

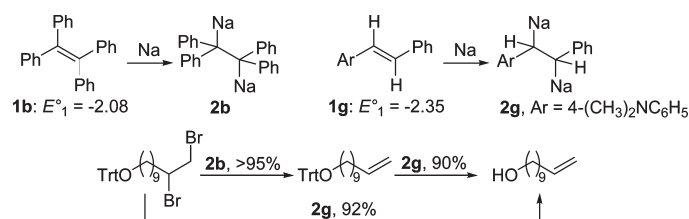
Tuning the Reducing Properties of 1,2-Diaryl-1,2-disodiummethanes

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We investigated the reducing properties of a series of 1,2-diaryl-1,2-disodiummethanes by means of equilibration reactions. The electron-donor power of these *vic*-diorganometals is strongly affected by the nature of substituents present either on the aromatic ring(s) or on the carbanionic centers, and it can be correlated with their ability to delocalize the arylmethyl carbanions. These findings are supported by electrochemical analysis of the reduction behavior of the parent 1,2-diarylethene. Applications of these results to the reduction of selected substrates are described.

1. Introduction

Owing to its availability, low price, and high reducing ability,¹ sodium metal is particularly attractive as a reducing agent for organic synthesis.² To take full advantage of its reducing power, several methods were developed for obtaining highly reactive forms of the metal, encompassing either homogeneous (e.g., sodium naphthalenide in THF,³ or solutions of the metal in liquid ammonia¹ or HMPA⁴) or heterogeneous (e.g., polymer-supported sodium naphthalenide,⁵

dispersions of the metal on solid supports like SiO₂,⁶ and others⁷) reagents. It is worth noting, however, that different active forms of the same metal may exhibit substantial differences in chemical performance.⁸

We recently reported^{2a,b} that reductive metalation of aryl-substituted alkenes **1** with Na metal in dry THF affords the corresponding 1,2-diaryl-1,2-disodiummethanes **2**. We also reported application of these dianions as effective “single electron” reductive elimination reagents toward functionalized and nonfunctionalized *vic*-dihalides, and related compounds. These *vic*-diorganometals can thus be considered as synthetic equivalents of an activated and highly reactive form of Na metal.

To further explore their synthetic utility as reducing agents, we have investigated the effect of substitution pattern on the reducing power of several 1,2-diaryl-1,2-disodiummethanes. In particular, we carried out a series of equilibration reactions between several different *vic*-diorganometals **2** and studied the electrochemical reductive behavior of the parent 1,2-diarylethanes **1** (Chart 1).

The results allowed us to establish a scale of the reducing power of these dianions. The chemical scale nicely correlates with the electroreduction order. Applications of these findings to the reduction of selected substrates will also be described.

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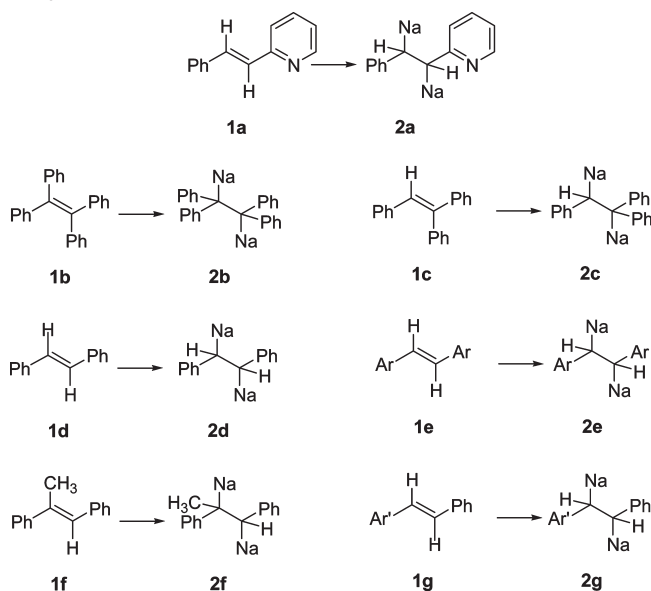
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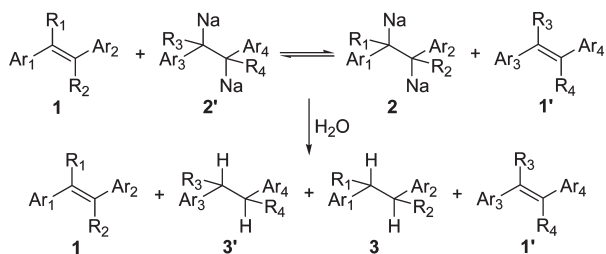
(7) (a) Fürstner, A.; Seidel, G. *Synthesis* **1995**, 63–68 and references cited therein. (b) Makosza, M.; Grela, K. *Synlett* **1997**, 267–268 and references cited therein.

(8) See, for example: (a) Cintas, P. *Activated Metals in Organic Synthesis*; CRC Press: Boca Raton, FL, 1993. (b) Fürstner, A. *Active Metals*; VCH: Weinheim, Germany, 1996.

CHART 1. Formulae of the Various Alkenes/Dianions Couples Investigated: 1e, 2e, Ar = 2-(CH₃O)C₆H₄; 1g, 2g, Ar' = 4-(CH₃)₂-NC₆H₄.



SCHEME 1. Equilibration Reaction between vic-Dianions 2



2. Results and Discussion

2.1. Chemical Determination of the Relative Scale of the Reductive Power of 1,2-Diaryl-1,2-disodiummethanes 2. To establish a scale of the reducing ability of substituted *vic*-diorganometals, we reacted a series of 1,2-diaryl-1,2-disodiummethanes (**2** or **2'**), with different 1,2-diaryl-substituted ethenes (**1'** or **1**). All reactions were run in THF, under dry Ar, and at 0 °C; the reactions involving dianion **2f** were run at -10 °C, as this species is unstable at higher temperatures.⁹ After equilibration for 12 h and quenching with H₂O, we obtained crude mixtures containing 1,2-diaryl-substituted alkenes (**1** and/or **1'**) and the corresponding aryl-substituted alkanes (**3** and/or **3'**) (Scheme 1 and Table 1).

The distribution of the reaction products was determined by ¹H NMR spectroscopy, and the ratio between bibenzyls **3** and **3'** was taken as an estimate of the equilibrium ratio between the corresponding dianions (**2** and **2'**).

The results (Table 1) were reproducible within ±5% independently of the specific alkene/dianion reactant couple (either **1** + **2'** or **1'** + **2** in Scheme 1). By assuming that equilibration is mainly governed by the relative stabilities of the different dianions, the results provide a measure of the relative reducing power of the corresponding *vic*-diorganometals,

TABLE 1. Equilibrium Ratio of *vic*-Diorganometal Couples 2/2'^a

Entry	<i>vic</i> -Diorganometal couple	T (°C)	Product ratio (3/3')
1		0	>95:<5
2		0	>95:<5
3		0	80:20
4		0	>95:<5
5		0	57:43
6		-10	>95:<5
7		0	70:30
8		-10	65:35

^aAll reactions were run in THF under dry Ar during 12 h.

and show that substituents, located either on the aromatic rings or on benzylic carbons, strongly affect the equilibration process. By taking 1,2-diphenyl-1,2-disodiummethane **2d** as the reference dianion, we can observe that whereas dianions bearing substituents able to delocalize the arylmethyl carbanion (as in compounds **2a-c**) accumulate in the equilibrium mixtures, the opposite trend is observed in the presence of electron-donating substituents (as in **2e-g**). Dianion **2e**, bearing two *o*-methoxy substituents,¹⁰ appears as only slightly less stable than dianion **2d**. Consequently, the investigated

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(10) Our procedure could not be applied to the generation of *p*-methoxy-substituted dianions **2**, due to competitive demethoxylation reactions (see ref 2a).

TABLE 2. Cyclic Voltammetry Data for 1,2-Diarylethenes 1

entry	substrate	E°_1 ^a (V vs. SCE)	E°_1 ^b (V vs. SCE)	$(E_p)_2$ ^a (V vs. SCE)
1	1a	-2.003	-2.026	-2.425
2	1b	-2.084		- ^c
3	1c	-2.119		-2.386
4	1d	-2.182	-2.177	-2.607
5	1e	-2.202		-2.619
6	1f	-2.323		-2.588
7	1g	-2.354	-2.369	-2.717

^aDMF/0.1 M TBAP, glassy carbon electrode, 25 °C. ^bTHF/0.1 M TBAP, glassy carbon electrode, 25 °C. ^cNot present, see text.

vic-dianions can be ordered according to the following scale of increasing reducing power: **2a** < **2b** < **2c** < **2d** ≤ **2e** < **2f** ≤ **2g**.

2.2. Electrochemical Determination of Reduction Potentials of 1,2-Diarylethenes 1. The above results were compared with those obtained by studying the electroreduction of diarylalkenes **1a–g**. The formal reduction potential (E°) and irreversible peak potential (E_p) values were determined at 25 °C by cyclic voltammetry in DMF. Tetrabutylammonium perchlorate (TBAP) was the supporting electrolyte and glassy carbon was the electrode material. DMF was the solvent of choice for its excellent electrochemical characteristics and for the sake of comparison with previous work.¹¹ Some representative cyclic voltammetry experiments, however, were carried out in the solvent used for equilibration reactions, THF, and led to similar results both in the shape and relative position of the alkene reduction peaks. Table 2 shows the results.

The reduction of alkenes **1** occurs via two one-electron steps, with stepwise formation of the corresponding radical anions and dianions. These reduction steps also correspond to separate voltammetric peaks, except for **1b** (see below).¹¹

Electroreduction of alkene **1a** to its radical anion (Table 2, entry 1, column 3) is chemically reversible even at low potential scan rate (ν) values, i.e., on a relatively long time scale. The E° was calculated as the average between the cathodic and anodic peak potentials. The same behavior was observed for alkenes **1d**, **1e**, and **1g** (Table 2, entries 4, 5, and 7, column 3). Figure 1 compares the first reduction peak of alkenes **1a–g**.

By extending the voltammetric scan to more negative potential values, a second reduction peak, related to the formation of the corresponding dianions, was observed.¹² For all compounds, this peak is irreversible due to the high basicity of these dianions and, therefore, their tendency to undergo protonation by residual water in the solvent/electrolyte system. Table 2 (column 5) shows the E_p values measured at 0.2 V s⁻¹. We found that E_p shifts toward more negative potentials by ~30 mV for a 10-fold increase of ν , which is the typical behavior indicating that a first-order (or pseudo-first-order) chemical reaction follows electron transfer.¹³

(11) The electrochemical behavior of **1b–d**, under various conditions, was already reported. **1b**: (a) Farnia, G.; Maran, F.; Sandonà, G. *J. Chem. Soc., Faraday Trans. 1*, **1986**, 82, 1885–1892. **1c**: (b) Farnia, G.; Maran, F.; Sandonà, G.; Severin, M. G. *J. Chem. Soc., Perkin Trans. II* **1982**, 1153–1158. **1d**: (c) Meerholz, K.; Heinze, J. *J. Am. Chem. Soc.* **1989**, 111, 2325–2326.

(12) A third wave was observed for **1a** ($E^{\circ}_3 = -2.780$ V vs. SCE). We assigned it to the formation of a pyridine-type radical anion. Indeed, pyridine itself is electrochemically reduced in DMF at -2.76 V vs. SCE; similarly, mono-, di-, and trimethylpyridines are reduced with E° ranging from -2.77 and -2.91 V vs. SCE: See: Tabner, B. J.; Yandel, J. R. *J. Chem. Soc. A* **1968**, 381–388.

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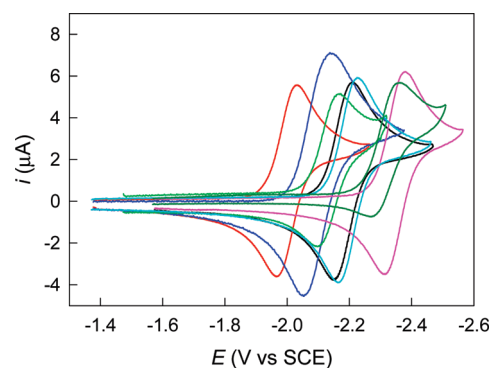


FIGURE 1. Cyclic voltammograms for the reduction of (from left to right) **1a**, **1b**, **1c**, **1d**, **1e**, **1f**, and **1g** in DMF/0.1 M TBAP (glassy carbon electrode, 25 °C, $\nu = 0.2$ V s⁻¹, $C = 1$ mM).

The separation between the first and second reduction peaks is very similar for **1a**, **1d**, and **1e** (392, 395, and 387 mV, respectively), which points to homogeneity of behavior and properties. A slightly smaller value, 333 mV, was determined for **1g**: this difference could be related to thermodynamic reasons (smaller difference between the two E° values) and/or a higher basicity of the dianion **2g**, and, therefore, to a faster protonation rate resulting in a larger positive shift of the second reduction peak.

Under otherwise identical conditions, a different behavior was observed for tetraphenylethylene **1b**. For this alkene, the reversibility of the reduction peak decreases for $\nu < 2$ V s⁻¹; we already showed that this behavior is caused by radical-anion disproportionation followed by protonation of the ensuing dianion by residual water in the solvent/electrolyte system.^{11b} A peculiar feature of the reduction of **1b** is the observation of a large peak current value, as the other alkenes of the series display very similar values of the peak current when normalized for the concentration (cf. Figure 1). Additionally, a distinct peak corresponding to dianion formation is absent. This behavior is caused by the fact that the difference between the E° values of the first and second reduction steps is only 60 mV (in the presence of tetraethylammonium cations, the value is 31 mV), which causes merging of the two reduction peaks.^{11a} Such a large positive shift of the second E° is caused by a favorable structural rearrangement associated with electron transfer.^{11a,14}

At low ν values, whereas the chemical reversibility of the first peak of **1c** is only partially affected by residual water in the solvent/electrolyte system, dianion formation is strongly affected by protonation of the dianion.^{11b} At 0.2 V s⁻¹, $(E_p)_2$ is 267 mV more negative than E°_1 ; on the other hand, when the reduction is carried out in the presence of highly activated alumina, the second peak also becomes chemically reversible and E°_2 is determined to be 317 mV more negative than E°_1 .^{11b} The reduction of α -methylstilbene, **1f**, proceeds along very similar lines: the first peak is reversible only for moderate ν values (Table 2, entry 6, column 3) and the $E^{\circ}_1 - (E_p)_2$ difference, 265 mV, is identical within error to that of **1c**, 267 mV.

2.3. Comparison between Chemical and Electrochemical Results. Overall, the results of Table 2 compare well with

(14) Szwarc, M.; Jagur-Grodzinski, J. In *Ions and Ions Pairs in Organic Reactions*; Szwarc, M., Ed.; Wiley: New York, 1974; Vol. 2, pp 1–150.

those obtained in the equilibration reactions. The formal potentials of the first reduction step, i.e., those corresponding to formation of the radical anions, steadily increase on going from **1a** to **1g**, in agreement with the empirical scale of reducing power described above. This trend is confirmed by the results obtained for the first reduction peak of alkenes **1a**, **1d**, and **1g** (Table 2, column 4) in THF, i.e., the solvent of the equilibration reactions described in the previous section. The same trend is also observed for the dianion-formation potentials of alkenes **1a**, **1d**, **1e**, and **1g**.

Indeed, the general agreement between chemical and electrochemical results calls for further analysis. The initial step of the equilibration reaction is electron transfer from the dianion to the alkene of the other species with formation of a couple of radical anions. From the large separation observed between the first and second reduction peaks, one can estimate an upper limit for the radical-anion disproportionation equilibrium constant (K_d). Except for **1b**, which we already saw to provide a peculiar case, the K_d values of the other alkenes are very small: the largest value pertains to **1c**, whose K_d is 4.4×10^{-6} .^{11b} Increasing the strength of ion pairing decreases the separation between the first and second peaks, as radical anion reduction potentials are much more affected by ion pairing than the E° values of their formation.¹⁵ Although strong ion pairing with alkali metal ions in ether solvents makes the K_d values even larger, K_d values are still, as a rule, very small.¹⁴ Because of these considerations, the equilibrium mixtures contain substantial amounts of either radical anion. By using the $(E_p)_2$ values of Table 2 as a proxy of the E°_2 values in the presence of sodium ions, the equilibrium concentrations of alkene, radical anion, and dianion for either species involved in the equilibration reaction (Scheme 1) could be calculated: in all cases (except for reactions involving **1b**, where the following trend is less pronounced) we found that while the two radical anions have a concentration essentially corresponding to that of the initial concentrations of the pertinent precursors, the other species are present at much lower concentrations. Quenching by water may occur according to two main mechanisms: (i) radical-anion disproportionation followed by protonation of the dianion and ensuing carbanion (for hydrocarbons, the basicity scale is dianion > carbanion > radical anion)^{11b,15} or (ii) radical-anion protonation, reduction of the ensuing neutral radical (whose reduction is generally much easier than that of the corresponding alkene),¹⁶ and protonation of the so-formed carbanion. Water, however, is a very weak proton donor and thus, as already shown for the radical anions of **1c** and **1b**,^{11a,b} it is likely that protonation occurs by the disproportionation mechanism.¹⁷ Protonation of the dianion of

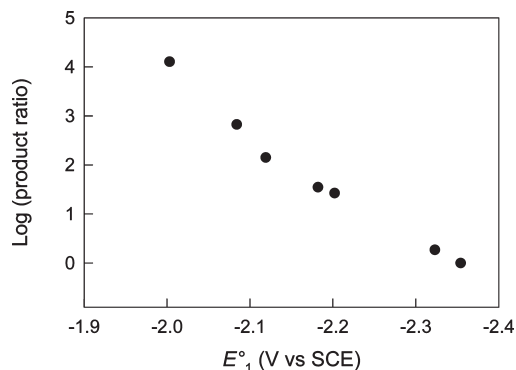


FIGURE 2. Correlation between relative yields ratios and formal potentials for reduction of **1a–g**.

the right-hand-side member of the equilibration reaction would drag the corresponding disproportionation reaction; in turn, further radical anion would form through the favored reaction between the corresponding alkene with the radical anion of the second species.

The relative stability of the two radical anions involved in the equilibration reactions is thus believed to be the key parameter dictating the outcome of the equilibration/quenching reactions. It is, therefore, not surprising that the reducing power scale observed in the chemical reactions (section 2.1) nicely matches the electrochemically established order of alkene reduction potentials (section 2.2). Even small differences match, as observed for the reaction outcomes or reduction potentials of couples **d/e** and **f/g**. To better appreciate this conclusion, we made a graph to verify how well the relative product ratios of Table 1 correlate with the E° values of Table 2, taking into account that electrochemical potentials are related to the logarithm of equilibrium constants. Given the general agreement between the chemical and the electrochemical results, when more than one yield ratio could be used to form the reactivity ladder we opted to use the ratios pertaining to compounds with smaller E° differences, which is expected to minimize errors. The chemical reactivity scale was arbitrarily referred to **1g**. Despite the assumptions of our approach, Figure 2 shows that the correlation is indeed quite good, surely beyond the result of fortuitous combinations of errors.

We now propose, and tests will be provided in the next section, to employ the reversible reduction potential of the parent alkene as a first-choice estimate of the reducing power of the corresponding *vic*-diorganometal. This approach could imply convenient implications on how to choose the most appropriate *vic*-diorganometal to carry out specific reductions, particularly when the acceptor molecule bears more than one reducible group and selectivity is required in the synthesis. The convenience of this approach also relies on the fact that several radical-anion formation potentials can be found in literature compilations (because of differences in reference electrodes, caution must always be exercised to select data) or, alternatively, that they can be directly determined by carrying out relatively simple cyclic voltammetry experiments.

2.4. Reductive Metalation of Benzophenone. To check the usefulness of the above results, we reinvestigated the reductive metalation of benzophenone **4** with various

(15) Jensen, B. S.; Parker, V. D. *J. Am. Chem. Soc.* **1975**, *97*, 5211–5217.

(16) Peover, M. E. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1967; Vol. 2, pp 1–51.

(17) The pK_a (DMF) of water can be calculated to be 31.7 by using the corresponding DMSO value^{17a} and the correlation pK_a (DMF) = $1.56 + 0.96pK_a$ (DMSO).^{17b} Electrochemical literature is rich of examples where addition of stronger, but still weak acids, such as phenol (pK_a (DMF) = 18.4),^{17b} cause radical anion protonation.^{17c} Disproportionation mechanisms, however, may provide the actual reaction path when very weak proton donors are present or added (such as alcohols or water): for example, see refs 11b and 4–7 and ref 10 cited therein. (a) Olmstead, W. N.; Margolin, Z.; Bordwell, F. G. *J. Org. Chem.* **1980**, *45*, 3295–3299. (b) Maran, F.; Celadon, D.; Severin, M. G.; Vianello, E. *J. Am. Chem. Soc.* **1991**, *113*, 9320–9329. (c) For example, see: Heinze, J. In *Organic Electrochemistry*, 4th ed.; Lund, H., Hammerich, O., Eds.; Marcel Dekker, Inc.: New York, 2001; pp 293–332.

SCHEME 2. Reductive Metalation of Benzophenone, 4, and Reaction with Electrophiles

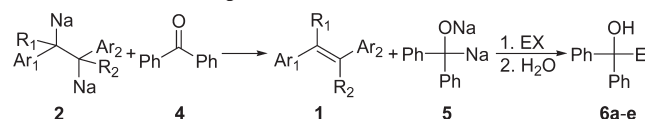


TABLE 3. Reductive Metalation of Benzophenone, 4, and Reaction with Electrophiles^a

entry	dianion	EX	product, E =	6, % ^b	4, % ^b
1	2a	H ₂ O	6a , H	72	28
2	2b	H ₂ O	6a , H	85	15
3	2d	H ₂ O	6a , H	92	8
4	2f ^c	H ₂ O	6a , H	> 95	< 5
5	2g	H ₂ O	6a , H	> 95	< 5
6	2d	Cl(CH ₂) ₃ NR ₂ ^d	6b , (CH ₂) ₃ NR ₂ ^d	90 ^{e,f}	n.d. ^g
7	2d	Cl(CH ₂) ₂ NR ₂ ^h	6c , (CH ₂) ₂ NR ₂ ^h	65 ^{e,f}	n.d. ^g
8	2d	Cl(CH ₂) ₂ NR ₂ ⁱ	6d , (CH ₂) ₂ NR ₂ ⁱ	58 ^{e,f}	n.d. ^g
9	2d	ClCH ₂ -2-Py ^j	6e , CH ₂ -2-Py ^j	50 ^{e,f}	n.d. ^g

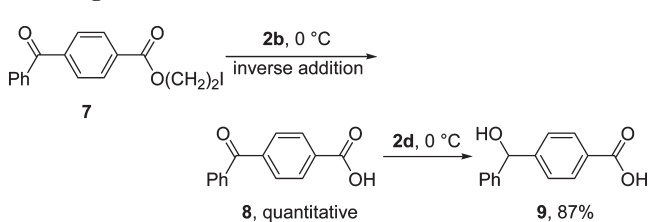
^aAll reactions were run at 0 °C during 8 h, unless otherwise indicated. ^bDetermined by ¹H NMR spectroscopy analysis of the crude reaction mixture, unless otherwise indicated. ^cThe reaction was run at -10 °C. ^dR = CH₃. ^eAs determined from isolated products. ^fReduction time 3 h. ^gn.d. = not determined. ^hR₂¹ = -(CH₂)₅-. ⁱR₂² = CH₂CH₃. ^j2-Py = 2-C₃H₄N.

1,2-diaryl-1,2-disodiummethanes.^{18,19} The reduction of ketone **4** was carried out by reaction with an excess (1.5 equiv) of diorganometals **2a**, **2b**, **2d**, **2f**, and **2g** in dry THF during 8 h (Scheme 2). Most reactions were quenched with H₂O and finally analyzed by ¹H NMR spectroscopy to determine the ratio between the expected reaction product, i.e., diphenylmethanol **6a**, and the starting material (Table 3, entries 1–5).

Whereas reductions run in the presence of dianions **2d**,²⁰ **2f**, and **2g** led to almost quantitative conversion of ketone **4** (Table 3, entries 3–5), lower conversions were observed with the less reactive diorganometals **2a** and **2b** (Table 3, entries 1 and 2). Intermediate formation of dianion **5** was evidenced by quenching some of the reduction mixtures with different electrophiles (1.3 equiv), thus affording, after aqueous workup, alcohols **6b–e** (Table 3, entries 6–9).

As a practical application of these findings, we investigated the reduction of the 2-iodoethyl ester of 4-benzoylbenzoic acid, **7**, with diorganometals **2b** and **2d**. Indeed, according to the above-reported findings, as well as to previous results on the reductive deprotection of 2-haloethyl esters,^{2b} we anticipated that the use of dianion **2b** as a reducing agent would have allowed, under appropriate reaction conditions,²¹ chemoselective deprotection of the ester moiety; on the other side, a more powerful reducing

SCHEME 3. Selectivity in the Reduction of Ketones 7 and 8 with vic-Diorganometals 2b and 2d



SCHEME 4. Reductive Cleavage of Trityl Methyl Ether 10

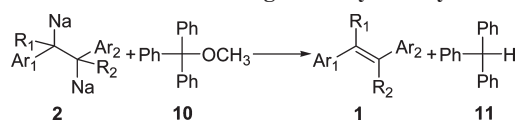


TABLE 4. Reductive Cleavage of Trityl Ether 10^a

entry	diorganometal (equiv)	T, °C	10, % ^b	11, % ^b
1	2a (1.6)	0	> 95	< 5
2	2b (1.6)	0	> 95	< 5
3	2c (1.6)	0	84	16
4	2d (1.0)	0	65	35
5	2d (1.6)	0	24	76
6	2e (1.6)	0	25	75
7	2f (1.0)	-10	36	64
8	2f (1.6)	-10	< 5	> 95
9	2g (1.6)	0	7	93

^aAll reactions were run under dry Ar during 16 h. ^bAs determined by ¹H NMR spectroscopy of crude reaction mixtures.

agent, such as **2d**, was expected to convert ketoacid **8** into hydroxyacid **9**.

The results, as summarized in Scheme 3, nicely confirmed our expectations.

2.5. Reductive Cleavage of Trityl Alkyl Ethers. As a further application of our findings, we also investigated the reductive cleavage of triphenylmethyl methyl ether (trityl methyl ether), **10**, taken as a model for tritylated alcohols (Scheme 4).

The reductions of ether **10** were run in THF, under dry Ar, with variable amounts of *vic*-diorganometals **2a–g**, at temperatures ranging from 0 to -10 °C. Aqueous workup afforded crude mixtures, which were analyzed by ¹H NMR spectroscopy to determine the ratio between the expected reaction product, i.e., triphenyl methane, **11**, and the starting material. As already seen for benzophenone **4**, the results (Table 4) were in good agreement with the scale of reducing powers that we could establish in the previous sections.

Very low or almost no conversion of **10** into **11** occurred in the presence of the less effective reducing agents, i.e., diorganometals **2a–c** (Table 4, entries 1–3), but conversion was satisfactory in the presence of dianions **2d** or **2e** (Table 4, entries 4–6) and quantitative or almost quantitative in the presence of an excess of the highly reducing dianions **2f** and **2g** (Table 4, entries 8 and 9).

The yield in **11** was sensibly dependent on the relative amount of the dianion, as shown by entries 4 vs. 5 and entries 7 vs. 8.

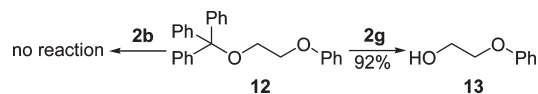
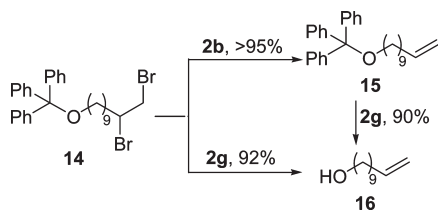
It also is worth noting that reaction of ether **10** with 3 equiv of Na metal in dry THF, at 0 °C and for the same time period,

(18) The reduction of benzophenone with 1,2-disodium-1,2-diphenylethane was already reported: Brook, A. G.; Cohen, H. L.; Wright, G. F. *J. Org. Chem.* **1953**, *18*, 447–463.

(19) Generation of dianion **5** under different reaction conditions, as well as its reactivity toward various electrophiles, was already reported. See, for example: (a) Na in NH₃(l): Hamrick, P. J. Jr.; Hauser, C. R. *J. Am. Chem. Soc.* **1959**, *81*, 493–496. (b) Na sand in DME: Selman, S.; Eastham, J. F. *J. Org. Chem.* **1965**, *30*, 3804–3809. (c) For the generation and reactivity of the corresponding dilithium derivative, see: Gujarró, D.; Mancheño, B.; Yus, M. *Tetrahedron* **1993**, *49*, 1327–1334.

(20) A reaction run with 1 equiv of **2d** led to the recovery of a reaction mixture containing, besides 50% unreacted **4**, 34% of **6a** as well as 16% of 1,2-dihydroxy-1,2,3,4-tetraphenylethane.

(21) Reduction of ketoester **7** to ketoacid **8** was run with 1 equiv of dianion **2b** under inverse addition reaction conditions (see the Supporting Information).

SCHEME 5. Selectivity in the Reaction of Ether 12 with vic-Diorganometals 2b and 2g

SCHEME 6. Selectivity in the Reduction of Ethers 14 and 15 with vic-Diorganometals 2b and 2g


afforded triphenylmethane **11** in less than 10% yield (by ^1H NMR spectroscopy analysis), thus supporting the remarkable effectiveness of 1,2-diaryl-1,2-disodiummethanes as activated forms of the alkali metal.

To test the versatility of our detritylation procedure, we investigated the reactivity of ether **12** toward dianions **2b** and **2g** (Scheme 5). In agreement with the above-reported findings, reduction of ether **12** with an excess (1.6 equiv) of the most powerful diorganometal reductant, **2g**, led to the expected detritylation product, **13**, in almost quantitative yield. Conversely, no reaction of ether **12** with a less reactive dianion, such as **2b**, was observed.

Finally, we investigated the reduction of 10,11-dibromoundecyl trityl ether, **14**, and 10-undecenyl trityl ether, **15**, with diorganometals **2b** and **2g**. The results, summarized in Scheme 6, show that dianion **2g** is able to cause both debromination and detritylation of ether **14**, as well as direct detritylation of ether **15**, to yield 10-undecen-1-ol, **16**. On the other hand, the less reactive dianion **2b** selectively debrominates ether **14** without affecting the trityl carbon–oxygen bond. In keeping with this result, **2b** was found unreactive toward trityl ether **15**.²²

3. Summary

In this paper we report that a simple competitive reaction can be employed to determine the relative reducing capabilities of differently substituted 1,2-diaryl-1,2-disodiummethanes **2**. The reliability of the proposed methodology is nicely consistent with the electrochemical determination of the reduction potentials of the corresponding 1,2-diarylalkenes **1**. In particular, based on a semiquantitative comparison of the chemical and electrochemical results, we propose that the formal potentials for radical-anion formation could be used to estimate the reducing power of vic-diorganometals. The outcome of reactions carried out with selected acceptors provides further support to our findings, thereby highlighting a potential interest of 1,2-diaryl-1,2-disodiummethanes as tunable synthetic equivalents of an activated form of Na metal

(22) Under similar conditions, low conversions (**12** to **13** and **14** to a mixture of **15** and **16**) were observed performing these reactions in the presence of Na metal.

that, however, function under homogeneous and mild reaction conditions.

4. Experimental Section

Equilibration Reactions. To 10 mL of a 0.1 M solution of a diorganometal **2** (1 mmol), chilled at the temperature reported in Table 1, was added a solution of the appropriate diarylalkene **1** (1 mmol) dissolved in 3 mL of dry THF. After stirring at the temperature and for the time reported in Table 1, the mixture was quenched by slow dropwise addition of H_2O (15 mL), the cold bath was removed, and THF was evaporated in vacuo. The resulting mixture was extracted with CH_2Cl_2 (3×10 mL), then the organic phases were collected, washed with H_2O (1×10 mL) and brine (10 mL), and dried (Na_2SO_4). After evaporation of the solvent, the resulting mixture were analyzed by ^1H NMR and/or GC-MS. Reaction products **3a**,²³ **3e**,²⁴ **3f**,²⁵ and **3g**²⁶ were characterized by comparison with literature data, while compounds **3b–d** were characterized by comparison with commercially available samples.

Electrochemistry. For the electrochemical experiments, an EG&G-PARC 173/179 potentiostat-digital coulometer, an EG&G-PARC 175 universal programmer, and a Nicolet 3091 12-bit resolution digital oscilloscope were used. The electrochemical experiments were conducted under an Ar atmosphere, in an all-glass cell that was thermostated at 25 °C. The experiments were carried out inside a double-wall copper Faraday cage. The cage and all instruments were connected to a common ground. To minimize the ohmic drop between the working and the reference electrodes, the feedback correction was employed.

The electrochemical experiments were performed by using homemade microdisk (1 mm diameter) glassy carbon (Tokai GC-20) electrodes that were prepared as previously reported.²⁷ The electrodes were stored in ethanol and, before experiments, were polished with a 0.25 μm diamond paste (Struers) and ultrasonically rinsed with ethanol for 5 min. The electrodes were electrochemically activated in the background solution by means of several voltammetric cycles at 0.5 V s^{-1} between the anodic and cathodic solvent/electrolyte discharges, until the quality features described in ref 28 were obtained. The reference electrode was a homemade Ag/AgI. Its potential was always

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calibrated after each experiment by adding ferrocene as an internal standard; the ferrocene/ferricenium couple has a formal potential in DMF of 0.464 V²⁷ against the KCl saturated calomel electrode (SCE). For the experiments carried out in THF, the electrode potential was measured directly versus SCE (Ingold). All potential values are reported against SCE. The counter-electrode was a 1 cm² Pt plate, positioned symmetrically under the working electrode. The scan rate was varied from 0.1 to 100 V s⁻¹.

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Supporting Information Available: Detailed experimental procedures and ¹H and ¹³C NMR spectra of noncommercially available prepared compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.