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Competition between Nucleophilic Addition and Electron-Transfer Process in the Reaction of 9-Diazo-10-Anthrone with Grignard Reagents*

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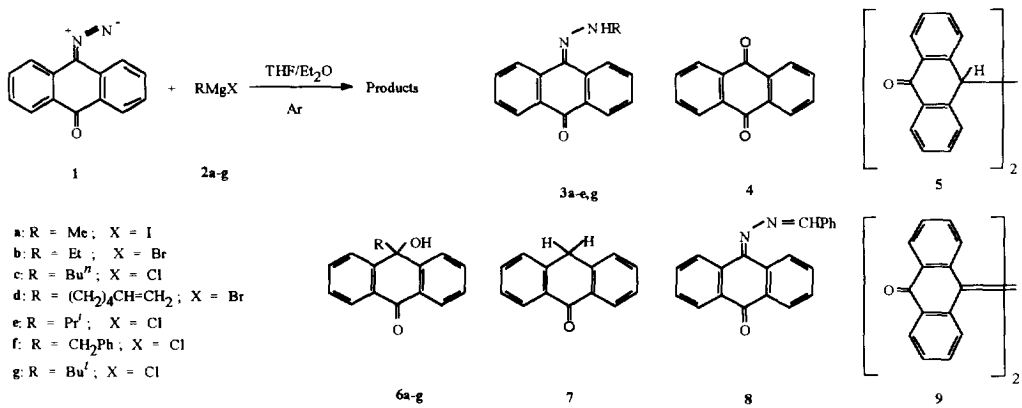
Abstract. 9-diazo-10-anthrone reacts with RMgX (R = Me, Et, Bu^n, 5-hexenyl, Pr^i, benzyl, Bu^t) essentially yielding 9-alkylazo-10-hydroxy derivatives, which are isolated in their tautomeric quinoid structure as alkylhydrazones of 9,10-anthraquinone. The yields of these compounds decrease as the oxidation potentials (E_{OX}) of the Grignards decrease: at the same time additional compounds, formed through a radical mechanism, are obtained in higher yields. The reaction has been interpreted as a competition between single electron transfer (SET) and nucleophilic attack, which occur with ratios varying with the oxidation potentials of the Grignard reagents. Evidences for the SET pathway have been found performing an experiment in the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as a scavenger of C-centered radicals.

Grignard reagents react with many compounds such as ketones,[1] quinones and quino-diimines,[2] azo[3,4] and azoxy[5] compounds, nitroso[6] and nitroarenes,[7] radical cations,[8] diazonium salts[9] and unsaturated hydrocarbons.[10] Most of the reactions were carried out many years ago and later reinvestigated from the mechanistic point of view to verify whether a radical pathway through an electron transfer between the substrate and the Grignard reagent was involved.[11] In a study carried out on 2-phenyl-3-phenylimino-3H-indole with Grignard reagents,[12] it was established on the basis of the experimental results and the Marcus theory, that an electron transfer process is possible when using Bu^nMgCl (which shows an oxidation potential of -0.53 V *vs* NHE) and substrates with a reduction potential of -0.8 V (*vs* NHE) or less negative. On the basis of this result and of the fact that oxidation potentials of Grignard reagents range from 0.00 V to -1.16 V (*vs* NHE),[13] the reaction of some Grignard reagents with 1,1'-dioxide-2,2'-diphenyl-3,3'-bi-3H-indole, showing a reduction potential of -0.125 V (*vs* NHE in DMF),[14] was studied: a redox process was observed in all cases and the radicals arising from Grignards were trapped with an indolinonic aminoxyl.[14] In the light of the above mentioned results, we have studied the reaction of 9-diazo-10-anthrone **1** (E_{red} = -0.62 V *vs* NHE in DMF), with Grignard reagents **2a-g**, with the aim to synthesize alkyl-azo compounds, not accessible by diazocoupling, and to verify whether an electron transfer process could compete with the normal nucleophilic addition.

RESULTS

The reactions between **1** and **2a-g** (Scheme 1) were carried out using a molar ratio 1:3 in an argon atmosphere at room temperature. Compounds **3-9** were obtained and their distribution and yields in the different reactions are listed in Table 1: overall yields around 80-90 % have been observed. Compounds **3** have been identified by their analytical and spectroscopic data; the IR spectra show the characteristic carbonyl and NH- stretching frequencies, while ^{1}H-NMR spectra show similar patterns in the aromatic region and typical $^3J_{HH}$ couplings between -NH- and the alkyl substituent (see experimental). Compound **8**, which is likely to arise from oxidation of **3f** during the reaction workup, has been characterized by its mass spectrum, which shows the correct molecular ion peak, and an appropriate IR spectrum. In addition, the ^{1}H-NMR spectrum shows a typical aromatic region pattern, but no signals attributable to any -NH-, as found in compounds **3a-e,g**.

Scheme 1



Even compounds **6** have been identified on the basis of their spectroscopic data. In particular it has been found that they show characteristic stretching frequencies due to the -OH and carbonyl in the IR spectra; these data are supported both by the full analysis of ^{1}H-NMR spectra using the ^{1}H-COSY two-dimensional technique, and by the analysis of the ^{1}H-^{1}H coupling constants (see experimental).

Compounds **4**,7 and **9** have been identified by comparison with authentic samples, while compound **5** by comparing its ^{1}H-NMR spectrum with the one reported in the "Aldrich Library of NMR Spectra".

DISCUSSION

As already mentioned, Grignard reagents with a E_{ox} ranging from 0.00 V to -1.07 V (*vs* NHE) were oxidized to the corresponding radicals by using a very strong oxidant such as 1,1'-dioxide-2,2'-diphenyl-3,3'-bi-3H-indole (E_{red} = -0.125 V *vs* NHE).[14] With other compounds such as 2-phenyl-3-phenylimino-3H-indole[12,15a] and 2-phenyl-3H-indole-3-one[15b], having E_{red} = -0.67[16] and -0.59[17] V *vs* NHE, respectively,

the electron transfer process is in competition with the nucleophilic attack. Since **1** shows an E_{red} = -0.62 V *vs* NHE (see experimental), one can expect the Grignards with an E_{ox} around -0.5 V *vs* NHE to undergo oxidation, even though partial.

Table 1. Yields of products isolated in the reactions of 1 with 2a-g.

Reactants	Products **3-12** (% Yields)								
1 + 2a-g	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**11**	**12**
a	(68)	(16)	(3)	(2)					
b	(60)	(19)	(9)	(2)					
c	(53)	(24)	(4)	(2)	(7)				
c[a]	(62)	(20)	(4)	(3)	(2)				
d	(50)	(16)	(8)	(7)					
d[b]	(15)	(17)	(6)	(3)	(2)			(28)	(15)
e	(26)	(16)	(10)	(6)	(15)		(9)		
f		(13)	(14)	(10)	(28)	(10)			
g	(27)	(24)	(10)	(2)	(18)				

[a]reaction in benzene; [b]reaction carried out in the presence of TEMPO (**10**).

One of the most applied methods to evidence an ET process, besides the theoretical approach through the application of the Marcus theory, is the use of 5-hexenylmagnesium bromide **2d**.

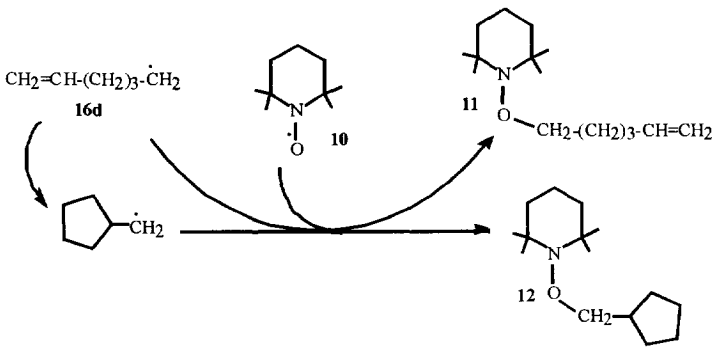
The 5-hexenyl radical formed from the corresponding anion by oxidation is known to undergo a rapid cyclization ($k \simeq 10^5$ s^{-1})[18] to cyclopentylmethyl radical.[19] On the basis of the E_{red} of **1** and of the E_{ox} of 5-hexenyl anion, which should be similar to the one of Bu^n anion, the Marcus theory[20] foresees a rate constant of 10^5 M^{-1} s^{-1} for the outer-sphere single electron transfer.[21] Nevertheless, no product containing the cyclopentylmethyl group was isolated in the reaction of **1** with **2d** because the intermediate radicals rapidly couple in the solvent cage before cyclization occurs. However in all cases, calculated data allow to state that the ET process can operate, in particular for Grignards having less negative E_{ox} (Table 2). High rate constants correspond to these compounds even when calculated using a λ value of 65 kcal mol^{-1}.

Table 2. Calculations of log(k_{ET}, M^{-1}, s^{-1}) for reactions between 1 and 2a-g, using the Marcus approach.

			λ(kcal mol^{-1})			
			40		65	
RMgX	E°(V) ($RMgX^{\cdot+}$/RMgX)	$\Delta G^{o'}$ (kcal mol^{-1})	$\Delta G^{\#}$ (kcal mol^{-1})	$\log(k_{ET})$	$\Delta G^{\#}$ (kcal mol^{-1})	$\log(k_{ET})$
2a	-0.25	-0.47	9.70	3.80	16.00	-0.78
2b	-0.66	-9.92	5.65	6.84	11.67	2.41
2c	-0.53	-6.92	6.84	5.97	12.97	1.45
2d	-0.53[a]	-6.92	6.84	5.97	12.97	1.45
2e	-0.95	-16.60	3.40	8.50	9.00	4.40
2f	-0.73	-11.50	5.10	7.20	11.00	2.90
2g	-1.07	-19.38	2.66	9.05	8.01	5.13

[a]Evaluated on the basis of $E°_{Bu^n}$

Scheme 2

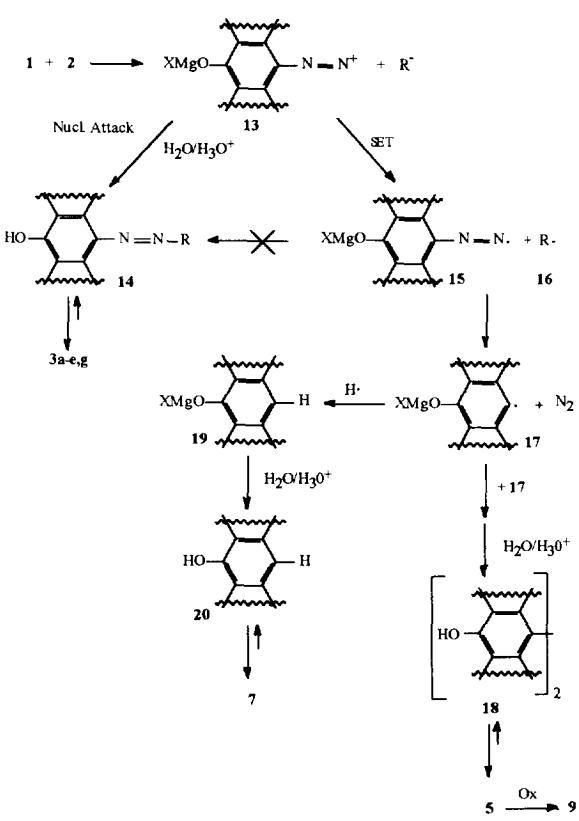


In order to prove the electron transfer process, compound **1** was reacted with **2d** in the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), being aminoxyls efficient traps for C-centered radicals.[22]

In this case, in addition to products isolated in the reaction without TEMPO, compounds **11** and **12** were isolated in 2:1 ratio, respectively, and identified[23] (TEMPO does not react with **2d** in the same experimental conditions).These two products were isolated as a mixture and their identification was done on the basis of GC-MS and ^{1}H NMR spectroscopic data (see experimental).

The formation of radical intermediates, and then the existence of a SET between the reactants, can be drawn from the evaluation of the reaction products distribution: dimer **5** can be formed by dimerization of radical **17** arising from **15**, followed by hydrolysis and tautomerization (Scheme 3). This is supported by the observation that **5** increases as the the oxidation potentials of the Grignard reagents decrease (see Table 1). The formation of **3** cannot be explained by the coupling of diazenyl radical **15** with radical **16**, the former lose nitrogen with a high rate constant[24] and no unambiguous example of trapping of diazenyl radicals is known.[25] Compound **5** or its tautomeric form **16** can also be considered as intermediates in the formation of **9**: the hydrogen abstraction from **5** can be caused by some of the radicals present in the reaction mixture. Thus, compounds **3**, which are the main products of all the reactions are necessarily formed by nucleophilic attack from the Grignard.

Scheme 3



Compound **4**, whose yield is practically the same in all the reactions, arises from hydrolysis of

unreacted **1** during the reaction workup as demonstrated experimentally.[26] Compounds **6** could be formed by addition of Grignard reagents to **4** formed in the reaction medium, or to the carbonyl group of the starting material followed by hydrolysis during the reaction workup[26]. The latter hypothesis is supported by the fact that Grignard reagents react with anthraquinone **4** leading to compound **6** in good yields.

Anthrone **7** can be considered the tautomeric form of 9-hydroxyanthracene **20**, which is formed from the intermediate **17** following the pathway described in Scheme 3: hydrogen abstraction by **17** from some of the species present in the reaction mixture leads to **19**, which is hydrolyzed to **20** during the reaction workup.

CONCLUSIONS

The highest yields of compounds **3** are obtained with Grignard reagents showing a more positive oxidation potential; whereas the highest yields of compounds **5** and **7**, which have the same origin, are observed with those reagents showing a lower oxidation potential.

Since the formation of compounds **3** can only be explained by a nucleophilic attack by the reagents on the starting diazonium **1,** and that of compounds **5** and **7** only by a free radical pathway, it could be concluded that in the reactions here described, ionic and radical mechanisms are both operating in competition. This conclusion is also supported by the reaction performed in the presence of TEMPO and by the results of the Marcus theory treatment.

EXPERIMENTAL

Melting points are uncorrected and were measured with an electrothermal apparatus. IR solid state spectra were measured on a Nicolet Fourier Transform Infrared 20-SX spectrophotometer equipped with a Spectra Tech "Collector" for DRIFT maesurements. ^{1}H-NMR spectra were recorded at room temperature in $CDCl_3$ solution on a Varian Gemini 200 spectrometer (TMS was taken as reference peak). Mass spectra were taken with a Carlo Erba QMD 1000 mass spectrometer, equipped with a Fisons GC 8060 gaschromatograph. Combustion analyses of new crystalline compounds were performed with a Carlo Erba CHNS-O EA1108 elemental analyzer.

9-Diazo-10-anthrone **1** was synthesized according to the literature.[27] Grignard reagents **2a-c,e-g**, 6-bromo-1-hexene and compounds **4**, **7**, **9** were purchased from Aldrich, while **2d** was prepared by the standard method. All solvents were Carlo Erba RP-ACS grade and were purified and dried according to the literature.[28]

*Reaction of 9-diazo-10-anthrone (1) with 2a-g. General procedure.*The Grignard reagent (15 mmol) was added dropwise, at room temperature in a stream of argon to a solution of **1** (5 mmol) in THF (20 ml). The mixture was stirred for 2 h, then poured into aqueous 5% NH_4Cl and extracted with $CHCl_3$. The $CHCl_3$ layer was dried with Na_2SO_4 and evaporated to dryness; the residue was chromatographed on a SiO_2 column using cyclohexane/ethyl acetate as eluant (with a ratio from 9/1 to 1/1). The yields of the products isolated are set out in Table 1, while the analytical and spectroscopic data of the new isolated compounds are reported below.

9-Methylhydrazono-10-anthrone (3a). M.p. 153-155°C (from diethylic ether); IR (DRIFT) ν_{NH} 3271 cm^{-1}, ν_{CO} 1639 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.28 (3H, d, -CH_3, J=4.3 Hz), 6.92 (1H, q-broad, -NH-, J=4.3 Hz), 7.45 (1H, ddd, arom., J=7.9, J=7.2, J=1.3 Hz), 7.57 (1H, ddd, arom., J=7.7, J=7.4, J=1.3 Hz), 7.62 (1H, ddd, arom., J=7.9, J=7.2, J=1.6 Hz), 7.72 (1H, ddd, arom., J=7.7, J=7.4, J=1.6 Hz), 8.22 (1H, ddd, arom., J=7.9, J=1.6, J=0.5 Hz), 8.25 (2H, m, arom.), 8.46 (1H, ddd, arom., J=7.7, J=1.6, J=0.5 Hz); MS (EI)

m/z 236 (M+, 100), 221 (15), 193 (12), 165 (42). Anal. Calcd for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86. Found: C, 76.30; H, 5.10; N, 11.83.

9-Ethylhydrazono-10-anthrone (3b). M.p. 135-137°C (from diethylic ether); IR (DRIFT) ν_{NH} 3235 cm^{-1}, ν_{CO} 1649 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.32 (3H, t, $-CH_3$, J=7.2 Hz); 3.53 (2H, dq, $-CH_2-$, J=7.2, J=4.4 Hz), 6.97 (1H, t, -NH-, J=4.4 Hz), 7.44 (1H, td, arom., J=7.8, J=1.4 Hz), 7.60 (2H, m, arom.), 7.73 (1H, td, arom., J=7.8, J=1.4 Hz), 8.24 (3H, m, arom.), 8.46 (1H, dd, arom., J=7.7, J=1.6 Hz); MS (EI) *m/z* 250 (M+, 100), 235 (82), 221 (25), 165 (77). Anal. Calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19. Found: C, 76.85; H, 5.62; N, 11.17.

9-Buthylhydrazono-10-anthrone (3c). M.p. 159-161°C (from diethylic ether); IR (DRIFT) ν_{NH} 3241 cm^{-1}, ν_{CO} 1639 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.98 (3H, t, $-CH_3$, J=7.3 Hz), 1.44 (2H, m, $-C\underline{H}_2CH_3$), 1.70 (2H, m, $-CH_2-C\underline{H}_2-CH_2-$), 3.50 (2H, td, -NH-$C\underline{H}_2-$, J= 7.0, J=4.6 Hz), 7.07 (1H, t, -NH-, J=4.6 Hz), 7.43 (1H, ddd, arom., J=7.8, J=7.2, J=1.2 Hz), 7.56 (1H, ddd, arom., J=7.8, J=7.2, J=1.2 Hz), 7.62 (1H, ddd, arom., J=8.1, J=7.2, J=1.5 Hz), 7.72 (1H, ddd, arom., J=8.1, J=7.2, J=1.5 Hz), 8.22 (1H, ddd, arom., J=7.8, J=1.5, J=0.4 Hz), 8.25 (2H, m, arom.), 8.46 (1H, ddd, arom., J=7.8, J=1.5, J=0.4 Hz); MS (EI) *m/z* 278 (M+, 75), 250 (64), 221 (51), 165 (100). Anal. Calcd for $C_{18}H_{18}N_2O$: C, 77.66; H, 6.52; N, 10.07. Found: C, 77.60; H, 6.54; N, 10.09.

9-(5-Hexenyl)hydrazono-10-anthrone (3d). M.p.: uncrystallizable material; IR (DRIFT) ν_{NH} 3263 cm^{-1}, ν_{CO} 1645 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.52 (2H, m, $-C\underline{H}_2-CH_2-CH=$), 1.74 (2H, m, $-CH_2-C\underline{H}_2-(CH_2)_2-$), 2.12 (2H, m, $-C\underline{H}_2-CH=$), 3.50 (2H, td, -NH-$C\underline{H}_2-$, J= 7.1, J=4.6 Hz), 5.00 (2H, m, $=CH_2$), 5.82 (1H, ddt, -CH=, J=17.1, J=10.2, J=6.6 Hz) 7.08 (1H, t, -NH-, J=4.6 Hz), 7.42 (1H, ddd, arom., J=7.8, J=7.2, J=1.6 Hz), 7.56 (2H, m, arom.), 7.69 (1H, ddd, arom., J=7.8, J=7.2, J=1.6 Hz), 8.22 (3H, m, arom.), 8.42 (1H, dd, arom., J=7.8, J=1.6 Hz); MS (EI) *m/z* 304 (M+, 100), 276 (69), 221 (45), 193 (61). Anal. Calcd for $C_{20}H_{20}N_2O$: C, 78.92; H, 6.62; N, 9.20. Found: C, 78.94; H, 6.61; N, 9.19.

9-Isopropylhydrazono-10-anthrone (3e). M.p. 150-152°C (from diethylic ether); IR (DRIFT) ν_{NH} 3225 cm^{-1}, ν_{CO} 1648 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.34 (6H, d, 2-CH_3, J=6.4 Hz), 3.73 (1H, heptd, -CH-, J=6.4, J=4.6 Hz), 6.85 (1H, d, -NH-, J=4.6 Hz), 7.43 (1H, td, arom., J=7.8, J=1.4 Hz), 7.60 (2H, m, arom.), 7.74 (1H, td, arom., J=7.8, J=1.4 Hz), 8.26 (3H, m, arom.), 8.46 (1H, dd, arom., J=7.7, J=1.6 Hz); MS (EI) *m/z* 264 (M+, 85), 249 (100), 234 (26), 221 (28), 165 (30). Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60. Found: C, 77.35; H, 6.08; N, 10.58.

9-Terbuthylhydrazono-10-anthrone (3g). M.p. 185-187°C (from diethylic ether); IR (DRIFT) ν_{NH} 3239 cm^{-1}, ν_{CO} 1639 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.37 (9H, s, 3-CH_3), 6.88 (1H, s, -NH-), 7.44 (1H, ddd, J=7.8, J=7.4, J=1.3 Hz), 7.58 (1H, m, arom.), 7.62 (1H, m, arom.), 7.74 (1H, ddd, arom., J=7.8, 7.4, J=1.6 Hz), 8.30 (3H, m, arom.), 8.49 (1H, ddd, arom., J=7.8, J=1.6, J=0.5 Hz); MS (EI) *m/z* 278 (M+, 75), 263 (100), 221 (70), 165 (48). Anal. Calcd. for $C_{18}H_{18}N_2O$: C, 77.66; H, 6.52; N, 10.07. Found: C, 77.62; H, 6.53; N, 10.08.

9-Methyl-9-hydroxy-10-anthrone (6a). M.p.: uncrystallizable material; IR (DRIFT) ν_{OH} 3428 cm^{-1}, ν_{CO} 1665 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.67 (3H, s, $-CH_3$), 2.94 (1H, s-broad, -OH), 7.43 (2H, ddd, $H_{3,6}$, J=7.6, J=7.3, J=1.3 Hz), 7.64 (2H, ddd, $H_{2,7}$, J=7.9, J=7.2, J=1.5 Hz), 7.92 (2H, ddd, $H_{1,8}$, J=7.9, J=1.2, J=0.5 Hz), 8.15 (2H, ddd, $H_{4,5}$, J=7.8, J=1.5, J=0.5 Hz); MS (EI) *m/z* 224 (M+, 12), 209 (100), 180 (25). Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.33; H, 5.40. Found: C, 80.30; H, 5.41.

9-Ethyl-9-hydroxy-10-anthrone (6b). M.p.: uncrystallizable material; IR (DRIFT) ν_{OH} 3430 cm^{-1}, ν_{CO} 1672 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.36 (3H, t, $-CH_3$, J=7.5 Hz), 2.05 (2H, q, $-CH_2-$, J=7.5 Hz), 2.67 (1H, s, -OH), 7.46 (2H, td, $H_{3,6}$, J=7.8, J=1.3 Hz), 7.65 (2H, ddd, $H_{2,7}$, J=7.9, J=7.3, J=1.5 Hz), 7.89 (2H, ddd, $H_{1,8}$, J=7.9, J=1.3, J=0.5 Hz), 8.19 (2H, ddd, $H_{4,5}$, J=7.8, J=2.0, J=0.6 Hz); MS (EI) *m/z* 238 (M+, 25), 209 (100), 180 (19). Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.93. Found: C, 80.67; H, 5.91.

9-Buthyl-9-hydroxy-10-anthrone (6c). M.p.: uncrystallizable material; IR (DRIFT) ν_{OH} 3432 cm^{-1}, ν_{CO} 1660 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.63 (3H, t, $-CH_3$, J=7.2 Hz), 0.64 (2H, m, $-CH_2-C\underline{H}_2-CH_2-$), 1.02 (2H, sext, $-CH_2-C\underline{H}_2-CH_3$, J=7.2 Hz), 2.03 (2H, m, $-C\underline{H}_2-(CH_2)_2-CH_3$), 2.47 (1H, s, -OH), 7.48 (2H, td, $H_{3,6}$, J=7.3, J=1.3 Hz), 7.68 (2H, ddd, $H_{2,7}$, J=7.9, J=7.2, J=1.4 Hz), 7.92 (2H, ddd, $H_{1,8}$, J=7.9, J=1.2, J=0.4 Hz), 8.23 (2H, ddd, $H_{4,5}$, J=7.7, J=1.4, J=0.4 Hz); MS (EI) *m/z* 266 (M+, 10), 209 (100), 180 (21). Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.16; H, 6.82. Found: C, 81.18; H, 6.81.

9-(5-Hexenyl)-9-hydroxy-10-anthrone (6d). M.p.: uncrystallizable material; IR (DRIFT) ν_{OH} 3433 cm^{-1}, ν_{CO} 1666 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.70 (2H, m, CH_2-C<u>H</u>$_2$-$(CH_2)_2$-CH=), 1.10 (2H, quintet, $(CH_2)_2$-C<u>H</u>$_2$-CH_2-CH=, J=7.2 Hz), 1.75 (2H, m, -C<u>H</u>$_2$-CH=), 2.02 (2H, m, -C<u>H</u>$_2$-$(CH_2)_3$-CH=), 2,46 (1H, s, -OH), 4.80 (2H, m, $=CH_2$), 5.54 (1H, m, -CH=), 7.47 (2H, ddd, $H_{3,6}$, J=7.8, J=7.2, J=1.2 Hz), 7.70 (2H, ddd, $H_{2,7}$, J=7.8, J=7.2, J=1.5 Hz), 7.90 (2H, dd, $H_{1,8}$, J=7.8, J=1.2 Hz), 8.24 (2H, dd, $H_{4,5}$, J=7.8, J=1.5 Hz); MS (EI) *m/z* 292 (M+, 100), 275 (58), 264 (36), 193 (77). Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89. Found: C, 82.24; H, 6.87.

9-Isopropyl-9-hydroxy-10-anthrone (6e). M.p. 126-127 °C (from diethylic ether); IR (DRIFT) ν_{OH} 3429 cm^{-1}, ν_{CO} 1668 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.63 (6H, d, 2-CH_3, J=6.8 Hz), 2.11 (1H, hept, -C<u>H</u>$(CH_3)_2$, J=6.8 Hz), 2.62 (1H, s-broad, -OH), 7.44 (2H, ddd, $H_{3,6}$, J=7.6, J=7.5, J=1.4 Hz), 7.61 (2H, ddd, $H_{2,7}$, J=7.9, J=7.3, J=1.6 Hz), 7.86 (2H, dd, $H_{1,8}$, J=8.1, J=1.4 Hz), 8.15 (2H, dd, $H_{4,5}$, J=7.7, J=1.4 Hz); MS (EI) *m/z* 252 (M+, 10), 221 (7), 209 (75), 165 (100). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.88; H, 6.41.

9-Benzyl-9-hydroxy-10-anthrone (6f). M.p.: uncrystallizable material; IR (DRIFT) ν_{OH} 3427 cm^{-1}, ν_{CO} 1663 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.86 (1H, s, -OH), 3.20 (2H, s, -C<u>H</u>$_2$-Ph), 6.12 (2H, dt-broad, -CH_2-<u>Ph</u>), 6.79 (2H, td-broad, -CH_2-<u>Ph</u>), 7.07 (1H, tt-broad, -CH_2-<u>Ph</u>), 7.43 (2H, td, $H_{3,6}$, J=7.5, J=1.4 Hz), 7.65 (2H, td, $H_{2,7}$, J=7.3, J=1.6 Hz), 7.88 (2H, dd, $H_{1,8}$, J=7.9, J=1.4 Hz), 7.99 (2H, dd, $H_{4,5}$, J=7.9, J=1.4 Hz); MS (EI) *m/z* 300 (M+, 22), 209 (100), 193 (15), 165 (18).

9-Terbuthyl-9-hydroxy-10-anthrone (6g). M.p.: uncrystallizable material; IR (DRIFT) ν_{OH} 3425 cm^{-1}, ν_{CO} 1665 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.79 (9H, s, 3-CH_3), 2.35 (1H, s, -OH), 7.44 (2H, td, $H_{3,6}$, J=7.5, J=1.5 Hz), 7.57 (2H, td, $H_{2,7}$, J=7.4, J=1.6 Hz), 7.89 (2H, ddd, $H_{1,8}$, J=7.8, J=1.6, J=0.5 Hz), 8.11 (2H, ddd, $H_{4,5}$, J=7.6, J=1.6, J=0.5 Hz); MS (EI) *m/z* 266 (M+, 52), 251 (25), 209 (100), 180 (13). Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.16; H, 6.82. Found: C, 81.13; H, 6.83.

9-Benzylidenehydrazono-10-anthrone (8). M.p. 118-120 °C (from diethylic ether); IR (DRIFT) ν_{CO} 1666 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.52 (3H, m, arom.), 7.67 (5H, m, arom.), 7.90 (2H, m, arom.), 8.38 (1H, m, arom.), 8.42 (1H, s, -N=C<u>H</u>-Ph), 8.51 (1H, m, arom.), 8.68 (1H, m, arom.); MS (EI) *m/z* 310 (M+, 55), 282 (50), 233 (100), 163 (62). Anal. Calcd for $C_{21}H_{14}N_2O$: C, 81.27; H, 4.55; N, 9.03. Found: C, 81.20; H, 4.57; N, 9.05.

Reaction of 9,10-anthraquinone (4) with 2a-g. General procedure. Grignard reagent **2** (15 mmol) was added dropwise, at room temperature in a stream of argon to a solution of **4** (5 mmol) in THF (20 ml). The mixture was stirred for 2 h, then poured into aqueous 5% NH_4Cl and extracted with $CHCl_3$. The $CHCl_3$ layer was dried with Na_2SO_4 and evaporated to dryness; the residue was chromatographed on a SiO_2 column using cyclohexane/ethyl acetate as eluant with a ratio 8/2. In all cases compounds **6** were isolated in good yields (69-80 %), the remaininig quantity being starting material **4**.

Reaction of 9-diazo-10-anthrone (1) with 2d in the presence of TEMPO. Grignard reagent **2d** (15 mmol) was added dropwise, at room temperature in a stream of argon, to a solution of **1** (5mmol) and TEMPO (5mmol) in THF (20 ml). The mixture was stirred for 2 h, then poured into aqueous 5% NH_4Cl and extracted with $CHCl_3$. The $CHCl_3$ layer was dried with Na_2SO_4 and evaporated to dryness; the residue was chromatographed on a SiO_2 column using cyclohexane/ethyl acetate as eluant with a ratio 8/2. The yields of the products isolated are set out in Table 1. Compounds **11** and **12**, that were impossible to separate, were identified by their ^{1}H NMR spectra. In fact the O-CH_2- group falls in a region where no other signals are present; in compound **11**, it appears as a triplet at 3.73 δ, whereas in **12** it is a doublet at 3.64 δ. From the integration of these two signals, a ratio of 2:1 between **11** and **12** was found. The complete description of the ^{1}H NMR spectra of these two compounds is reported below.

2,2,6,6-Tetramethyl-N-(O-5-hexenyl)-piperidine (11). ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.10 (6H, s, 2-CH_3), 1.15 (6H, s, 2-CH_3), 1.45 (10H, m, O-CH_2-C<u>H</u>$_2$-C<u>H</u>$_2$-, 3-CH_2- piperidine), 2.08 (2H, m, -C<u>H</u>$_2$-CH=), 3.73 (2H, t, O-CH_2-, J=6.4 Hz), 4.94 (1H, ddt, $=CH_2$, J=10.2, J=2.2, J=1.2 Hz), 5.01 (1H, ddt,$=CH_2$, J=17.1, J=2.2, J=1.5 Hz), 5.82 (1H, ddt, -CH=, J=17.1, J=10.2, J=6.6 Hz).

2,2,6,6-Tetramethyl-N-(O-cyclomethylpenthyl)-piperidine (12). ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.10 (6H, s, 2-CH_3), 1.15 (6H, s, 2-CH_3), 1.50 (14H, m, 4-CH_2 -, 3-CH_2- piperidine), 1.70 (1H, m, -CH-), 3.64 (2H, d, O-CH_2-, J=6.8 Hz).

Cyclic Voltammetry. Reduction potential of **1** was determined at room temperature in a three electrode cell using nitrogen purged DMF solutions of the compound (10^{-3} mol dm^{-3}), containing 0.1 mol dm^{-3} TEAP. A stationary platinum disk (AMEL 492) of about 1 mm diameter was used as working electrode and a platinum wire as auxiliary electrode. Hg-Hg_2Cl_2, NaCl (sat.aq.)-DMF-TEAP/sintered glass disk[29] was used as reference electrode. A multipolarograph AMEL 472/WR coupled with a digital x/y recorder AMEL 863 was used: details of the apparatus and the cell have been described elsewhere.[30] An E_{red} of -0.85 V was determined.

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