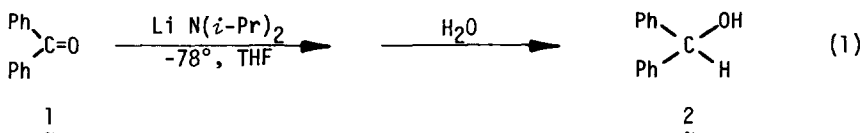


REDUCTION OF A KETONE BY LITHIUM DIISOPROPYL AMIDE
EVIDENCE FOR AN ELECTRON-TRANSFER MECHANISM

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The widespread use of lithium diisopropyl amide (LDA) as a strong base has revolutionized numerous facets of mechanistic and synthetic organic chemistry in recent years;¹ however, it is less widely appreciated that amide bases can function also as reducing agents.² LDA, for example, reduces benzophenone (1) to benzhydrol (2) even at -78°C in tetrahydrofuran (eq 1). Certain enolizable aliphatic ketones (*e.g.*, phenacyl bromide)³ even suffer reduction in competition with deprotonation by LDA.



We have found that LDA in 20% HMPA/THF (60°C, 24 hr) reduces benzophenone (1) not only to benzhydrol (2) but also to other products of higher molecular weight, including tetraphenylethylene oxide (3). Benzpinacol (4) could *not* be found among the reduction products but was independently shown also to give tetraphenylethylene oxide (3), benzhydrol (2) and benzophenone (1) under identical conditions.

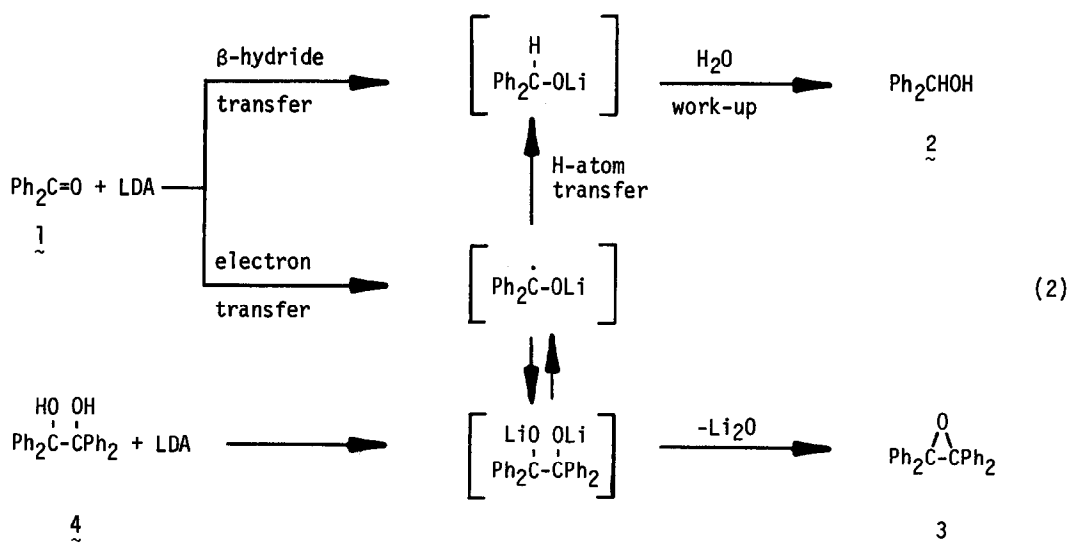


(1) M. Fieser and L. Fieser, "Reagents for Organic Synthesis", vols. 2-6, Wiley-Interscience, New York, N. Y. (1969-77).

(2) G. Wittig, H. J. Schmidt, and H. Renner, *Chem. Ber.*, **95**, 2377 (1962); G. Wittig and H.-D. Frommelt, *ibid.*, **97**, 3541 (1964); G. Wittig and U. Thiele, *Liebigs Ann. Chem.*, **726**, 1 (1969); G. Wittig, H. F. Ebel and G. Häusler, *ibid.*, **743**, 120 (1971); G. Wittig and A. Hesse, *ibid.*, **746**, 149 and 174 (1971); E. P. Woo and K. T. Mak, *Tetrahedron Lett.*, 4095 (1974).

(3) C. Kowalski, X. Creary, A. J. Rollin, and M. C. Burke, *J. Org. Chem.*, **43**, in press (1978). We thank these authors for exchanging information prior to publication.

Direct β -hydride transfer² from LDA to benzophenone (1) could certainly account for the formation of benzhydrol (2); however, the concomitant production of tetraphenylethylene oxide (3) suggests a possible radical mechanism (eq 2). Lithium-2,2,6,6-tetramethylpiperidide (which has no β -hydrogens) also reduces benzophenone (1) in THF at room temperature but gives only the higher molecular weight reduction products and *no* benzhydrol (2). This result demonstrates that the carbinol hydrogen of benzhydrol (2) must come from the base and not from solvent; however, it remains undetermined whether the hydrogen is transferred in a single step as hydride or as a hydrogen atom following an initial 1-electron transfer (eq 2).



We intend by this note simply to draw attention to the fact that ketones (and perhaps other functional groups)⁴ can suffer reduction by LDA, especially when proton transfer is slow or not feasible, and that an electron-transfer mechanism may be involved in certain instances.⁵

(4) Chalcone, a nonenolizable α,β -unsaturated ketone, yields more than eight products on treatment with LDA in THF at room temperature; see also C. L. Kissel and B. Rickborn, *J. Org. Chem.*, **37**, 2060 (1972).

(5) We thank the Petroleum Research Fund, administered by the American Chemical Society and the University of Nevada Research Advisory Board for financial support.