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Active-sodium-promoted reductive cleavage of halogenated benzoic acids

Ugo Azzena [a,*], Giovanna Dettori [a], Sarah Mocci [a], Luisa Pisano [a], Giovanni Cerioni [b], Francesca Mocci [b]

[a] *Dipartimento di Chimica, Università di Sassari, via Vienna 2, I—07100 Sassari, Italy*
[b] *Dipartimento di Scienze Chimiche, Università di Cagliari, Complesso Universitario, S.S. 554 bivio per Sestu, I—09042 Monserrato (Ca), Italy*

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ABSTRACT

The outcome of the reaction between 1,2-diaryl-1,2-disodioethanes and halogenated benzoic acids strongly depends on the nature of both reaction partners. Indeed, whilst chloro-, bromo- and iodobenzoic acids are easily dehalogenated, the reductive cleavage of fluorobenzoic acids proceeds to a high extent only in the presence of the dianions endowed with more powerful reducing properties. Moreover, it was observed that *ortho*-substituted benzoic acids are more easily dehalogenated than the corresponding *para* or *meta* isomers. These observations allowed the development of reaction conditions for the exhaustive or regioselective cleavage of selected polyhalogenated benzoic acids.

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1. Introduction

Environmental concerns on the chemical behaviour of halogenated aromatic compounds under incineration or high-temperature pyrolysis conditions have stimulated the development of alternative chemical treatments in the decomposition of halogenated organic pollutants.[1] From this point of view, chemical reduction of the carbon-halogen bond is developing as an interesting alternative to thermal decomposition.[2]

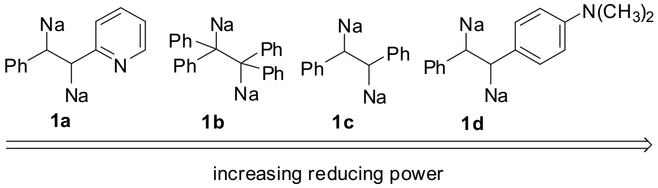
We have recently shown that 1,2-diaryl-1,2-disodioethanes represent an easily accessible class of *vic*-diorganometals[3] functioning as a highly activated form of Na metal and promoting, e.g., the reductive β-elimination reactions on *vic*-disubstituted aliphatic halides.[4] Furthermore, we provided clear evidence that their reducing power strongly depends on the substitution pattern of the parent 1,2-diarylethene employed as a starting material in their generation.[5,6]

We wish now to report that 1,2-diaryl-1,2-disodioethanes can be employed as effective reducing agents towards halogenated benzoic acids,[7,8] a class of compounds which can be considered not only as a model for aromatic halogenated pollutants but, at least in the case of the chlorides, as widespread environmental contaminants, arising as by-products of PCB or chlorinated herbicide degradation.[9]

2. Results and discussion

2.1. Reductive dehalogenation of monohalogenated benzoic acids 2a–h

For convenience purposes, numbering of 1,2-diaryl-1,2-disodioethanes, **1a–d**, follows their relative order of increasing reducing power, i.e., **1a** is the least powerful and **1d** is the most powerful reducing agent employed in the present study (Scheme 1).[5]



Scheme 1. Formulae of the various dianions employed as reducing agents.

The reaction of a dicarbanion with a halogenated carboxylic acid can be foreseen to give rise to deprotonation as well as to dehalogenation. By taking into account that deprotonation of the carboxylic moiety should require an acid vs dianion ratio of 1:0.5, and

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* Corresponding author. Tel.: +39079229549; fax: +39079229559; e-mail address: ugo@uniss.it (U. Azzena).

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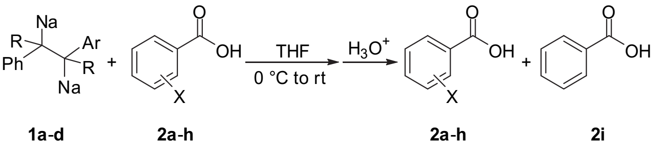
that reductive cleavage of an aromatic carbon–halide bond is usually considered as an overall two electrons reaction process[10–12] (aromatic halide versus dianion ratio=1:1, see below) at the outset of our investigation we decided to test the reactivity of halogenated benzoic acids **2a**–**h** with an excess of the different dianions, i.e., we run a first set of reactions with a benzoic acid/dianion molar ratio of 1:2.

Accordingly, deep red (0.20–0.25 M) solutions of these 1,2-diaryl-1,2-disodioethanes in THF, were prepared and filtered from unreacted sodium metal as described elsewhere.[3–5] THF solutions (0.12 M) of halogenated benzoic acids **2a**–**f** were added dropwise to a solution of the appropriate dianion chilled to 0 °C, under dry Ar. No attempt was made to determine the minimum reaction time required for the reaction to go to completion. Accordingly, reaction mixtures were stirred during 12 h and allowed to warm to rt, quenched with H_2O and the resulting carboxylic acids were recovered after acidifying the aqueous phase with 1 N HCl (Scheme 2). Independently of the work up procedure, it is worth noting that we found no evidence of the formation of significant amounts of product(s) of reduction of the carboxylic moiety and/or of the aromatic ring.



Scheme 2. Reductive cleavage of 4-halogenated benzoic acids **2a**–**d** with *vic*-diorganometals **1a**–**d**. **1a**, Ar=2-C_5H_4N, R=H; **1b**, Ar=R=C_6H_5; **1c**, Ar=C_6H_5, R=H; **1d**, Ar=4-$(CH_3)_2NC_6H_4$, R=H; **2a**, X=4-F; **2b**, X=3-F; **2c**, X=2F; **2d**, X=4-Cl; **2e**, X=3-Cl; **2f**, X=2-Cl; **2g**, X=4-Br; **2h**, X=4-I.

The results, reported in Table 1, clearly show that the amount of benzoic acid, **2i**, recovered in the reaction of 4-fluorobenzoic acid, **2a**, with an excess of 1,2-diaryl-1,2-disodioethane, **1a**–**d**, increases according to the increasing reactivity of the dianion employed as a reducing agent. Indeed, relatively high conversion of the starting material was achieved with dianions **1c** and **1d**, whilst low conversions were obtained in the presence of the less effective reducing agents **1a** and **1b** (Table 1, entries 1–4). Whilst a relatively lower reactivity was observed with the *meta* isomer **2b** (Table 1, entries 5 and 6), higher conversions were observed in the dehalogenation of 2-fluorobenzoic acid, **2c**, exhaustively dehalogenated in the presence of dianion **1c** (Table 1, entries 7 and 8).

Table 1
Reductive cleavage of halobenzoic acids **2a**–**h**[a]

Entry	Dianion	Substrate (X=)	Products distribution	
			2 (%)[b]	**2i** (%)[b]
1	**1a**	**2a**, 4-F	**2a**, 69	31
2	**1b**	**2a**, 4-F	**2a**, 63	37
3	**1c**	**2a**, 4-F	**2a**, 20	80
4	**1d**	**2a**, 4-F	**2a**, 15	85
5	**1a**	**2b**, 3-F	**2b**, 80	20
6	**1c**	**2b**, 3-F	**2b**, 40	60
7	**1b**	**2c**, 2-F	**2c**, 26	74
8	**1c**	**2c**, 2-F	**2c**, <5	>95
9	**1a**	**2d**, 4-Cl	**2d**, <5	>95
10	**1b**	**2d**, 4-Cl	**2d**, <5	>95
11	**1c**	**2d**, 4-Cl	**2d**, <5	>95
12	**1c**	**2e**, 3-Cl	**2e**, <5	>95
13	**1c**	**2f**, 2-Cl	**2f**, <5	>95
14	**1b**	**2g**, 4-Br	**2g**, <5	>95
15	**1b**	**2h**, 4-I	**2h**, <5	>95

[a] All reactions were run in dry THF, under Ar, during 12 h.
[b] As determined by ^1H NMR spectroscopic analyses of crude reaction mixtures.

As it is well known that the ease of reductive dehalogenation of organic halides follows the order I>Br>Cl≫F,[2a] it was not surprising to find that quantitative reductive dehalogenations of benzoic acids **2d**–**h** was easily achieved in the presence of every dianion under investigation (Table 1, entries 9–15).

The above reported results suggest that the ease of cleavage of the carbon–fluorine bond is affected by its relative position with respect to the carboxyl moiety and, in particular, that the *ortho* derivative is cleaved more easily than the corresponding *para* or *meta* isomers (Table 1, entries 1–8).

Similar results were observed in the dehalogenation of chloro derivatives **2d**–**f**. Indeed, the reduction of 1:1 mixtures of isomeric chlorobenzoic acids with 1.5 equiv of dianion **1b** confirmed this trend affording, besides different amounts of benzoic acid, **2i**, the unreacted starting materials in the following ratio: *para*/*ortho*=1.6:1, *meta*/*ortho*=1.8:1, and *para*/*meta*=1.1:1. Accordingly, one can state the following order for the reducibility of the C–Cl bonds of these acids: *ortho*>*para*≈*meta*. Interestingly, the higher reactivity of the *ortho* isomer parallels the results obtained in the electrochemical reduction of isomeric methyl chlorobenzoates[10] and chloroacetophenones[11] although, in these examples, the order of reducibility is: *ortho*>*para*≫*meta*.

Finally, the effectiveness of this procedure was emphasised by the observation that reaction of either 4-fluorobenzoic acid, **2a**, or 4-chlorobenzoic acid, **2d**, with Na metal (1:4 M ratio, THF, 0 °C to rt, 12 h) led to the recovery, after aqueous work up, of the respective starting materials.

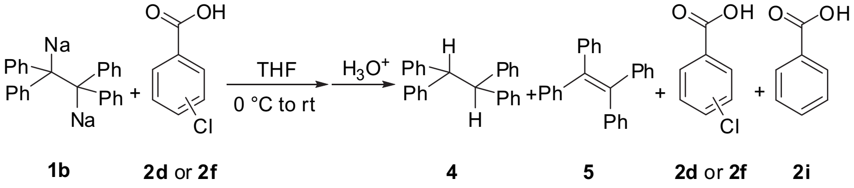
2.2. Competitive deprotonation vs reductive cleavage reactions

From a mechanistic point of view, the reactivity highlighted in the above paragraph is the result of two competing reactions, i.e., deprotonation of the carboxylic moiety and reductive dehalogenation.

To underline the competition between these reactions, we investigated in some details the reaction of chloroacids **2d** and **2f** with increasing amounts of dianion **1b**, thereafter submitting to ^1H NMR spectroscopic analyses both acidic and neutral recovered reaction products (Scheme 3 and Table 2).[13]

Reaction of **2d** with **1b** in a 2:1 M ratio afforded an acidic fraction containing chloroacid **2d** and benzoic acid, **2i**, in a 89:11 ratio, as well as a neutral fraction containing 1,1,2,2-tetraphenylethane, **4** (the product of protonation of dianion **1b**), and 1,1,2,2-tetraphenylethene, **5** (the product of oxidation of dianion **1b**[4]) in a 80:20 M ratio (Table 2, entry 1).

Reaction of acid **2d** with dianion **1b** in a 1:1 or in a 1:1.5 M ratio led to the recovery of increasing amounts of the dehalogenated reaction product, as well as to an increase of the relative amount of the oxidation product **5** (Table 2, entries 2 and 3, respectively).



Scheme 3. Reaction of 4-chlorobenzoic acid, **2d**, and 2-chlorobenzoic acid, **2f**, with dianion **1b**.

Table 2
Dehalogenation vs deprotonation in the reaction of chlorobenzoic acids **2d** and **2f** with different amounts of dianion **1b**[a]

Entry	Substrate	**2/1b**	Neutral fraction	Acidic fraction
		Molar ratio	**4/5**[b]	**2/2i**[b]
1	**2d**	2:1	80:20	89:11
2	**2d**	1:1	50:50	46:54
3	**2d**	1:1.5	35:65	<5:>95
4	**2f**	2:1	53:47	73:27
5	**2f**	1:1.2	33:67	22:78
6	**2f**	1:1.5	33:67	<5:>95

[a] All reactions were run in dry THF, under Ar, during 12 h.
[b] As determined by ^{1}H NMR spectroscopic analyses of crude reaction mixtures; estimated error±5%.

Comparable results were obtained in the reduction of the isomeric *ortho*-derivative **2f** (Table 2, entries 4–6).

By taking into account the relative amounts of the products of the redox reactions (**2i** and **5**) as well as the molar ratio between the reactants, the results described in Table 2 strongly suggest that the dehalogenation reaction is an overall two electrons process, as supported by the electrochemical reductions of isomeric methyl chlorobenzoates,[10] chloroacetophenones[11] and other aromatic chlorides.[12] In view of the minimal amount of the dianion required to accomplish the deprotonation step (0.5 equiv), the overall reaction demands a 1:1.5 M ratio between the chloroacid and the *vic*-diorganometal.

However, some additional comments are necessary to better understand the outcome of our reactions. Indeed, bearing in mind the reaction mechanism usually accepted for the reductive cleavage of aromatic halides,[14] we can consider the reduction of halogenated carboxylic acids (or their Na salts) to occur as depicted in Eqs. 1–5 (M=H or Na).

$$\mathrm{X{-}C_6H_4{-}COOM} + e^- \rightarrow [\mathrm{X{-}C_6H_4{-}COOM}]^{\bullet}- \tag{1}$$

$$[\mathrm{X{-}C_6H_4{-}COOM}]^{\bullet}- \rightarrow [\mathrm{C_6H_4{-}COOM}]^{\bullet} + X^- \tag{2}$$

$$[\mathrm{C_6H_4{-}COOM}]^{\bullet} + e^- \rightarrow [\mathrm{C_6H_4{-}COOM}]^- \tag{3}$$

$$[\mathrm{C_6H_4{-}COOM}]^- + \mathrm{SH} \rightarrow \mathrm{C_6H_5{-}COOM} + \mathrm{S}^- \tag{4}$$

$$[\mathrm{C_6H_4{-}COOM}]^{\bullet} + \mathrm{SH} \rightarrow \mathrm{C_6H_5{-}COOM} + \mathrm{S}^{\bullet} \tag{5}$$

A first step led to the formation of a π^* radical anion, as a result of a Single Electron Transfer (SET) from the reducing agent to the substrate (Eq. 1).

The fragmentation reaction (Eq. 2), requiring an intramolecular electron transfer from the π^* radical anion to the scissile bond (σ^* radical anion), affords an aryl radical, which could be further reduced to the corresponding carbanion in a second SET step (Eq. 3). Once formed, the carbanion could deprotonate some components of the reaction medium (SH, e.g., the carboxyl moiety or the solvent) (Eq. 4), whilst the radical intermediate could abstract an hydrogen atom from the reaction medium (Eq. 5), thus affording the dehalogenated benzoic acid and a new radical; finally, the newborn radical (s) and carbanion(s) could be involved in other reaction paths (e.g., the radical could dimerize or be further reduced), thus affecting the overall process. Accordingly, it is the competition between all the reaction paths outlined above that determines the apparent number of electrons required for the reductive cleavage step,[15] i.e., the relative amount of a specific 1,2-diaryl-1,2-disodioethane needed for the complete conversion of a definite halogenated benzoic acid.

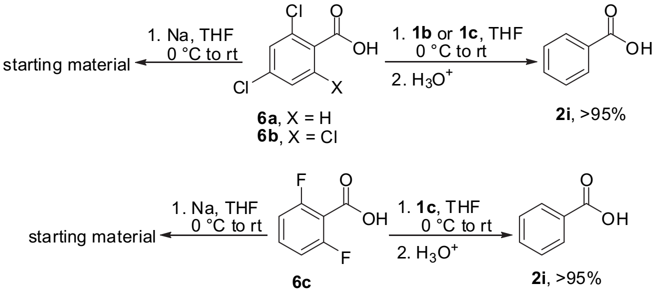
Furthermore, it appears that the deprotonation of the carboxylic moieties and the reductive cleavage of the C–Cl bonds proceed with comparable reaction rates. Indeed, the reactions described in entries 1 and 4 of Table 2, i.e., the reactions run with an excess of each carboxylic acid, show that dehalogenation occurred also in presence of a reduced amount of the *vic*-diorganometal. Accordingly, quenching these reaction mixtures with D_2O led to the recovery of nondeuterated 1,1,2,2-tetraphenylethane, **4**, thus showing formation of this product in the reaction mixtures before the aqueous work up.[16]

2.3. Reductive cleavage of polyhalogenated benzoic acids 6a–d

To further test the usefulness of the proposed dehalogenation procedure, we next investigated the reactivity of several polyhalogenated benzoic acids, **6**, with different *vic*-diorganometals.

Accordingly, we investigated the reactivity of 2,4-dichloro- and 2,4,6-trichlorobenzoic acid (**6a** and **6b**, respectively) with an excess of dianions **1b** or **1c** (**1**/**6a**=3:1 M ratio; **1**/**6b**=4:1 M ratio), as well as the reactivity of 2,6-difluorobenzoic acid, **6c**, with an excess of dianion **1c** (**1c**/**6c**=3:1 M ratio).

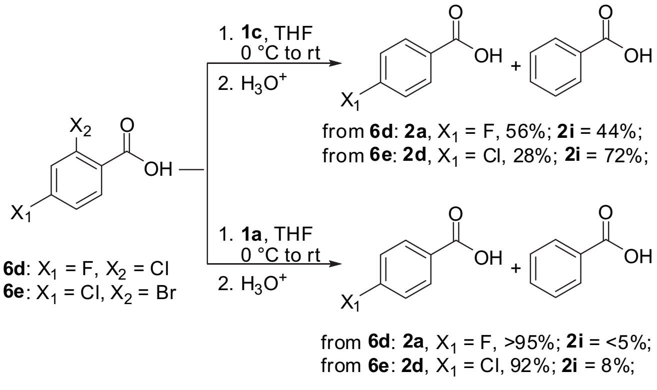
The results, summarized in Scheme 4, show that the employment of an excess of the appropriate dianion led to complete dehalogenation of the starting materials. In Scheme 4 it is also shown that Na metal proved useless in promoting the reductive cleavage of benzoic acids **6a–c**. Indeed, their reaction with the alkali metal (**6a**/Na or **6c**/Na=1:6 and **6b**/Na=1:8 M ratio, respectively), followed by aqueous work up, led to the quantitative recovery of the respective starting materials.



Scheme 4. Reductive cleavage of polyhalogenated benzoic acids **6a–c**.

Finally, by taking into account the different ease of cleavage of different and/or isomeric carbon–halide bonds outlined above, we investigated the reaction of 2-chloro-4-fluorobenzoic acid, **6d**, and 2-bromo-4-chlorobenzoic acid, **6e**, with different dianions.

Reduction of 2-chloro-4-fluorobenzoic acid, **6d**, with 1.5 equiv of dianion **1c** led to the recovery of a reaction mixture containing benzoic acids **2a** and **2i** in an almost equimolar ratio, whilst the employment of a milder reducing agent, such as dianion **1a**, allowed the highly regioselective cleavage of the C–Cl bond (Scheme 5).



Scheme 5. Selectivity in the reductive cleavage of 2,4-dihalogenobenzoic acids, **6d** and **6e**.

A similar result, i.e., preferential or regioselective cleavage of an *ortho* C–Br bond vs a *para* C–Cl bond, was obtained reacting 2-bromo-4-chlorobenzoic acid, **6e**, with 1.5 equiv of dianion **1c** or **1a**, respectively (Scheme 5).[17]

2.4. Conclusion

The results reported above show that 1,2-diaryl-1,2-disodioethanes behave as an activated form of Na metal, which find useful application in the reductive cleavage of halogenated benzoic acids, a reaction which cannot be promoted by the metal alone.

Accordingly, by taking into account the dependence of the reducing power of these *vic*-diorganometals on their substitution pattern (i.e., the less delocalized dianions are the more powerful reducing agents, and vice versa) as well as the different order of reducibility of the carbon–halogen bonds (either due to their relative bond strength and/or position with respect to the carboxylic moiety), it was possible to obtain either the regioselective or the exhaustive dehalogenation of a series of polyhalogenated benzoic acids.

3. Experimental section

3.1. General

Starting materials were of the highest commercial quality and were purified by distillation or recrystallization immediately prior to use. THF was distilled from Na/K alloy under N_2 immediately prior to use. All reactions were run under dry N_2. ^1H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra were recorded at 75 MHz in $CDCl_3$ or DMSO-d_6 with $SiMe_4$ as an internal standard on a Varian VXR 300 spectrometer. IR spectra were recorded on a FTIR Jacso 680 P.

3.2. Starting materials

Benzoic acids **2a**–**g** and **6a**–**e** are commercially available. 0.2–0.25 M solutions of dianions **1a**–**d** in dry THF were prepared as already described.[3–5]

3.3. General procedure for the reductive dehalogenation of benzoic acids 2a–h and 6a–e

A 0.20–0.25 M solution of a diorganometal **1** (1.8–4.8 mmol, see Tables 1 and 2, and text) was added dropwise to a solution of the appropriate halogenated benzoic acid (1.2 mmol) in dry THF (10 mL), chilled at 0 °C. The mixture was vigorously stirred and allowed to reach rt during 12 h, after which time it was quenched by slow dropwise addition of H_2O (15 mL). The organic solvent was evaporated in vacuo and the resulting mixture was extracted with CH_2Cl_2 (3×10 mL). The organic phases were collected, extracted with 1 N NaOH (3×10 mL), dried (Na_2SO_4) and, after evaporation of the solvent, the residue was analyzed by ^1H NMR. The aqueous phases were collected, acidified with 1 N HCl and extracted with CH_2Cl_2 (3×10 mL). The new organic phases were collected and dried (Na_2SO_4). After evaporation of the solvent, the residue was analyzed by ^1H NMR.

Quenching with D_2O was realized by adding 0.75 mL of the electrophile to the reaction mixture, followed by aqueous work up as described above.

Reaction products were characterized (^1H NMR and IR) by comparison with commercially available samples.

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.09.072.

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17. Reduction of either **6d** or **6e** with dianion **1c** in a 3:1 M ratio led to the recovery of benzoic acid, **2i**, in almost quantitative yield.