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THE INVENTION OF RADICAL REACTIONS. PART XIX†. THE SYNTHESIS OF VERY HINDERED QUINONES

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Abstract. On photolysis with tungsten light, the acyl derivatives of N-hydroxy-2-thiopyridone afford carbon radicals which readily add to quinones. In the case of benzoquinone radical addition is followed by 2-thiopyridyl transfer to afford adducts of type **4**. Two different procedures were developed for the conversion of type **4** compounds into hindered quinones of type **7**.

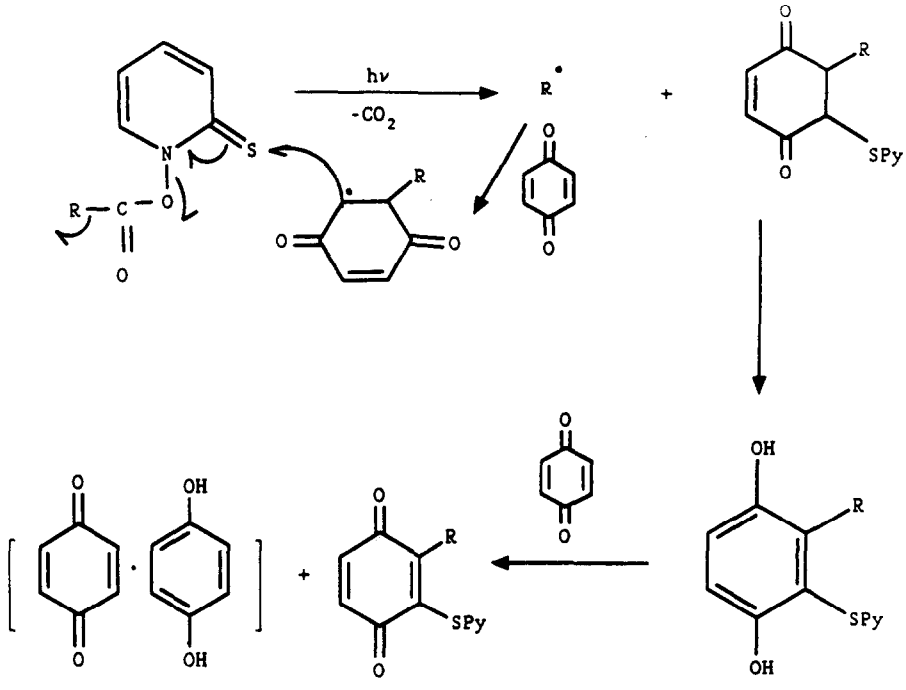
Since saturated carbon radicals are not solvated, whereas ions are, it should be possible to synthesise highly hindered compounds more easily using radical chemistry than using ionic chemistry. We decided to test this proposition by the synthesis of highly hindered quinones.

In the past, radicals for quinone addition have been generated by oxidation of carboxylic acids with lead tetracetate[1] or by persulfate with silver ion catalysis.[2]

The acyl derivations of thiohydroxamic acids, especially of N-hydroxy-2- thiopyridone, are an excellent source of carbon radicals.[3] In a recent article[3] we studied the addition of carbon radicals, generated in this way, to benzoquinone, 1,4-naphthoquinone and several analogues. Scheme 1 summarises the results of most of this work. Using an excess of the quinone, the initial cyclohex-2-ene-1,4-dione adducts were isomerised to the corresponding hydroquinones and then oxidised to quinones bearing the original carbon radical and the 2-thiopyridyl residue resulting from the chain propagation step. This has advantages since the 2-thiopyridyl group lends itself to further manipulation. However, the need for excess quinone means that valuable quinones would not be usable.

In view of the high radicophilicity of quinones[4], we decided to synthesise hindered quinones using only a slight excess of quinone with respect to the radical precursor. The well-known derivative **3a** of 1-adamantoic acid was photolysed in CH_2Cl_2 at 0° under argon in the presence of benzoquinone **1a**. The NMR and IR spectra of the product showed it to be

† Part XVIII. Barton, D. H. R.; Bridon, D.; Zard, S. Z. *Tetrahedron* **1989**, *45*, 2615.



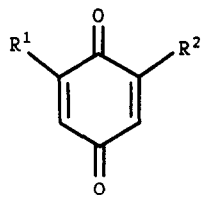
Scheme 1

4a. It was stable to recrystallisation in methanol. With acetic anhydride it gave diacetate **5b**. Small quantities of hydroquinone **5a** could be detected in **4a**. The stereochemistry of **4a** was not obvious from the N.M.R. spectrum.

The mass spectrum of **4a** gave two peaks with different fragmentation patterns at two different temperatures. HRMS for the molecular ion was in good agreement with **4a** (or the isomeric **5a**). Support for **5a** as the less volatile component came from the intense peak at [M^+(353)-17] suggesting structure **6**. (Found: 336.1437. Calc. for **6** 336.1408).

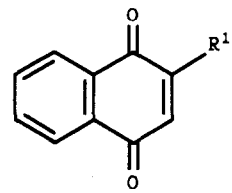
Be this as it may, the recrystallised compound is clearly **4a**. As judged by NMR and IR spectra, a similar compound **4b** was formed from the photolysis of acyl derivative **3b**. The compound **4b** was obtained in lesser yield than that of **4a**, which is understandable in terms of radical stability.[5]

Compounds of type **4**, which are available directly from quinones for the first time, should be interesting intermediates. However, the object of our present study was the synthesis of alkylated quinones. We have developed two methods for the conversion of **4** into alkylquinones.



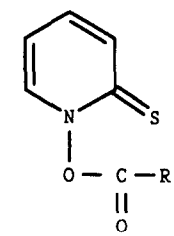
1

a $R^1 = R^2 = H$
b $R^1 = H \quad R^2 = CH_3$
c $R^1 = R^2 = CH_3$



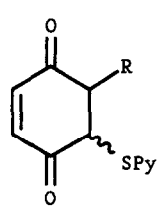
2

a $R^1 = H$
b $R^1 = CH_3$

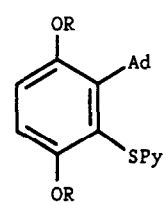


3

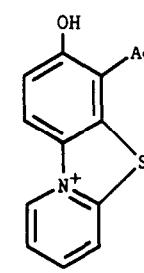
a R = 1-adamantyl (Ad)
b R = *t*-butyl
c R = cyclohexyl
d R = $PhCH_2CH_2$
e R = *i*-Pr
f R = $CH_3O_2CCH_2CH_2$



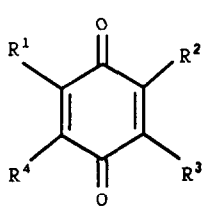
4a R = Ad
4b R = *t*-Bu



5a R = H
5b R = CH_3CO

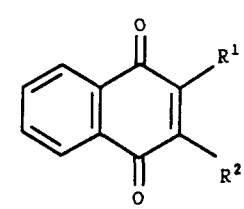


6



7

a R^1 = Ad $R^2 = R^3 = R^4 = H$
b R^1 = *t*-Bu $R^2 = R^3 = R^4 = H$
c R^1 = Ad $R^3 = CH_3$ $R^2 = R^4 = H$
d R^1 = Ad $R^2 = CH_3$ $R^3 = R^4 = H$
e R^1 = Ad R^3 = Ad $R^2 = R^4 = H$
f R^1 = Ad R^2 = Ad $R^3 = R^4 = H$
g $R^1 = R^2 = CH_3$ $R^3 = c\text{-}C_6H_{11}$ $R^4 = H$
h $R^1 = R^2 = CH_3$ $R^3 = R^4 = c\text{-}C_6H_{11}$



8

a $R^1 = H \quad R^2$ = Ad
b $R^1 = H \quad R^2$ = *t*-Bu
c R^1 = Me $R^2 = CH_2CH_2Ph$
d R^1 = Me R^2 = *i*-Pr
e R^1 = Me $R^2 = C\text{-}C_6H_{11}$
f R^1 = Me $R^2 = CH_2CH_2CO_2H$

Table 1

Alkylation of Quinones with Carbon Radicals

Entry	Quinone	Acyl Derivative	Method	Product (Yield, %)
1	**1a**	**3a** (0.87) **3a** (1.1)	A B	**7a** (51.5) (60.5)
2	**1a**	**3b** (1.15)	B	**7b** (30.5)
3	**1b**	**3a** (1.1)	B	**7c** + **7d** (60.5)
4	**7a**	**3a** (1.1)	B	**7e** (29.7) **7f** (22.7)
5	**2a**	**3a** (1.0)	B	**8a** (71.8)
6	**2a**	**3b** (1.05)	B	**8b** (44.5)
7	**2b**	**3c** (1.25)	reflux benzene	**8c** (75.0)
8	**2b**	**3d** (1.25)	CH_2Cl_2, AcOH, r.t.	**8d** (73.7)
9	**2b**	**3e** (1.25)	CH_2Cl_2, Cl_3CCO_2H. r.t.	**8e** (70.0)
10	**2b**	**3f** (1.25)	HCl, dioxan, H_2O reflux	**8f** (64.5)
11	**1c**	**3c** (1.25)	B	**7g** (79.0)[a]
12	**7g**	**3c** (1.25)	B	**7h** (65.0)

[a] **7h** (4%) was also isolated.

Method A. Reduction of **4** with zinc dust in methanol containing ammonium acetate gave the desulfurised hydroquinone. Without isolation, this was oxidised to quinone by hydrogen peroxide and a catalytic amount of phenylseleninic acid.[6]

Method B. This took advantage of the 2-pyridylthio residue to introduce the needed second double bond. After the photolysis was complete, and without work-up, the adduct **4** was oxidised with *m*-chloroperbenzoic acid. The elimination of phenylsulfenic acid was spontaneous. Work-up then afforded the desired alkylquinone.

The results are summarised in Table 1. The 1'-adamantylquinone **7a** is obtained easily by either method. Similarly the 1-adamantyl radical was added to toluquinone **1b** to afford the isomers **7c** and **7d**. Then the 1-adamantyl radical was added to 1'-adamantylquinone **7a** to give two isomers **7e** and **7f**. To distinguish between these two isomers was simple. Isomer **7e** showed only one ^{13}C signal for carbonyl, whereas isomer **7f** showed two. We were not able to add a further adamantyl radical to either **7e** or **7f**, However, these two isomers must be the most hindered quinones known.

Starting with 2,6-dimethylquinone **1c** we were able to add easily the cyclohexyl radical to furnish eventually **7g** in good yield. Then **7g** was again reacted with the cyclohexyl radical without difficulty to give the symmetrical dicyclohexyldimethylquinone **7h**.

In our previous study[3d] of radical addition to quinones, we had shown that naphthaquinone **2a** added readily the radical and the thiopyridyl residue, whereas 2-methylnaphthaquinone **2b** gave only a small yield (20%) of the simple alkylquinone. An unstable intermediate was detected.

The modified procedure now reported gave better results. Thus naphthaquinone **2a** gave a good yield of the 1-adamantyl derivative **8a**. The addition of the *t*-butyl radical from photolysis of **3b** gave a lower yield of **8b**.

We then turned to 2-methylnaphthoquinone **2b** and developed various procedures for eliminating the -S-pyridyl residue. Because the adducts are now tertiary, it was possible to eliminate the thiopyridyl residue simply by heating or by acid treatment. In this way, the disubstituted naphthoquinones **8c, 8d, 8e and 8f** were prepared in satisfactory yield. **8d** and **8e** show medium steric interaction.

Experimental

^{13}C and HNMR spectra were recorded at 200 MHz with a Varian GEMINI 200 Spectrometer in $CDCl_3$ solution. Chemical shifts are in ppm with respect to internal TMS. Coupling constants are in Hz. First order approximation was used for determination of spectral parameters. IR spectra were measured with a Perkin-Elmer 881 Spectrometer and only major absorptions are reported. Electron impact mass spectra were carried on with VG Analytical 705 high resolution double focusing magnetic sector mass spectrometer with attached VG Analytical 11/250 J data system. Microanalyses were performed at Atlantic Microlab, Inc. P. O. Box 228, Norcross, GA 30092-9990. Melting points were determined on a Kofler hot stage and are uncorrected. All solvents used in photolysis were freshly distilled under nitrogen. The quinones were purchased from Aldrich (**1a**, **2a**, **2b**), Fluka (**1b**) and Lancaster (**1c**). The quinones **1a**, **2a**, and **1b** were purified by filtration through silica gel using dichloromethane as eluent and crystallization from heptane or hexane-dichloromethane mixture. The quinones **1c** and **2b** were used without purification. *N*-Hydroxypyridine-2-thione was prepared[7] from the aqueous solution of its sodium salt, (Olin Corp.). The derivatives **3a**[8], **3b**, **3c** and **3d**[9] were prepared according to the literature. All acyl derivatives **3** are somewhat light sensitive and all manifulation should be performed under protection against light. For thin-layer chromatographic (TLC) analysis, Merck precoated TLC plates (Kieselgel 60 F_{254}, 0.2mm) were used and column chromatography was performed on Merck Kieselgel 60 (230-400 mesh) as stationary phase. Preparative TLC separations were done on glass precoated TLC plates (Analtech, Inc., 2 mm).

N-(Isobutyroyloxy)pyridine-2-thione (**3e**). Isobutyric acid (2.9 ml, 0.034 mol) *N*-hydroxypyridine-2-thione (3.815 g, 0.03 mol) were dissolved in dry dichloromethane (20 ml) and cooled to 0°. To this solution 1,3-dicyclohexylcarbodiimide (6.18 g, 0.03 mol) was added at once. After 30 min. the cooling bath was removed and the mixture was magnetically stirred for 3h. A precipitate was filtered off and washed with dichloromethane. The yellow filtrate was subsequently washed with saturated aqueous sodium bicarbonate (twice), water, brine and dried over sodium sulfate. The resulting mixture was kept in a freezer overnight. This was filtered through a short column of silica gel and washed with the same solvent. The solvent was distilled off under reduced pressure and the yellow crystalline residue was crystallized from ethyl acetate-hexanes mixture. The yield of ester **3e** was 4.5 g (76%) with m.p. 88.5-93°. Calculated for $C_9H_{11}NO_2S(M^+)$: 197.0510; Found: 197.0509; IR(CH_2Cl_2): 2978, 1803 cm^{-1}; NMR (δ): 7.67 (m, 1H), 7.58 (dd, J=7.0, J=1.6, 1H), 7.22 (m, 1H), 6.65 (td,

J=7.0, J=1.8, 1H), 3.00 (sp, J=7.1, 1H), 1.41 (d, J=7.1, 6H).

N-(3'-Carbomethoxypropionyloxy) pyridine-2-thione (**3f**). *N*-Hydroxy-pyridine-2-thione (6.36 g, 0.05 mol) was dissolved in dry dichloromethane (30 ml) and the solution was cooled to 0°. 3-Carbomethoxypropionyl chloride (Aldrich, 6.16 ml, 0.05 mol) was added portionwise followed by addition of dry pyridine (4.4 ml) in the same manner. When the addition was completed the mixture was stirred for 1 h at 0°, then 3 h at ambient temperature. The mixture was washed with water, saturated aqueous sodium bicarbonate, water, brine and dried with sodium sulfate. The solvent was removed under reduced pressure. The crystalline residue was crystallized from ethyl acetate yielding derivative **3f** (6.23 g, 51.7%) with m.p. 75-80°. Calculated for: $C_{10}H_{11}NO_4S(M^+)$: 241.0409; Found: 241.0413; IR (CH_2Cl_2): 2955, 1812, 1736, 1073 cm^{-1}; NMR (δ): 7.67 (m, 2H), 7.23 (m, 1H), 6.66 (td, J=6.9, J=1.7, 1H), 3.73 (s, 3H), 3.03 (t, J=6.8, 2H), 2.85 (t, J=6.8, 2H).

General Procedure for Preparation of Quinone Derivatives. Quinone **1** or **2** (1 mmol), acyl derivative **3** (see Table 2), and dichloromethane were placed in a round bottomed flask previously flushed with argon. The resulting solution was cooled to 0 ± 3°C. Argon was bubbled through for ca. 30 min. then bubbling was stopped and mixture was irradiated with tungsten lamp (150W) under slight positive pressure of argon. To improve the effectiveness of light, the back side of the reaction flask was covered with aluminum foil. The progress of photolysis was followed by IR at the absorption of **3** around 1800 cm^{-1} and/or by TLC with dichloromethane as eluent and ethanol solution of iron (III) chloride as developing reagent. The acyl derivatives give blue spots on heating. When one of the reagents was consumed, which usually needed a few hours, the adduct was converted to the quinone derivative by one of the methods described below.

2-(1'-Adamantyl)-*p*-benzoquinone (**7a**).

Method A. For the photolysis, there was used 2.4 g (22.2 mmol) of quinone **1a** and acyl derivative **3a** (5.61 g, 19.4 mmol). The solvent was distilled off under reduced pressure. The residue was mixed with methanol (100 ml) zinc dust (5.2 g, 79.5 mmol), activated by washing with diluted hydrochloric acid (5%), and ammonium acetate (4.6 g, 60 mmol). The resulting mixture was sonicated at 20-25° under nitrogen using an ultrasound cleaning bath (Branson 2200). The reaction was followed by TLC with dichloromethane-ethyl acetate (15:1, v/v) as eluent. After 1.5 h, the reaction was completed. Zinc was filtered off and methanol removed under reduced pressure. After extraction with ethyl acetate, the solution was washed with diluted sulfuric acid (1:20, v/v), water and brine. The solvent was distilled off and the residue was mixed with dichloromethane

(100 ml), hydrogen peroxide (30%, 6.6 ml) and benzeneseleninic acid (0.3 g 1.6 mmol). After 1 h of intensive stirring the starting material had disappeared (TLC). The mixture was diluted with water, the organic layer was separated and the water one was extracted with the same solvent. The organic solutions were combined, washed with water, saturated aqueous sodium bicarbonate solution, water, brine and dried with magnesium sulfate. The quinone was purified by column chromatography with hexanes-dichloromethane (3:2, v/v) mixture as eluent, to give **7a** (2.48 g) (51.5% calculated on **3a**) with m.p. 136-138° (from hexanes). Calculated for $C_{16}H_{18}O_2$: C 79.31%, H 7.49%; found: C 79.20, H 7.59; IR (CH_2Cl_2): 2910, 2855, 1656, 1590 cm^{-1}; NMR (δ): 6.56 (m, 2H), 6.51 (m, 1H), 2.07 (m, 3H), 1.92 (m, 6H), 1.76 (m, 6H).

Method B. When the photolysis was completed *m*-chloroperbenzoic acid (Aldrich, 50-60%, 0.35 g) was added and the mixture was stirred at 0°. Usually after 1 h the adduct was no longer detected by TLC (CH_2Cl_2). The cooling bath was removed, saturated aqueous sodium bicarbonate solution (4 ml) was added and the resulting mixture was stirred at ambient temperature for 4 h. The mixture was diluted with water. The organic layer was separated, washed with water, brine and dried over sodium sulfate. The quinone was purified by column chromatography with dichloromethane-hexanes (1:1, v/v) as eluent, if another solvent system is not mentioned. The yields are given in Table 2.

2-*tert*-Butyl-*p*-benzoquinone (**7b**). Method B, 3 mmol scale. M.p. 54-56° (lit.[10] 54-55°; 57-58° [3a]). IR (CCl_4): 2963, 2922, 1651, 1588 cm^{-1}, NMR (δ): 6.68 (m, 2H), 6.60 (m, 1H), 1.29 (s, 9H).

2-(1'-Adamantyl)-5-methyl-*p*-benzoquinone (**7c**) and 2-(1'Adamantyl)-6-methyl-*p*-benzoquinone (**7d**). Method B. Mixture of isomers **7c** and **7d**, ratio **7c**:**7d** = 1:2 (by NMR). The mixture (90 mg) was separated on two preparative TLC plates with the standard eluent. Quinone **7c** (13 mg) had m.p. 145-146.5° after crystallization from methanol. Calculated for: $C_{17}H_{20}O_2$ (M^+): 256.1463; found: 256.1459; IR (CCl_4): 2905, 2851, 1646, 1593 cm^{-1}; [NMR (δ): 6.47-6.51 (q and s, J=1.5, 2H), 2.06 (m, 3H), 2.00] (d, J=1.5, 3H), 1.92 (m, 6H), 1.75 (m, 6H). The more polar isomer **7d** (25 mg) had m.p. 150-152° after crystallization from methanol. Calculated for $C_{17}H_{20}O_2$ (M^+): 256.1463; found 256.1458; IR (CCl_4): 2908, 2852, 1649, 1596 cm^{-1}; NMR (δ): 6.52 (sx, 1H), 6.44 (d, J=2.6, 1H), 2.06 (m, 3H), 2.03 (d, J=1.6, 3H), 1.92 (m, 6H), 1.76 (m, 6H).

2,5-(**7e**) and 2,6-Di (1'adamantyl)-*p*-benzoquinone (**7f**). Method B (1.52 mmol scale). The reaction mixture was taken up in a small volume of dichloromethane. A yellow crystalline precipitate formed and was filtered off. It was almost pure quinone **7e** (0.123 g). The filtrate was

concentrated to dryness and purified by column chromatography. Elution with carbon tetrachloride afforded further **7e** (0.047 g). Overall yield of quinone **7e** was 0.17 g (30%) with m.p. 306-308° after crystallization from 1,2-dichloro- methane-ethyl acetate mixture. Calculated for $C_{26}H_{32}O_2$ (M^+): 376.2402; found: 376.2409; IR ($CHCl_3$): 2909, 2853, 1638, 2551 cm^{-1}; ^{1}HNMR (δ): 6.35 (s, 2H), 2.05 (bs, 6H), 1.91 (m, 12H), 1.75 (m, 12H); ^{13}C NMR (δ): 189.2, 154.3, 134.8, 40.6, 37.3, 36.9, 28.6. Elution further with dichloromethane- hexanes (1:1 v/v) afforded quinone **7f** (0.13 g, 23%) with m.p. 266-268° after crystallization from ethyl acetate-ethanol mixture. Calculated for $C_{26}H_{32}O_2$ (M^+): 376.2402; found: 376.2382; IR ($CHCl_3$): 2906, 2852, 1644, 1592 cm^{-1}. ^{1}HNMR (δ): 6.40 (s, 2H), 2.05 (m, 6H), 1.93 (m, 12H), 1.76 (m, 12H); ^{13}C NMR (δ): 190.0, 188.5, 158.5, 130.8, 40.8, 38.4, 36.9, 28.7.

2-(1'Adamantyl)-1,4-naphthoquinone (**8a**). The photolysis was performed at 20-30°. Method B. **8a** had m.p. from 143.5-145.5°. Calculated for $C_{20}H_{20}O_2$ (M^+): 292.1463; found: 292.1459; IR (CCl_4): 2910, 2852, 1657, 1591 cm^{-1}, NMR (δ): 8.06 (m, 2H), 7.72 (m, 2H), 6.76 (s, 1H), 2.10 (m, 3H), 2.04 (m, 6H), 1.80 (m, 6H).

2-tert.-Butyl-1,4-naphthoquinone (**8b**). Method B. **8b** had m.p. from 72.5-74.5° (lit.[2e] 75-76°), IR (CCl_4): 2963, 2922, 1659, 1595 cm^{-1}. NMR (δ): 8.07 (m, 2H), 7.72 (m, 2H), 6.85 (m, 1H), 1.38 (s, 9H).

2-Methyl-3-(2'-phenylethyl)-1,4-naphthoquinone (**8c**). After photolysis dichloromethane was replaced by benzene (10 ml). The mixture was refluxed for 2h. The mixture was cooled and chromatographed with hexanes-dichloromethane (3:2, v/v) mixture as eluent. **8c** had m.p. 72-73.5° (lit.[2a] 73-73.5°) after crystallization from methanol. IR (CCl_4): 3025, 2945, 2862, 1655, 1592 cm^{-1}; NMR (δ): 8.10 (m, 2H), 7.70 (m, 2H), 7.25 (m, 5H), 2.94 (m, 2H), 2.79 (m, 2H), 2.04 (s, 3H).

2-Methyl-3-(isopropyl)-1,4-naphthoquinone (**8d**). When the photolysis was completed, acetic acid (~0.5 ml) was added and the resulting mixture was allowed to stand at ambient temperature until the next day. The solution was washed with water, saturated aqueous sodium bicarbonate, water, brine, and dried with sodium sulfate. Purification by column chromatography afforded quinone **8d** with m.p. from 109.5-111.5 (lit.[1a] 110-112°). IR (CCl_4): 2988, 2961, 1653, 1593 cm^{-1}; NMR (δ): 8.05 (m, 2H), 7.67 (m, 2H), 3.27 (sp, J=7.1, 1H), 2.22 (s, 3H), 1.36 (d, J=7.1, 6H).

2-Cyclohexyl-3-methyl-1,4-naphthoquinone (**8e**). Trichloroacetic acid (0.17 g, 1.04 mmol) was added to the photolysis mixture. The cooling bath was removed and the resulting mixture was kept at room temperature for 3.5 h. The work-up as described for **8d** gave quinone **8e** with m.p. 77.5-79° after crystallization from methanol (lit.[2c] 78-79°). IR (CCl_4): 2925, 2853,

1652, 1591 cm^{-1}, NMR (δ): 8.05 (m, 2H), 7.67 (m, 2H), 2.88 (tt, J=12.0, J=3.5, 1H), 2.24 (s, 3H), 2.20-1.25 (m, 10H).

2-Methyl-3-(2'-carboxyethyl)-naphthoquinone (**8f**). After photolysis (3 mmol scale) the solvent was removed and the residue was taken up in dioxane- water-concentrated hydrochloric acid (15 ml -15 ml -8 ml). The resulting mixture was refluxed for 2.5 h, and then it was cooled, diluted with water (15 ml) and extracted with dichloromethane. The organic solution was washed with water followed by extraction with saturated aqueous sodium bicarbonate (twice). These extracts were combined, washed with dichloromethane and acidified with diluted hydrochloric acid (1:1, v/v). A yellow precipitate was filtered off, washed with water and dried. Crystallization from ethyl acetate-octane (1:1, v/v) provided acid **8f** (65%) with m.p. 145-147° (lit. [1b] 142-144°). IR ($CHCl_3$): 3360-2754, 2928, 1707, 1651, 1592 cm^{-1}; NMR (δ): 8.08 (m, 2H), 7.70 (m, 2H), 2.99 (m, 2H), 2.61 (m, 2H), 2.24 (s, 3H).

2-Cyclohexyl-3,5-dimethyl-*p*-benzoquinone (**7g**). Method B (3 mmol scale) with hexanes-dichloromethane (2.5:1, v/v) afforded quinone **7g** (79%) as a yellow oil. Calculated for $C_{14}H_{18}O_2$: C 77.03%, H 3.31%; found: C 76.87%, H 8.35%; IR (neat): 2923, 1637, 1598 cm^{-1}; ^{1}HNMR (δ): 6.47 (q, J=1.6, 1H), 2.73 (tt, J=12.1, J=3.4, 1H), 2.089 (s, 3H), 2.01 (d, J=1.6, 1H), 2.00-1.20 (m, 10H); ^{13}C NMR (δ): 189.2, 188.4, 148.2, 144.8, 140.9, 134.4, 40.0, 30.0, 27.0, 25.9, 15.7, 12.2. The first fraction was quinone **7h** (4%).

2,6-Dicyclohexyl-3,5-dimethyl-*p*-benzoquinone (**7h**). Method B. (0.54 mmol scale) with hexanes-dichloromethane (3:1, v/v) gave quinone **7h** (65%) with m.p. 101.5-103° after crystallization from methanol. Calculated for $C_{20}H_{28}O_2$: C 79.95%, H 9.39%; found: C 79.80%, H 9.44%; IR (CCl_4): 2927, 2885, 1638, 1602 cm^{-1}; ^{1}H NMR (δ): 2.69 (tt, J=1.20, J=3.4, 2H), 2.04 (s, 6H), 2.00-1.20 (m, 20H); ^{13}C NMR (δ): 189.3, 189.0, 148.7, 139.5, 40.3, 30.1, 27.1, 26.0, 12.0.

5-(1'-Adamantyl)-6-(pyridine-2-thiyl)-cyclohex-2-ene-1,4-dione (**4a**). *p*-Benzoquinone (1.19 g, 11 mmol) and **3a** (2.89 g 10 mmol) were photolyzed at 0° in dichloromethane (50 ml) as described previously. After ca. 4h **3a** was not detectable. The reaction mixture was quickly filtered through a short pad of silica. The filtrate was concentrated to dryness at 0° under reduced pressure. The dark yellow oil was mixed with methanol-pentane mixture (15 ml, 2:1, v/v) at 0°. The yellow crystals were filtered off and washed with the same solvent. The yield of adduct **4a** was 2.74 g (77.5%) with m.p. 109-113° (with decomp.) crystallization from hexanes-carbon tetrachloride increased m.p. up to 112-119° (with decomp.). TLC (CH_2Cl_2) showed the presence of a more polar component. Calculated

for: $C_{21}H_{23}NO_2S$ (M^+): 353.1449; found: 353.1452 (at 167°) and 353.1445 (at 200°); mass spectra m/z (relative intensity): 353 (11.5), 244 (36), 242 (100), 135 (75.5), 111 (82), 67 (73); 353 (88.6), 336 (99.7), 320 (47.6), 244 (100), 187 (39.7), 111 (37), 78 (31), 67 (32.5); IR (CH_2Cl_2); 2912, 2852, 1679, 1579 cm^{-1}; NMR (δ): 8.46 (m, 1H), 7.53 (m, 1H), 7.18 (m, 1H), 7.08 (m, 1H); 6.75 (dd, J=10.5, J=1.2, 1H), 6.70 (dd, J=10.5, J=0.8, 1H) 5.24 (t, 1H), 2.78 (bs, 1H), 2.02 (bs, 4H), 1.63 (m, 14H).

Diacetate **5b**. Adduct **4a** (0.103 g), acetic anhydride (1.5 ml) and dry pyridine (0.2 ml) were mixed together and kept in a refrigerator for 24 h. The mixture was poured into water. When organic layer had disappeared, the white crystals were filtered off, washed with water and dried. The yield of diacetate **5b** was 0.058 g (45.5%) after crystallization from ethyl acetate-hexanes mixture. It showed m.p. 188-190.5°. Calculated for: $C_{25}H_{27}NO_4S$ (M^+-59): 378.1528; found: 378.1535; IR ($CHCl_3$): 2912, 2850, 1758, 1213 cm^{-1}; NMR (δ): 8.38 (m, 1H), 7.42 (m, 1H), 6.99 (ABq, J=8.8, Δ_{AB}=0.07 ppm, 2H), 6.96 (m, 1H), 6.60 (m, 1H), 2.41 (m, 6H), 2.29 (s, 3H), 2.00 (bs, 3H), 1.83-1.61 (m, 6H).

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Addendum. After we had completed this work and had the manuscript ready for submission, we made a final check of Chem. Abs. The quinones **7a** and **7e** were prepared before by electrophilic substitution into hydroquinone of 1-bromoadamantane followed by oxidation.[11] The m.ps. recorded are in agreement with our data.

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