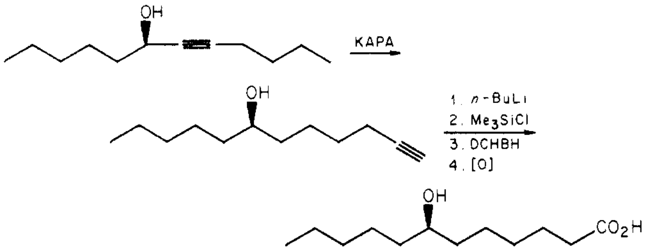
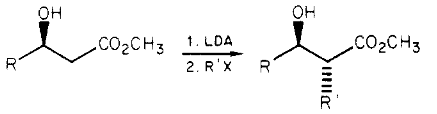
minal acetylenes without racemization[13] now provides a general route to optically-active hydroxy carboxylic acids in which the hydroxy center may be placed at any position in the aliphatic chain. Thus 5-dodecyn-7-ol (78% ee) was converted to 7-hydroxydodecanoic acid[14] through the trimethylsilyl acetylene in 76% yield. Analysis of the methyl ester with the NMR shift reagent revealed an enantiomeric purity of 82%.[15]



The reduction of propargyl ketones with *B*-3-pinanyl-9-borabicyclo[3.3.1]nonane generally proceeds in 74–100% ee. The limiting factor in obtaining high optical purity is usually the optical purity of the α-pinene.[16] Methods exist for obtaining (+)- or (−)-α-pinene of essentially 100% optical purity.[17] Alternatively, many α- and β-hydroxy carboxylic acids may be enriched by simple recrystallization.[18]

These acids are useful intermediates for organic synthesis. For example, the dianion of β-hydroxy esters may be alkylated with a very high degree of threo selectivity.[19]



It should be noted that the relative configuration is the opposite of that obtained in most aldol-type condensations.[3]

Acknowledgment. We thank the National Institutes of Health and the Committee on Research, University of California, Riverside, for financial support.

Registry No. (*R*)-1-Octyn-3-ol, 32556-70-0; (*R*)-1-octyn-3-ol acetate, 54315-41-2; (*R*)-2-acetoxyheptanoic acid, 78672-88-5; (*R*)-2-hydroxyheptanoic acid, 52437-20-4; (*R*)-methyl-2-hydroxyheptanoate, 78672-89-6; (*R*)-3-hydroxyoctanoic acid, 44987-72-6; (*R*) methyl 3-hydroxyoctanoate, 78672-90-9; (*R*)-5-dodecyn-7-ol, 78672-91-0; (*R*)-7-hydroxydodecanoic acid, 78737-61-8; (*R*) methyl 7-hydroxydodecanoate, 78672-92-1.

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[12] Brown, C. A.; Yamashita, A. *J. Chem. Soc., Chem. Comm.* **1976,** 959.

[13] Midland, M. M.; Halterman, R. L.; Brown, C. A.; Yamaichi, A., *Tetrahedron Lett.,* in press.

[14] It has been discovered recently that this acid is produced by various *Mucor* species of fungi. See Tahara, S.; Hosokawa, K.; Mizutani, J. *Agric. Biol. Chem.* **1980,** *44,* 193.

[15] In this case the methyl ester signal was split by the NMR shift reagent.

[16] With use of commercially available α-pinene (92% ee), most propargyl alcohols are obtained in 80–90% ee.

[17] Brown, H. C.; Yoon, N. M. *Isr. J. Chem.* **1976/1977,** *15,* 12. Cocker, W.; Shannon, P. V. R.; Staniland, P. A. *J. Chem. Soc. C* **1966,** 41. Also, research in progress with R. Graham.

[18] For an example, see ref 1b.

[19] Frater, G. *Helv. Chim. Acta* **1979,** *62,* 2825, 2829.

[20] A. P. Sloan Foundation Fellow, 1978–1982.

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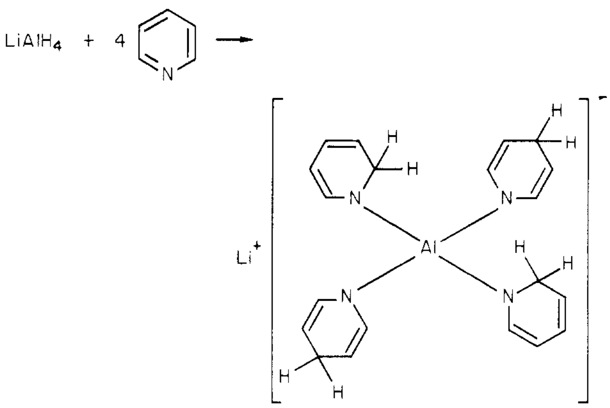
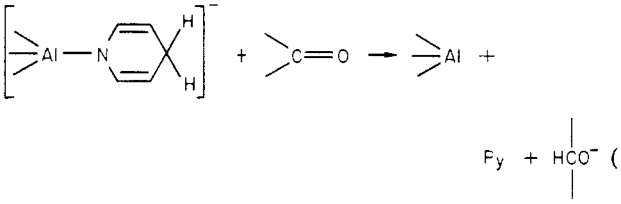
Evidence of Single Electron Transfer in the Reduction of Various Organic Substrates by Lithium Tetrakis(*N*-dihydropyridyl)aluminate

Summary: Aromatic ketones, polynuclear hydrocarbons, and alkyl halides react wih $LiAl(PyH)_4$ by a single electron transfer process.

Sir: In the early 1960's, Lansbury and co-workers[1-3] investigated reactions of $LiAlH_4$ dissolved in pyridine with organic substrates and made some unusual observations. Sometime later the same workers discovered that $LiAlH_4$ reacted with pyridine to form lithium tetrakis(*N*-dihydropyridyl)aluminate (LDPA, I) as a result of $LiAlH_4$ attack on the pyridine ring[4] (eq 1) and also found that LDPA was the responsible reducing agent when $LiAlH_4$ was allowed to react in pyridine. Further work by Lansbury and co-workers demonstrated that the 1,2- or 1,4-hydrogens on the dihydropyridyl group were transferred to the organic substrate (e.g., ketone) via a polar mechanism during the course of reduction (eq 2).



(1)



(2)

Recently, we demonstrated that simple and complex metal hydrides of the main group elements reduce certain aromatic ketones via a single electron transfer (SET) mechanism,[5] although the mechanism of this reaction was also considered previously to be of a polar nature. In view of these recent findings, we decided to investigate the possible involvement of SET mechanisms in reactions of

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[1] P. T. Lansbury, *J. Am. Chem. Soc.,* **83,** 429 (1961).

[2] P. T. Lansbury, J. R. Rogozinski, and F. L. Coblentz, *J. Org. Chem.,* **26,** 2277 (1961).

[3] P. T. Lansbury and R. Thedford, *J. Org. Chem.,* **27,** 2383 (1969).

[4] P. T. Lansbury and J. O. Peterson, *J. Am. Chem. Soc.,* **83,** 3537 (1961); **86,** 1756 (1962); **85,** 2236 (1963).

[5] E. C. Ashby, A. B. Goel, and R. N. DePriest, *J. Am. Chem. Soc.,* **102,** 7779 (1980).

[6] E. C. Ashby, A. B. Goel, R. N. DePriest, and H. S. Prasad, *J. Am. Chem. Soc.,* **103,** 973 (1981).

[7] E. C. Ashby, R. N. DePriest, and A. B. Goel, *Tetrahedron Lett.,* in press (1981).

[8] E. C. Ashby, A. B. Goel, and R. N. DePriest, *J. Org. Chem.,* **46,** 2429 (1981).

[9] E. C. Ashby and A. B. Goel, *Tetrahedron Lett.,* in press (1981).

[10] EPR spectrum consists of four sets (or a quartet) of well-resolved peaks. The appearance of a quartet is consistent with the large splitting (≃4–5 G) displayed by the ortho and para protons of the phenyl ring.

[11] D. H. Paskovich, A. H. Reddoch, and D. F. Williams, *J. Chem. Soc., Chem. Commun.,* 1195 (1972).

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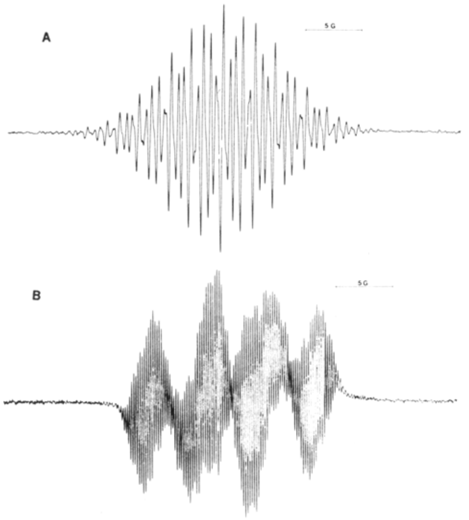
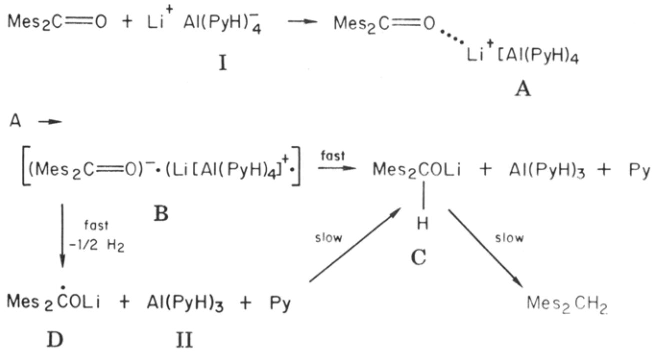


Figure 1. EPR spectrum of the radical intermediate of the reaction between lithium tetrakis(*N*-dihydropyridyl)aluminate (LDPA) with (A) dimesityl ketone and (B) mesityl phenyl ketone in THF at room temperature.

Scheme I



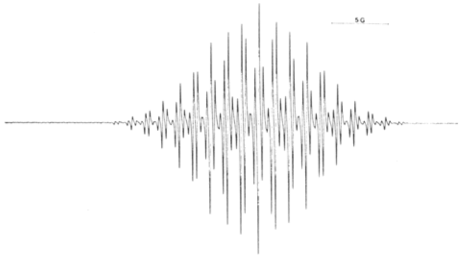


Figure 2. EPR spectrum of the 2,3-benzanthracene radical anion generated in the reaction of LDPA with 2,3-benzanthracene in THF at room temperature.

(LDPA, I) with various organic substrates. Indeed we have observed radical intermediates in the reactions of LDPA with organic substrates such as aromatic ketones [dimesityl ketone (DMK) and mesityl phenyl ketone (MPK)], polynuclear hydrocarbons (perylene, 2,3-benzanthracene, benzo[*a*]pyrene, phenanthrene, chrysene, and anthracene), alkyl halides [trityl halides (Ph_3CX, where X = Cl or Br) and 5-hexenyl iodide]. A preliminary account of these results are presented here.

When DMK and LDPA were allowed to react in THF in a dry nitrogen atmosphere, a blue-colored solution (λ_{max} 667 nm) resulted within a few minutes. Similarly, a violet color ($\lambda_{max} \simeq 520$ nm) was generated in the reaction of MPK. These colored solutions were found to be EPR active, suggesting the formation of paramagnetic species in solution. Both the intensity of the EPR signals as well as the visible absorption increased with time at the same rate in a particular reaction, indicating that both the color and the EPR signal are due to the same species. The concentration of the intermediate as determined by both visible and EPR spectroscopy was found to reach a maximum beyond which it slowly decayed. At the maximum, the amount of paramagnetic species was estimated to be about 4–18%. The reduction products [Mes_2CHOH and Mes(Ph)CHOH] were formed continuously during the entire course of the reactions. Typically, when DMK (0.02 M) and LDPA were mixed in equimolar ratio, about 8% paramagnetic species[5] were observed after 1 day. However, when the reaction mixture was hydrolyzed and analyzed, it contained 87% alcohol (Mes_2CHOH), 5% hydrocarbon product (Mes_2CH_2), and 8% ketone. It is worth mentioning here that when the free ketyl of dimesityl ketone (prepared independently) was hydrolyzed, it produced only dimesityl ketone. Thus the above results indicate that the ketone formed in the reaction of DMK with LDPA resulted from the free ketyl (8%) present in the reaction mixture. The formation of free ketyl in this reaction was further supported by the EPR spectrum of the reaction mixture (Figure 1), which was found to be identical with that of the free lithium ketyl (prepared independently). Formation of hydrocarbon product, Mes_2CH_2 (5%), can be explained in terms of a further reaction of alkoxide[9] (most likely Mes_2CHOLi) with LDPA (I) or with $Al(PyH)_3$ (II) (formed as the byproduct in the reaction). In order to confirm this point we allowed Mes_2CHOLi prepared independently to react with I and II, respectively; in both cases, Mes_2CH_2 was obtained. It was further observed that I reduced the alkoxide faster than II, although both of the reactions were quite slow. On the basis of the above results, Scheme I is proposed. In this mechanism, the radical pair intermediate B can give product C by hydrogen radical transfer or can generate free ketyl D by the loss of hydrogen radical by either self-coupling or hydrogen abstraction from THF solvent.

The slow decay of the intensity of ketyl D beyond its maximum is probably due to the abstraction of hydrogen from II, which was found to be possible by reacting the ketyl D with II and studying its rate. Formation of the free ketyl in the reaction by escape from B is further supported by the fact that when the reaction of DMK with LDPA was carried out in a 1:4 ratio, a larger amount of free ketyl (~18%) was observed. Thus in the reaction, the concentration of A is increased by increasing the concentration of LDPA (bimolecular reaction), thus increasing the probability of ketyl escape. A similar behavior has been observed in the reaction of LDPA with MPK, where the EPR spectrum (Figure 1) was found to be identical with that of the free ketyl.

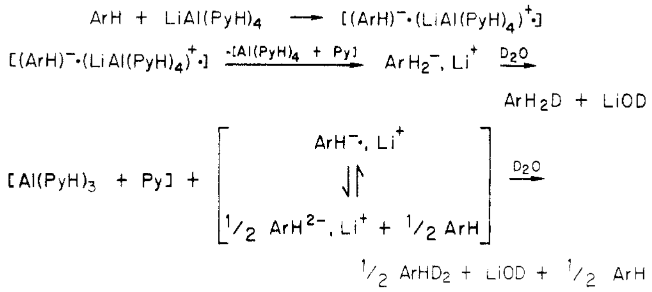
Polynuclear hydrocarbons have been shown to be excellent probes for the observation of SET since the radical intermediates are stable and show strong, well-defined visible and EPR spectra.[6,11] Reactions of LDPA with perylene, 2,3-benzanthracene, benzo[*a*]pyrene, phenanthrene, chrysene, and anthrancene have been carried out in THF at room temperature. Reasonably rapid radical formation was observed in the cases of hydrocarbons with low reduction potentials, whereas slow radical formation was observed for hydrocarbons of higher reduction potentials. In each case, the rate of SET was accelerated by using an excess of LDPA. The intensity of the EPR signal increased with time, and the concentrations of radical intermediates after a specific time are given in Table I. The EPR spectrum in each case was found to be identical with that of the respective radical anion generated independently. The EPR spectrum of the radical anion obtained from the reaction of LDPA with 2,3-benzanthracene

Table I. Reactions of LDPA with Polynuclear Hydrocarbons in THF at 24 °C[a]

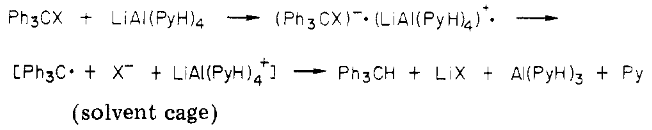
hydrocarbon	10^{-4} M	time, days	color	% radical anion[b]	EPR data: g value	EPR data: no. of lines
anthracene	200	15	light blue	6	2.0029	43
benzo[*a*]pyrene	1	7	violet	38	2.0031	93
chrysene	4	10	blue-green	10	2.0033	111
2,3-benzanthracene	1	5	yellow-green	>55	2.0032	65
phenanthrene	4	10	blue	9	2.0030	73
perylene	1	4	blue	71	2.0029	59

[a] LDPA was used in 20-fold excess. [b] Percentages of radical anion intermediates were calculated from the values of the extinction coefficient as well as by integrating the EPR spectra. Values are within ±5% of the reported values.

Scheme II



Scheme III



is shown in Figure 2. When the mixture obtained from the reaction of LDPA with anthracene was hydrolyzed by D_2O and the products analyzed, both ArH_2D and $ArHD_2$ (ArH = anthracene) were formed. $ArHD_2$ is the expected product when the radical anion is hydrolyzed by D_2O, and the formation of ArH_2D indicates that hydrogen is already transferred from LDPA to the radical anion prior to hydrolysis.

Thus it appears from EPR and visible spectroscopic as well as product formation studies that a single electron is transferred from LDPA to the hydrocarbon, forming initially a radical anion–radical cation pair $[(ArH)^{-}\cdot(LiAl(PyH)_4)^{+}\cdot]$, which not only proceeds to form the product ArH_2Li but also dissociates to generate the radical anion $ArH^{-}\cdot Li^{+}$. The suggested mechanism is shown in Scheme II.

Reactions of LDPA have also been carried out with alkyl halides. When trityl halides (Ph_3CX, where X = Cl or Br) were allowed to react with LDPA in THF, a yellow-orange color developed immediately. The reaction solution was found to be EPR active and showed an EPR spectrum consistent with that of the trityl radical, $Ph_3C\cdot$. This signal was not present in the spectrum of the starting materials. The intensity of the signal increased rapidly and reached a maximum (estimated intensity ~6%) beyond which it decreased slowly. The reduction product of the reaction was triphenylmethane, which continuously formed during the course of the reaction. The suggested mechanism is described in Scheme III. Preliminary results[12] concerning the reaction of 5-hexenyl iodide with LDPA show the formation of cyclized hydrocarbon product, which indicates the involvement of a SET mechanism.[7] We have also found that aryl halides can be reduced by LDPA. Currently we are engaged in exploring the possible involvement of SET in these reactions.

Registry No. Anthracene, 120-12-7; benzo[*a*]pyrene, 50-32-8; chrysene, 218-01-9; 2,3-benzanthracene, 92-24-0; phenanthrene, 85-01-8; perylene, 198-55-0; anthracene radical anion, 34509-92-7; benzo[*a*]pyrene radical anion, 34505-58-3; chrysene radical anion, 34488-57-8; 2,3-benzanthracene radical anion, 34512-30-6; phenanthrene radical anion, 34510-03-7; mesityl phenyl ketone, 78609-86-6; LDPA, 36393-24-5.

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[12] E. C. Ashby, R. N. DePriest, and A. B. Goel, work in progress.

A Greatly Improved Procedure for Ruthenium Tetraoxide Catalyzed Oxidations of Organic Compounds

Summary: Addition of acetonitrile to the traditional CCl_4/H_2O solvent system for ruthenium tetraoxide catalyzed oxidations leads to a greatly improved system; some applications to olefins, alcohols, aromatic rings, and ethers are described.

Sir: In 1953 ruthenium tetraoxide was introduced by Djerassi and Engle as an organic oxidant.[1] Since that time its utility for a variety of oxidative transformations has been recognized.[2] The expense of ruthenium metal provided incentive for the development of catalytic procedures, the most popular of which involve use of periodate or hypochlorite as the stoichiometric oxidants.[2] The periodate- and hypochlorite-based catalytic methods can be very effective; however, we and others have often encountered problems such as very slow and/or incomplete reactions. These sluggish or failed reactions must be due to inactivation of the ruthenium catalyst (normally present in amounts of 1–5%). We noted that the difficult cases shared a common feature: carboxylic acids were either present or being generated during the course of the oxidation. This led us to speculate[3] that lower valent ruthenium carboxylate complexes[4] might be responsible for the loss of catalyst activity.

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[1] Djerassi, C.; Engle, R. R. *J. Am. Chem. Soc.* **1953**, *75*, 3838.

[2] Lee, D. G.; van den Engh, M. In "Oxidation in Organic Chemistry"; Trahanovsky, W. S., Ed.; Academic Press: New York, 1973; Part B, Chapter 4.

[3] Dark-colored, ruthenium containing precipitates can usually be observed in inactive systems.

[4] Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1972**, 1570.

0022-3263/81/1946-3936$01.25/0 © 1981 American Chemical Society