide.
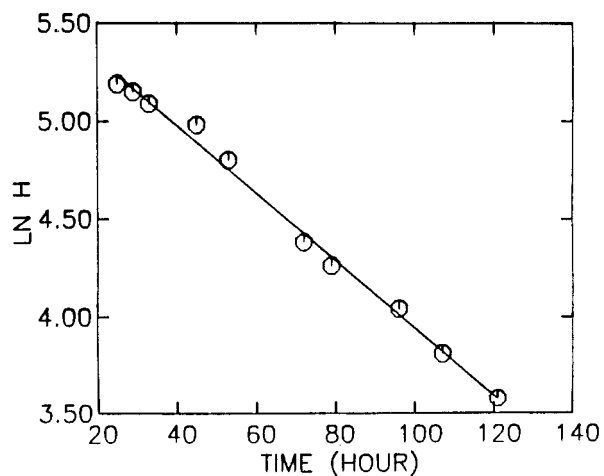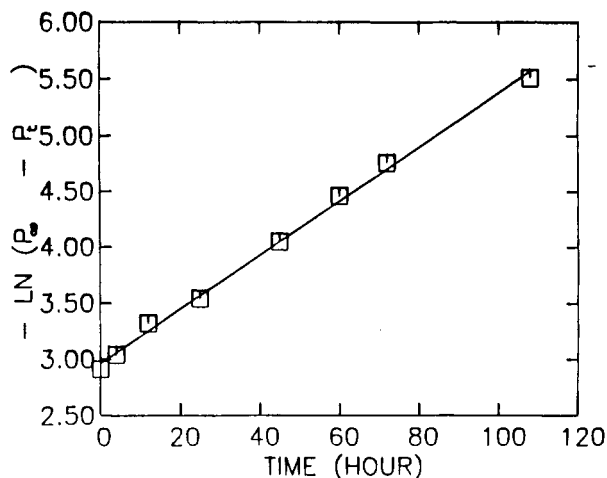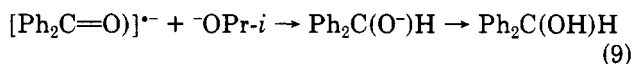

Figure 7. Plot of ln H vs. time for the first-order decay of benzophenone ketyl in the reaction of the ketyl with lithium isopropoxide.

experimental error of the pseudo-first-order rate constant for the appearance of product. These data are consistent with the notion that the product comes from the ketyl intermediate although it is possible that the formation of the ketyl is a dead-end step and the product formation is independent of the ketyl (eq 8).

$$\text{product} \leftarrow \text{LiOR} + \text{Ph}_2\text{C}{=}\text{O} \rightleftharpoons [\text{Ph}_2\text{C}{=}\text{O}]^{\bullet-} \quad (8)$$
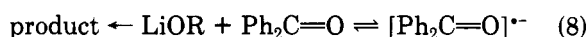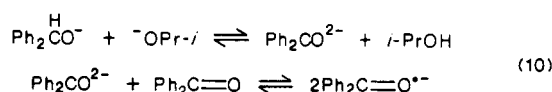
In order to verify that the intermediate to the reaction product (benzhydrol) is indeed benzophenone ketyl, benzophenone was allowed to react with lithium metal in THF, and the resulting ketyl was transferred to a solution of lithium isopropoxide in THF (molar ratio of alkoxide to ketyl was 20 to 1, respectively). Interestingly, the concentration of ketyl decreased 1000-fold over a 60-h period. The decay of the ketyl was monitored by EPR spectroscopy and found to be first order (Figure 7) with an apparent first-order rate constant $k = 3.4 \times 10^{-5}$ s^{-1} (similar to the rate constant $k = 2.0 \times 10^{-5}$ s^{-1} for the reaction of lithium isopropoxide with benzophenone under similar conditions). When the ketyl was completely consumed, the reaction was quenched to give benzhydrol quantitatively (eq 9). Hence, the lithium ketyl of benzophenone

$$[\text{Ph}_2\text{C}{=}\text{O})]^{\bullet-} + {}^-\text{OPr-}i \rightarrow \text{Ph}_2\text{C}(\text{O}^-)\text{H} \rightarrow \text{Ph}_2\text{C}(\text{OH})\text{H} \quad (9)$$

in the presence of lithium isopropoxide was shown to behave in a similar manner to the paramagnetic intermediate formed in the reaction of benzophenone with lithium isopropoxide directly.

The possibility that benzophenone ketyl is originating from the disproportionation of benzophenone with its dianion (eq 10) was specifically investigated. Lithium

$$\overset{\text{H}}{\text{Ph}_2\text{CO}^-} + {}^-\text{OPr-}i \rightleftharpoons \text{Ph}_2\text{CO}^{2-} + i\text{-PrOH}$$

$$\text{Ph}_2\text{CO}^{2-} + \text{Ph}_2\text{C}{=}\text{O} \rightleftharpoons 2\text{Ph}_2\text{C}{=}\text{O}^{\bullet-} \quad (10)$$

isopropoxide and benzhydrol were allowed to react in a 20:1 molar ratio, respectively, in THF at 22 °C and the characteristic deep red color of the benzophenone dianion was not observed. Furthermore, an aliquot from the reaction mixture was treated with oxygen at time zero and 12 h as described by Newcomb. Whitesides had previously shown that treatment of benzophenone dianion with oxygen gives benzophenone quantitatively.[7] No benzophenone was
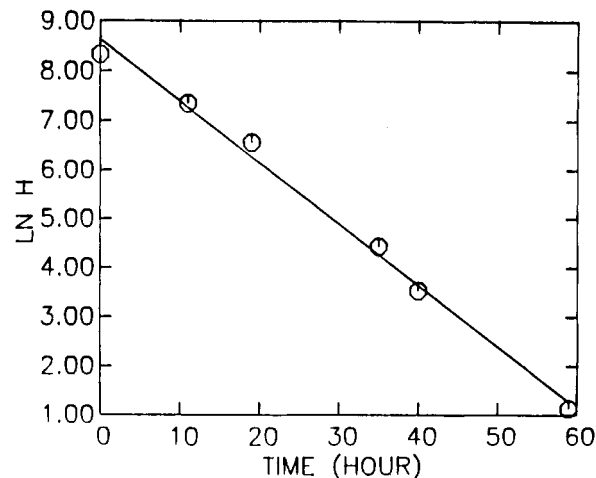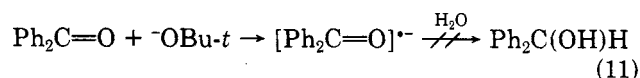
observed from time zero to 12 h, suggesting that the dianion was not present in detectable concentration. Hence, lithium isopropoxide, unlike lithium dialkylamides, is not a strong enough base to deprotonate lithium benzhydrolate (eq 3) to give a detectable amount of the dianion by the method previously used to detect the dianion.

Nevertheless, if the rate of formation of benzophenone dianion from the deprotonation of lithium benzhydrolate is much slower than the reaction of the dianion with benzophenone, then the direct detection of dianion may not be possible and yet it could still be a significant source of the ketyl. Hence, lithium benzhydrolate and lithium isopropoxide were allowed to react in a 1:20 molar ratio, respectively, for 60 h in the presence of 1.0 equiv of i-PrOD in order to determine whether deuterated benzhydrol was formed by the trapping of the dianion with i-PrOD. The amount of deuterium incorporation was found to be very low (1.3%) by mass spectroscopy. These results suggest that a small amount of dianion could have been formed by the deprotonation of lithium benzhydrolate with lithium isoproxide; however, it is formed in such low concentration that the dianion cannot account for the major reaction pathway to form product.

On the other hand, there is another pathway to benzophenone ketyl in the reactions of benzophenone with lithium alkoxides and that is the SET pathway in which the alkoxide acts as a one-electron donor toward benzophenone. In order to test this possibly, lithium and potassium $tert$-butoxide (which do not contain a β-hydrogen needed for reduction) were allowed to react with benzophenone. Over a 60-h period benzophenone ketyl was formed in high concentration (3% relative to the amount of ketone). Indeed, no reduction product was observed after 60 h, yet the alkoxides gave EPR-active solutions (eq 11). Hence lithium alkoxides can act as one-electron

$$\text{Ph}_2\text{C}{=}\text{O} + {}^-\text{OBu-}t \rightarrow [\text{Ph}_2\text{C}{=}\text{O}]^{\bullet-} \overset{\text{H}_2\text{O}}{\nrightarrow} \text{Ph}_2\text{C}(\text{OH})\text{H} \quad (11)$$

donors toward benzophenone to form the ketyl which was shown to react with the alkoxide to form the reduction product, benzhydrol.

On the basis of the above results, the reduction of benzophenone by lithium alkoxides is proposed to proceed by the pathway depicted in Scheme I. In step a the alkoxide is shown to be a one-electron donor toward the ketone to form the ketyl and the alkoxide radical. The credibility of this step is based on the fact that lithium $tert$-butoxide reacts with benzophenone to form benzo-

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(7) Trzupek, L. S.; Newirth, T. L.; Kelly, E. G.; Sbarbati, N. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 8118.

Scheme I

(a) $Ph_2C=O + R\underset{H}{\overset{OLi}{C}}CH_3 \rightleftharpoons Ph_2\dot{C}-OLi + R\underset{H}{\overset{O\cdot}{C}}CH_3$

(b) $Ph_2\dot{C}-OLi + R\underset{H}{\overset{OLi}{C}}CH_3 \rightarrow Ph_2C-OLi(H) + R\overset{OLi}{\underset{H}{C}}CH_3$

(c) $2 R\overset{OLi}{\underset{\cdot}{C}}CH_3 \rightarrow R\overset{OLi}{\underset{H}{C}}CH_3 + R\overset{OLi}{C}=CH_2$

(d) $R\overset{OLi}{\underset{\cdot}{C}}CH_3 + Ph_2C=O \rightleftharpoons R\overset{O}{C}CH_3 + Ph_2\dot{C}-OLi$

(e) $Ph_2C-OLi(H) + R\underset{H}{\overset{OLi}{C}}CH_3 \rightleftharpoons (Ph_2C-O)^{2-}2Li^+ + R\underset{H}{\overset{OH}{C}}CH_3$

(f) $(Ph_2C-O)^{2-}2Li^+ + Ph_2C=O \rightarrow 2Ph_2\dot{C}-OLi$
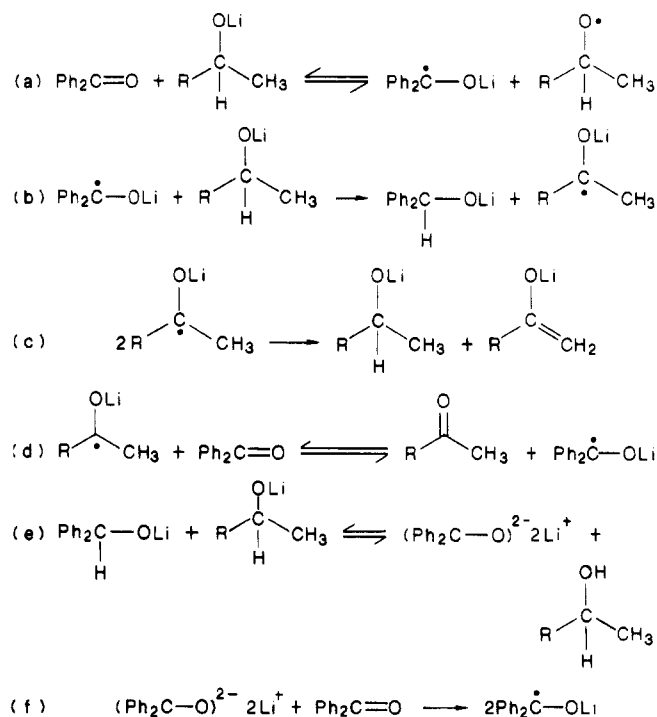
phenone ketyl. In step b the lithium ketyl of benzophenone is converted to lithium benzhydrolate by abstracting a β-hydrogen atom from the alkoxide[8] as indicated by the kinetic studies. The alkoxide is thus converted to the lithium ketyl of an aliphatic ketone. Rautenstrauch[9] has shown that the lithium ketyls of aliphatic ketones containing β-hydrogens undergo a rapid intramolecular disproportionation in THF to give a 1:1 enolate/alcoholate mixture as shown in step c. The lithium ketyl of the aliphatic ketone can also undergo an intermolecular electron transfer to benzophenone to give benzophenone ketyl and free ketone (step d).[10] Hence steps b and d constitute a radical chain process for the observed conversion of benzophenone to lithium benzhydrolate. The viability of a radical chain pathway was tested by allowing benzophenone to react with lithium isopropoxide in the presence of ambient fluorescent light, in the absence of light, and with a catalytic amount of p-dinitrobenzene. The rate of the above reaction was not affected by light or a catalytic amount of p-dinitrobenzene, suggesting that a nonradical chain process is in effect. p-Dinitrobenzene has been shown to accept an electron from various radical anions,[11] including benzophenone ketyl.[12] Its effectiveness as a radical anion trap in the presence of lithium isopropoxide has also been demonstrated.[13] Furthermore, the reactions of benzophenone with lithium alkoxides did not appear to give free ketone (see next paragraph) as required by step d. Step e shows that the alkoxide[14] can extract a proton from lithium benzhydrolate to form the dianion of the ketone and step f shows the disproportionation of the dianion with the ketone to form the ketyl.

As suggested from the oxidation and deuterium exchange studies, steps e and f are thought to be of minor importance.

In order to determine the fate of the alkoxide, the lithium salt of 2-heptanol was allowed to react with benzophenone in a 3:1 molar ratio, respectively, in THF at 24 °C. A blue solution developed slowly and after 4 days an aliquot from the reaction mixture was analyzed by GLC and shown to give benzhydrol in 78% yield. An analysis based on total alkoxide used gave 15% 2-heptanone and 84% 2-heptanol. Hence the alkoxide involved in the reduction (26% of the total alkoxide employed due to the extent of reduction) was converted to 15% ketone and 11% alcohol (26–15% isolated as ketone). The ratio of ketone to alcohol is within experimental error of a 1:1 mixture which should result if the lithium ketyl of 2-heptanone is present and undergoes disproportionation to give a 1:1 enolate/alcoholate mixture. Further evidence that a major portion of the ketone resulted from quenching the enolate was provided by a control study which showed that 2-heptanone in the presence of excess alkoxide undergoes condensation, and therefore is not stable over the time period of this reaction in the presence of excess alkoxide. Interestingly, an enolate anion was also suggested as a precursor to ketone in a similar reaction (Oppenauer oxidation).[15]

The SET pathway depicted in Scheme I indicates that 1.5 mol of alkoxide are needed to reduce 1 mol of benzophenone. Conversely, the polar pathway involving a cyclic transition state (eq 1) requires only 1 mol of alkoxide to participate in reduction. Interestingly, when lithium isopropoxide and benzophenone were allowed to react in a 1:1 molar ratio in THF, the reaction did not go to completion.

In view of the above results with lithium alkoxides, the classic Meerwein–Ponndorf–Verley reduction of benzophenone with aluminum isopropoxide was also studied. When benzophenone and aluminum isopropoxide were allowed to react in a 1:3 molar ratio, respectively, in THF at 24 °C, the characteristic blue-colored solution observed with lithium alkoxides did not develop. EPR analysis of the reaction mixture showed that benzophenone ketyl was not produced in a detectable concentration over a 7-day period, yet 92% benzhydrol was formed after 1 week. The inability to observe benzophenone ketyl in the above reaction suggests that aluminum isopropoxide is a poorer one-electron donor than lithium alkoxides. The latter have been shown to produce radical intermediates in their reactions with polynuclear hydrocarbons,[13] whereas aluminum isopropoxide does not give a detectable amount of radical when allowed to react with perylene.

Conclusion

The Meerwein–Ponndorf–Verley reduction of benzophenone by lithium alkoxides was determined to proceed via a radical intermediate. The radical intermediate was identified as the lithium ketyl of benzophenone and was found to be reduced to lithium benzhydrolate by abstracting a β-hydrogen atom from the lithium alkoxide. The major pathway to benzophenone ketyl appears to be the result of a one-electron transfer from the lithium alkoxide to benzophenone. The formation of benzophenone ketyl from the corresponding dianion, formed in low concentration by deprotonation of lithium benzhydrolate by the alkoxide, should be a minor alternate source of ketyl

(8) Rossi, R. A.; DeRossi, R. H. *Aromatic Substitution by the S_{RN}1 Mechanism*; American Chemical Society, Washington, D.C., 1983; p. 19.
(9) Rautenstrauch, V.; Geoffroy, M. *J. Am. Chem. Soc.* 1977, 99, 6280.
(10) This possibility was suggested by a referee.
(11) Bunnett, J. F. *Acc. Chem. Res.* 1978, 11, 413.
(12) Ashby, E. C.; Wiesemann, T. L. *J. Am. Chem. Soc.* 1978, 100, 189.
(13) Ashby, E. C.; Bae, D.-H.; Park, W. S.; DePriest, R. N.; Su, W.-Y. *Tetrahedron Lett.* 1984, 25, 5107.
(14) The lithium enolate generated by the disproportionation of the aliphatic ketyl can also extract a proton from lithium benzhydrolate, but it is present in very low concentration relative to the amount of alkoxide employed in the reaction.

(15) Woodward, R. B.; Wendler, N. L.; Brutschy, F. *J. J. Am. Chem. Soc.* 1945, 67, 1425.

as determined by a deuterium exchange experiment. Conversely, aluminum isopropoxide gave no indication that it reduces benzophenone via a radical intermediate.

Experimental Section

Materials. Aluminum isopropoxide (99.999%) was purchased from Aldrich and used as received. Reagent-grade tetrahydrofuran (THF) from Fisher was distilled under nitrogen from a deep purple solution of sodium benzophenone ketyl. Reagent-grade isopropyl alcohol from Aldrich was distilled under nitrogen from magnesium isopropoxide prior to use. Reagent-grade *tert*-butyl alcohol and 1-butanol from Fisher and 2-heptanone and 2-heptanol from Aldrich were stirred over CaH_2 for 24 h and then distilled under nitrogen. Benzophenone and benzhydrol from Aldrich were distilled under vacuum. Deuterated isopropyl alcohol (98% d_1) from Aldrich was used as received.

General Procedures. Methods of manipulation of reagents under an inert atmosphere and instrumentation were discussed in a previous paper.[16] For the kinetic studies, a constant temperature water bath was used to maintain the solutions at ± 0.5 °C.

GLC yields were determined by utilizing internal standards and comparing peak areas which were corrected for response factors. For quantitative GLC analyses, the following columns and conditions were used (t_R are given relative to the internal standard): column A, 5% Carbowax 20M on Chromosorb G, 2.5 ft × $^1/_4$ in., 190 °C, benzophenone (0.74), mesityl phenyl ketone (1.00), benzhydrol (1.58); column B, DB-1 fused silica capillary column, 30 m, 50 °C for 3 min to 150 °C at 15° per min, 2-heptanone (0.76), 2-heptanol (0.80), n-decane (1.00).

Miscellaneous Reactions. Reaction of Benzophenone with Lithium Isopropoxide. Isopropyl alcohol (0.96 g, 16 mmol) was added dropwise to a cold (0 °C) solution of MeLi (15 mmol) in 9.5 mL of Et_2O. After being stirred for 0.5 h, the Et_2O and excess alcohol were evaporated under vacuum to give lithium isopropoxide as a white powder. The alkoxide was dissolved in 5.0 mL of THF and 0.14 g (0.76 mmol) of benzophenone in 5.0 mL of THF was added all at once. A 1.0-mL portion of the solution was transferred into a quartz tube equipped with a ground glass stopcock for the EPR study. Aliquots of the reaction mixture were taken at appropriate time intervals for the product study and quenched in vials containing saturated NH_4Cl solution and internal standard. The organic layer was then extracted with hexane (2 × 2.0 mL), and the combined hexane layers were washed twice with water, dried, and then analyzed by GLC (column A). After 1 week, the remainder of the reaction mixture was worked up to yield one product, benzhydrol (NMR and IR spectra were identical with those of an authentic sample). In a similar manner, the reactions of benzophenone with lithium n-butoxide and aluminum isopropoxide were also studied.

Reaction of Benzophenone Ketyl with Lithium Isopropoxide. The lithium ketyl of benzophenone was prepared by adding 0.14 g (0.77 mmol) of benzophenone in 5.0 mL of THF to a round-bottomed flask containing 0.0056 g (0.80 mmol) of lithium wire under argon. After stirring for 24 h, the characteristic dark-blue of benzophenone ketyl developed. The flask was then transferred into a drybox and 0.50 mL (0.077 mmol) of the ketyl solution was added to a quartz EPR tube containing 1.5 mmol of lithium isopropoxide in 0.50 mL of THF. An additional 0.50 mL of the ketyl solution was added to a second EPR tube containing 0.50 mL of THF (blank). The concentration of ketyl for the blank remained constant over a 3-day period, whereas the concentration of ketyl in the EPR tube containing lithium isopropoxide decreased 1000-fold over the same period. When the ketyl was completely consumed, the reaction mixture was worked up as described above and analyzed by GLC (column A).

Reaction of Benzophenone with the Lithium Salt of 2-Heptanol. 2-Heptanol (0.33 g, 2.8 mmol) was added dropwise to a cold (0 °C) solution of MeLi (2.8 mmol) in 5.0 mL of Et_2O. After stirring for 0.5 h, the Et_2O was evaporated under vacuum and the resulting alkoxide was dissolved in 3.0 mL of THF. Benzophenone (0.17 g, 0.93 mmol) in 4.0 mL of THF was then added to the alkoxide solution. After 4 days, an aliquot of the reaction mixture was worked up as described before and analyzed by GLC for benzhydrol (column A) and for 2-heptanol and 2-heptanone (column B). An aliquot was also taken after 6 days and an analysis for 2-heptanone showed no change in its concentration. In a control study, 2-heptanone (0.11 g, 0.93 mmol) was added to the lithium salt of 2-heptanol (2.8 mmol) in 7.0 mL of THF and the concentration of 2-heptanone was monitored over time by GLC and found to decrease rapidly (25% 2-heptanone after 2 days, 8.2% after 6 days).

Deprotonation of Lithium Benzhydrolate. Method A. To a 5.0-mL solution of lithium isopropoxide (10 mmol) in THF was added 0.092 g (0.50 mmol) of benzhydrol dissolved in 5.0 mL of THF. Aliquots of the reaction mixture were taken after 10 s and 12 h and quenched with oxygen. This was done by fitting a vial with a rubber septum, flushing with oxygen, and then adding the aliquot (0.50 mL) and gently mixing. Saturated NH_4Cl solution (0.50 mL) was added after 60 s, followed by 1.0 mL of Et_2O. After separation of the phases, the Et_2O layer was analyzed by GLC (column A).

Method B. To a 2.5-mL solution of lithium benzhydrolate (0.50 mmol) in THF was added 2.5 mL of a 4.0 M solution of lithium isopropoxide in THF. The reaction flask was transferred into a drybox and 0.031 g (0.50 mmol) of i-PrOD was then added (the sealed vial containing the alcohol was broken in the drybox to avoid contamination). The reaction mixture was stirred for 60 h and then saturated NH_4Cl solution (10 mL) was added, followed by 30 mL of Et_2O. After separation of the phases, the ethereal layer was washed twice with saturated NH_4Cl solution and twice with water, dried, and concentrated to give benzhydrol. Utilizing mass spectroscopy, the ratio of the (M + 1)/M peaks for the treated alcohol was determined by scanning the peaks 50 times and taking an average ((M + 1)/M = 15.2133 ± 0.5795). An authentic sample of benzhydrol was also analyzed ((M + 1)/M = 13.8718 ± 0.1617).

EPR Studies. For the EPR studies, the above-named reactions were performed in quartz EPR tubes equipped with a ground glass stopcock under identical conditions used for the product studies. Immediately after mixing the reagents, the measurements of the EPR signal intensities were made at appropriate time intervals. The plot of ln H vs. time, where H represents the height of the first derivative EPR signal obtained at high modulation and measured in mm, yielded a straight line in the region where the intensity of the EPR signal was decreasing. The concentration of radical species was estimated by a comparison of the peak height of the first derivative EPR signal generated in the reaction being studied with the peak height of the signal obtained from a standard solution of 3-carbamoyl-2,2,4,4-tetramethylpyrrolidine-1-oxyl.

(16) Ashby, E. C.; Argyropoulos, J. N. *J. Org. Chem.* **1985**, *50*, 3274.