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A new and highly effective organometallic approach to 1,2-dehalogenations and related reactions

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Dedicated to Professor Miguel Yus on the occasion of his 60th birthday.

Abstract

We investigated the reductive elimination of several functionalized and non-functionalized *vic*-dibromides with 1,2-diphenyl-, 1,1,2,2-tetraphenyl- and 1-phenyl-2-(2-pyridyl)-1,2-disodioethane. The reaction, involving some of the less expensive organic and inorganic reagents, proceeds under mild conditions, and is tolerant of a variety of functional groups. Extension of this procedure to similar 1,2-disubstituted compounds was also investigated. Reductive eliminations run on stereochemical probe compounds strongly suggest that this reaction proceeds via a "single electron" reductive elimination reaction pathway.

Keywords: Sodium; *vic*-Diorganometals; Reduction; Elimination

1. Introduction

Reductive dehalogenation of *vic*-dihalides is a useful and long time known reaction, and many reagents have been developed to achieve this goal [1]. Indeed, halogenation/dehalogenation of alkenes has been employed either to protect double bonds towards oxidations, reductions or electrophilic additions [2], or as a useful way to achieve alkene purification [3]. Furthermore, reductive dehalogenation allows the employment of 1,2-dihaloethenes as synthetic equivalents of acetylene in cycloaddition reactions [4–6]. Recently, the dehalogenation procedure was successfully employed in the synthesis of isotopically labelled compounds, like [1-^{14}C]-*E*-isomers of fatty acids [7] and [1-^{79}Br]-1-bromo- or [1-^{37}Cl]-1-chloro-2-fluoroethylene [8]. Finally, it is worth mentioning the application of reductive dehalogenation procedures to the abiotic degradation of organohalide contaminants [9].

We recently reported that reaction of 1,2-diarylethenes with Na metal in dry THF allows the generation of a wide array of 1,2-diaryl-1,2-disodioethanes, whose reaction with 1,3-dichloropropane led to a highly stereoselective synthesis of *trans*-1,2-diaryl-substituted cyclopentanes [10]. At odds with these results, reaction of 1,2-diaryl-1,2-disodioethanes with 1,2-dihaloethanes affords the parent *trans*-1,2-diarylethenes, probably with concurrent formation of ethene [11]. Although the ability of delocalized polycarbanions to act either as nucleophiles or reducing agents towards alkyl halides is well known [12], the latter reaction was never synthetically exploited.

Following our interest in the development of efficient alkali metal-mediated reaction procedures, and with the aim to expand the synthetic utility of these interesting *vic*-diorganometallics, we investigated the reductive dehalogenation of several *vic*-disubstituted compounds

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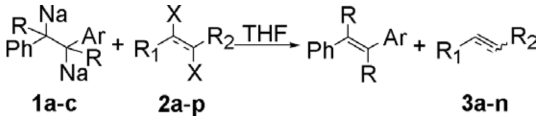

Scheme 1. Reductive eliminations of *vic*-disubstituted compounds. **1a**, Ar = Ph, R = H; **1b**, Ar = R = Ph; **1c**, Ar = 2-C_5H_4N, R = H; R_1, R_2, X = see text and Tables 1–3.

with 1,2-diphenyl-, 1,1,2,2-tetraphenyl- and 1-phenyl-2-(2-pyridyl)-1,2-disodioethane (Scheme 1). A preliminary communication on this topic already appeared [13].

2. Results and discussion

2.1. Reductive elimination reactions

0.1–0.2 M deep red solutions of 1,2-diaryl-1,2-disodioethanes (**1a**–**c**) were obtained by the reaction of *trans*-stilbene, tetraphenylethene or *trans*-stilbazole, respectively, with an excess of Na metal in dry THF, under Ar [10]. Yields of the diorganometals were determined by quenching samples of the resulting solutions with D_2O, followed by ^1H NMR analysis of crude reaction mixtures, to determine the percentage of deuterium incorporation in the arylmethyl positions. The same procedure was employed to determine that solutions of organometals **1a**–**c** can be stored under Ar in a freezer, for at least one week, without detrimental effects.

Solutions of **1** were decanted from excess metal immediately prior to use, a procedure allowing a simple way to recycle the excess of the metal [14].

Reductive eliminations were carried out by adding a solution of the appropriate *vic*-disubstituted compound **2** to a chilled solution of **1a**–**c**, followed by stirring the reaction mixture at the same temperature before aqueous work up. Inverse addition of the organometallic reagent to the substrate is usually equally effective. It is worth noting that the last procedure is particularly effective for those reactions requiring stoichiometric amounts of the reducing agent. Indeed, under these conditions, addition of the diorganometal can be stopped as soon as a faint red colour persists in the reaction mixture.

Besides the desired unsaturated reaction products, reactions run with the disodium-derivative **1a** (or **1b**) led to the formation of *trans*-stilbene (or tetraphenylethene), as well as to the formation of minor amounts of 1,2-diphenylethane (or 1,1,2,2-tetraphenylethane), the product of protonation of **1a** (or **1b**). In a similar way, *trans*-stilbazole is the main by-product of reductions run with the pyridine derivative **1c**, usually accompanied by minor amounts of 2-phenethylpyridine (i.e., the product of protonation of **1c**); the relative basicity of these pyridine derivatives allowed their easy separation form the reaction mixture upon acid washings with 1 N HCl.

Results obtained in the reductive elimination of several simple *vic*-disubstituted compounds (Chart 1) are reported in Table 1.

Reaction of *meso*-1,2-dibromo-1,2-diphenylethane (**2a**) with 1.1 equiv. of dianion **1a** led, within 10 min at 0 °C, to the recovery of a reaction mixture containing *trans*-stilbene (**3a**) as the major reaction product, as well as a minor amount of 1,2-diphenylethane (Table 1, entry 1). Running this reaction without removing the excess of the metal, to check the feasibility of an operatively simpler reaction procedure, led to a comparable result.

Under similar reaction conditions, the dibromo derivative **2b** (as a 9:1 *erythro*/*threo* mixture of diastereoisomers) was quantitatively converted into *trans*-anetole (**3b**), which, however, was inseparable from *trans*-stilbene (Table 1, entry 2).

Therefore, dehalogenation of **2b** was performed in the presence of 1.2 equiv. of dianion **1c**: after aqueous work up and acid washings to separate basic derivatives, *trans*-anetole (**3b**) was recovered in almost quantitative yield (Table 1, entry 3) [15].

The procedure was successfully applied to *vic*-dichlorides: in a first experiment (not reported in Table 1), treatment of dianion **1a** with 1 equiv. of 1,2-dichloroethane led to the quantitative recovery of stilbene. According to this preliminary finding, reduction of 1,2-dichlorododecane

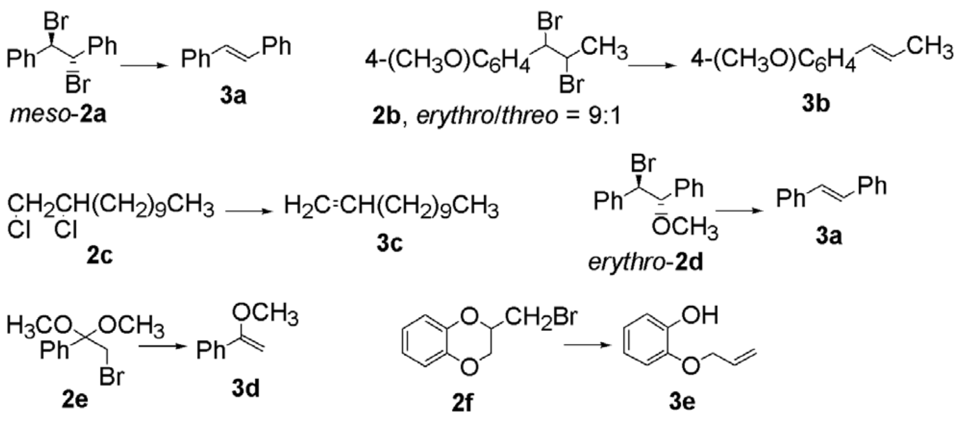

Chart 1. *Vic*-disubstituted compounds **2a**–**2f**, and resulting alkenes **3a**–**3e**.