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Thermal and Photochemical Electron-Transfer Reactions of 4-Chlorobiphenyl with Lithium Diisopropylamides and Diisopropylamine

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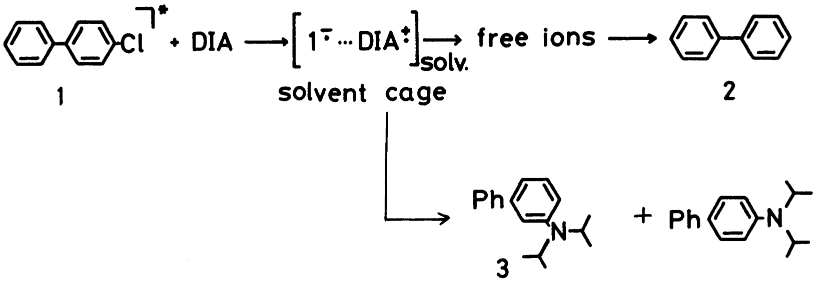
Synopsis. A reaction of 4-chlorobiphenyl with lithium diisopropylamide in a polar solvent gave 3- and 4-(diisopropylamino)biphenyl together with biphenyl, similar to the case of photoinduced reactions of 4-chlorobiphenyl with diisopropylamine. A common electron-transfer mechanism is proposed.

Lithium diisopropylamide (LDA) has been widely used for deprotonation and lithiation as a very strong nucleophile.[1] Recently, Ashby reported that the reaction of an alkyl halide with LDA proceeds through an electron-transfer rather than a lithiation or nucleophilic attack and gives a radical ion pair which collapses via concomitant reactions.[2] If the reaction starts from electron-transfer, the products are expected to be similar to those obtained from the well-known photoinduced electron-transfer reactions of halides with amines.[3–6] In accord with this expectation, comparing the products of reaction between 4-chlorobiphenyl (4-CB, **1**) and LDA with those of the photoinduced reactions of **1** with diisopropylamine (DIA), we found that the products of a thermal reaction in a polar solvent was similar to those of photochemical reactions, and their formation could be accounted for in terms of electron-transfer reactions. However, the features of a thermal reaction in THF at 0 °C were different from those of the photochemical reactions and the product ratios may be explained on the basis of a benzyne intermediate.[7]

We tried thermal reactions under two different reaction conditions; i) 0 °C in tetrahydrofuran(THF) and ii) 0 °C in THF-hexamethylphosphoramide(HMPA) (8:2). The yields of products, 3-and 4-(diisopropylamino)biphenyls (**3** and **4**) and biphenyl (**2**) were calculated by the standard GC analyses. On the other hand, irradiations of **1** in the presence of DIA were carried out in three different solvents, i.e., hexane, THF and acetonitrile. The yields of the products were analyzed in the same way as cases involving thermal reactions. The results are summarized in Table 1.

The major product of photochemical reactions is **2**, in accordance with our previous results.[3] Small amounts of amination products **3** and **4** were also isolated together with **2**. The yields of amination products seem to depend on the solvent polarity, i.e., the relative yield [**3**]/[**4**] is 1.8 in hexane, while 0.04 in acetonitrile. There is ample evidence that photoaddition of aromatics to a primary or secondary amine proceeds through proton-transfer in an exciplex to give a solvent caged radical pair in a nonpolar solvent, while in a polar solvent a solvent separated radical cation-radical anion pair is produced.[8] The solvent depen-



Scheme 1.

Table 1. Yields of Products Obtained from Thermal Reactions of **1** with LDA and from Photochemical Reactions of **1** with DIA[a)]

Reagent	Light	Temp °C	Solv.	Time/h	Conv. %	**5**[b)] %	**2** %	**3** %	**4** %	[**3**]/[**4**]
LDA	—	0	THF	3	90	0	18	31	21	1.5
LDA	—	0	THF-HMPA[c)]	2	100	0	57	18	5.4	3.3
DIA	d)	r.t	Hex	5	38	0	92	1.5	0.8	1.8
DIA	d)	r.t	THF	5	81	1.1	83	1.2	2.4	0.5
DIA	d)	r.t	MeCN	5	100	43	19	0.3	7.8	0.04

a) Yields were calculated based on GC analyses by using 2% OV-17 on Chromosob W NAW. b) 1,4-dihydrobiphenyl which may be produced by further reduction of biphenyl.[10] c) A mixture of THF-HMPA (8:2). d) A 6W low pressure mercury lamp was used.

dency of the product ratio observed in these photochemical reactions may reflect the different behavior of those different intermediate species. However, since the processes leading to the amination products are minor, discussion regarding the reaction mechanism based on the product ratios should be avoided at this stage. We would like to emphasize here that the major product of photoinduced electron-transfer is the reduction product **2**. The mechanism for formation of **2** may be complicate as shown in the case of 1-triethylamine system.[4-6]

The product ratios of thermal reaction of **1** with LDA carried out at 0 °C in THF-HMPA were similar to those of photochemical reactions, i.e., the major product is **2** and small amounts of the amination products **3** and **4** are also produced. Thus, the mechanism of this thermal reaction seems to be similar to that of photochemical reaction. A radical cation radical anion pair formed through thermal electron-transfer may participate in the reaction sequence. We, thus, propose path A in Scheme 2 as the most plausible mechanism for the major reaction between **1** and LDA in the polar solvent.

In sharp contrast with the thermal reaction in a polar solvent, the reaction in THF gave **3** and **4** as the major products and **2** as the minor one. This result is consistent with the case of thermal reaction between 4-bromobiphenyl and lithium piperidide in ether reported previously,[9] where the formation of the major products, 3- and 4-piperidinobiphenyl (47 and 37%), is explained in terms of the well known benzyne intermediate (Scheme 2, path B).[7,9] It is evident that both processes, i.e., electron-transfer and benzyne routes, participate in the thermal reactions aforementioned; however, the former is predominant in a polar solvent, while the latter is the major process in a nonpolar solvent.

In conclusion, on the basis of product analyses of photochemical reactions of **1** with DIA and of thermal reactions of **1** with LDA, we conclude that the reaction of **1** with LDA in a polar solvent proceeds through the electron-transfer mechanism similar to that in the photochemical reactions of **1** with DIA.

Experimental

IR spectra were determined on a JASCO IRA-1 spectrometer. H-and C-13 NMR were taken by using a JEOL GX-270 spectrometer in a $CDCl_3$ solution. UV-VIS spectra were taken on a Hitachi 320 spectrometer. Quantitative GC analyses were conducted with a Shimadzu GC-8 gas chromatograph using Pyrex column (2.5 mm i.d.×2 m) packed with 2% OV-17 on Chromosorb W NAW (80/100) at 130 to 230 °C. **1** and four products showed the following retention times; **1**, 7.5′; **2**, 4′; **3**, 10′; **4**, 10.5′ and 1,4-dihydrobiphenyl (**5**), 3′. GC-MS analyses were carried out on a Hitachi RMU-6MG mass spectrometer (20 eV). High resolution MS were measured with a Hitachi M-80 instrument.

THF was purified by refluxing over and distillation from $LiAlH_4$ under nitrogen. DIA and hexane were distilled from calcium hydride. Acetonitrile was distilled from P_2O_5 before use. *n*-BuLi in hexane was titrated immediately before use.

Typical Thermal Reaction of 1 with LDA. To a solution of LDA (3.13 mmol) prepared from DIA (316 mg, 3.13 mmol) and 1.20 mol dm^{-3} of *n*-BuLi in hexane (2.61 cm^3) was added a solution of **1** (200 mg, 1.06 mmol) in THF (1 cm^3) at 0 °C under nitrogen. The colorless solution gradually turned to deep red (λ_{max}=508 nm). After being allowed to stand for 3 h at 0 °C, the mixture was quenched with methanol, while the color was discharged, and extracted with ether to give 29% of **3**, 19% of **4**, 16% of **2** and 10% of recovered **1**. 1,3-(diisopropylamino)biphenyl (**3**): Bp 170—180 °C/0.5 mmHg# (Kugelrohr) ^{1}H NMR ($CDCl_3$) δ=7.60—6.85 (9H, m), 3.84 (2H, septet, J=6.8 Hz) and 1.25 (6H, d, J=6.8 Hz); ^{13}C NMR ($CDCl_3$) δ=148.35 (C-1), 118.06 (C-2), 142.21 (C-3), 118.12 (C-4), 117.22 (C-6), 141.57 (C-1′), 47.66 (methine) and 21.42 (methyl); IR (liquid film) 790 cm^{-1}; MS (20 eV) *m/z* (rel intensity) 253 ($M^{+\cdot}$ 11), 238 (37), 196 (100), 180 (18), 154 (26), 153 (26), and 152 (26): Found; *m/z* 253.1834, Calcd, for $C_{18}H_{23}N$; $M^{+\cdot}$ 253.1830. 4-(diisopropylamino)biphenyl (**4**): Bp 170—185 °C/0.5 mmHg (kugelrohr); ^{1}H NMR ($CDCl_3$) δ=7.69—7.20 (5H, m), 6.93 (2H, d, J=8.79 Hz) and 7.45 (2H, d, J=8.79 Hz) ^{13}C NMR ($CDCl_3$) δ=147.44 (C-1), 118.22 (C-2), 129.59 (C-4), 141.18 (C-1′), 47.54 (methine) and 21.32 (methyl); IR (liquid film) 830, 760 and 700 cm^{-1}; MS (20 eV) *m/z* (rel intensity) 253 (($M^{+\cdot}$ 16), 239 (18), 238 (46), 223 (8.2), 210 (23), 196 (100), 180 (16), 154 (23), 153 (17) and 152 (16). Found; *m/z* 253.1815, Calcd. for $C_{18}H_{23}N$; $M^{+\cdot}$ 253.1830.

Alternative Preparation of 4. A suspension of 4-aminobiphenyl (34 mg), KOH (28 mg) and isopropyl iodide (69 mg) in THF (2 cm^3) was refluxed overnight. Extraction with ether gave a crude oil (35 mg). To a solution of the oil in 1,2-dimethoxyethane (2 cm^3) was added 1.20 mol dm^{-3} *n*-BuLi in hexane (0.2 cm^3) at 0 °C under nitrogen. The mixture was refluxed over 2 d and extracted with ether to give 33 mg of a yellow oil in 65% yield.

Typical Photoreaction of 1 with Diisopropylamine. Irradiation of a solution of **1** (20 mg, 0.106 mmol) and diisopropylamine (0.3 cm^3) in acetonitrile (1 cm^3) with a 6 W low-pressure mercury arc for 5 h gave **3** and **4** in 0.30 and 7.8% yields, respectively, in addition to 43% of 1,4-dihydrobiphenyls (**5**)[10] and 19% of **2** as major products.

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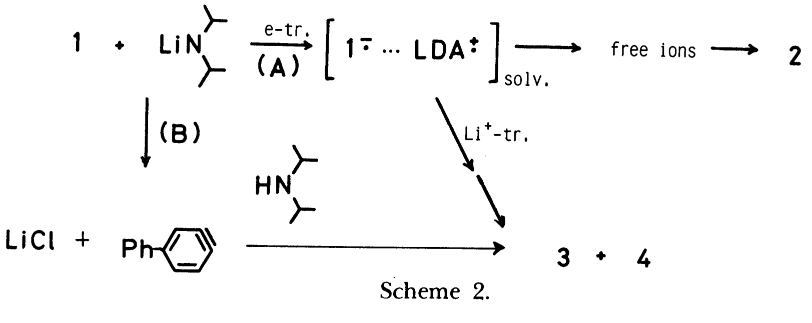

Scheme 2.

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#) 1mmHg≈133.322 Pa.