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Reductive dearomatization of biphenyl: sequential one-pot regioselective introduction of two different electrophiles

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Dedicated to Professor Teruaki Mukaiyama on occasion of his 80th birthday

Abstract—The reaction of biphenyl (**1**) with an excess of lithium in THF at room temperature leads to a solution of the corresponding dianion (**I**), which by successive reactions with an alkyl fluoride [$E_1 = n\text{-}C_8H_{17}F$, $c\text{-}C_5H_9CH_2F$, $CH_2{=}CH(CH_2)_4F$] at 0 °C and another electrophile [$E_2 = n\text{-}C_4H_9Br$, Et_2CO, $Me_2C(O)CH_2$, $i\text{-}Pr_3SiCl$] at −78 °C yields the corresponding 1,4-disubstituted 1,4-dihydrobiphenyls **3** in a regioselective manner, as mixtures of cis- and trans-isomers. The diastereomers of **3** are separated by column chromatography.

Aromatic compounds are widely distributed in nature and represent a potentially useful pool of synthetically versatile molecules. In general, arenes are easily accessible, highly stable and readily derivatized through reactions such as electrophilic and nucleophilic substitution,[1] tandem *ortho*-lithiation/S_E reaction,[2] and metal-catalyzed coupling processes.[3] However, for the preparation of alicyclic synthetic building blocks it is necessary to perform the controlled dearomatization of the aromatic ring, which is not an easy reaction because it requires disruption of the aromatic π-system.[4] Among different methodologies to carry out the controlled dearomatization of an arene, reduction processes have been commonly used,[5–8] the Birch reaction being the most versatile and efficient one for that purpose.[9]

On the other hand, in the last few years we have been employing an arene-catalyzed lithiation[10] for the preparation of very reactive organolithium intermediates[11] (such as functionalized organolithium compounds[12] or dilithium synthons[13]) or the activation of other metals[14] under mild reaction conditions. Concerning the mechanism of this reaction, we have found that the most reactive electron transfer agent in the process is the corresponding arene dianion,[15] and not just the radical-anion commonly accepted to take part in the stoichiometric version of the arene-promoted lithiation.[16] Very recently,[17] we have reported that the dianion intermediate has a special reactivity so, for instance, in the case of biphenyl (**1**) it can add a terminal olefin ($R^1R^2C{=}CH_2$) followed by reaction with a carbonyl compound ($R^3_2C{=}O$) to yield the corresponding *trans*-3,4-disubstituted compounds **2** (Scheme 1). Apart from the initially formed dianion **I**, intermediates **II** (after addition to the olefin), **III** (resulting from a proton abstraction by the non-stabilized organolithium **II** from the reaction medium[18]) and **IV** (after regio- and stereoselective reaction with the carbonyl compound), are involved in the process.

In this Letter, we report a new and different reactivity of dianion **I** with two subsequent electrophilic reagents, namely, an alkyl fluoride[15c,d] and a variety of conventional electrophiles, which give compounds resulting from a 1,4-disubstitution instead of the 3,4-disubstitution observed for products **2**.

The reaction of biphenyl (**1**) with an excess of lithium powder (1:12 molar ratio) in THF at room temperature gave a deeply coloured greenish-blue solution of dianion **I**, which was successively treated with an alkyl fluoride[19] as the first electrophile [$E_1 = n\text{-}C_8H_{17}F$, $c\text{-}C_5H_9CH_2F$,

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Keywords: Biphenyl dianion; Electrophilic substitution; Alkyl fluorides; Electron transfer.

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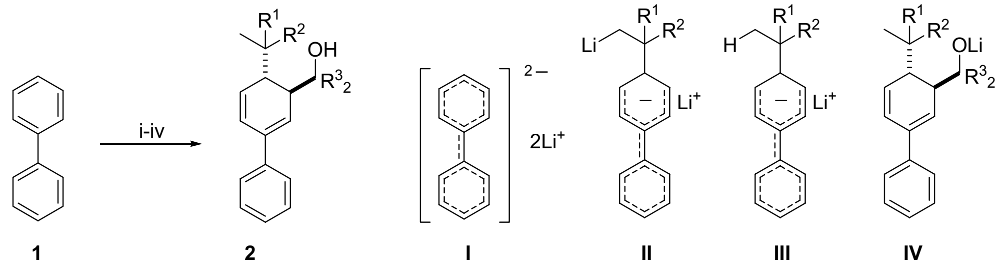
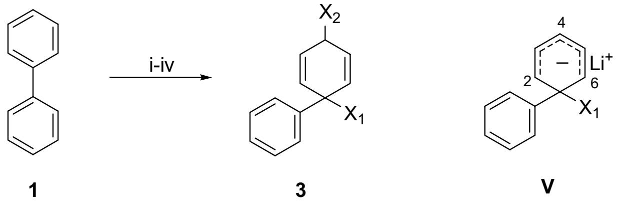


Scheme 1. Reagents and conditions: (i) Li, THF, rt; (ii) $R^1R^2C{=}CH_2$; (iii) R^3_2CO, −78 °C; (iv) H_2O, −78 °C to rt.

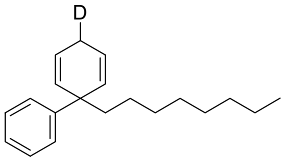
$CH_2{=}CH(CH_2)_4F$; 1:1.1 molar ratio, 0 °C, 30 min], and a second electrophile [$E_2 = n\text{-}C_4H_9Br$, Et_2CO, $Me_2C(O)CH_2$, $i\text{-}Pr_3SiCl$; 1:1.1 molar ratio, −78 °C, 15 min], giving after final hydrolysis with water (−78 °C to rt) the corresponding 1,4-disubstituted compounds **3** as a mixture of cis/trans-diastereomers (Scheme 2 and Table 1).[20]

The reactions with the unsaturated fluoride (Table 1, entries 7 and 8) and the fact that no cyclopentylmethyl derivatives were obtained within the detection limits of GLC (Table 1, entries 5 and 6), point towards a bimolecular substitution reaction as the key step of the process, rather than a SET reaction from dianion intermediate **I** to the electrophile. That SET reaction pathway is well described to occur with other alkyl halides.[15c] After the introduction of the first electrophilic fragment, the resulting intermediate of type **V** reacts regio but not stereoselectively with the second electrophile to give, after hydrolysis, a cis/trans-mixture of the 1,4-disubstituted diastereomers **3**.[21] From a preparative point of view it is worthy to note that both diastereomers could be separated by column chromatography in all cases except for the minor components *trans*-**3c**,**d** (Table 1, entries 3 and 4), which were contaminated with variable amounts of the major cis-diastereomer (ca. 30% for *trans*-**3c**) or other byproducts (ca. 20% for *trans*-**3d**). The stereochemistry of both cis and trans-diastereomers was assigned in all cases by NMR experiments, especially NOESY measurements.

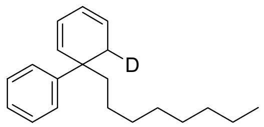
A especial case was the use of deuterium oxide as the second electrophile: after introduction of the octyl group, together with the expected mixture of 1,4-disubstituted deuterated products **4**-D (47%, 53:47 dr, >98.5% deuterium incorporation from MS and ^{1}H NMR, natural isotopic distribution corrected), the corresponding mixture of 1,2-disubstituted deuterated adducts **5**-D (31%, 62:38 dr, >99.8 deuterium incorporation, determined as above) was also isolated. It is well known that the cyclohexadienyl anion is kinetically more reactive at the central position (e.g., $C_{(4)}$ of **V** in Scheme 2), which is endowed with a higher HOMO coefficient. However, for the highly polarized H–O bond of water, the protonation step may be primarily controlled by electrostatic interactions. The density of charge is more equally distributed between $C_{(2)}$, $C_{(4)}$ and $C_{(6)}$ positions than the weight of these atoms in the HOMO of **V**, therefore a loss of selectivity is expected in a reaction pathway driven by polar interactions. PM3 calculations on **V** ($X_1 = n$-octyl, free anion) confirm these findings: relevant data for the lowest C_s conformer of **V** ($X_1 = n$-octyl, no counterion) are, $C_{(2)}{=}C_{(6)}$: 0.52 (−0.52); $C_{(4)}$: 0.62 (−0.57) (HOMO coefficients at the given atom, Mulliken charges in parenthesis).[22]



Scheme 2. Reagents and conditions: (i) Li excess (1:12 molar ratio), THF, rt, 30 min; (ii) $E_1 = n\text{-}C_8H_{17}F$, $c\text{-}C_5H_9CH_2F$, $CH_2{=}CH(CH_2)_4F$ (1:1.1 molar ratio), 0 °C, 30 min; (iii) $E_2 = n\text{-}C_4H_9Br$, Et_2CO, $Me_2C(O)CH_2$, $i\text{-}Pr_3SiCl$; 1:1.1 molar ratio, −78 °C, 15 min; (iv) H_2O, −78 °C to rt.



4-D

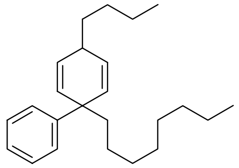
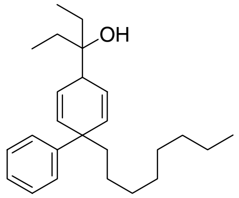
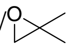
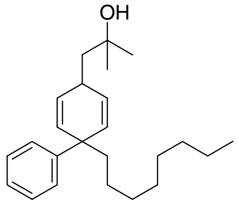
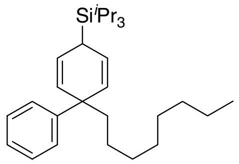
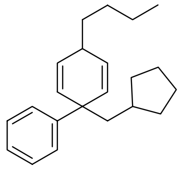
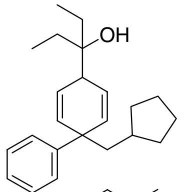
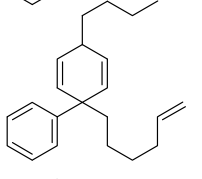
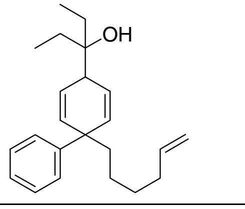


5-D

The choice of primary alkyl fluorides as first alkylating reagents is a critical matter, as it has been stated in a previous work.[15c,d] Alkyl fluorides are not generally viewed as good electrophiles in the reaction with conventional nucleophiles. However, it is not so when facing arene dianions, in which case they react in a regioselective manner affording alkylated dihydroarenes in good yields. On the other hand, arene dianions and radical-anions are a kind of highly reduced organic species that tend to react as SET reagents versus conventional alkylating reagents (such as RX, X = Cl, Br, I, OSO_2R),[15b,c] affording in general complex mixtures derived from the development of radicals. The reason for this behaviour may rely on an adequate energy levelling between the MO of both reagents, involving a high laying LUMO of the alkyl fluoride, but also a high laying HOMO of the biphenyl dianion. The resulting interaction favours the nucleophilic substitution pathway, rather than an SET mechanism.

As a conclusion, the successive reaction of the dianion of biphenyl (**I**) with an alkyl fluoride as the first electro-

Table 1. Preparation of compound **3**

Entry	Electrophiles E_1/E_2	Product **3**				
		Structure[a]	No.	Yield (%)[b]	cis/trans[c]	(t_R values)[d]
1	n-$C_8H_{17}F$/n-C_4H_9Br		**3a**	98	0.9/1	14.11/14.18
2	n-$C_8H_{17}F$/Et_2CO		**3b**	61	1/0.7	15.69/15.84
3	n-$C_8H_{17}F$/		**3c**	58	1/0.4	15.15/15.21
4	n-$C_8H_{17}F$/i-Pr_3SiCl		**3d**	82	1/0.4	16.77/17.00
5	c-$C_5H_9CH_2F$/n-C_4H_9Br		**3e**	81	0.9/1	13.38/13.48
6	c-$C_5H_9CH_2F$/Et_2CO		**3f**	59	0.5/1	14.70/14.87
7	$CH_2{=}CH(CH_2)_4F$/n-C_4H_9Br		**3g**	86	0.9/1	13.48/13.62
8	$CH_2{=}CH(CH_2)_4F$/Et_2CO		**3h**	58	1/0.6	14.57/14.77

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[a] All compounds **3** (both diastereomers) were >95% pure [except for *trans*-**3c** (ca. 70%) and *trans*-**3d** (ca. 80%); GLC and/or 300 MHz ^1H NMR] and were fully characterized by spectroscopic means (IR, ^1H and ^{13}C NMR, LRMS and HRMS).

[b] Isolated yield after column chromatography (silica gel, hexane/ethyl acetate).

[c] Determined by GLC and/or 300 MHz ^1H NMR of the reaction crude.

[d] Measured with a Hewlett–Packard HP-5890 instrument equipped with a flame ionization detector and a HP-5 capillary column (30 m, 0.32 mm diam.), using nitrogen as gas carrier, $T_{injector} = 275$ °C; $T_{detector} = 300$ °C; $T_{column} = 60$ °C (3 min) and 60–270 °C (15 min), $P = 12$ psi; t_R are given under these conditions.

phile and with a different second electrophile works regio but not stereoselectively, the 1,4-regiochemistry being drastically different than the 1,2 observed when the same dianion reacts first with an olefin and then with a carbonyl compound as electrophile. At this moment we do not have any clear explanation to justify the change in the regiochemistry observed for dianion **I** depending on the nature of the electrophiles used. A full mechanistic study involving both the dianion and the electrophilic counterpart (i.e., the alkene or the alkyl fluoride) and their respective low energy reaction pathways is ongoing.

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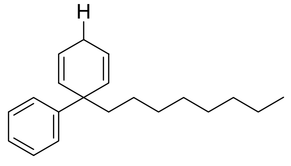
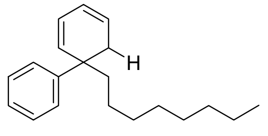
18. It is well known that THF can suffer α-deprotonation by reacting with organolithiums. See, for instance: (a) Stanetty, P.; Koller, H.; Mihovilovic, M. *J. Org. Chem.* **1992**, *57*, 6833–6837; For a recent report, see also: (b) Clayden, J.; Yasin, S. A. *New J. Chem.* **2002**, *26*, 191–192, However, in this case the alkene used (excess) is the proton source suffering deprotonation at the allylic position (see Ref. 17).
19. *n*-Octyl fluoride is commercially available (Aldrich). Cyclopentylmethyl and 5-hexenyl fluorides were prepared from the corresponding alcohols according to the literature procedure: (a) Pattison, F. L. M.; Norman, J. J. *J. Am. Chem. Soc.* **1957**, *79*, 2311–2316; (b) Filipo, J. S., Jr.; Romano, L. J. *J. Org. Chem.* **1975**, *40*, 1514–1515.
20. In a *typical reaction* to a stirred (rt, 30 min) greenish-blue suspension of a mixture of biphenyl (1 mmol) and lithium powder (12 mmol) in dry THF (10 mL) was added the corresponding alkyl fluoride[19] (1.1 mmol) at 0 °C and after 30 min at the same temperature the mixture was cooled at −78 °C. The second commercially available (Aldrich) electrophile (1.1 mmol) was then added and after 15 min stirring the resulting mixture was hydrolyzed with water (5 mL) allowing the temperature to rise to room temperature. The mixture was extracted with diethyl ether (3×20 mL), the organic layer dried over Na_2SO_4 and evaporated (15 Torr) to give a residue that was purified by column chromatography (silica gel, hexane/ethyl acetate). Spectroscopic data for compounds **3f** follow: *cis*-**3f**: IR (film): ν (cm^{-1}) = 3475, 3083, 3056, 3023, 2941, 2866, 1597, 1491, 1460, 1446, 1154, 1122, 952, 937, 913, 697; ^1H NMR (300 MHz, $CDCl_3$): $\delta_H = 0.93$ (t, $J = 7.5$ Hz, 6H, $2 \times C\mathit{H}_3CH_2$), 1.03–1.14 (m, 2H, $2 \times C\mathit{H}H$ of cyclopentyl), 1.36–1.47 (m, 2H, $2 \times C\mathit{H}H$ of cyclopentyl), 1.52–1.68 (2m, 7H, $2 \times C\mathit{H}H$ of cyclopentyl, $2 \times C\mathit{H}_2CH_3$, OH), 1.73–1.86 [2m, 3H, $2 \times C\mathit{H}H$ of cyclopentyl, $CH_2C\mathit{H}(CH_2)_2$], 1.92 [d, $J = 5.5$ Hz, 2H, $CC\mathit{H}_2CH(CH_2)_2$], 2.94–2.98 [m, 1H, $(CH{=}CH)_2C\mathit{H}COH$], 5.80–5.91 [m, 4H, $(CH{=}C\mathit{H})_2C(Ph)$, $(CH{=}C\mathit{H})_2CHCOH$], 7.12–7.20 (m, 1H, Ph), 7.26–7.39 (m, 4H, Ph); ^{13}CNMR: $\delta_C = 7.56$ ($2 \times CH_3$), 24.96 (2C of cyclopentyl), 29.00 ($2 \times \mathit{C}H_2CH_3$), 34.87 (2C of cyclopentyl), 36.90 [$CH_2\mathit{C}H(CH_2)_2$], 42.24 [$(CH{=}CH)_2\mathit{CH}COH$], 44.79 [$(CH{=}CH)_2\mathit{C}(Ph)$], 47.16 [$\mathit{C}H_2CH(CH_2)_2$], 76.27 (COH), 123.62 [2C, $(CH{=}\mathit{C}H)_2$-CHCOH], 125.85 (CH_{Ph}), 126.59 (2C, CH_{Ph}), 128.24 (2C, CH_{Ph}), 135.69 [2C, $(CH{=}\mathit{C}H)_2C(Ph)$], 147.73 ($C_{Ph}$); MS: *m*/*z* (%): 306 (3.43%, $M^+{-}18$), 223 (26), 181 (14), 167 (32), 156 (17), 155 (65), 154 (38), 153 (11), 87 (100), 69 (12), 55 (14); HRMS: calcd. for $C_{23}H_{30}$306.2348; found 306.2371. *trans*-**3f**: IR (film): ν (cm^{-1}) = 3473, 3024, 2941, 2867, 1492, 1447, 910, 763, 733, 698; ^1H NMR (300 MHz, $CDCl_3$): $\delta_H = 0.87$ (t, $J = 7.50$ Hz, 6H, $2 \times C\mathit{H}_3CH_2$), 1.13–1.01 (m, 2H, $2 \times C\mathit{H}H$ of cyclopentyl), 1.40–1.46 (m, 2H, $2 \times C\mathit{H}H$ of cyclopentyl), 1.46–1.62 (2m, 7H, $2 \times C\mathit{H}H$ of cyclopentyl, $2 \times C\mathit{H}_2CH_3$, OH), 1.70–1.86 [2m, 3H, $2 \times C\mathit{H}H$ of cyclopentyl, $CH_2C\mathit{H}(CH_2)_2$], 1.90 [d, $J = 5.7$ Hz, 2H, $CC\mathit{H}_2CH(CH_2)_2$], 2.94–3.01 [m, 1H, $(CH{=}CH)_2C\mathit{H}COH$], 5.85 [dd, $J = 10.5$ Hz, $J = 3.1$ Hz, 2H, $(CH{=}C\mathit{H})_2CHCOH$, 5.92 [dd, $J = 10.5$ Hz, 1.7 Hz, 2H, $(CH{=}C\mathit{H})_2C(Ph)$]. 7.12–7.18 (m, 1H, Ph), 7.24–7.31 (m, 2H, Ph), 7.34–7.39 (m, 2H, Ph); ^{13}C NMR: $\delta_C = 7.61$ ($2 \times CH_3$), 25.08 (2C of cyclopentyl), 28.84 ($2 \times \mathit{C}H_2CH_3$), 34.76 (2C of cyclopentyl), 37.19 [$CH_2\mathit{C}H(CH_2)_2$], 42.39 [$(CH{=}CH)_2\mathit{CH}COH$], 44.75 [$(CH{=}CH)_2\mathit{C}(Ph)$], 48.38 [$\mathit{C}H_2CH(CH_2)_2$], 76.74 (COH), 124.03 [2C, $(CH{=}\mathit{C}H)_2$-CHCOH], 125.75 (CH_{Ph}), 126.43 (2C, CH_{Ph}), 128.25 (2C, CH_{Ph}), 135.67 [2C, $(CH{=}\mathit{C}H)_2C(Ph)$], 148.35 ($C_{Ph}$); MS: *m*/*z* (%): 306 (9.91%, $M^+{-}18$), 277 (25), 224 (18), 223 (26), 222 (12), 181 (46), 178 (13), 168 (17), 167 (100), 165 (19), 156 (15), 155 (71), 154 (36), 153 (15), 152 (15), 87 (66), 69 (23), 55 (18); HRMS: calcd for $C_{23}H_{30}$306.2348; found 306.2381.
21. Regarding the assignment of structures **3** (i.e., the correct position of X_1 and X_2 versus the hypothetical compound in which X_1 and X_2 are permuted, which otherwise would be the expected product based on calculations and our previous experience with the biphenyl dianion), it was unequivocally established based on the ^{13}C NMR and DEPT experiments of compounds **4**-H and **5**-H. These two compounds clearly display one methylenic carbon [$\mathit{C}H_2(CH{=}CH)_2$ and $C\mathit{C}H_2CH{=}CH$ in **4**-H and **5**-H, respectively], in addition to the 7 methylene groups of the *n*-octyl moiety, as well a quaternary aliphatic centre [$Ph\mathit{C}(n\text{-octyl})(CH{=}CH)_2$ and $Ph\mathit{C}(n\text{-octyl})(CH{=}CH)CH_2$ in **4**-H and **5**-H, respectively], compatible only with the proposed structures.



4-H



5-H

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