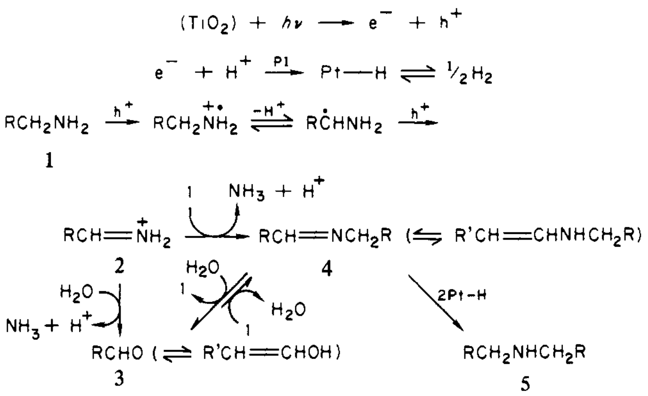
Scheme I



beled):d_1 (102):d_2 (103):d_3 (104):d_4 (105):d_5 (106) = 3:17:23:37:17:3.

A possible mechanism based on photoelectrochemical principles[1] is outlined in Scheme I. The initial step involves the creation, on the illuminated TiO_2, of an electron–hole pair, which is effectively separated by the partial Pt coverage. The electron (e^-) reduces a proton on the Pt site, producing an adsorbed hydrogen atom (Pt–H) and H_2. The hole (h^+) oxidizes the primary amine **1** at the TiO_2–water interface to form immonium ion **2**, which is expected to undergo hydrolysis to aldehyde **3** and NH_3.[12] The key step leading to secondary amine **5** would be the formation of a Schiff base intermediate **4** by reactions of **1** with **2** and more probably with **3**.[13] Although the aqueous solution system does not favor the formation of **4**, which is in equilibrium with **1** and **3**, hydrogenation across the C=N and/or C=CN bond of **4** by the Pt–H may occur to produce **5**. Indeed, dipropylamine (42%) was obtained from a H_2-purged aqueous solution (5 mL) of equimolar (122 μmol) mixture of propylamine and propionaldehyde when treated with Pt (2.5 mg) for 20 h in the dark.[14]

According to Scheme I, the Pt-catalyzed deuteration of **4** can lead to the d_2 product in D_2O and additional (≥3) deuterium incorporation can be accounted for by the keto–enol and imine–enamine tautomerisms of **3** and **4**. Upon raising the pH, the concentration of **4** would decrease, which would be responsible for the decreased yield of **5**. It is also obvious that the conversion of **1** to **5** depends on a dual function of the TiO_2/Pt, which has oxidizing and reducing sites acting as short-circuited electrode systems. Bard et al. have previously demonstrated the analogous property of partially metalized semiconductor photocatalysts in the Kolbe reaction,[2] but these results provide a potentially new mode of photocatalytic synthetic application.

Table I also shows a few extensions of this photocatalytic reaction. A 1:1 mixture of ethylamine and propylamine (entry 3) led to unsymmetrical *N*-ethylpropylamine (12%) accompanied by symmetrical diethylamine (9%) and dipropylamine (7%). Several cyclic secondary amines could be derived from polymethylene-α,ω-diamines (entries 4–6). Clearly, the present method is more favorable for intramolecular conversion of primary diamines to cyclic secondary amines (ca. 70–90% selectivity).[15]

Further extensions of this photocatalytic synthesis are now being explored.

Registry No. Anatase, 1317-70-0; platinum black, 7440-06-4; ethylamine, 75-04-7; propylamine, 107-10-8; 1,4-butanediamine, 110-60-1; 1,5-pentanediamine, 462-94-2; 1,6-hexanediamine, 124-09-4; *N*-(2-aminoethyl)-1,2-ethanediamine, 111-40-0.

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[12] Barnes, K. K.; Mann, C. K. *J. Org. Chem.* **1967**, *32*, 1474.

[13] Recently, Fox et al. have suggested a similar mechanism of the Schiff base formation (see ref 5b).

[14] Similar treatment of propionaldehyde (125 μmol) gave 1-propanol (3%, 24 h) under H_2.

[15] Reaction of 1,3-butanediamine (100 μmol) in the presence of $RuCl_2(Ph_3P)_3$ (2 μmol) in 5 mL of THF (26 h at 30 °C under Ar) resulted in a negligible amount of pyrrolidine (<1 μmol). At much higher temperature a good yield has been achieved (see ref 8b).

Homoenolate Dianions. Intramolecular Rearrangements of 1,4-Dilithio-*N*-phenyl Amides

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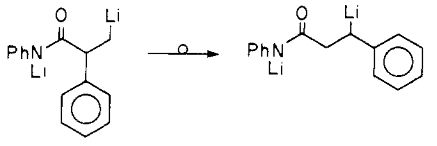
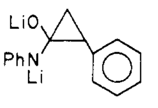
We report here the rearrangement of α-phenyl-1,4-dilithio-*N*-phenyl amide **1** to the more stable β-phenyl-1,4-dilithio derivative **2** (at −40 °C in THF). This rearrangement most likely proceeds through a transient dilithiocyclopropane intermediate such as **3**.



1 2



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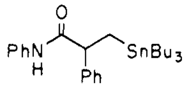

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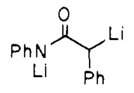

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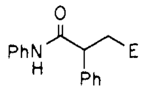

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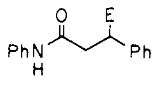

7

In contrast to the transient homoenolates generated by the well-known base-catalyzed opening of cyclopropanol derivatives,[1] the homoenolate dianion **2**, derived from **3**, can be used to functionalize the β-carbon atom with various electrophiles.[2] Although the highly deactivated carbonyl groups of *N*-lithio-*N*-phenyl amides are quite inert toward intermolecular nucleophilic attacks by organolithium reagents,[3] they appear susceptible to intramolecular reactions to form dilithiocyclopropane derivatives.[4]

The precursor *N*-phenyl-2-phenyl-3-(tri-*n*-butylstannyl)propionamide (**4**) was prepared in 80% yield by treatment of the 1,3-dilithio derivative **5** with (iodomethyl)tri-*n*-butyltin in THF.[5] Addition of 2 equiv of *n*-butyllithium to a cold (−70 °C) THF solution of **4** containing 1,4-diazabicyclo[2.2.2]octane (DABCO, 2 equiv) produced a light yellow solution containing **1**.[6,7] This dilithio species is stable at −70 °C for >90 min. Reaction of electrophiles (D_2O and Me_3SiCl) with this light yellow solution at −70 °C gave only **6** (E = D and E = Me_3Si) (Table I). When the light yellow solution was warmed to 0 °C, it turned dark orange. Addition of various electrophiles (D_2O, Me_3SiCl, Bu_3SnCl, and 5-nonanone) to this orange solution gave only **7** (Table I).

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[1] For a review, see: Werstiuk, N. H. *Tetrahedron* **1983**, *39*, 206–268.

[2] Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1983**, *105*, 651–652.

[3] Gay, R. L.; Hauser, C. R. *J. Am. Chem. Soc.* **1967**, *89*, 1647–1651. Goswami, R. Ph.D. Dissertation, Washington State University, Pullman, WA, 1977, p 78; *Diss. Abstr. Int. B* **1977**, *38* (3), 1206–1207. Fuhrer, W.; Gschwend, H. W. *J. Org. Chem.* **1979**, *44*, 1133–1136. Baldwin, J.; Dupont, W. *Tetrahedron Lett.* **1980**, *21*, 1881–1882. Mpango, G. B.; Mahalanabis, K. K.; Mahdavi-Damghani, Z.; Snieckus, V. *Ibid.* **1980**, *21*, 4823–4826.

[4] Houlihan, W. J.; Parrino, V. A.; Uike, Y. *J. Org. Chem.* **1981**, *46*, 4511–4515 and references cited therein.

[5] (a) Seyferth, D.; Andrews, S. B. *J. Organomet. Chem.* **1971**, *30*, 151–166. (b) Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481–1487.

[6] For previous reports, see: Goswami, R. *J. Am. Chem. Soc.* **1980**, *102*, 5973–5974. Goswami, R.; Corcoran, D. E. *Tetrahedron Lett.* **1982**, *23*, 1463–1466.

[7] Meyer, N.; Seebach, D. *Chem. Ber.* **1980**, *113*, 1290–1303.

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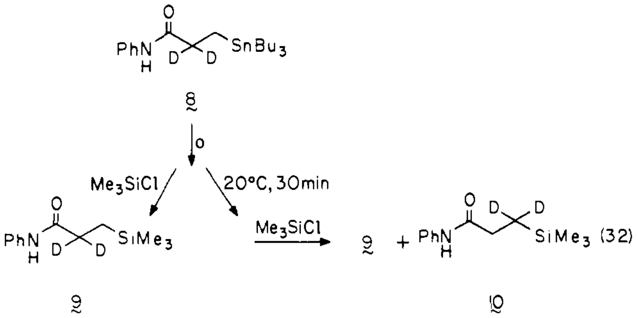
Table I. Reactions of 1 and 2 with Various Electrophiles

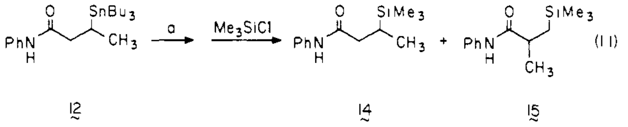
organolithium reagent	electrophile	product	yield, %
1	D_2O	6, E = D	84.5 (89 d_1)
1	Me_3SiCl	6, E = Me_3Si	72.0
2	D_2O	7, E = D	72.2 (95 d_1)
2	Me_3SiCl	7, E = Me_3Si	76.2
2	Bu_3SnCl	7, E = Bu_3Sn	64.0
2	$[CH_3(CH_2)_3]_2CO$	7, E = $[CH_3(CH_2)_3]_2COH$	67.2

Scheme I



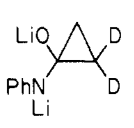
(a) THF, 2 DABCO, 2 n-BuLi, -70°C, 10 min.

Scheme II

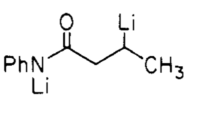


(a) THF, 2 DABCO, 2 n-BuLi, -70°C, 4 h.

To find out whether the rearrangement of **1** to **2** constitutes the migration of the phenyl ring or the involvement of a cyclopropane intermediate such as **3**, we prepared *N*-phenyl-3-(tri-*n*-butylstannyl)propionamide-*2*-d_2 (**8**).[8] Reactions of dilithio derivatives generated from **8** with chlorotrimethylsilane are described in Scheme I.[9] The formation of **10** indicates involvement of dilithiocyclopropane intermediate **11** in such a rearrangement.



11



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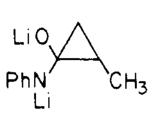

16

An attempt to detect the cyclopropyl intermediate **3** by using ^{1}H NMR spectroscopy was unsuccessful. The initial dilithio derivative **1**, generated from **4**, was stable below -40 °C. New signals,[10] consistent with the rearranged acyclic dilithio species **2**, started appearing at -40 °C. The rearrangement was complete in 1 h at this temperature, and quenching the reaction mixture with chlorotrimethylsilane produced **7** (E = $SiMe_3$). Consequently, the acyclic derivative **2**, rather than the cyclopropane **3**, is the major reactive species responsible for the formation of **7**.[11]

The tin-lithium exchange of **12** to produce the corresponding secondary dilithio derivative **13** was very slow at -70 °C (80% in 4 h).[12] Quenching the reaction mixture with chlorotrimethylsilane produced a 1:1 mixture of **14** and **15** (Scheme II). Tin-lithium exchange of **12** was much faster at -10 °C (complete within 30 min), but pure rearranged product **15** was isolated from the reaction mixture upon addition of chlorotrimethylsilane. We are considering other ways of generating such dilithiocyclopropane derivatives as well as attempting to trap these intermediates with other substrates.[13]

Acknowledgment. We thank Larry W. Kelts and Dr. J. John Uebel for obtaining the low-temperature ^{1}H NMR spectra of the organolithium reagents.

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[8] Acetyl-d_3 chloride was purchased from KOR Isotopes. Compound **8** was prepared from (iodomethyl)tri-*n*-butyltin and the 1,3-dilithio derivative derived from acetanilide-d_3.

[9] The unequal amounts of **9** and **10** (3:2) obtained may signify the incomplete formation of the intermediate **11** under the reaction conditions.

[10] The observed characteristic signals of **2**: ^{1}H NMR (THF-d_8) δ 2.42 (t, 1, J = 6.1 Hz, LiCH), 2.73 (d, 2, J = 6.1 Hz, CH_2), 5.10 (t, 1, J = 6.7 Hz, para H), 5.59 (d, 1, J = 7.3 Hz, ortho H), 5.94 (d, 1, J = 7.3 Hz, ortho′ H), 6.16 (appt, 1, J = 7.3, 6.7 Hz, meta H), 6.31 (appt, 1, J = 7.3, 6.7 Hz, meta′ H). DABCO was not present in this reaction mixture. Ortho and meta protons were nonequivalent up to 10 °C, above which **2** decomposed. Sandel, V. R.; McKinley, S. V; Freedman, H. H. *J. Org. Chem.* **1968**, *33*, 495-497.

[11] It is possible that **3**, even though present in low concentration, is the true reactive species for the formation of the rearranged products **7**. This is unlikely, as **2**, generated independently from **7** (E = $SnBu_3$) under conditions where cyclopropane formation is not expected (THF, 2 DABCO, 2 BuLi, -70 °C, 10 min), reacts with electrophiles such as Me_3SiCl to give exclusively **7** (E = $SiMe_3$).

[12] Compound **12** was prepared by the reaction of dilithioaniline with ethyl 3-(tributylstannyl)butyrate in THF.

[13] All compounds gave satisfactory spectral and analytical data.

Orientation of Complex Molecules Chemisorbed on Metal Surfaces: Near-Edge X-ray Absorption Studies

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Structural definition of chemisorbed states is essential to a molecular understanding of surface chemistry.[1] A large family of molecules of great significance in surface chemistry has in common π and π^* molecular orbitals that interact strongly with surfaces.[2] We describe here the general structural utility of a surface technique to the chemisorption states and surface reaction intermediates derived from such molecules. The technique is NEXAFS, which is based on the analysis of the polarization dependence of the *n*ear-*e*dge- *X*-ray-*a*bsorption *f*ine *s*tructure of the 1s core excitation of chemisorbed species. This technique has been previously applied to chemisorbed atoms[3] and diatomic molecules.[4,5]

The theory and technique of NEXAFS have been described previously.[3-5] In brief, the crystal is exposed to a monochromatic, linearly polarized beam of X-rays, and the X-ray absorption coefficient is measured as a function of X-ray beam angle with respect to the surface plane in the region near the K edge of an atom (e.g., C or N) in the adsorbed molecules. Absorption in this region is dominated by resonant transitions into bound (usually π^*) and pseudobound (usually σ^*) molecular orbital states. It has been shown for cylindrically symmetric molecules such as CO that the polarization dependence for transitions from an s initial

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