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Stereoselective Cyclopropanation to Homoquinones from Phenacyl Carbenes Obtained through Quinone-Electrogenerated Bases

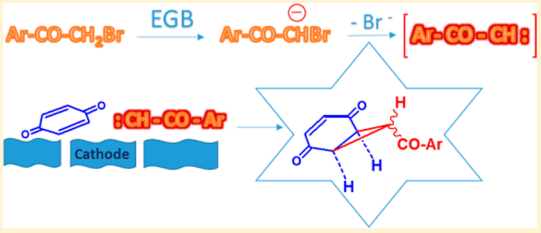
Kaouthar Hamrouni,[‡] Fructuoso Barba,[†] Mohamed Lamine Benkhoud,[‡] and Belen Batanero*[,†]

[†]Department of Organic Chemistry, University of Alcala, 28871 Alcalá de Henares, Madrid, Spain

[‡]Laboratoire de Chimie Analytique et d'Electrochimie, Faculté des Sciences, Université Tunis El Manar, 2092 El-Manar, Tunis, Tunisia

Supporting Information

ABSTRACT: A series of new (*E*) and (*Z*)-benzoyl-homoquinones have been prepared in good yield by the parent quinone-electrogenerated base (EGB) in the presence of α-bromoacetophenones or α-bromopropiophenone. The EGB, obtained when electrolysis of *p*-benzoquinone, or 1,4-naphthoquinone, is carried out at the reduction potential of their first voltammetric peak, conducted to electrogenerated phenacyl carbenes after halide evolution on the first obtained bromo-enolates. The stereoselectivity of the [2 + 2]cycloaddition of the carbene to the quinoid substrate is highly dependent on the electrode nature. Reaction mechanism proposal is discussed.



INTRODUCTION

Quinones are historically highly significant reagents, being the very first example of dienophiles used by Diels and Alder.[1a] Great number of reported applications of this reaction with quinones have been employed in the total synthesis of relevant natural products such as morphine[1b] (Gates, 1952), reserpine[1c] (Woodward, 1956), Gibberellic acid[1d] (Corey, 1978) or tetracycline analogues[1e] (Myers, 2011) to mention only some examples. However, some quinones, as anthraquinones, have been more recently[2] utilized for electrochemical labeling of biomolecules, linked to purines, pyrimidines, nucleosides, and even chemically incorporated into DNA to study charge transport properties or linked to oligonucleotides to stabilize the triplexes. The biological importance of quinones has been long time recognized[3] since their electrochemistry[4] demonstrates that are able to modulate the redox balance in cancer cells.[5]

Homoquinone moieties are interesting and important building-blocks in organic chemistry that have a fused cyclopropane ring in the quinone frame. The homoquinone scaffold occurs rarely in nature, spite of that some molecules with biological activity, such as (±)-car-3-ene-2,5-dione or (±)-Asarinol, are homoquinones isolated from *Asari radix* and identified as antilisterial compounds exhibiting potent inhibitory activity against *L. monocytogenes* strains.[6]

Fusion of a quinone rest to a cyclopropane ring is expected to endow new structural and electronic features to the quinone function by increasing its potential as synthetic intermediate, because cyclopropane derivatives undergo a variety of ring-cleavage reactions.[7] Very limited number of methods are reported for direct construction of homoquinones. The classical strategy for the preparation of *p*-homobenzoquinones either via addition of diazo-alkanes to the parent *p*-benzoquinone and thermolysis of the resulting adducts,[8,9] or addition of dihalocarbenes to *p*-benzoquinone[10] is limited to substituted derivatives. For this reason it was devised an involved indirect (three stage) synthesis of these compounds via the singlet oxygenation of cycloheptatrienes that affords norcaradiene derived [2 + 4]-*endo*-peroxides, which are readily isomerized into 4-hydroxy-2-enones on base treatment. This leads to desired *p*-homobenzoquinones on manganese dioxide oxidation.[11]

The reaction of 2-chloro-1,4-naphthoquinone with 1-phenyldiazoethane gave the corresponding 1-pyrazoline, that decomposed in refluxing benzene to give 1a,7a-dihydro-1a-chloro-1-methyl-*endo*-1-phenyl-1*H*-cyclopropa[*b*]naphthalene-2,7-dione.[12]

Two principally different methods[10] for the preparation of bis-homo-*p*-quinones are (1) debrominative, as well as dehydrobrominative, cyclopropanations of 2,4,6,8-tetrabromocyclooctane-1,5-diones yielding mostly the *anti*-isomer, and (2) double addition of one-carbon units to *p*-quinone derivatives, which was achieved in two ways: (a) by the action of diazomethane or diazoethane on duroquinones followed by nitrogen elimination, and (b) by the action of dimethylsulfoxonium methylide on a *p*-quinone-monoacetal. The formation of bis-homo-*p*-quinones as byproducts, with 8−12% yields, has been observed in the reactions of 3,3-dichloropentane-2,4-dione with benzaldehyde in the presence of sodium ethoxide,[13] or 3,3-dichloropentane-2,4-dione with aldehydes under the conditions of the *Darzens* condensation.[14]

It has been reported that irradiation of bromo-homonaphthoquinone in the presence of alkylamine donors provides a

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dimer and the corresponding hydrogen bromide salt of the amine via an initial electron-transfer from amine to excited homoquinone.[15] This photochemical reaction is a photo-induced electron transfer (PET) that changed dramatically when catalyzed[16] by BF_3 or when the amines were replaced by arene donors, to give xanthylium salts.[17] Irradiation of substituted homobenzoquinones with ethyl vinylether gave the [2 + 2] photoadducts, tricyclic diones, regio- and *endo*-selectively in good yields.[18] These authors have also described the photocycloaddition reaction of homobenzoquinone with alkenes and alkynes.[19] However, thermolysis of diphenyl- and biphenyl-2,2′-diyl-substituted-homobenzoquinones and homo-naphthoquinones has also been described.

The high potential of homoquinones in the construction of structurally useful target molecules, together with the interest itself of these rare scaffolds, prompted us to explore the possibility to synthesize them at the electrode. The cathodic reduction of quinones, under aprotic organic solvents has been deeply studied in our research group. Quinones can be easily transformed, by direct and by mediated electron transfer processes, into many interesting heterocycle derivatives such as 1,3-dioxoles when electrolyses are performed in dichloro-methane as the solvent,[20] or into 1,3,4-oxadiazol-2(3*H*)-ones and dibenzo[*c*,*e*]azepines using dry *N*-methylformamide in the presence of benzenediazonium salt.[21] The last reaction being a concomitant reduction of the salt and 9,10-phenanthrenequi-none followed by a radical coupling reaction with electro-generated solvent radicals.[21,22]

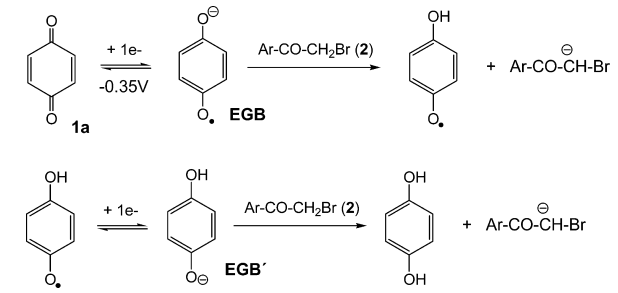
On the other hand, the use of electrogenerated bases (EGB) in organic synthesis is well-known. Recently we have described the formation of new biological active 5-imino-4-thioxo-2-imidazolidinones involving acetonitrile electrogenerated base.[23] However, the highly negative reduction potential needed to produce such bases entails the use of magnesium sacrificial anode at time that easier reducible groups are forbidden. These reasons led us to try the possibility of employing the quinone anion radicals as recycling electrogenerated bases, that simultaneously, unless in some cases, could act as further reactants involved in the structure of final products. Considering such preceding results, herein we report our findings on the proton abstraction, by quinone-EGB, to phenacyl halide molecules present in solution, that provide a new broadly useful methodology to the synthesis of highly valuable and desired homoquinone systems.

RESULTS AND DISCUSION

The electrochemically reversible quinoid systems are well-known to be conducted, under aprotic organic solvents and by applying low reduction potentials, to the corresponding stabilized radical anions, that could be used as electrogenerated bases (EGB) in the appropriate conditions. With the aim of preparing these easily obtained intermediates, the reduction of *p*-benzoquinone (**1a**) or 1,4-naphthoquinone (**1b**) were carried out at the reduction potential of their first voltammetric peak, in the presence of low concentrated solution of phenacyl halides (**2**) or α-bromo propiophenone (**2′**). Under the applied potential only the quinone molecules are being reduced (not the phenacyl halide, even when this compound is close to the electrode surface waiting to be discharged at higher voltage) to the corresponding radical anions in a heterogeneous single-electron transfer. The latter, that once formed are cathodically desorbed, migrate to the solution where behave as a base regarding to the α-halocarbonyl derivative.

As indicated in Scheme 1, under the applied voltage (−0.35 V vs Ag/Ag^+), the finally obtained neutral radical of the *p*-

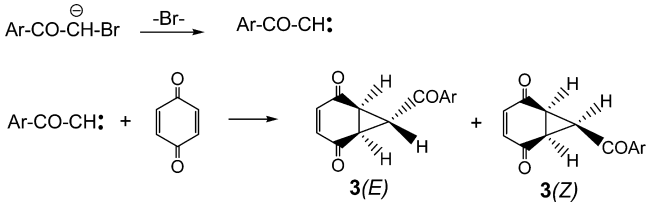
Scheme 1. EGBs from Parent *p*-Benzoquinone and Formation of Brominated Enolate of 2



benzoquinone, that is easier reduced than starting molecule **1a**, provides a new electrogenerated base EGB′ that can abstract the proton of another new molecule of **2**. The formation of two phenacyl halide anions and one hydroquinone molecule is the overall balance of this first electrochemical step.

The brominated phenacyl enolate can evolve, under these experimental conditions, to a plausible and highly reactive phenacyl carbene species after the halide leak. The attack of this carbene intermediate to a new starting quinone molecule, through a [2 + 2] cycloaddition reaction, as summarized in Scheme 2, successfully afforded the corresponding homoqui-none (**3**).

Scheme 2. Evolution of Brominated Phenacyl Enolate to Phenacyl Carbene and Further Formation of Homoquinones 3



This cyclopropanation reaction has been performed with different 4-substituted (with electron-withdrawing and electron-donating groups) phenacyl halides **2**(**a**−**f**), and it was conducted to **3**(**a**−**f**) in good yield, as summarized in Table 1. The results showed that when platinum is employed as cathode material, both stereoisomers *E* and *Z* were almost equally yielded, being the more stable *E*-homoquinone (*exo*-) slightly predominant (in which both carbonyl groups, from quinone and benzoyl substituent, are respectively in a favorable *anti* orientation). These new cyclopropane systems (both diastereomers) were now isolated and fully characterized (see the Experimental Section).

The formation of homoquinones **3**, as outlined in Scheme 2, is rationalized on the basis of a proposed phenacyl carbene intermediate, that undergo C═C bond insertion, instead of a Michael type addition reaction, of the brominated anion to the quinone.

Quinones **1** are Michael acceptors that can incorporate phenacyl groups when attacked by pyridinium ylides.[24] However, under the described ionic pathway using ylides, the plausible homoquinone formation was never observed. This fact let us to discard the possibility to get the cyclopropane by a

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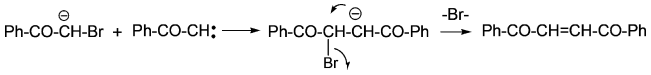
Table 1. Obtained Yields of Homoquinones 3(a–f) and *E*/*Z* Ratio at Pt/Hg Electrode from *p*-Benzoquinone (1) and Phenacyl Bromides 2(a–f)[a]

phenacyl halide (2) Ar–CO–CH_2Br	isolated yield homoquinones 3(a–f)	ratio (*E*/*Z*) homoquinones 3(a–f)
	Pt/Hg	Pt/Hg
a: Ar= C_6H_5-	77/67	53:47/70:30
b: Ar = 4-CH_3-C_6H_4-	75/71	55:45/75:25
c: Ar = 4-CH_3O-C_6H_4-	80/70	52:48/80:20
d: Ar = 4-Cl-C_6H_4-	78/74	53:47/84:16
e: Ar = 4-Br-C_6H_4-	68/65	65:35/92:8
f: Ar = 4-NO_2-C_6H_4-	84/78	60:40/97:3

[a] *E*/*Z* ratios obtained by ^{1}HNMR integration of the signals corresponding to the cyclopropane ring protons in the electrolysis crude.

nucleophilic conjugate addition of the brominated phenacyl enolate to the quinone. Instead of that we propose that a free phenacyl carbene intermediate is bypassed in this reaction. This mechanism proposal is supported by the trace formation of 1,2,3-tri-(4-chloro-benzoyl)cyclopropane MS-GC (CI, *m*/*z* (relative intensity): 497 (M^++41, 0.1), 485 (M^++29, 2), 459 (M^++3, 9.4), 457 (M^++1, 9.1) and 1,4-diphenyl-but-2-ene-1,4-dione as side product, detected in MS-GC (EI, *m*/*z* (relative intensity): 236 (M^+, 62), 208 (M^+-CO, 31), 179(3), 159(3), 131(9), 105(100), 77(91), 51(42). This compound should be formed via carbene, as indicated in Scheme 3, because the phenacyl anions (brominated or not) behave, as already described,[25,26] through addition processes (not substitution) with regard to another phenacyl halide molecule.

Scheme 3. Evidence of phenacyl carbene intermediate: formation of 1,4-diphenyl-but-2-ene-1,4-dione



The most common reactions associated with divalent carbon intermediates are insertion into saturated C–H or C–X bonds and addition to unsaturated centers. The latter reaction, in particular the addition to olefins yielding cyclopropanes, has been demonstrated to be of great preparative value.

Electronic configuration of carbenes determines their reactivity. Highly reactive singlet carbene (electrophiles) are not selective with regard the concerted *syn*-cycloaddition to olefins, providing a mixture of equal stereoisomers ratio. This is our mechanism proposal to occur when platinum cathode is used in the electrolysis of *p*-benzoquinone in the presence of phenacyl halides. Because the phenacyl halides are not adsorbed over platinum (no reduction is achieved even applying the adequate reduction potential) the [2 + 2] cycloaddition of electrogenerated carbene to quinones takes place in solution, not at the electrode surface, and subsequently the delivered stereoselectivity *E*/*Z* is tiny.

In contrast to singlet carbenes, carbenoid species (synthetic equivalents of a triplet carbene) behave as radical intermediates producing, in the presence of olefins, highly stereoselective isomeric cyclopropane mixtures, as described in the styrene photoredox catalysis[27] or in the presence of metal-carbene species, as recently reported[28] (Co^{III}-carbene radical intermediate).

To further investigate the effect of electrode nature on the stereoselectivity of this cyclopropanation reaction, the reduction of **1** was carried out using mercury as working electrode, due to the well-known adsorption properties of organic substrates at this material, that could modify (by environment influence) the steric hindrance on the cycloaddition reaction, compared to previous platinum electrolysis.

Surprisingly, since the first attempt with mercury as cathode, the *E*/*Z* yield ratios on homoquinones **3** were clearly increased, as indicated in Table 1, pointing out that in the cyclopropanation, the appropriate election of the electrode nature, allows a control on delivered homoquinone diastereomers.

These interesting results on the stereochemistry effect caused by mercury can be explained in base to the strong adsorption that both starting compounds **1** and **2** suffer at this electrode surface. Electroactive quinone, that prior to be reduced is adsorbed in parallel to the surface, is attacked by the previously oriented electrogenerated carbene, with the phenone carbonyl group situated (electrically attracted) closely to the negative charged cathode surface. This more stabilized *exo*-adduct, affords the sterically less hindered *E* homoquinone that is preferentially formed compared to the less favored *endo*-adduct (see Figure 1)

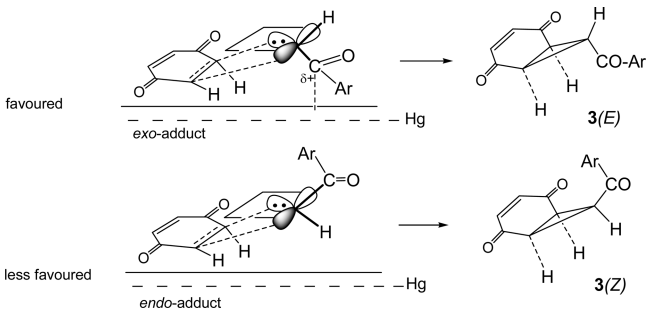


Figure 1. Orientation at the mercury surface of the *endo*- and *exo*-adducts on the [2 + 2]cycloaddition of phenacylcarbene to 1,4-quinone.

Instead of that, at platinum electrode the poor stereoselectivity is explained by the fact that the quinone is attacked by the carbene in solution, not at the electrode surface, because of the lower adsorption properties of this material. At platinum both the sterically less crowded (*E*)-homoquinone and the *Z* isomer are almost equally formed. It indicates that in the absence of a strong quinone adsorption and a phenacyl carbene electric field orientation, the fast cycloaddition reaction produces a *E*/*Z* ratio close to unity, being the *trans* (*E*) preferentially formed probably due to the rather bulky *endo*-adduct. The stereoselectivity is however increased, even at platinum, when a hindered substituent (Br or NO_2) is located at the 4-position of the aryl group.

Nevertheless, the highly diastereoselective isomeric cyclopropane mixtures obtained at mercury electrode, is not discarded to be simultaneously justified by involving a metal-carbenoid (carbenoid radical) intermediate similarly to the described Hg-complexes containing carbene ligands[29] or the already suggested carbenoid specie in the amalgam reduction of sulfones.[30] Such organometal-carbenoid intermediate never could be formed at a noble platinum electrode.

In all cases a low concentration of phenacyl halide could be convenient to avoid the further attack of the initially formed brominated phenacyl anion to a new molecule of **2**, as it was

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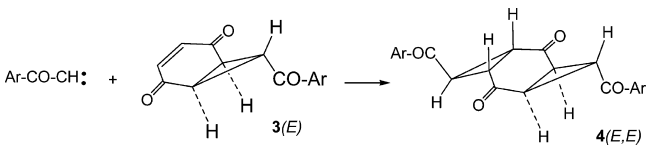
already described to produce undesired halogenated ketoepoxides.[25] However, in the presence of 1,4-quinone molecules the ketoepoxide was never detected.

It is noteworthy that trace amounts of the corresponding bis-homoquinone (**4**), was possible to be detected. This compound was formed after a second phenacylcarbene insertion over the free C−C double bond of the homoquinone **3**, that presumable[14] should be *anti*-configured, as indicated in Scheme 4.

Scheme 4. Formation of Trace Amounts of Bis-homoquinone (4) from Phenacyl Carbene and (*E*)-Homoquinone 3



To explore the scope of this carbene cycloaddition and to extend and increase the utility of the method, 1,4-naphthoquinone (**1b**) was used as electroactive substrate and as precursor of another electrogenerated bases (EGB) that subsequently conducted to different cyclopropanation products. When **2a**, **2b** or **2d** were located at the cathodic compartment, at time that **1b** was electrolyzed, the expected homonaphthoquinones **3g**, **3h** and **3i** were respectively obtained. It should be noticed that in this case it was needed a higher reduction potential to be applied to produce the radical anion of the quinone (E_{pc1} of 1,4-naphthoquinone is −0.55 V, vs Ag/Ag^+). For this reason phenacyl chloride (instead of bromide) was used to avoid a simultaneous cathodic discharge of **1b** and **2**. Table 2 summarizes the obtained yields on homonaphthoquinones **3(g−i)**.

Table 2. Obtained Yields and *E*/*Z* Ratios at Mercury Cathode in Homoquinones 3(g−i) from 1,4-Naphthoquinone (1b) and Phenacyl Chlorides 2a, 2b or 2d

phenacyl halide (**2**) Ar−CO−CH_2Cl	isolated yield homonaphthoquinones **3(g−i)**	yield ratio *E*/*Z*-homonaphthoquinones **3(g−i)**
a: Ar = C_6H_5-	77	98:2 (93:7)[a]
b: Ar = 4-CH_3-C_6H_4-	74	85:15
d: Ar = 4-Cl-C_6H_4-	71	89:11

[a]At Pt electrode.

The *E*-diastereomers were curiously preferentially obtained, both when reduction of naphthoquinone was conducted on Hg but also on Pt as cathode. A plausible explanation is that the aromatic ring, condensed with the 1,4-quinone frame, even in solution avoids the formation of the sterically less favored *endo*-adduct when reacted with the phenacyl carbene, being the *trans*-stereoisomer afforded as the main product.

Finally, in order to improve the scope of the reaction, it was extended to α-bromo-propiophenone (**2′**) that was examined as acidic substrate (instead of α-halo-acetophenones **2**) and as precursor of a carbenoid feature intermediate.

When *p*-benzoquinone (**1a**) was reduced in the presence of **2′**, the expected homonaphthoquinone (**3′**) was obtained only as a detected product (MS *m*/*z* (relative intensity) EI 240 (M^+, 8), 225(7), 212(13), 197(7), 196(7), 184(5), 158(100), 129(29), 115(9), 105(15), 77(33)). In this case, the anion radical of the *p*-benzoquinone does not behave as an EGB related the α-bromo-propiophenone (probably is not strong enough due to the lower acidity of **2′** related to **2**) but acts as a nucleophile, displacing the halogen atom and providing the phenolic ether (**5a′**) as the main product (see Scheme 5). The homologous 2-(4-hydroxyphenoxy)-1-phenylethanone (**5a**) was also delivered, however as traces, in the above-described reaction with phenacyl bromide (**2a**).

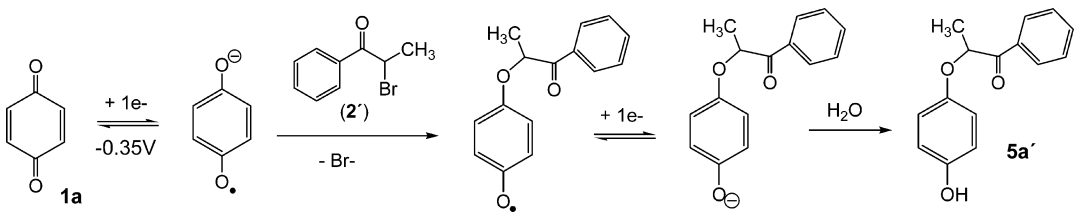
Contrary to this reaction, when 1,4-naphthoquinone (**1b**) was electrolyzed in the presence of α-bromo-propiophenone, the corresponding homonaphthoquinone (**3′**) was achieved, as indicated in Scheme 6, although not quantified due to its low yield, however compensated for the simultaneous formation of 2-(1-methylphenacyl)-1,4-naphthoquinone (**4′**) that should be obtained by C−H insertion from the methyl phenacyl carbene to the naphthoquinone frame, and the undesired double phenolic ether (**5b′**).

Unexpected similar nucleophilic substitution reaction was also observed[31] in direct electrolysis of **2′** that afforded 3,4-dimethyl-2,5-diphenylfuran contrary to the expected 3,5-dimethyl-2,4-diphenylfuran.

The 1,4-naphthoquinone radical anion (formed at more negative reduction potential), as stronger base than that of **1a**, affords the brominated enolate of **2′**, precursor of the phenacyl methyl carbene. The interesting achievement of 1,2-diphenyl-propan-1-one (MS *m*/*z* (relative intensity) EI 210 (M^+, 36), 132(12), 105(100), 77(57)), justifies the decreasing yield on homonaphthoquinone **3′**, compared with those of **3**. The formation of the former ketone only can be explained by involving the stabilized brominated ketene indicated in Scheme 7.

One of the advantages of the now described reaction is that the corresponding hydroquinone, obtained as side product, can be easily transformed into the starting quinone either by "in situ" electrode polarity change, once the reduction is finished, or by a further oxidation after being recovered in the final isolation of the homoquinones.

Scheme 5. Competitive Nucleophilic Substitution Reaction to Undesired 5a′



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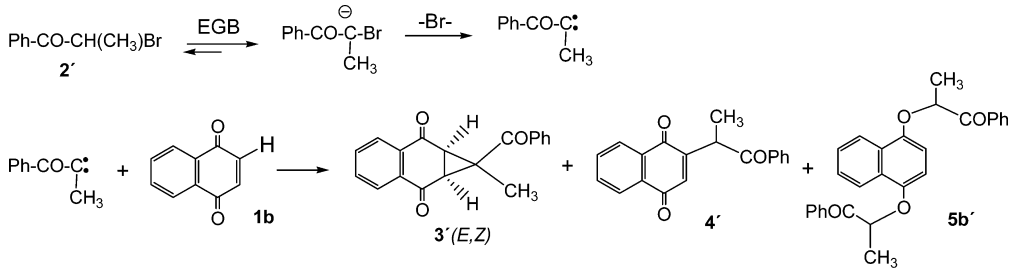
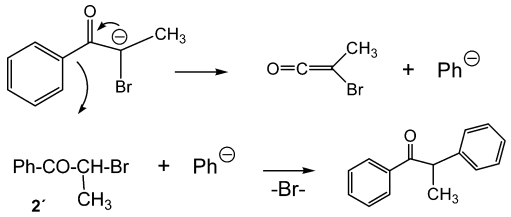
Scheme 6. Electrode Pathway Followed by 2′ in the Electrolysis of 1b



Scheme 7. Another Stabilization Pathway Followed by the Brominated Enolate of 2′



CONCLUSION

A new and high yielded electrochemical protocol for the room-temperature synthesis, in one-pot, of a variety of benzoyl homoquinones is now described. *p*-Benzoquinone and 1,4-naphthoquinone have proven to be suitable starting materials, at time that precursors of electrogenerated bases (EGB) involved in the first proton abstraction to α-halophenones. Reductive electrochemical discharge of those conducted, in the presence of phenones to phenacyl carbene intermediates that provided cyclopropanes after a stereoselective [2 + 2] cycloaddition to the C=C double bond of the quinone. Diastereoselectivity dependence on the electrode nature is justified in base to the adsorption of reactant at the electrode surface.

EXPERIMENTAL SECTION

Electrolyses were performed in an Amel potentiostat Model 552 with electronic integrator Amel Model 721. IR spectra of the products were recorded as dispersions in KBr or NaCl films on a PerkinElmer FT-IR Frontier spectrometer. ^{1}H,^{13}C NMR, correlation COSY, NOE-2D and other resonance spectra were recorded in $CDCl_3$ or CD_3OD on a Varian Unity 300 (300 MHz) or a Bruker 500 MHz spectrometers, with tetramethylsilane (TMS) as the internal standard. The chemical shifts are given in ppm. Mass spectra (EI, ionizing voltage 70 eV) were determined using a THERMOFISHER ITQ-900 DIP/GC-MSn mass-selective detector. All melting points were measured on a Reichert Thermovar microhot stage apparatus and are uncorrected. Elemental analyses were performed on a Leco CHNS Model 932 analyzer. All starting materials were obtained from commercial sources and used without purification.

The electrochemical reduction of 1,4-quinone (**1a** or **1b**, 1.2 mmol) in the presence of phenacyl bromides (**2**(**a**–**f**), 1 mmol), or in the presence of α-bromo-propiophenone (**2′**, 1 mmol), was carried out under potentiostatic conditions (E = −0.40 V/or −0.55 V, vs Ag/AgCl, with **1a**/or **1b**, respectively), which corresponds to the first quinone one-electron wave reduction potential, not being reduced the phenacyl halide. The solvent-supporting electrolyte system (SSE) was dry DMF/0.2 M $LiClO_4$ solutions. As cathode a platinum sheet (8 cm^2) (or a mercury pool of 12 cm^2) was used. The anode was a platinum plate, and the reference electrode was a Ag/AgCl (saturated) electrode.

The electrolyses were performed at room temperature (20 °C) under an argon atmosphere, to exclude air, in a concentric and divided electrochemical cell where both compartments were separated by a porous (D4) glass frit diaphragm, and equipped with a magnetic stirrer. The catholyte was 70 mL of the SSE solution containing 1.2 mmol of **1** and 1.0 mmol of the corresponding phenacyl halide (**2**). Initial current values proximate to 80 mA were accompanied to a change in catholyte solution appearance that became dark-blue, indicating the quinone radical anion formation.

Once the reduction was finished and the current was decreased to residual values, the catholyte solution was stirred overnight under an argon atmosphere. The solvent, in the cathodic solution, was finally removed under reduced pressure; the residue was then three times extracted with ether/water and the organic phase was dried over Na_2SO_4 and concentrated by evaporation. The resulting solid or oil was chromatographed on a GC-MS (HP-5 cross-linked 5% PhMe silicone 30 m−0.25 mm−0.25 μm chromatographic column) instrument and purified by a silica gel 60 (35−70 mesh) (24 × 3 cm) column using mixtures chloroform/methanol (20/1) or petroleum ether/ethyl acetate (5/1) as eluents. Homoquinones (**3**) were characterized by its IR, MS, ^{1}H NMR, ^{13}C NMR, NOE-2D and correlation COSY spectroscopic properties. Also by comparison with other, already described, homoquinone frames.[32]

Complete spectra description of these new obtained products is given below.

7-Benzoyl bicyclo[4.1.0]hepta-3-en-2,5-dione (3a-*E*). (92 mg, white solid, 41% yield (Pt cathode)). mp 131−133 °C. IR(KBr) ν_{max} = 3061, 2920, 1679, 1597, 1223, 1021, 690 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.12 (d, J = 4.0 Hz, 2H), 3.65 (t, J = 4.0 Hz, 1H), 6.61 (s, 2H), 7.48−7.54 (m, 2H), 7.64 (tt, J_1= 7.4 Hz, J_2= 1.5 Hz, 1H), 7.96 (dd, J_1= 8.7 Hz, J_2= 1.5 Hz, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 34.7, 34.8, 128.4, 128.9, 134.2, 136.0, 138.1, 191.5, 192.3. MS m/z (relative intensity) EI 226 (M^+, 23), 225 (M^+-1, 14), 198 (49), 197(28), 182(2), 170(13), 148(97), 144(53), 115(29), 105(100), 77(78), 65(7), 51(34). Anal. Calc. for $C_{14}H_{10}O_3$: C, 74.33; H, 4.42. Found: C, 74.21; H, 4.37.

7-Benzoyl bicyclo[4.1.0]hepta-3-en-2,5-dione (3a-*Z*). (82 mg, white solid, 36% yield (Pt cathode)). mp 124−126 °C. IR(KBr) ν_{max} = 3060, 2927, 1677, 1599, 1224, 1103, 691 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.96 (d, J = 9.8 Hz, 2H), 3.42 (t, J = 9.8 Hz, 1H), 6.5 (s, 2H), 7.44−7.49 (m, 2H), 7.59 (tt, J_1= 7.3 Hz, J_2= 1.5 Hz,1H), 7.93 (dd, J_1= 8.3 Hz, J_2= 1.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.4, 36.8, 129.0, 129.1, 134.5, 135.7, 139.3, 191.8, 192.0. MS m/z (relative intensity) EI 226 (M^+, 47), 225 (M^+-1, 25), 198 (47), 197(31), 182(27), 170(33), 156(29), 144(70), 115(36), 105(100), 77(97), 65(7), 51(35). Anal. Calc. for $C_{14}H_{10}O_3$: C, 74.33; H, 4.42. Found: C, 74.08; H, 4.45.

7-(4-Methylbenzoyl)bicyclo[4.1.0]hepta-3-en-2,5-dione (3b-*E*). (99 mg, pale yellow solid, 41% yield (Pt cathode)). mp 130−133 °C. IR(KBr) ν_{max} = 3044, 2924, 1672, 1603, 1509, 1303, 1232, 1023, 980, 827 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.44 (s, 3H), 3.10 (d, J = 4.4 Hz, 2H), 3.64 (t, J = 4.4 Hz, 1H), 6.60 (s, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.83 (d, J = 8.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.8, 34.8, 128.6, 129.7, 133.5, 138.0, 145.4, 191.6, 191.7. MS m/z (relative intensity) EI 240 (M^+, 42), 225 (6), 212(13), 197 (10), 184(7), 169(4), 158(33), 148(78), 129(12), 119(100), 115(8),

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91(51), 65(21). Anal. Calc. for $C_{15}H_{12}O_3$: C, 75.00; H, 5.00. Found: C, 74.82; H, 5.13.

7-(4-Methylbenzoyl)bicyclo[4.1.0]hepta-3-en-2,5-dione (3b-*Z*). (81 mg, white-yellow solid, 34% yield (Pt cathode)). mp 102−104 °C. IR(KBr) ν_{max} = 3042, 2961, 2961, 1676, 1607, 1508, 1227, 1102, 1015, 910 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 2.42(s, 3H), 2.85 (d, J = 9.7 Hz, 2H), 3.49 (t, J = 9.7 Hz, 1H), 6.47 (s, 2H), 7.27 (d, J = 7.7 Hz, 2H), 7.83 (d, J = 7.7 Hz, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 21.8, 31.3, 36.8, 129.2, 129.7, 133.2, 139.2, 145.7, 191.2, 192.2. MS m/z (relative intensity) EI 240 (M^+, 96), 212 (56), 197 (16), 184(38), 169(14), 158(35), 145(29), 129(22), 119(100), 115(17), 91(70), 65(26). Anal. Calc. for $C_{15}H_{12}O_3$: C, 75.00; H, 5.00. Found: C, 74.90; H, 4.87.

7-(4-Methoxybenzoyl)bicyclo[4.1.0]hepta-3-en-2,5-dione (3c-*E*). (108 mg, yellow solid, 42% yield (Pt cathode)). mp 139−141 °C. IR(KBr) ν_{max} = 3065, 2935, 1680, 1600, 1574, 1511, 1461, 1263, 1172, 1025, 836. ^1H NMR (500 MHz, $CDCl_3$) δ 3.10 (d, J = 4.4 Hz, 2H), 3.62 (t, J = 4.4 Hz, 1H), 3.89 (s, 3H), 6.60 (s, 2H), 6.97 (d, J = 8.8 Hz, 2H), 7.94 (d, J = 8.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 34.7, 55.6, 114.2, 128.9, 130.9, 138.1, 164.4, 190.4, 191.8. MS m/z (relative intensity) EI 256 (M^+, 63), 227 (2), 174(10), 159(11), 135(100), 131(5), 108(13), 107(10), 92(10), 77(27), 63(13). Anal. Calc. for $C_{15}H_{12}O_4$: C, 70.30; H, 4.70. Found: C, 70.11; H, 4.63.

7-(4-Methoxybenzoyl)bicyclo[4.1.0]hepta-3-en-2,5-dione (3c-*Z*). (97 mg, yellow solid, 38% yield (Pt cathode)). mp 165−167 °C. IR(KBr) ν_{max} = 3054, 2921, 2844, 1675, 1603, 1506, 1441, 1230, 1170, 1013, 905, 834 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 2.92 (d, J = 9.7 Hz, 2H), 3.4 (t, J = 9.7 Hz, 1H), 3.87 (s, 3H), 6.45 (s, 2H), 6.93 (d, J = 9.0 Hz, 2H), 7.94 (d, J = 9.0 Hz, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 31.3, 36.8, 55.6, 114.2, 128.9, 131.6, 139.1, 164.5, 190.0, 192.3. MS m/z (relative intensity) EI 256 (M^+, 77), 228(7), 212(9), 200(10), 174(16), 161(25), 159(16), 135(100), 131(7), 107(12), 92(12), 77(31), 63(17). Anal. Calc. for $C_{15}H_{12}O_4$: C, 70.30; H, 4.70. Found: C, 70.60; H, 4.51.

7-(4-Chlorobenzoyl)bicyclo[4.1.0]hepta-3-en-2,5-dione (3d-*E*). (107 mg, yellow solid, 41% yield (Pt cathode)). mp 160−163 °C. IR(KBr) ν_{max} = 3042, 2923, 1678, 1590, 1509, 1299, 1220, 1092, 1012, 979, 832, 741 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 3.11 (d, J = 4.4 Hz, 2H), 3.59 (t, J = 4.4 Hz, 1H), 6.60 (s, 2H), 7.47 (d, J = 8.8 Hz, 2H), 7.89 (d, J = 8.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 34.8, 35.2, 129.5, 130.0, 134.4, 138.2, 141.1, 191.3, 191.4. MS m/z (relative intensity) EI 262 (M^++2, 8), 260 (M^+, 24), 234 (5), 232(16), 225(30), 197(31), 180(18), 178(54), 169(9), 148(79), 141(34), 139(100), 115(26), 113(14), 111(41), 75(26). Anal. Calc. for $C_{14}H_9ClO_3$: C, 64.50; H, 3.50. Found: C, 64.79; H, 3.67.

7-(4-Chlorobenzoyl)bicyclo[4.1.0]hepta-3-en-2,5-dione (3d-*Z*). (97 mg, yellow solid, 37% yield (Pt cathode)). mp 130−133 °C. IR(KBr) ν_{max} = 3057, 2924, 1678, 1591, 1403, 1336, 1221, 1094, 1007, 905, 837, 786 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 2.96 (d, J = 9.8 Hz, 2H), 3.39 (t, J = 9.8 Hz, 1H), 6.49 (s, 2H), 7.46 (d, J = 8.8 Hz, 2H), 7.89 (d, J = 8.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.1, 36.3, 129.3, 130.3, 133.9, 139.2, 141.1, 190.4, 191.7. MS m/z (relative intensity) EI 262 (M^++2, 15), 260 (M^+, 46), 234 (7), 232(21), 216(10), 204(5), 197 (53), 180(18), 178(54), 169(11), 141(35), 139(100), 115(32), 113(15), 111(45), 95(11), 75(30). Anal. Calc. for $C_{14}H_9ClO_3$: C, 64.50; H, 3.50. Found: C, 64.55; H, 3.91.

7-(4-Bromobenzoyl)bicyclo[4.1.0]hepta-3-en-2,5-dione (3e-*E*). (134 mg, pale orange solid, 44% yield (Pt cathode)). mp 168−171 °C. IR(KBr) ν_{max} = 3040, 2924, 1668, 1584, 1301, 1224, 1069, 1006, 979, 871, 848, 740 cm^{-1}. ^1H NMR (500 MHz, CD_3OD-$CDCl_3$) δ 3.10 (d, J = 3.9 Hz, 2H), 3.58 (t, J = 3.9 Hz, 1H), 6.61 (s, 2H), 7.64 (d, J = 8.8 Hz, 2H), 7.81 (d, J = 8.8 Hz, 2H). ^{13}C NMR (125 MHz, CD_3OD-$CDCl_3$) δ 34.4, 34.8, 129.7, 129.8, 132.3, 134.6, 138.0, 191.2, 191.4. MS m/z (relative intensity) EI 306 (M^++2, 37), 304 (M^+, 37), 278 (10), 276(10), 250(3), 248(3), 225(34), 224(44), 222(44), 197(67), 185(100), 183(99), 169(17), 157(28), 155(28), 148(70), 141(11), 115(34), 76(13), 75(16). Anal. Calc. for $C_{14}H_9BrO_3$: C, 55.10; H, 3.00. Found: C, 55.23; H, 2.78.

7-(4-Bromobenzoyl)bicyclo[4.1.0]hepta-3-en-2,5-dione (3e-*Z*). (73 mg, pale orange solid, 24% yield (Pt cathode)). mp 164−167 °C. IR(KBr) ν_{max} = 3058, 2925, 1680, 1585, 1299, 1219, 1070, 1008, 979 cm^{-1}. ^1H NMR (500 MHz, CD_3OD-$CDCl_3$) δ 2.95 (d, J = 9.8 Hz, 2H), 3.39 (t, J = 9.8 Hz, 1H), 6.49 (s, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 8.4 Hz, 2H). ^{13}C NMR (125 MHz, CD_3OD-$CDCl_3$) δ 31.2, 36.4, 129.8, 130.4, 132.4, 134.4, 139.3, 190.7, 191.7. MS m/z (relative intensity) EI 306 (M^++2, 61), 304 (M^+, 67), 278 (18), 276(16), 262(11), 260(11), 250(18), 248(18), 225(18), 224(54), 222(54), 197(80), 185(99), 183(100), 169(24), 157(30), 155(40), 148(20), 115(40), 76(7), 75(12). Anal. Calc. for $C_{14}H_9BrO_3$: C, 55.10; H, 3.00. Found: C, 54.87; H, 3.03.

7-(4-Nitrobenzoyl)bicyclo[4.1.0]hepta-3-en-2,5-dione (3f-*E*). (136 mg, yellow solid, 50% yield (Pt cathode)). mp 217−219 °C. IR(KBr) ν_{max} = 3047, 1680, 1601, 1524, 1349, 1302, 1281, 1217, 1126, 1033, 860, 713, 691 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 3.16 (d, J = 3.2 Hz, 2H), 3.63 (t, J = 3.2 Hz, 1H), 6.64 (s, 2H), 8.12 (d, J = 8.4 Hz, 2H), 8.36 (d, J = 8.4 Hz, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 36.2, 124.2, 130.0, 139.5, 139.7, 150.9, 190.4, 191.2. MS m/z (relative intensity) EI 271 (M^+, 14), 254 (52), 243(100), 226(22), 224(26), 216(10), 197(17), 189(28), 173(35), 159(30), 150(70), 148(18), 131(12), 120(30), 115(25), 104(17), 92(41), 82(16), 76(21), 75(18). Anal. Calc. for $C_{14}H_9NO_5$: C, 62.00; H, 3.30; N, 5.20. Found: C, 61.75; H, 3.57; N, 5.31.

7-(4-Nitrobenzoyl)bicyclo[4.1.0]hepta-3-en-2,5-dione (3f-*Z*). (92 mg, yellow solid, 34% yield (Pt cathode)). mp 153−157 °C. IR(KBr) ν_{max} = 3058, 3002, 2925, 1684, 1603, 1530, 1347, 1217, 1105, 1006, 856, 736, 713. ^1H NMR (300 MHz, $CDCl_3$) δ 3.0 (d, J = 9.3 Hz, 2H), 3.44 (t, J = 9.3 Hz, 1H), 6.52 (s, 2H), 8.11 (d, J = 8.4 Hz, 2H), 8.33 (d, J = 8.4 Hz, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 34.6, 35.1, 124.1, 129.4, 138.0, 140.1, 151.9, 190.5, 191.1. MS m/z (relative intensity) EI 271 (M^+, 41), 270(19), 243(24), 242(19), 227(56), 215(22), 201(76), 189(24), 173(35), 169(17), 159(28), 150(100), 131(13), 120(30), 115(27), 104(19), 92(51), 82(12), 76(23), 65(14), 63(17). Anal. Calc. for $C_{14}H_9NO_5$: C, 62.00; H, 3.30; N, 5.20. Found: C, 62.31; H, 3.11; N, 4.89.

1-Benzoyl-1,1a-dihydro-7a*H*-cycloprop[*b*]naphthalene-2,7-dione (3g-*E*). (208 mg, white solid, 75% yield (Hg cathode)). mp 136−139 °C. IR(KBr) ν_{max} = 3064, 3047, 2921, 1674, 1597, 1449, 1288, 1224, 1018, 786, 711 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 3.28 (d, J = 4.4 Hz, 2H), 3.60 (t, J = 4.4 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.57 (tt, J_1= 7.5 Hz, J_2= 1.2 Hz, 1H), 7.76 (d, J = 5.9 Hz, 1H), 7.77 (d, J = 5.9 Hz, 1H), 7.88 (dt, J_1= 7.3 Hz, J_2= 1.2 Hz, 2H), 8.05 (d, J = 5.9 Hz, 1H), 8.06 (d, J = 5.9 Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 34.6, 35.8, 127.3, 128.4, 128.8, 132.3, 134.1, 134.6, 136.1, 190.4, 192.4. MS m/z (relative intensity) EI 276 (M^+, 100), 259 (8), 248(9), 247(21), 232(27), 231(21), 219(6), 203(20), 198(24), 191(8), 171(7), 143(9), 115(32), 105(56), 104(12), 89(11), 77(51). Anal. Calc. for $C_{18}H_{12}O_3$: C, 78.30; H, 4.30. Found: C, 77.99; H, 4.44.

(*Z*-Isomer): MS m/z (relative intensity) EI 276 (M^+, 98), 259 (7), 247(8), 232(78), 231(30), 204(28), 203(28), 198(14), 191(7), 171(8), 143(7), 115(38), 105(100), 89(16), 77(87), 51(33).

1,1a-Dihydro-1-(4-methyl-benzoyl)-7a*H*-cycloprop[*b*]-naphthalene-2,7-dione (3h-*E*). (182 mg, white solid, 63% yield (Hg cathode)). mp 128−130 °C. IR(KBr) ν_{max} = 3055, 2921, 1682, 1603, 1324, 1299, 1234, 1186, 1041, 959, 737, 697 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 2.38 (s, 3H), 3.28 (d, J = 4.4 Hz, 2H), 3.56 (t, J = 4.4 Hz, 1H), 7.22 (d, J = 7.8 Hz, 2H), 7.76−7.79 (m, 4H), 8.06 (d, J = 5.8 Hz, 1H), 8.07 (d, J = 5.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.7, 34.6, 35.7, 127.3, 128.4, 128.5, 129.4, 129.5, 132.4, 133.6, 134.5, 145.2, 190.5, 191.8. MS m/z (relative intensity) EI 290 (M^+, 45), 275(8), 247(11), 246(20), 231(10), 203(16), 198(25), 129(7), 119(100), 115(43), 104(14), 91(70), 89(28), 76(19). Anal. Calc. for $C_{19}H_{14}O_3$: C, 78.60; H, 4.80. Found: C, 78.91; H, 4.83.

(*Z*-Isomer): MS m/z (relative intensity) EI 290 (M^+, 31), 275(4), 246(37), 231(8), 218(17), 203(13), 198(7), 128(7), 119(100), 115(34), 104(13), 91(54), 89(23), 76(17).

1,1a-Dihydro-1-(4-chloro-benzoyl)-7a*H*-cycloprop[*b*]-naphthalene-2,7-dione (3i-*E*). (196 mg, yellow solid, 63% yield (Hg cathode)). mp 161−164 (descomp) °C. IR(KBr) ν_{max} = 3094, 2923, 1678, 1589, 1326, 1300, 1227, 1089, 1012, 958, 776, 725, 689 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 3.30 (d, J = 4.3 Hz, 2H), 3.53 (t,

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J = 4.3 Hz, 1H), 7.42 (d, J = 8.7 Hz, 2H), 7.79(d, J = 5.9 Hz, 1H), 7.80(d, J = 5.9 Hz, 1H), 7.84(d, J = 8.7 Hz, 2H), 8.08(d, J = 5.9 Hz, 1H), 8.09 (d, J = 5.9 Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 34.4, 35.8, 127.3, 129.2, 129.8, 132.2, 134.4, 134.6, 140.7, 190.2, 191.3. MS m/z (relative intensity) EI 312 (M^++2, 29), 310 (M^+, 88), 281(10), 275(48), 268(10), 266(32), 247(30), 231(33), 219(10), 203(17), 198(33), 191(10), 141(35), 139(100), 115(30), 113(14), 111(42), 104(24), 89(10), 76(17), 75(20). Anal. Calc. for $C_{18}H_{11}ClO_3$: C, 69.60; H, 3.50; Found: C, 69.37; H, 3.78.

(*Z*-Isomer): MS m/z (relative intensity) EI 312 (M^++2, 17), 310 (M^+, 55), 268(39), 266(100), 238(15), 231(37), 203(21), 141(31), 139(99), 115(13), 113(14), 111(40), 104(7), 76(14), 75(13).

1-Benzoyl-1a,7a-dihydro-1-methyl-cycloprop[*b*]-naphthalene-2,7-dione (3′-*E*). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39 (s, 3H), 3.21 (s, 2H), 7.54−7.64 (m, 3H), 7.7 (d, J = 5.9 Hz, 1H), 7.8 (d, J = 5.9 Hz, 1H), 8.16 (d, J = 5.9 Hz, 1H), 8.17 (d, J = 5.9 Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 13.3, 35.1, 126.8, 129.1, 133.4, 134.3, 134.6, 134.7, 136.2, 190.8. MS m/z (relative intensity) EI 290 (M^+, 13), 275 (15), 262(9), 247(28), 246(100), 231(21), 218(11), 203(13), 185(12), 157(9), 128(20), 105(42), 104(11), 77(58). Anal. Calc. for $C_{19}H_{14}O_3$: C, 78.62; H, 4.82; Found: C, 79.00; H, 5.17.

(*Z*-Isomer): (trace) MS m/z (relative intensity) EI 290 (M^+, 17), 275 (17), 262(8), 247(30), 246(100), 231(14), 218(11), 203(11), 185(13), 157(6), 128(15), 104(12), 77(33).

2-(1-Methylphenacyl)-1,4-naphthoquinone (4′). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.48 (d, J = 7.0 Hz, 3H), 5.08 (q, J = 7.0 Hz, 1H), 6.89 (s, 1H), 7.48 (t, J = 7.2 Hz, 2H), 7.58 (t, J = 7.2 Hz, 1H), 7.70−7.78 (m, 2H), 8.02 (d, J = 7.2 Hz, 2H) 8.04−8.1 (m, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 16.2, 39.9, 126.2, 126.8, 128.7, 128.8, 129.9, 131.9, 133.5, 133.8, 134.0, 135.6, 135.7, 136.2, 150.7, 184.3, 199.4. MS m/z (relative intensity) EI 290 (M^+, 5), 187(1), 157(1), 128(8), 105(100), 77(50).

Bis(4-bromo-phenacyl)-homo-*p*-quinone (4e). 2,6-Dioxo-4,8-di(4-bromophenacyl)triciclo[5.1.0^{3,5}] octane: (trace) MS m/z (relative intensity) EI 504 (M^++4, 4), 502 (M^++2, 3), 500 (M^+, 3), 319 (65), 317(67), 224(49), 222(47), 185(97), 183(100), 157(30), 155(30), 115(20), 95(17), 75(8).

2-(4-Hydroxyphenoxy)-1-phenylethanone (5a). mp 111−113 °C [Lit.[33] 114−115 °C]. IR(KBr) ν_{max} = 3393, 2923, 1693, 1510, 1216, 828, 737 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.25 (d, 2H, J = 2.8 Hz), 6.78 (d, 2H, J = 8.9 Hz), 6.88 (d, 2H, J = 8.9 Hz), 7.50−7.58 (m, 2H), 7.64 (t, J = 7.4 Hz, 1H), 8.0 (d, J = 7.7 Hz, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 71.8, 116.1, 116.2, 128.1, 128.8, 133.8, 134.6, 150.4, 152.2, 195.0. MS m/z (relative intensity) EI 229 (M^++1, 10), 228 (M^+, 64), 105(100), 91(7), 77(54), 65(9), 51(12).

2-(4-Hydroxyphenoxy)-2-methyl-1-phenylethanone (5a′). MS m/z (relative intensity) EI 243 (M^++1, 9), 242 (M^+, 57), 137(100), 110(18), 109(13), 105(26), 91(4), 77(43), 65(11), 51(22).

1,4-Bis(propionylphenyl-2-oxy)-naphthalene (5b′). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.8 (d, J = 6.8 Hz, 6H), 5.5 (q, J = 6.8 Hz, 2H), 6.46 (d, J = 12.4 Hz, 2H), 7.42 (t, J = 7.2 Hz, 4H), 7.50−7.58 (m, 4H), 8.10 (d, J = 7.2 Hz, 4H), 8.3 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 18.7, 18.8, 77.5, 105.2, 105.4, 122.0, 126.2, 126.6, 126.7, 128.7, 128.8, 128.9, 133.6, 134.1, 147.7, 147.8, 199.1, 199.3.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b00925.

Copies of ^{1}H and ^{13}C NMR spectra, IR and MS of (*E*) and (*Z*) stereoisomers of homoquinones **3a−i** (all of them new compounds); a COSY (of representative homoquinone **3d**-*E*) and NOE-2D (of representative homoquinone **3g**-*E*); Characterization spectra copies of compounds **3′**, **4′**, **4e**, **5a**, **5a′** and **5b′**; MS of 1,4-Diphenyl-but-2-ene-1,4-dione, 1,2,3-Tri-(4-chloro-benzoyl)cyclopropane and 1,2-Diphenylpropan-1-one; Figure of the electrochemical reactor (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +34-91-8854617. Fax: +34-91-8854686. E-mail: belen.batanero@uah.es.

ORCID

Belen Batanero: 0000-0003-2630-4814

Notes

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