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Additions of Crotonaldehyde N,N-Dimethylhydrazone to *p*-Quinones under Ultrasonic and Thermal Conditions

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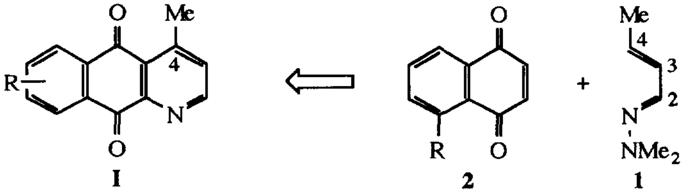
Abstract: The additions of crotonaldehyde N,N-dimethylhydrazone to juglone and azanaphthoquinones are performed under sonochemical and thermal conditions. The rates and products of the reactions, Diels-Alder cycloaddition and amination of the quinones are largely modified by ultrasonic irradiation. In addition, the study reveals an apparent similarity between high pressure and ultrasonic effects.

In the synthesis of 1-azaanthraquinone compounds, the Diels-Alder reaction between α,β-unsaturated N,N-dimethylhydrazones and naphthoquinones constitutes an important pathway.[1] A substitution at C-3 by an electron releasing group facilitates the [4+2] cycloadditions.[1b] In order to obtain some functionalized derivatives of Cleistopholine[2,3] **I** (R=H), a natural 1-azaanthraquinone bearing a methyl at the C-4 position, we envisaged to study the Diels-Alder reaction between crotonaldehyde N,N-dimethylhydrazone **1** and naphthoquinones **2**[1e] (Scheme 1). However, since the activating C-3 substituent is absent in this heterodiene, the cycloadditions are rather slow, reducing the practical interest of this synthetic route.

Scheme 1



2 (**2a** : R = OH)

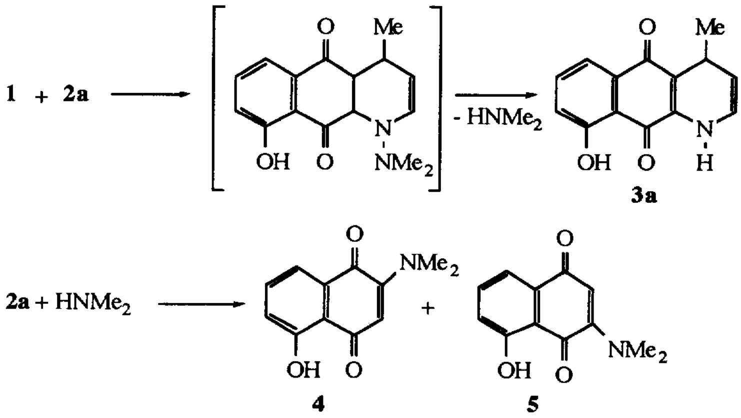
Numerous works describe rate and selectivity enhancements in [4+2] cycloadditions by new or "unusual" methods.[4] Among these, ultrasonic irradiation seems very attractive. Indeed, it is generally considered that the large negative activation volume of the Diels-Alder reaction as well as its dependence towards heat and pressure should make it sensitive to ultrasonic cavitation, according to the hot spot theory.[5] In fact, only a limited number of studies related to the sonochemical Diels-Alder synthesis have been published till now. A sonochemical effect is observed in the reactions of 3-methyl-4,5-benzofurandione with vinyl cyclohexenes,[6] and interesting observations were recently published for styrenes reacting with *p*-quinones.[7] In contrast, some other cycloadditions are reported to be less influenced,[8] and others left unchanged,[9] by sonication.

Due to such a small number of cases reported, a general interpretation of the sonochemical Diels-Alder reaction cannot reasonably be proposed. In order to bring up new elements for a future understanding, and also to try to solve a synthetic problem, a comparative study of the cycloadditions of azadiene **1** with juglone **2a** under traditional conditions and under sonication was undertaken, and is reported in this paper together with high pressure experiments.

RESULTS AND DISCUSSION

The cycloadditions were carried out at room temperature under an inert atmosphere. To the deoxygenated toluene or methanol solution of quinone **2a**, azadiene **1** in 50 % excess was added, and the experiments were run in parallel under sonication and stirring. Experimental observations, shown in Table 1, are as follows. In all the cases, the primary tetrahydro adduct is not isolated due to a rapid elimination of dimethylamine (Scheme 2) and the dihydro azaanthraquinone **3a**[1e] is obtained as the single 1,8-regioisomer. An important qualitative difference between the thermal and sonicated reactions is immediately found. In the latter, the aminoquinones **4** and **5**,[10] are isolated in 15 % yield each. These compounds, which result from an addition-oxidation of dimethylamine to the starting quinone, are formed in traces in the thermal reaction.

Scheme 2



Ultrasonic irradiation increases the rate of the Diels-Alder reaction in toluene. The highest yield of **3a** is obtained in this solvent after 6 h sonication or 24 h stirring of a 7.10^{-2} M solution (entries 1 and 3). Using a *ca.* 4 times more concentrated solution (entries 4 and 5) gives degradation products and an important yield decrease. In methanol solution (entries 8 and 9) or in the absence of solvent (entries 10 and 11), **3a** forms in lower amounts, without sonochemical effect. These results contrast with those of Snyder *et al.* From *o*-quinones and vinylcyclohexenes, methanol was found to be a good medium for the sonochemical cycloaddition, toluene has a strong negative influence, and optimal yields are obtained in the absence of solvent.[6] The rate enhancement of the cycloaddition of **1** to quinone **2a** was confirmed by following the process as a function of time (Figure 1).

Table 1. Cycloadditions of azadiene **1** towards quinone **2a** under various experimental conditions.

Entry	Concentration of **2a** (x10^{-2})	**1/2a** ratio	Solvent	Conditions	Reaction time (h)	**3a** Yield (%)	**4+5** Yield (%)
1	7	1.5	Toluene	))))	6[a]	52	15 + 15
2	7	1.5	Toluene	Stirring	6	25	Traces[b]
3	7	1.5	Toluene	Stirring	24[c]	48	Traces[b]
4	28	1.5	Toluene	))))	6[a,e]	32	10 + 10
5	28	1.5	Toluene	Stirring	24[c,e]	26	Traces[b]
6[d]	28	1.5	Toluene	10 kbars	6[e,f]	48	Traces[b]
7	28	1.5	Toluene	10 kbars	24[e]	24	15 + 15
8	7	1.5	Methanol	))))	6[a]	14	Traces[b]
9	7	1.5	Methanol	Stirring	6[c]	15	Traces[b]
10	-	3	Neat	))))	6[a,e]	15	Traces[b]
11	-	3	Neat	Stirring	6[c,e]	14	Traces[b]

[a] Maximum irradiation time with our generator. [b] Detected by TLC. [c] Time required for total consumption of the quinone. [d] Similar results are observed when the cycloaddition is carried out under the same conditions with a concentration of 7x10^{-2} in **2a**. [e] A large amount of polar products is formed in the black reaction mixture. [f] A small proportion (1.5%) of juglone is recovered.

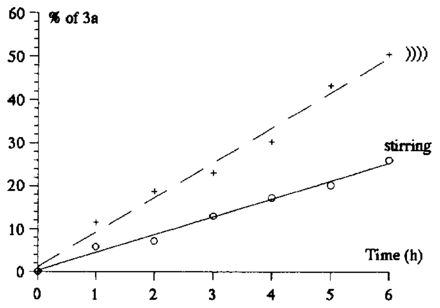


Figure 1. Kinetic study of the sonicated and thermal Diels-Alder reaction of azadiene **1** with juglone **2a**.

The use of high pressure conditions in the Diels-Alder reaction, mentioned in the introduction,[4] allows heat-sensitive or poorly reactive substrates to cycloadd. To compare the effects of this activation method with those of sonication, azadiene **1** and quinone **2a** were reacted under 10 kbars (entries 6 and 7). It is interesting to note that after sonication or application of high pressure for 6 h, a similar yield in the dihydro adduct **3a** was obtained (entries 1 and 6). The pressure effects of the cavitational collapse are frequently mentioned in the literature,[11] but their direct influence is not clearly established, since most authors consider the "hot spot" theory only through its thermal effects. The results given in the table above constitute one of the rare direct comparisons of the respective roles of a static high pressure and the transient (*ca.* 10^{-6} s) so-called "high-pressures" developed in the collapsing bubble. Furthermore, ultrasound favours the nucleophilic addition-oxidation of the liberated dimethylamine to the starting quinone,[12] (entries 1 and 4) while a subsequent formation of aminoquinones **4** and **5** is only observed after 24 h of high pressure application (entry 7).

Based on these results, an extrapolation to cycloadditions using azanaphthoquinones **6** and **7** was undertaken. The unstable tetrahydro adducts can be oxidized to the dihydro compounds **8** or **11**,[13] or eliminate dimethylamine to give **9** and **10**, or **12** and **13** respectively. The proportion of these compounds depends on the reaction conditions, and again, sonication has an important influence (Scheme 3 and Table 2). Aminoquinones **14**,[14] **15** on one hand and **16** and **17** on the other hand, are also isolated, in larger amounts for the sonicated reaction of **6** or **7**.

Scheme 3

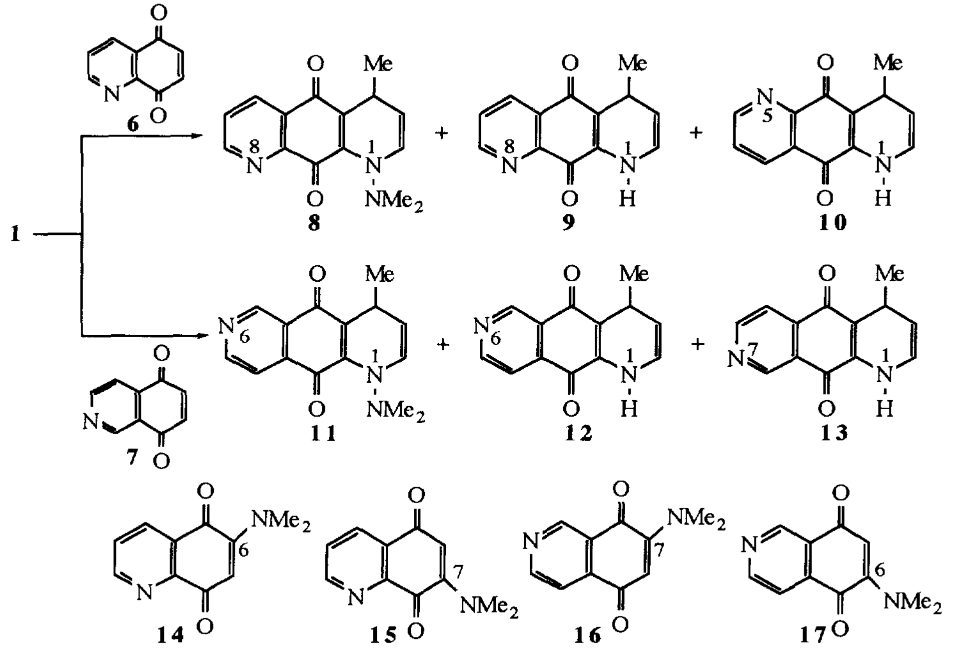


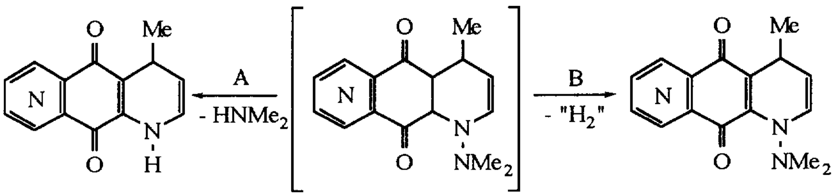
Table 2. Cycloadditions of azadiene **1** to azanaphthoquinones **6** and **7**.

Entry	Quinone	Cond's	Reaction time (h)	Adducts overall yield (%)	Adducts (%)	Aminoquinone (%)
12	**6**	))))	6[a]	35	**9**(28) + **10**(7)	**14**(15) + **15**(5)
13	**6**	Stirring	6[b]	45	**8**(10) + **9**(28) + **10**(7)	**14**(10)
14	**7**	))))	6[a]	48	**11**(18) + **12**(18) + **13**(12)	**16**(10) + **17**(2)
15	**7**	Stirring	6	Traces[c]	-	Traces[c]
16	**7**	Stirring	48[b]	65	**11**(33) + **12**(22) + **13**(10)	**16**(10) + **17**(2)

[a] Maximum irradiation time with our generator. [b] Time required for consumption of the quinone. [c] Detected by TLC.

With quinone **6**, sonication leads to an overall yield lower by 10 % than under stirring (entries 12 and 13) but this effect is due to the absence of the hydrazine adduct **8**, which is formed in 10 % amount in the thermal reaction. In contrast, quinone **7** yields 48 % of compounds **11-13** (entry 14) after 6h sonication, and only traces of adduct after the same time of stirring (entry 15). A longer reaction time gives a high overall yield. But in this case also, this beneficial effect is due to the presence of the N,N-dimethylamino compound **11** in higher amounts (entry 16). Thus, an unexpected effect of ultrasound irradiation consists in enhancing the elimination of dimethylamine from the unstable tetrahydro primary adduct via pathway A (Scheme 4).

Scheme 4



The regioselectivity of the cycloadditions, assigned in a previous work,[15] is not noticeably affected by sonication. The ratio of compounds **9**/**10** is identical in entries 12 and 13, and the difference in the ratios of **12** and **13** in entries 14 and 16 should not be considered as significant.

CONCLUSION

This work describing the Diels-Alder reactions of crotonaldehyde N,N-dimethylhydrazone with juglone and azanaphthoquinones under sonochemical and traditional conditions leads to some observations. The first one is the rate of the reactions, which is significantly increased by sonication. Repetition of the experiments confirms that the differences observed fall far outside of the experimental error (± 2%). A second point is related to the nature of the products. Under thermal conditions, hydrazine adducts are isolated in reactions of azanaphthoquinones, but their formation is suppressed or decreased by sonication. On the other hand, applying this activation method does not solve the chemoselectivity problem, since amination of the quinone partner is enhanced, in all the cases reported here. Interesting questions are opened by these results. The elimination of dimethylamine from the primary tetrahydro adduct seems to be rather strongly influenced by sonication as well as the addition of the latter compound to the quinone. No satisfactory explanation can be proposed at the present time for both reactions, since, to the best of our knowledge, the latter has been mentionned only once in the sonochemical literature, and the former is observed for the first time in this work. However, the probably more important point raised here is a similarity between the high pressure and the sonochemical activations, in terms of yields and or nature of the reaction products from additions of the azadiene to juglone. Even if the synthetic problem (high yields and selectivity) cannot reasonably be considered as resolved, we observe here that the pressure parameter may have some fundamental importance, or, in other terms, that analogous phenomena may take place in both activation methods. Due to the controversial situation presently developed in the fundamental aspects of sonochemistry,[16] the data presented in this paper should constitute experimental elements to be taken into account for further interpretations. Lastly, the diversity of the results illustrates the complexity of the mechanism of this hetero Diels-Alder process in connection with ultrasonic irradiation. Indeed, each pair of diene-dienophile seems to be a particular case, excluding in the present state of the knowledge, a global interpretation of the phenomenon.

EXPERIMENTAL SECTION

^{1}H-NMR spectra were recorded on a Bruker AM 300 (300 MHz) with tetramethylsilane as an internal standard. IR spectra were obtained on a Perkin-Elmer 1310 spectrophotometer. High-resolution mass spectra (HRMS) were recorded on a AE 1 MS 902 spectrometer. Elemental analyses were performed at the Service Central de Microanalyse du CNRS (Solaize, France). Melting points were determined with a Kofler apparatus. Thin-layer chromatographic analyses (TLC) were performed on silica gel 60 F_{254} on aluminum sheets (Merck). Column chromatography is carried out with Matrex Amicon (60 Å, 35-70 μm) silica gel. Sonications were effected with a cleaning bath (50 kHz, thermostated at 20°C) and a thermostated Labsonic U probe (20°C, 4 mm diameter, 30 W electrical input) for preparative experiments. Toluene was freshly distilled on sodium under nitrogen. All the reactions were carried out under a an inert atmosphere. Azadiene **1**[17] and azanaphthoquinones **6** and **7**[18] were prepared according to the methods described in the literature.

Cycloaddition of azadiene 1 to 5-hydroxy-1,4-naphthoquinone 2a. Typical procedure

Quinone **2a** (0.2 g, 1.15 mmol) was dissolved in 10 mL of toluene. The solution was deoxygenated by bubbling nitrogen for 1h. A solution of azadiene **1** (0.193 g, 1.725 mmol) in 5 mL of the same solvent was added under nitrogen. The mixture was stirred for 24 h at room temperature. The solvent was removed under vacuum to afford a dark residue purified by column chromatography (eluent CH_2Cl_2) to yield **3a** (0.13 g, 48 %). In the sonochemical experiments, the same solution as above is sonicated for 6h. The reaction mixture was purified as above to give **3a** (0.143 g, 52 %), **4** (0.038 g, 15 %) and **5** (0.038 g, 15 %).

General procedure for the cycloadditions under high pressure

In a 1 mL high pressure rigid PTFE tube previously degassed with argon, was introduced a solution of quinone **2a** (0.05 g, 0.3 mmol) in 1 mL of toluene and azadiene **1** (0.05 g, 0.45 mmol). The external diameter of the tube was designed so as to fit exactly the diameter of the inner cylinder of the high pressure cell. Then, a pressure of 1000 MPa (uniaxial compression) was applied at 20°C for 6 or 24 h. The reaction mixture was treated as above.

General procedure for the kinetic study

A solution of azadiene **1** (0.05 g, 0.45 mmol) in 1.5 mL of toluene, deoxygenated as above, was added to 5-hydroxy-1,4-naphthoquinone **2a** (0.05 g, 0.3 mmol) in the same solvent (3.5 mL) at room temperature under N_2 with stirring or sonication for 1 to 6h. After evaporation of the solvent, the residue was purified by flash chromatography (30 mm diameter column, 150 mL of silica gel, CH_2Cl_2/hexane, 1/1). The yields were calculated from the pure isolated dihydro azaanthraquinone **3a**.

1-Aza-1,4-dihydro-8-hydroxy-4-methyl-9,10-anthraquinone 3a

Dark blue solid, m.p. 186°C ; IR (KBr) ν 3370, 3400-3200, 1635, 1625 cm^{-1} ; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ ppm 11.48 (s, 1H, OH), 7.60 (m, 2H, H-5 and H-6), 7.13 (dd, 1H, J=7 and 2.6 Hz, H-7), 6.79 (br s, 1H, NH), 6.17 (dd, 1H, J=7.7 and 4.4 Hz, H-2), 4.98 (m, 1H, H-3), 3.75 (m, 1H, H-4), 1.19 (d, 3H, J=6.7 Hz, CH_3). Anal. Calcd for $C_{14}H_{11}NO_3$: C, 69.70 ; H, 4.60 ; N, 5.80. Found : C, 69.66 ; H, 4.77 ; N, 5.51. HRMS calcd for $C_{14}H_{11}NO_3$: 241.0739. Found : 241.0739.

Cycloaddition of azadiene 1 to quinoline-5,8-dione 6

A mixture of quinone **6** (0.2 g, 1.26 mmol) and azadiene **1** (0.211 g, 1.89 mmol) was stirred in 15 mL of toluene for 6h. After the usual work-up and purification, compounds **8** (0.03 g, 10 %), **9** (0.08 g, 28 %), **10** (0.02 g, 7 %), and **14** (0.025 g, 10 %) were isolated. The same solution as above was sonicated for 6h. After the usual work-up and purification, compounds **9** (0.08 g, 28 %), **10** (0.02 g, 7 %), **14** (0.038 g, 15 %) and **15** (0.013g, 5 %) were isolated.

1-N,N-Dimethylamino-1,8-diaza-1,4-dihydro-4-methyl-9,10-anthraquinone 8

Purple solid, m.p. 85°C ; IR (KBr) ν 1690, 1670 cm^{-1} ; ^{1}H-NMR (CD_3COCD_3, 300 MHz) δ ppm 8.90 (dd, 1H, J=4.7 and 1.8 Hz, H-7), 8.32 (dd, 1H, J=7.8 and 1.8 Hz, H-5), 7.59 (dd, 1H, J=7.8 and 4.7 Hz, H-6), 6.53 (d, 1H, J=7.8 Hz, H-2), 5.27 (dd, 1H, J=7.8 and 5.1 Hz, H-3), 3.68 (dq, 1H, J=6.6 and 5.1 Hz, H-

4), 2.72 (s, 6H, $(CH_3)_2N$), 1.16 (d, 3H, J=6.6 Hz, CH_3). HRMS calcd for $C_{15}H_{15}N_2O_2$: 269.1164. Found : 269.1163. The poor stability of this compound did not permit a satisfactory microanalysis.

1,8-Diaza-1,4-dihydro-4-methyl-9,10-anthraquinone 9

Dark blue solid, m.p. 176°C ; IR (KBr) ν 3390, 1690, 1660 cm^{-1} ; ^1H-NMR ($CDCl_3$, 300 MHz) δ ppm 8.92 (dd, 1H, J=4.7 and 1.7 Hz, H-7), 8.43 (dd, 1H, J=7.8 and 1.7 Hz, H-5), 7.65 (dd, 1H, J=7.8 and 4.7 Hz, H-6), 6.99 (br s, 1H, NH), 6.20 (dd, 1H, J=7.7 and 4.4 Hz, H-2), 5.02 (m, 1H, H-3), 3.80 (m, 1H, H-4), 1.22 (d, 3H, J=6.7 Hz, CH_3). Anal. Calcd for $C_{13}H_{10}N_2O_2$: C, 69.02 ; H, 4.46 ; N, 12.38. Found : C, 69.05 ; H, 4.52 ; N, 11.94. HRMS calcd for $C_{13}H_{10}N_2O_2$: 226.0742. Found : 226.0742.

1,5-Diaza-1,4-dihydro-4-methyl-9,10-anthraquinone 10

Dark blue solid, m.p. 190°C ; IR (KBr) ν 3280, 1680, 1660 cm^{-1} ; ^1H-NMR ($CDCl_3$, 300 MHz) δ ppm 9.0 (dd, 1H, J=4.8 and 1.7 Hz, H-6), 8.35 (dd, 1H, J=7.8 and 1.7 Hz, H-8), 7.57 (dd, 1H, J=7.8 and 4.8 Hz, H-7), 6.83 (br s, 1H, NH), 6.19 (dd, 1H, J=7.7 and 4.4 Hz, H-2), 5.03 (m, 1H, H-3), 3.87 (m, 1H, H-4), 1.23 (d, 3H, J=6.7 Hz, CH_3). Anal. Calcd for $C_{13}H_{10}N_2O_2$: C, 69.02 ; H, 4.46 ; N, 12.38. Found : C, 69.18 ; H, 4.72 ; N, 11.80. HRMS calcd for $C_{13}H_{10}N_2O_2$: 226.0742. Found : 226.0742.

6-N,N-dimethylaminoquinoline-5,8-dione 14

Red solid; m.p. 178°C (lit.[14] 164-167°C) ; IR (KBr) ν 1675, 1625 cm^{-1} ; ^1H-NMR ($CDCl_3$, 300 MHz) δ ppm 8.98 (dd, 1H, J=4.7 and 1.7 Hz, H-2), 8.33 (dd, 1H, J=7.8 and 1.7 Hz, H-4), 7.57 (dd, 1H, J=7.8 and 4.7 Hz, H-3), 6.05 (s, 1H, H-7), 3.27 (s, 6H, $(CH_3)_2N$).

7-N,N-dimethylaminoquinoline-5,8-dione 15

Red solid ; m.p. 164°C ; IR (KBr) ν 1700, 1625 cm^{-1} ; ^1H-NMR ($CDCl_3$, 300 MHz) δ ppm 8.91 (dd, 1H, J=4.7 and 1.7 Hz, H-2), 8.38 (dd, 1H, J=7.8 and 1.7 Hz, H-4), 7.63 (dd, 1H, J=7.8 and 4.7 Hz, H-3), 5.90 (s, 1H, H-6), 3.28 (s, 6H, $(CH_3)_2N$). Anal. Calcd for $C_{11}H_{10}N_2O_2$: C, 65.34 ; H, 4.99 ; N, 13.85. Found : C, 65.51 ; H, 5.13 ; N, 13.40.

Cycloaddition of azadiene 1 with isoquinoline-5,8-dione 7

A mixture of quinone **7** (0.2 g, 1.26 mmol) and azadiene **1** (0.211 g, 1.89 mmol) was stirred in 15 mL of toluene for 48h. Purification by column chromatograpy using acetone/hexane (3:7) as the eluent affords compound **11** (0.11 g, 33%), a mixture of the regioisomeric compounds **12**+**13** (0.09 g, 32% with the ratio **12**/**13** : 70/30) and a mixture of the regioisomeric aminoquinones **16**+**17** (0.03 g, 12 %, with the ratio **16**/**17** : 90/10). In the sonochemical experiment, the solution prepared as above was sonicated for 6h. Purification affords compound **11** (0.06 g, 18%), a mixture of the regioisomeric compounds **12**+**13** (0.086 g, 30% with the ratio **12**/**13** : 60/40) and a mixture of aminoquinones **16**+**17** (0.03 g, 12%, with the ratio **16**/**17** : 90/10).

1-N,N-Dimethylamino-1,6-diaza-1,4-dihydro-4-methyl-9,10-anthraquinone 11

Purple solid ; m.p. 144°C ; IR (KBr) ν 1690, 1660 cm^{-1} ; ^1H-NMR ($CDCl_3$, 300 MHz) δ ppm 9.28 (s, 1H, H-5), 8.95 (d, 1H, J=4.9 Hz, H-7), 7.76 (d, 1H, J=4.9 Hz, H-8), 6.28 (d, 1H, J=7.8 Hz, H-2), 5.24 (dd, 1H, J=7.8 and 5.3 Hz, H-3), 3.73 (dq, 1H, J=6.7 and 5.3 Hz, H-4), 2.73 (s, 6H, $(CH_3)_2N$), 1.18 (d, 3H, J=6.7 Hz, CH_3). Anal. Calcd for $C_{15}H_{15}N_3O_2$, 0.5 H_2O : C, 64.73 ; H, 5.80 ; N, 15.09. Found : C, 65.01 ; H, 5.88 ; N, 14.50. HRMS calcd for $C_{15}H_{15}N_3O_2$: 269.1164. Found : 269.1164.

1,6- and 1,7-Diaza-1,4-dihydro-4-methyl-9,10-anthraquinone 12 and 13

Dark blue solid, m.p. 70°C ; IR (KBr) ν 3340, 1680, 1655 cm^{-1} ; ^1H-NMR ($CDCl_3$, 300 MHz) δ ppm **12** : 9.35 (s, 1H, H-5), 8.98 (d, 1H, J=4.9 Hz, H-7), 7.79 (d, 1H, J=4.9 Hz, H-8), 6.82 (br s, 1H, NH), 6.18 (m, 1H, H-2), 5.02 (m, 1H, H-3), 3.78 (m, 1H, H-4), 1.21 (d, 3H, J=6.7 Hz, CH_3). **13** : 9.34 (s, 1H, H-8), 9.0 (d, 1H, J=5Hz, H-6), 7.90 (d, 1H, J=5Hz, H-5), 6.94 (br s, 1H, NH), 6.18 (m, 1H, H-2), 5.02 (m, 1H, H-3), 3.78 (m, 1H, H-4), 1.21 (d, 3H, J=6.7 Hz, CH_3). **12**+ **13** HRMS calcd for $C_{13}H_{10}N_2O_2$: 226.0742. Found : 226.0735. A partial aromatization occurs with these derivatives. Therefore, microanalysis data are not satisfactory.

7- and 6-N,N-Dimethylaminoisoquinoline-5,8-diones 16 and 17

Red solid ; m.p. 122°C ; IR (KBr) ν 1680, 1640 cm^{-1} ; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ ppm **16** : 9.21 (s, 1H, H-1), 8.97 (d, 1H, J=5 Hz, H-3), 7.85 (d, 1H, J=5 Hz, H-4), 5.92 (s, 1H, H-6), 3.28 (s, 6H, $(CH_3)_2N$). **17** : 9.30 (s, 1H, H-1), 8.96 (d, 1H, J=5 Hz, H-3), 7.77 (d, 1H, J=5 Hz, H-4), 5.86 (s, 1H, H-7), 3.24 (s, 6H, $(CH_3)_2N$). **16+17**. Anal. Calcd for $C_{11}H_{10}N_2O_2$, 0.33 H_2O : C, 63.47 ; H, 5.16 ; N, 13.46. Found : C, 63.23 ; H, 5.11 ; N, 13.34. HRMS calcd for $C_{11}H_{10}N_2O_2$: 202.0742. Found : 202.0741.

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