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Indirect electrografting of aryl iodides

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ABSTRACT

Keywords:

Iodoaryl

Electrografting

2,6-Dimethylbenzene diazonium

Facilitated grafting

The electrografting of 4-iodonitrobenzene that is not possible directly is demonstrated while that of 5-iodo-2-amino-pyridine, 4-iodoaniline and iodobenzene is performed with a decrease of overpotential > 2 V. The electrografting of aryl iodides is achieved through an iodine abstraction reaction: in the presence of a sterically hindered diazonium salt (2,6-dimethylbenzenediazonium), the aryl iodide is grafted to gold at the much less negative reduction potential of the diazonium salt.

1. Introduction

Many electro or photografting reactions rely on radicals that are obtained by cleavage of weak bonds, either thermally with peroxides [1] (--O--O-- bonds, $\sim 40 \text{ kcal mol}^{-1}$ [2]), electrochemically with diazoniums [3] ($\text{Ar-N} \equiv \text{N}^+$, $\sim 38.5 \text{ kcal mol}^{-1}$ [4,5]), photochemically with azides [6] ($\text{Ar-N} = \text{N}^+ = \text{N}^-$, $\sim 37 \text{ kcal mol}^{-1}$ [2]). The bond dissociation energy (BDE) of alkyl and aryl iodides is somewhat higher ($n\text{-Bu-I}$, $\sim 56 \text{ kcal mol}^{-1}$, Ph-I , $\sim 65 \text{ kcal mol}^{-1}$ [2]) and their reduction takes place at quite negative potentials (-2.3 V/SCE for $n\text{-Hex-I}$ [7], -2.2 V/SCE for Ph-I [8]).

However, alkyl iodides can be grafted at their reduction potential on GC, Au, Cu, Fe [7] and Al [9] and also at much more positive potential using a crossover reaction where the 2,6-dimethylphenyl radical (derived from 2,6-dimethylbenzenediazonium, 2,6-DMBD) cannot react with surfaces due to steric hindrance. Instead it abstracts an iodine atom from the alkyl iodide to give an alkyl radical (Scheme 1, R1), which finally binds to the surface. As 2,6-DMBD is reduced at much more positive potential than alkyl iodides or alkyl bromides, a potential gain of $\sim 1.7 \text{ V}$ and $\sim 2.35 \text{ V}$ was attained in the case of $\text{I}(\text{CH}_2)_2\text{C}_6\text{F}_{13}$ [10] and 6-bromohexanoic acid, respectively [11].

Since the BDE of iodobenzene is higher than that of alkyl iodides ([2]), the formation of the phenyl radical from iodobenzene and therefore the grafting should be more difficult (Scheme 1, R2). However, when heating bis(p-chlorobenzoyl)peroxide in the presence of iodobenzene in a benzene solution, 4-chloriodobenzene was obtained, testifying for an iodine atom abstraction [12]. Since i) 1-iodo-2,6-dimethylbenzene is sterically hindered, and ii) the buttressing effect of two methyl groups is $1.46 \text{ kcal mol}^{-1}$ [10,13], R2 should be endothermic by this value. As the entropy variation should be small for

R2, R2 should be slightly endergonic.

The experiments described thereafter starting from different aryl iodides demonstrate that R2 is possible.

2. Results and discussion

2.1. 4-Iodonitrobenzene

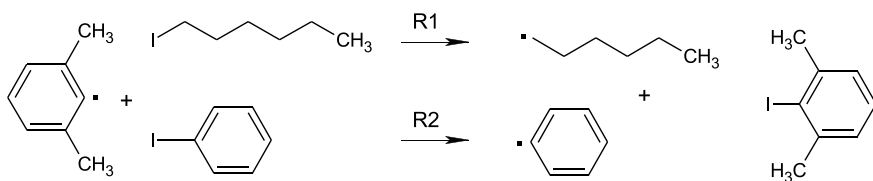
The voltammogram of 4-iodonitrobenzene in DMF at a Pt electrode presents two close waves at ~ -1.07 and -1.11 V/SCE . The first irreversible one corresponds to the transfer of 1 e^- ; it becomes reversible upon increasing the scan rate to 10 Vs^{-1} . The second one pertains to nitrobenzene that is formed through an H-atom transfer. Based on these data the following ECE mechanism [14] was proposed [15–20] with a slow cleavage of the radical anion: $k = 1.1 \text{ s}^{-1}$ [19]:

Upon repetitive scanning (up to 100 cycles) from -0.4 to -1.4 V/SCE in acetonitrile, the voltammogram of 4-iodonitrobenzene on various electrodes (Au, Pt, GC) remains stable and does not indicate significant grafting. This was confirmed by IRRAS: under the above conditions, a gold plate does not present the strong characteristic signals of the NO_2 group. This is due to the slow cleavage of the radical anion (Scheme 2, R2); the nitrophenyl radical that should be responsible for the grafting of 4-nitrobenzenediazonium is formed in solution and trapped by the solvent (Scheme 2, R3) before diffusing back to the electrode. Note that 4-bromonitrobenzene that cleaves somewhat faster [19] can be electrografted [8]. Therefore, it is not possible to graft directly 4-iodonitrobenzene onto metals.

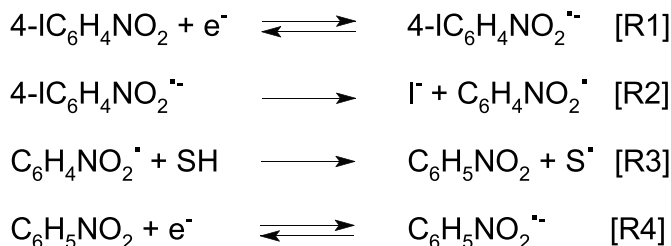
But if 2,6-DMBD is reduced ($E_{\text{red}} = -0.28 \text{ V/SCE}$) in the presence of 4-iodonitrobenzene, its reduction wave decreases upon repetitive scanning (Fig.1A). After rinsing the electrode under sonication and

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Scheme 1. Iodine exchange between an aryl radical and an alkyl or aryl iodide.



Scheme 2. Electrochemical reduction of 4-iodonitrobenzene [19].

transfer to an ACN + 0.1 M NBu₄BF₄ solution, the characteristic reversible signal of nitrobenzene is observed at $E^\circ = -1.10$ V/SCE (Fig. 1B). The indirect electrografting of the nitrophenyl group is confirmed by a redox probe experiment, IRRAS and XPS. The reversible voltammogram of Fe(CN)₆³⁺/Fe(CN)₆²⁺ nearly disappears on the modified electrode (Fig. 1C). The IRRAS spectrum of the modified electrode presents two stretching vibrations of the nitrophenyl group at 1350 and 1525 cm⁻¹ (Fig. 1D). The XPS spectrum (not shown) presents a N1s signal (7.3%) with a contribution of the nitrophenyl group at

406 eV (3%) and no iodine signal in the 620–635 eV region; the spectrum of a blank sample obtained in the absence of 2,6-DMBD does not show the latter peak but a N1s peak at 400 eV (1.3%), likely due to some contamination.

The surface concentration of the modified electrode was obtained by integration of the voltammogram of the grafted nitrophenyl group (Fig. 1B): $\Gamma = 5.4 \times 10^{-9}$ mol.cm⁻² that corresponds to a film thicker than a monolayer [21]; it agrees with the thickness of the film measured by ellipsometry as 7.9 ± 2 nm. However, thinner layers (1.4 nm) are obtained through a single voltammetric cycle.

This indirect method should apply to all aromatic derivatives that cleave slowly to a radical upon electron transfer (DISP situation). Let us mention, for example, 4-nitrophenyl-*tert*-butylazosulfide ($E_{\text{red}} = -0.95$ V/SCE, $k = 4.1 \times 10^{-2}$ s⁻¹) that cleaves slowly to a radical that does not react with the electrode [22].

2.2. 5-Iodo-2-aminopyridine

Diazopyridinium salts are highly unstable (their unstability decreases from 3 to 4 to 2-diazopyridinium) and must therefore be prepared in situ by diazotation of the corresponding aminopyridine

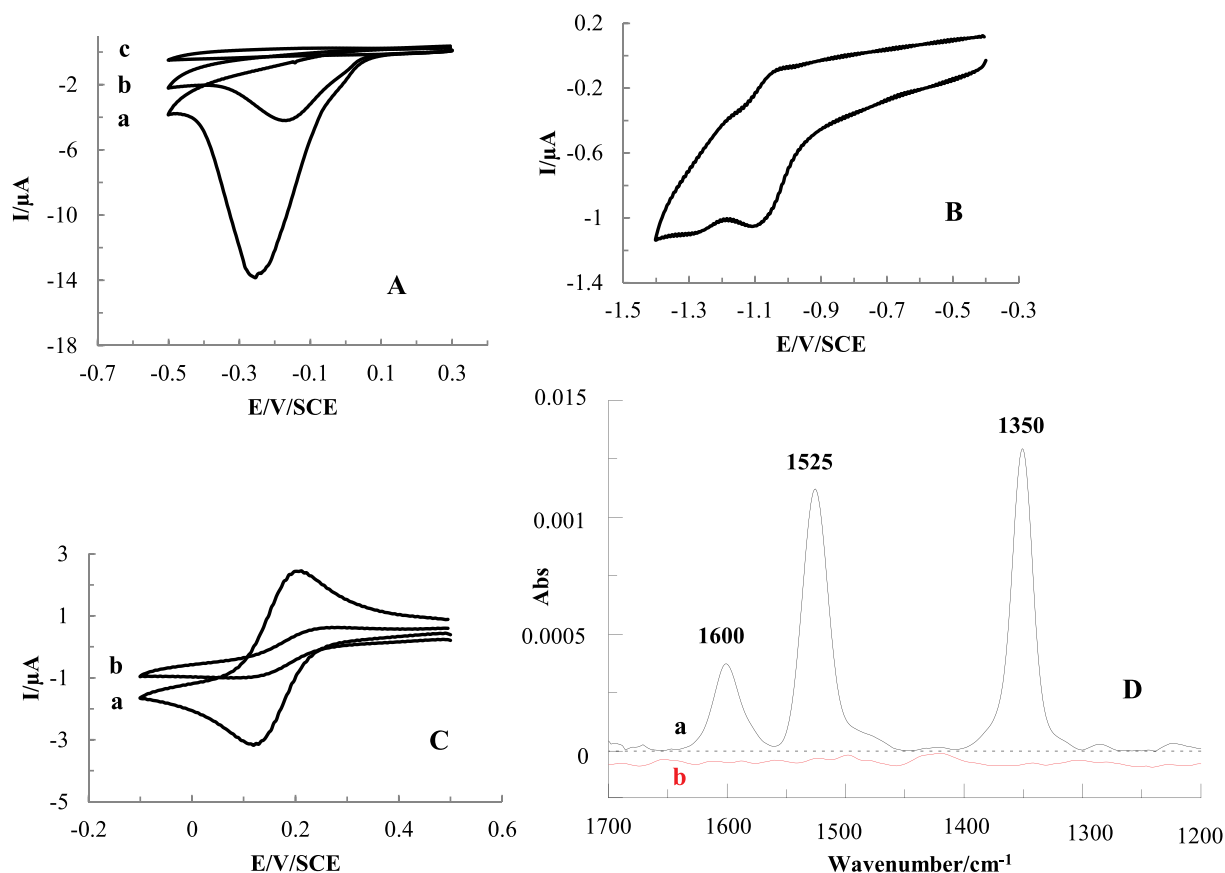


Fig. 1. A–C) Cyclic voltammetry on A) Au electrode (1 mm diameter, 0.1 V.s⁻¹) in ACN + 0.1M NBu₄BF₄ of 2,6-DMBD (10 mM) in the presence of 4-iodonitrobenzene (12 mM), a) first and b) second cycle; Ac) 4-iodonitrobenzene (12 mM) without 2,6-DMBD; B) Au electrode modified by 4-nitrophenyl groups; C) redox probe experiment, Ca) 2 mM K₃[Fe(CN)₆] + 0.1 M LiClO₄ on a bare Au electrode and Cb) on the same modified electrode as in B); D) IRRAS spectrum of Da) Au plate modified as in B) and Db) Au plate treated with 4-iodonitrobenzene in the absence of 2,6-DMBD.

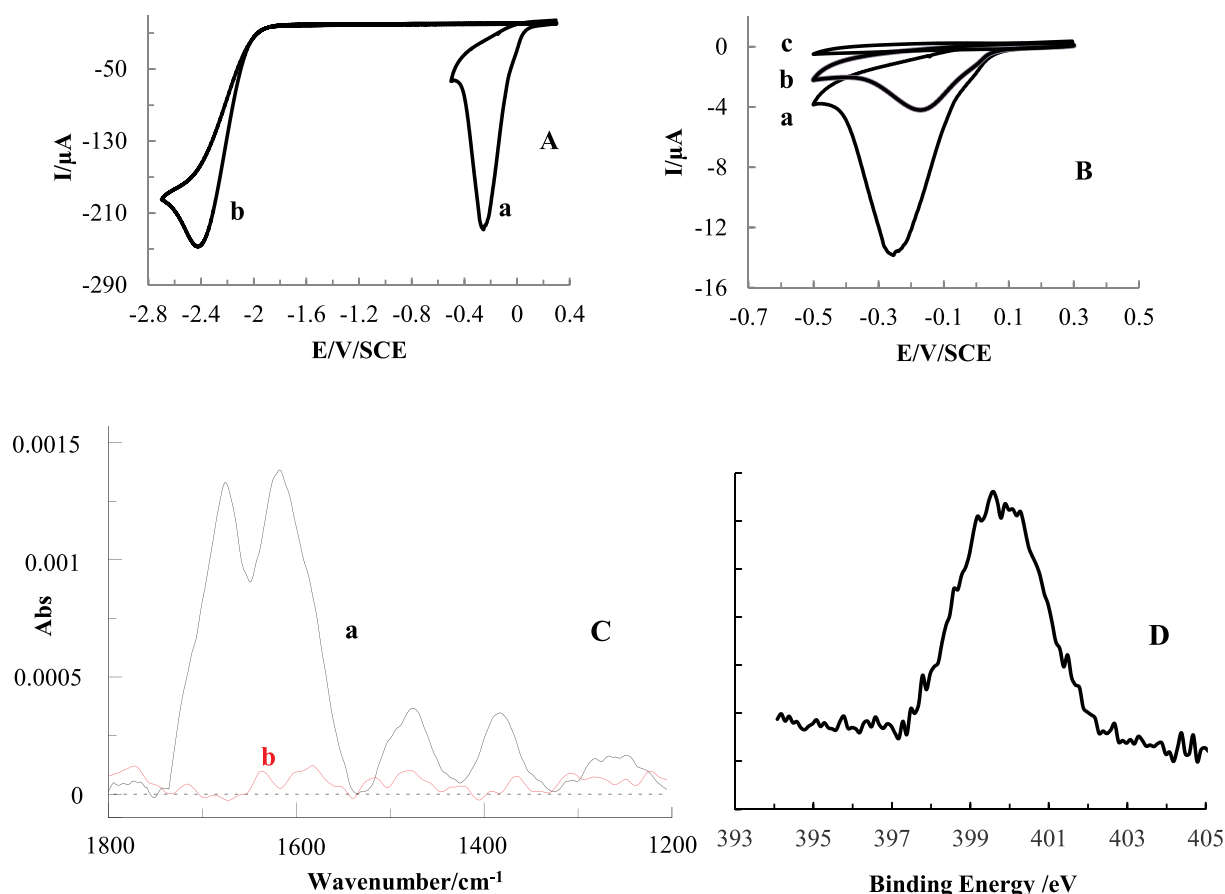


Fig. 2. A, B) Cyclic voltammetry on Au electrode (1 mm diameter, $0.1\text{ V}\cdot\text{s}^{-1}$) of Aa) 2,6-DMBD (10 mM), Ab) 5-iodo-2-aminopyridine (20 mM) (recorded separately and presented on the same scale, currents are not on scale), B) DMBD in the presence of 5-iodo-2-aminopyridine (10 and 20 mM, respectively), a) first and b) second cycle and Bc) 5-iodo-2-aminopyridine (20 mM) without 2,6-DMBD. C,D) IRRAS and high resolution XPS spectrum, N1s contribution of Ca, D) Au plate grafted by 5-iodo-2-aminopyridine (20 mM) in the presence of 2,6-DMBD (10 mM); Cb) blank spectrum in the absence of 2,6-DMBD.

[23,24], which mainly leads to the corresponding hydroxypyridine. However, electrografting is possible starting from iodonium or iodo derivatives [25]. We have tried to graft pyridyl radicals starting from an iodo derivative rather than from a diazonium salt.

Fig. 2A presents, on the same potential scale, the voltammograms of 2,6-DMBD ($E_{red} = -0.28\text{ V/SCE}$, Fig. 2Aa) and 5-iodo-2-aminopyridine ($E_{red} = -2.43\text{ V/SCE}$, Fig. 2Ab) recorded separately. The peak potentials difference is $\Delta E_p = 2.15\text{ V}$. When both compounds are present in the same solution and the potential of an Au electrode is scanned repetitively between 0.3 and -0.5 V/SCE , the voltammogram decreases steadily (Fig. 2B), pointing to a grafting reaction. This reaction is confirmed by i) a redox probe experiment, ii) the IR spectrum of a modified Au plate that presents four characteristic peaks at 1676, 1658, 1475 and 1380 cm^{-1} (to compare with 1637, 1582, 1478, 1378 cm^{-1} for 5-iodo-2-aminopyridine) and iii) the XPS spectrum that presents a N1s peak at 400 eV (9.3%, to compare with 3.2% in the absence of 2,6-DMBD, already present on the untreated Au wafer), and a small amount of iodine at 619 eV (0.24%, already present on the untreated Au wafer), and iv) the thickness of the film: $10.3 \pm 5\text{ nm}$.

2.3. 4-Iodoaniline

4-Iodoaniline is reduced at $E_{red} = -2.0\text{ V/SCE}$ on Au and at a similar potential on GC with a very spread out wave. Fig. 3A,B presents the voltammograms of 2,6-DMBD in the presence of 4-iodoaniline on Au and GC electrodes. On both substrates a fast decrease of the voltammogram is attributed to the grafting of the 4-aminophenyl radical, indicating the grafting of the phenyl group. This is confirmed by the IR

and XPS spectra on Au plate after only two scans that present the characteristic signals of the attached aniline groups: by IR 3367, 3236, 1600, 1513, 1281 cm^{-1} (by comparison: 3432, 3358, 1614, 1497, 1275 cm^{-1} for aniline); by XPS: N1s signal at 400 eV, (6.7%) and a small amount of iodine at 619 eV (0.29%); in the absence of 2,6-DMBD only 3.7% N1s and 2.5% iodine at 619 eV (the presence of iodine is due, as above, to the Au wafer and also to a photochemical reaction under the cool white light of the laboratory that does not occur in the presence of 2,6-DMBD). The thickness of the film measured by ellipsometry is $6.7 \pm 3.0\text{ nm}$.

2.4. Iodobenzene

Its reduction on GC at $E_{red} = -2.23\text{ V/SCE}$ involves a two-electron irreversible wave corresponding to the formation of the aromatic anion that cleaves to iodine and benzene (after protonation) [26]. However, after 100 cycles its reduction peak decreases and the grafting of phenyl groups is observed on the GC surface [8]. Considering such a difficult grafting, the indirect approach described herein should be an efficient alternative.

When iodobenzene is grafted on gold through an iodine abstraction from the 2-dimethylphenyl radical as above, the presence of phenyl groups is attested by a weak IR-ATR spectrum with aromatic bands at 1558, 1487 and 1427 cm^{-1} (by comparison 1570, 1471 and 1438 cm^{-1} for iodobenzene), these bands are not observed when the same reaction is performed in the absence of 2,6-DMBD. The thickness of the film measured by ellipsometry is $8.5 \pm 4.6\text{ nm}$. Therefore reaction R2 in Scheme 1 is possible in spite of its small calculated endergonicity, likely

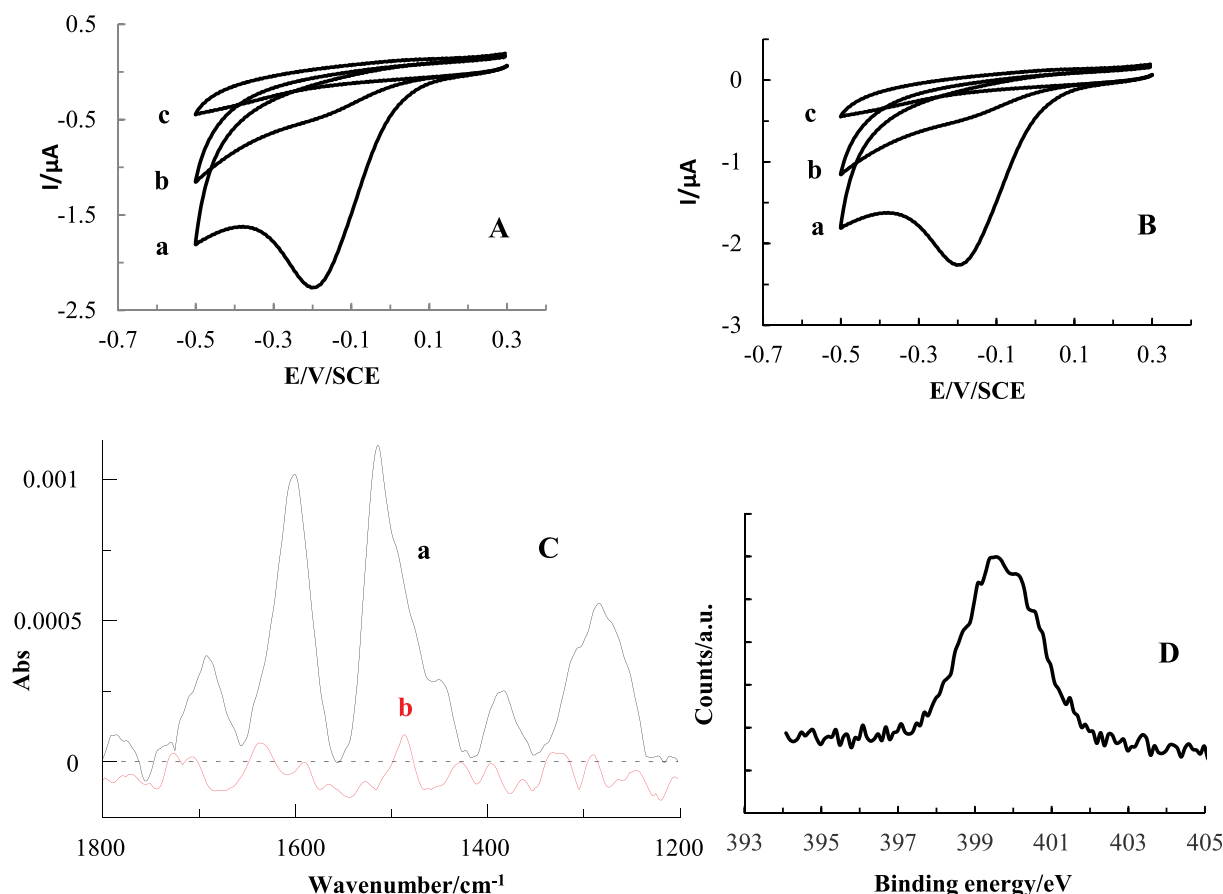


Fig. 3. Cyclic voltammetry on A) Au and B) GC electrodes (1 mm diameter, 0.1 V.s^{-1}): a) 1st and b) 2nd scan in ACN + $0.1 \text{ M NBu}_4\text{BF}_4$ + 10 mM 2,6-DMBD + $20 \text{ mM IC}_6\text{H}_4\text{NH}_2$ and c) in the absence of 2,6-DMBD. Ca, D) Au plate grafted by 5-iodo-2-aminopyridine (20 mM) in the presence of 2,6-DMBD (10 mM). Ca) IRRAS spectrum, D) high resolution XPS spectrum, N1 s contribution. Cb) blank spectrum in the absence of 2,6-DMBD.

because the reaction is equilibrated and the driving force provided by the irreversible grafting reaction ($\Delta H = -38.5 \text{ kcal.mol}^{-1}$) [5].

3. Conclusions

The indirect electrografting of aromatic iodides owing to the 2-dimethylphenyl radical provides a valuable option when the direct grafting i) is not possible (4-iodonitrobenzene), or ii) occurs inefficiently at very negative potentials (5-iodo-2-aminopyridine, iodoaniline, iodobenzene). This reaction can also be an alternative to the grafting of diazonium salts when the latter are highly unstable or too difficult to prepare.

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