Photolytic, Thermal, Addition, and Cycloaddition Reactions of

2-Diazo-5,6- and 3,8-disubstituted-acenaphthenones

Patricia A. Blair, Sou-Jen Chang and Harold Shechter*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

shechter@chemistry.ohio-state.edu

Supporting Information

Table of Contents

Methods and Materials	S3
1,8-Diphenylnaphthalene	S3
5,6-Diphenylacenaphthenequinone (19b)	S3
5,6-Diphenylacenaphthenenequinone 2- <i>p</i> -Tosylhydrazone (17b)	S4
2-Diazo-5,6-diphenylacenaphthenone (11b)	S4
Photolysis of 2-Diazo-5,6-diphenylacenaphthenone (11b) in Methanol	S4
Photolysis of 11b in Benzene	S5
Thermolysis of 11b in Aniline	S5
Photolysis of 11b in Aniline in the Presence of Excess Oxygen	S6
Thermolysis of 11b	S6
Thermolysis of 11b in Dimethyl Acetylenedicarboxylate	S6
1,8-Di(<i>m</i> -tolyl)naphthalene and 8,8'-Di(<i>m</i> -tolyl)-1,1'-binaphthyl	S7
5,6-Di(<i>m</i> -tolyl)acenaphthenequinone (19c)	S7
5,6-Di(<i>m</i> -tolyl)acenaphthenequinone 2- <i>p</i> -Tosylhydrazone (17c)	S8
2-Diazo-5,6-di(<i>m</i> -tolyl)acenaphthenone (11c)	S8
Photolysis of 11c in Methanol	S8
Photolysis of 11c in Benzene	S9
Thermolysis of 11c in Aniline	S10

Thermal Decomposition of 11c	S10
Thermolysis of 11c in Dimethyl Acetylenedicarboxylate	S10
5,6-Dinitroacenaphthenequinone (19d)	S10
5,6-Dinitroacenaphthenequinone 2- <i>p</i> -Tosylhydrazone (17d)	S11
2-Diazo-5,6-dinitroacenaphthenone (11d)	S11
Photolysis of 11d in Benzene	S11
Photolysis of 11d in Acetonitrile	S11
Photolysis of 11d in Benzonitrile	S12
Photolysis of 11d in Phenylacetylene	S12
Thermolysis of 11d in Dimethyl Acetylenedicarboxylate	S12
2,7-Dimethoxynaphthalene	S12
3,8-Dimethoxyacenaphthenequinone (20)	S13
3,8-Dimethoxyacenaphthenequinone 2- <i>p</i> -Tosylhydrazone (18)	S13
2-Diazo-3,8-dimethoxyacenaphthenone (12)	S13
Photolysis of 12 in CH ₃ OH	S14
Photolysis of 12 in Tetrahydrofuran	S14

Experimental Section

Methods and Materials. Melting points were determined in capillary tubes or on block and are uncorrected. ^1H NMR spectra were recorded on 360 and 390 MHz spectrometers in which the chemical shifts were measured in ppm downfield from tetramethylsilane. Column chromatography was effected on MN-Kieselgel (70-270 mesh) or neutral alumina (80-200 mesh). All photolyses were conducted by irradiating the diazo compounds in the solvent (220 mL) specified using a Hanovia 450 W medium pressure Hg lamp dipped in a pyrex well. All solvents for photolyses were dried and distilled before use. Dry N_2 was bubbled through the reaction mixtures before and/or during photolyses. Photolyses were conducted at room temperatures unless otherwise indicated. All thermolyses were carried out by refluxing solutions of the diazo compounds in the indicated solvents under purified N_2 . The vacuum decompositions of **11a-d** and **1a** at $\sim 450^\circ\text{C}$ and 0.15 mm Hg in quartz were effected as detailed for **11a**.

1,8-Diphenylnaphthalene^{1a}. Iodobenzene (48.6 mL, $D = 1.82$, 0.432 mmol) in dry ethyl ether (360 mL) was added dropwise over 1.5 h to Mg (16.0 g, 0.641 mmol) in dry ethyl ether (50 mL). The phenylmagnesium iodide reagent was refluxed 0.5 h, filtered, and added in 4 h to 1,8-diiodonaphthalene^{1b,c} (20.0 g, 53 mmol) in ethyl ether (230 mL)/benzene (230 mL) containing nickel acetylacetonate (90 mg, 0.486 mmol). During and after addition (2 h), the reaction mixture was cooled in ice-salt and then stirred overnight at room temperature. After adding saturated NH_4Cl solution slowly, the H_2O layer was extracted with ethyl ether. The ethyl ether layer was washed with H_2O , dried over Na_2SO_4 , and concentrated to a dark oil which was chromatographed on silica gel (hexane). Biphenyl (8.87 g, mp 60°C) was eluted followed by 1,8-diphenylnaphthalene (6.67 g, 45%, mp $149\text{--}150^\circ\text{C}$) (hexane); lit.^{1a} mp $149\text{--}150^\circ\text{C}$) as white crystals; NMR (CDCl_3 , δ) 8.07-7.30 (m, 6H), 6.93 (s, 10H). Finally, 8,8'-diphenyl-1,1'-binaphthyl was obtained (2.80 g, 13%, mp $208\text{--}210^\circ\text{C}$); lit.^{1a} mp $210.5\text{--}212^\circ\text{C}$) as white prisms when recrystallized from hexane; NMR (CDCl_3 , δ) 7.67-6.80 (m, 12H), 6.74-6.07 (m, 10H).

5,6-Diphenylacenaphthenequinone (19b). Oxalyl chloride (6.6 mL, $D = 1.46$, 76 mmol) was

added to a cooled slurry (ice-salt) of anhydrous AlCl_3 (6.67 g, 50 mmol) in CS_2 (40 mL). 1,8-Diphenylnaphthalene (6.23 g, 22 mmol)^{1a} and then CS_2 (20 mL) were added at 0 °C. The dark red mixture was stirred at 0 °C for 1 h and then at room temperature for 2 h. Water was added slowly and the CS_2 was removed by heating the mixture at ~ 100 °C. After addition of CH_2Cl_2 , the organic layer was washed with dilute HCl, then with aqueous NaHCO_3 and finally with saturated aqueous NaCl. Drying over Na_2SO_4 and evaporation of the solvent gave a golden semi-solid. Chromatography on silica gel with benzene as eluent yielded **19b** (2.29 g, 31%, mp 288-290 °C) as yellow crystals; IR (KBr, cm^{-1}) 1730 (C=O, s); NMR (CDCl_3 , δ) 7.98 (d of d, 4H), 7.00 (s, 10H). *Anal.* Calcd for $\text{C}_{24}\text{H}_{14}\text{O}_2$: C, 86.21, H, 4.22. Found: C, 86.31; H, 4.34.

5,6-Diphenylacenaphthenequinone 2-*p*-Tosylhydrazone (17b). *p*-Tosylhydrazine (0.57 g, 3.0 mmol) was added to a suspension of **17b** (1.04 g, 3.0 mmol) in refluxing CH_3OH (20 mL). The resulting solution was refluxed 1 h. The yellow crystals obtained upon cooling were filtered and dried to yield **17b** (1.43 g, 93%, mp 121-123 °C); IR (KBr, cm^{-1}) 3200 (NH, w), 1690 (C=O, s), 1389, 1171 (SO_2 , s); NMR (CDCl_3 , δ) 8.13-7.13 (m, 8H), 6.98 (s, 10H), 2.38 (s, 3H). *Anal.* Calcd for $\text{C}_{32}\text{H}_{22}\text{N}_2\text{SO}_3$: H, 4.41; N, 5.57. Found: H, 4.42; N, 5.03.

2-Diazo-5,6-diphenylacenaphthenone (11b). A CH_2Cl_2 (30 mL) solution of **17b** (0.77 g, 1.3 mmol) and aqueous NaOH (14.3 mL, 0.1 N, 1.4 mmol) was stirred vigorously overnight. The water layer was extracted several times with CH_2Cl_2 . The CH_2Cl_2 layer was washed with H_2O and dried over Na_2SO_4 . Removal of solvent and chromatography on neutral alumina (CH_2Cl_2) yielded **11b** (0.47 g, 100%, mp 178-180 °C) as yellow crystals; IR (KBr, cm^{-1}) 2092 ($=\text{N}_2$, s), 1678 (C=O, s); NMR (CDCl_3 , δ) 7.83 (d of d, 2H), 7.40 (d, 2H), 6.93 (d, 10H). *Anal.* Calcd for $\text{C}_{24}\text{H}_{14}\text{N}_2\text{O}$: C, 83.22; H, 4.07; N, 8.09. Found: C, 83.31; H, 4.12; N, 7.90.

Photolysis of 11b in CH_3OH (23a). In a typical experiment, **11b** (0.4 g, 1.2 mmol) was photolyzed in **23a** (125 mL) for 8 h. After vacuum evaporation of the solvent, the IR and the NMR of the crude product revealed no ester absorptions expected if ketene **15b** had formed and was converted by **23a** to methyl 4,5-diphenyl-1*H*-cyclobuta[de]naphthalene-1-carboxylate (**49a**).

Chromatography of the residue on silica gel (benzene) yielded 5,6-diphenylacenaphthenone (**48a**, 46 mg, 13.1% based on reacted starting material, mp 189-190.5 °C) as yellow plates after being recrystallized from benzene:petroleum ether; IR (KBr, cm^{-1}) 1717 (C=O, s); NMR (CDCl_3 , δ) 8.17-7.20 (m, 4H), 6.97 (s, 10H), 3.90 (s, 2H); m/e calcd for $\text{C}_{24}\text{H}_{16}\text{O}$: 348.15140, obsd: 348.15094. *Anal.* Calcd for $\text{C}_{24}\text{H}_{16}\text{O}$: C, 89.97; H, 5.03. Found: C, 89.75; H, 5.11.

Next eluted was **11b** (44 mg, 11%) as characterized earlier. Elution with CH_2Cl_2 gave, in addition to intractables, 2-methoxy-5,6-diphenylacenaphthenone (**47a**, 0.11 g, 29% based on reacted starting material, mp 302-303 °C (benzene:petroleum ether)), light yellow crystals; IR (KBr, cm^{-1}) 2835 (OCH_3 , w), 1727 (C=O, s); NMR (CDCl_3 , δ) 8.07-7.14 (m, 4H), 6.90 (s, 10H), 5.11 (s, 1H), 3.60 (s, 3H); m/e calcd $\text{C}_{25}\text{H}_{18}\text{O}_2$: 350.13067, obsd: 350.13137. *Anal.* Calcd for $\text{C}_{25}\text{H}_{18}\text{O}_2$: C, 85.69; H, 5.18. Found: C, 85.43; H, 5.05.

Photolysis of 11b in Benzene. A benzene (225 mL) solution of **11b** (0.4 g, 1.2 mmol) was irradiated 4.5 h. Removal of the benzene and chromatography on silica gel (benzene) yielded two products: (1) 2,5,6-triphenylacenaphthenone (**50a**, 0.13 g, 25%, mp 179-181 °C (benzene:petroleum ether)) as yellow crystals; IR (KBr, cm^{-1}) 1723 (C=O, s); NMR (CDCl_3 , δ) 7.73 (d of d, 2H), 7.54-7.30 (m, 2H), 7.14 (s, 5H), 6.83 (d, 10H), 4.83 (s, 1H); m/e calcd for $\text{C}_{30}\text{H}_{20}\text{O}$: 396.15140, obsd: 396.15224. *Anal.* Calcd for $\text{C}_{30}\text{H}_{20}\text{O}$: C, 90.88; H, 5.08. Found: C, 91.03; H, 5.06 and (2) *cis*-7a,11a-dihydro-3,4-diphenylacenaphtho[1,2-*b*]-benzo[*d*]furan (**51a**, 0.21 g, 44%, mp 151-153 °C) (benzene)), orange crystals; IR (KBr, cm^{-1}) 1628 (C = C, s); NMR (CDCl_3 , δ) 8.90-5.60 (m, 8H), 7.00 (s, 10H), 3.23 (d, 2H); m/e calcd for $\text{C}_{30}\text{H}_{20}\text{O}$: 396.15141, obsd: 396.15224. *Anal.* Calcd for $\text{C}_{30}\text{H}_{20}\text{O}$: C, 90.88; H, 5.08. Found: C, 90.67; H, 5.12.

Thermolysis of 11b in Aniline. A mixture of **11b** (0.3 g, 0.87 mmol) in aniline (5 mL) under N_2 was refluxed for 1h in a heated silicone bath (~186° C). After cooling to room temperature, the dark red solution was poured into a conc. HCl-ice slurry and then extracted several times with benzene. The organic layers were combined, dried over MgSO_4 , and concentrated. Chromatography of the resulting dark orange semi-solid on silica gel (benzene) and

recrystallization from benzene yielded 3,4-diphenylacenaphtho[1,2-*b*]indole (**53a**, 60 mg, 17%, mp 255-256.5 °C) as shiny red crystals; IR (KBr, cm^{-1}) 3402 (NH, w); NMR (CDCl_3 , δ) 8.47 (bs, 1H), 8.06-7.08 (m, 8H), 6.96 (s, 10H); m/e calcd for $\text{C}_{30}\text{H}_{19}\text{N}$: 393.15174, obsd: 393.15229. *Anal.* Calcd for $\text{C}_{30}\text{H}_{19}\text{N}$: C, 91.57; H, 4.87; N, 3.56. Found: C, 91.65; H, 4.83; N, 3.56.

The next compound eluted was 4,5-diphenyl-1,8-naphthalic anhydride (**54**, 60 mg, 20%, mp > 300 °C) as light yellow crystals when recrystallized from benzene:petroleum ether; IR (KBr, cm^{-1}) 1765, 1730 (C=O, s); NMR (CDCl_3 , δ) 8.22 (d of d, 4H), 7.00 (s, 10H); m/e calcd for $\text{C}_{24}\text{H}_{14}\text{O}_3$: 350.09428, obsd: 350.09494. *Anal.* Calcd for $\text{C}_{24}\text{H}_{14}\text{O}_3$: C, 82.27; H, 4.03. Found: C, 82.40; H, 4.37.

Further elution yielded **19b** (0.14 g, 48%, mp 288-290 °C) as previously characterized.

Photolysis of 11b in Aniline in the Presence of Excess O_2 . Oxygen was bubbled through a solution of **11b** (0.24 g, 1.1 mmol) in aniline (125 mL) for 1 h before and during a 3 h photolysis. The aniline was removed under vacuum to yield a dark oil which was chromatographed on silica gel (benzene) to give : (1) 3,4-diphenylacenaphth[1,2-*b*]indole (**53a**, 10 mg, 2.3%, mp 255-256.5 °C), identical with an authentic sample and (2) N,4,5-triphenyl-1,8-naphthalimide (**55**, 70 mg, 14.5 %, mp 271-274 °C), a light brown solid; IR (CCl_4 , cm^{-1}) 1712, 1678 (C=O, s); NMR (CDCl_3 , δ) 8.23 (d of d, 4H), 7.57-7.20 (m, 5H), 7.00 (s, 10H); m/e calcd for $\text{C}_{30}\text{H}_{21}\text{NO}$: 425.14157, obsd: 425.14248. *Anal.* Calcd for $\text{C}_{30}\text{H}_{19}\text{NO}_2$: C, 84.69; H, 4.50; N, 3.29. Found: C, 84.69; H, 4.73; N, 3.22.

Thermolysis of 11b. Finely-ground **11b** (0.3 g, 0.87 mmol) was decomposed at 450 °C at 0.15 mm Hg pressure and condensed in **23a** as described for **11a**. After removal of **23a**, the dark orange solid was chromatographed on silica gel (benzene) to give **48a** (20 mg, 7%, mp 189-190.5 °C) as characterized previously.

Thermolysis of 11b in Dimethyl Acetylenedicarboxylate. A mixture of **11b** (0.2 g, 0.58 mmol) and dimethyl acetylenedicarboxylate (1 mL) in toluene (15 mL) was refluxed 5 h. After the solution had been concentrated a yellow fluorescent precipitate formed which was filtered

and identified as dimethyl 7-oxo-3,4-diphenyl-7*H*-benzo[*de*]pyrazolo[5,1-*a*]isoquinoline-10,11-dicarboxylate (**68h**, 0.21 g, 74%, mp 237-239 °C); IR (KBr, cm^{-1}) 1745, 1725, 1720 (C=O, s); NMR (CDCl_3 , δ) 8.97 (d of d, 2H), 7.94-7.53 (m, 2H), 7.03 (s, 10H), 4.07 (s, 6H); *m/e* calcd for $\text{C}_{30}\text{H}_{20}\text{N}_2\text{O}_5$: 488.13721, obsd: 488.13856. *Anal.* Calcd for $\text{C}_{30}\text{H}_{20}\text{N}_2\text{O}_5$: C, 73.76; H, 4.13; N, 5.73. Found: C, 73.53; H, 4.20; N, 5.62.

1,8-Di(*m*-tolyl)naphthalene. *m*-Iodotoluene (24.8 mL, $D = 1.70$, 0.193 mmol) in anhydrous ethyl ether (180 mL) was added in 1.5 h to Mg (7.12 g, 0.296 mmol) in ethyl ether (25 mL) to form *m*-tolylmagnesium iodide. The Grignard reagent solution was refluxed 0.5 h, filtered through glass wool, and added dropwise (3 h) to cooled (ice-salt) 1,8-diiodonaphthalene^{1b,c} (9.12 g, 24 mmol) in ethyl ether (115 mL)/benzene (115 mL) containing nickel acetylacetonate (40 mg, 0.216 mmol). Cooling was continued for 2 h after addition was complete. The mixture was stirred overnight at room temperature and then quenched by slow addition of saturated aqueous NH_4Cl . The H_2O layer was extracted with ethyl ether. The organic layer was washed with water and dried over Na_2SO_4 . Removal of the solvent produced a dark oil which was chromatographed on silica gel (petroleum ether).

3,3'-Dimethylbiphenyl (mp 5-7 °C) eluted first as a clear oil. The next compound obtained was 1,8-di(*m*-tolyl)naphthalene (3.26 g, 44%), a clear oil; NMR (CDCl_3 , δ) 7.86 (d of d, 2H), 7.73-7.20 (m, 4H), 7.13-6.33 (bm, 8H), 2.03 (bs, 6H); *m/e* calcd for $\text{C}_{24}\text{H}_{20}$: 308.15649, obsd: 308.15716. *Anal.* Calcd for $\text{C}_{24}\text{H}_{20}$: C, 93.46; H, 6.54. Found: C, 93.30; H, 6.69. The third compound separated was 8,8'-di(*m*-tolyl)-1,1'-binaphthyl (0.68 g, 6.5%) as a fluorescent oil; NMR (CDCl_3 , δ) 7.70-6.78 (m, 12H), 6.76-5.87 (m, 8H), 19.3 (d, 6H); *m/e* calcd for $\text{C}_{34}\text{H}_{26}$: 434.20344, obsd: 434.20486.

5,6-Di(*m*-tolyl)acenaphthenequinone (19c). Aluminum chloride (3.6 g, 27 mmol) and then oxalyl chloride (3.6 mL, $D = 1.46$, 41 mmol) were added to stirred CS_2 (30 mL) cooled in an ice-salt mixture. 1,8-Bis(*m*-tolyl)naphthalene (3.8 g, 12 mmol) in CS_2 (40 mL) was then dropped into the cooled slurry in 0.5 h. The dark red solution was stirred at ice-salt temperatures for 2 h

and then at 20-25 °C for 1 h. Water was added slowly and the CS₂ was removed by heating. After cooling the residue, CH₂Cl₂ was added and the H₂O layer was extracted with CH₂Cl₂. The organic phase was washed with dilute aqueous HCl, then with aqueous NaHCO₃, and finally with saturated aqueous NaCl. Drying over Na₂SO₄ and evaporation of the solvent produced a dark yellow semi-solid which, after chromatography on silica gel (benzene), yielded **19c** (1.22 g, 28%, mp 277-279 °C) (benzene)) as light orange crystals; IR (KBr, cm⁻¹) 1724 (C=O, s); NMR (CDCl₃, δ) 7.98 (d of d, 4H), 7.13-6.53 (m, 8H), 2.06 (s, 6H); m/e calcd for C₂₆H₁₈O₂: 362.13067, obsd: 362.13143. *Anal.* Calcd for C₂₆H₁₈O₂: C, 86.16; H, 5.01. Found: C, 86.22; H, 5.14.

5,6-Di(*m*-tolyl)acenaphthenequinone 2-*p*-Tosylhydrazone (17c). A solution of **19c** (1.35 g, 3.7 mmol) in CH₃OH (30 mL) was refluxed. *p*-Tosylhydrazine (0.78 g, 4.1 mmol) was added and the resulting solution was boiled for 5 h. Upon cooling, yellow crystals formed which on filtration and drying were identified as **17c** (1.99 g, 100%, mp 199-201 °C); IR (KBr, cm⁻¹) 3180 (NH, w), 1685 (C=O, s), 1392, 1162 (SO₂, s); NMR (CDCl₃, δ) 8.10-7.10 (m, 8H), 7.10-6.32 (m, 8H), 2.37 (s, 3H), 2.06 (s, 6H). *Anal.* Calcd for C₃₃H₂₆N₂SO₃: H, 4.94; N, 5.28; S, 6.04. Found: H, 5.07; N, 5.67; S, 6.03.

2-Diazo-5,6-di(*m*-tolyl)acenaphthenone (11c). A CH₂Cl₂ (25 mL) solution of **17c** (0.4 g, 0.68 mmol) and aqueous NaOH (8.2 mL, 0.1 N, 0.82 mmol) was vigorously stirred overnight. The water layer was extracted several times with H₂O, dried over Na₂SO₄, and concentrated to dryness. Chromatography of the residue on silica gel (benzene) produced **11c** (0.25 g, 84%, mp 191-192.5 °C (benzene:petroleum ether)) as yellow crystals; IR (KBr, cm⁻¹) 2080 (=N₂, s), 1675 (C=O, s); NMR (CDCl₃, δ) 8.23-7.20 (m, 4H), 7.18-6.50 (m, 8H), 2.07 (s, 6H); m/e calcd for C₂₆H₁₈N₂O: 374.14190, obsd: 374.14100. *Anal.* Calcd for C₂₆H₁₈N₂O: C, 83.40; H, 4.85; N, 7.48. Found: C, 83.49; H, 4.87; N, 7.19.

Photolysis of 11c in CH₃OH (23a). A solution of **11c** (0.34 g, 0.9 mmol) in **23a** (225 mL) was photolyzed 1 h (the time of the photolysis was long because of the poor solubility of **11c** in

CH₃OH). Upon evaporation of the solvent, the crude photolysate exhibited no spectral evidence for methyl 4,5-di(*m*-tolyl)-1*H*-cyclobuta[de]naphthalene-1-carboxylate (**49b**) as possibly formed by trapping ketene **15c** by **23a**. Chromatography on silica gel (benzene) yielded two products:

(1) 5,6-di(*m*-tolyl)acenaphthenone (**48b**, 50 mg, 16%, mp 185.5-187 °C) which was recrystallized from benzene:hexane to give off-white needles; IR (KBr, cm⁻¹) 1717 (C=O, s); NMR (CDCl₃, δ) 7.65 (d of d, 2H), 7.43-7.07 (m, 2H), 6.97-6.26 (m, 8H), 3.74 (s, 2H), 1.93 (s, 6H); m/e calcd for C₂₆H₂₀O: 348.15141, obsd: 348.15094. *Anal.* Calcd for C₂₆H₂₀O: C, 89.62; H, 5.79. Found: C, 89.37; H, 5.91 and (2) 2-methoxy-5,6-di(*m*-tolyl)acenaphthenone (**47b**, 0.12 g, 36%, mp 270-272 °C) (benzene:hexane)), yellow crystals; IR (neat, cm⁻¹) 2812 (OCH₃, w), 1723 (C=O, s); NMR (CDCl₃, δ) 8.10-7.50 (m, 4H), 7.17-6.40 (bm, 8H), 5.20 (s, 1H), 3.70 (s, 3H), 2.10 (s, 6H); m/e calcd for C₂₇H₂₂O₂: 378.16197, obsd: 378.16152. *Anal.* Calcd for C₂₇H₂₂O₂: C, 85.68; H, 5.86. Found: C, 85.27; H, 6.36.

Photolysis of 11c in Benzene. Irradiation of a benzene (225 mL) solution of **11c** (0.4 g, 1.1 mmol) for 4 h and removal of solvent produced a dark orange semi-solid which was chromatographed on silica gel (benzene:petroleum ether 1:1).

First eluted was 2-phenyl-5,6-di(*m*-tolyl)acenaphthenone (**50b**, 60 mg, 13%), a yellow semi-solid; IR (CCl₄, cm⁻¹) 1723 (C=O, s); NMR (CDCl₃, δ) 7.83 (d of d, 2H), 7.60-6.41 (m, 10H), 7.32 (s, 5H), 4.97 (s, 1H), 2.10 (s, H); m/e calcd for C₃₂H₂₄O: 424.18270, obsd: 424.18164. *Anal.* Calcd for C₃₂H₂₄O: C, 90.53; H, 5.70. Found: C, 90.52; H, 5.70.

5,6-Di(*m*-tolyl)acenaphthenone (**48b**, 50 mg, 13%), previously characterized, was obtained next.

Further elution yielded *cis*-7a,11a-dihydro-3,4-bis(*m*-tolyl)acenaphtho[1,2-*b*]benzo[*d*]furan (**51b**, 0.18 g, 39%, mp 180-182 °C) which was recrystallized from benzene:hexane to give orange crystals; IR (KBr, cm⁻¹) 1629 (C=C, s); NMR (CDCl₃, δ) 8.76-5.46 (m, 16H), 3.17 (d, 2H), 2.10 (s, 6H); m/e calcd for C₃₂H₂₄O: 424.18270, obsd: 424.18164. *Anal.* Calcd for C₃₂H₂₄O: C, 90.53, H, 5.70. Found: C, 90.15; H, 5.83.

Thermolysis of 11c in Aniline. A mixture of **11c** (0.22 g, 0.59 mmol) and aniline (5 mL) under nitrogen was refluxed at ~ 180 °C for 1 h, cooled to room temperature, poured into a conc. HCl - ice slurry and then extracted several times with benzene. The benzene layer was dried over Na₂SO₄ and evaporated. Chromatography of the dark red semi-solid on silica gel (benzene) yielded 3,4-di(*m*-tolyl)acenaphth[1,2-*b*]indole (**53b**, 90 mg, 36%), a red film; IR (KBr, cm⁻¹) 3400 (NH, w); NMR (CDCl₃, δ) 8.23 (s, 1H), 8.04-6.53 (m, 16H), 2.03 (s, 6H); m/e calcd for C₃₂H₂₃N: 421.18304, obsd: 421.18196. *Anal.* Calcd for C₃₂H₂₃N: N, 3.32. Found: N, 3.06.

Next to be eluted was **19c** (70 mg, 32%) as previously characterized, along with intractables.

Thermal Decomposition of 11c. Finely-ground **11c** (0.2 g, 0.53 mmol) was vacuum-pyrolyzed (~ 450 °C/0.15 mm Hg) as described for **11a**. Evaporation of the **23a** in the condensate produced a brown solid which was chromatographed on silica gel (benzene) to yield reduction product **48b** (20 mg, 11%, mp 185.5-187 °C) as previously characterized.

Thermolysis of 11c in Dimethyl Acetylenedicarboxylate. A toluene (15 mL) solution of **11c** (0.1 g, 0.27 mmol) and dimethyl acetylenedicarboxylate (1 mL) was refluxed 9 h. Concentration to a small volume and filtration of the resulting yellow fluorescent precipitate yielded dimethyl 3,4-di(*m*-tolyl)-7-oxo-7*H*-benzo[*de*]pyrazolo[5,1-*a*]isoquinoline-10,11-dicarboxylate (**69i**, 0.14 g, 100%, mp 234-236 °C) after recrystallization from benzene:hexane; IR (KBr, cm⁻¹) 1736, 1720 (C=O, s); NMR (CDCl₃, δ) 8.98 (d of d, 2H), 7.94-7.58 (m, 2H), 7.20-6.54 (m, 8H), 4.07 (s, 6H), 2.12 (s, 6H); m/e calcd for C₃₂H₂₄N₂O₅: 516.16851, obsd: 516.16988. *Anal.* Calcd for C₃₂H₂₄N₂O₅: N, 5.42. Found: N, 5.47.

5,6-Dinitroacenaphthenequinone (19d). Acenaphthenequinone (**19e**, 2.0 g, 11 mmol) in conc. H₂SO₄ (30 mL) was cooled to 0 °C. A solution of conc. HNO₃ (1.5 mL, 70%, D = 1.42, 24 mmol) in conc. H₂SO₄ (4 mL) was added dropwise to the mixture keeping the temperature at 0-5 °C. After the addition, the mixture was warmed to 65 °C for 3 h and then poured into ice/H₂O. The precipitate that formed was filtered, washed with H₂O, and dried to give yellow-orange crystals

of 5,6-dinitroacenaphthenequinone (**19d**, 2.43 g, 81%, mp 300 °C (toluene/CH₃CN); lit.² mp 300 °C); IR (KBr, cm⁻¹) 1765, 1750 (C=O, s), 1545, 1370 (NO₂, s); m/e calcd for C₁₂H₄N₂O₆: 272.00693, obsd: 272.0756.

5,6-Dinitroacenaphthenequinone 2-*p*-Tosylhydrazone (17d). A suspension of **19d** (1.0 g, 3.67 mmol) and *p*-tosylhydrazine (0.753 g, 4.03 mmol) in tetrahydrofuran (15 mL) was refluxed 4 h. The yellow crystals which separated on cooling were filtered and recrystallized from toluene/CH₃CN to give **17d** (1.36 g, 84%; mp 213 °C (dec.)); IR (KBr, cm⁻¹) 3200 (NH, w), 1700 (C=O, s), 1535, 1370 (NO₂, s), 1350, 1170 (SO₂, s). *Anal.* Calcd for C₁₉H₁₂N₄O₇S: S, 7.32. Found: S, 7.17.

2-Diazo-5,6-dinitroacenaphthenone (11d). A CH₂Cl₂ (200 mL) solution of **17d** (4.0 g, 9.1 mmol) and aqueous NaOH (100 mL, 0.1 N, 10 mmol) was vigorously stirred for 9 h. The CH₂Cl₂ layer was separated, washed with H₂O, and dried over CaCl₂ to give **11d** (2.0 g, 78%, mp 234-236 °C (dec.)(toluene/CH₃CN)) as orange needles; IR (KBr, cm⁻¹) 2100 (=N₂, s), 1700 (C=O, s), 1540, 1370 (NO₂, s); NMR (CDCl₃ + DMSO-d₆, δ) 8.39 (d, 1H), 8.37 (d, 1H), 8.17 (d, 1H), 7.43 (d, 1H); m/e calcd for C₁₂H₄N₄O₅: 284.01816, obsd: 284.01897. *Anal.* Calcd for C₁₂H₄N₄O₅: C, 50.70; H, 1.41; N, 19.72. Found: C, 51.14; H, 1.78; N, 20.00.

Photolysis of 11d in Benzene. A benzene solution of **11d** (0.4 g, 1.4 mmol) under N₂ was photolyzed 5 h. Removal of benzene, chromatography (silica gel, CHCl₃), and handling led to isolation of 2-hydroxy-5,6-dinitro-2-phenylacenaphthenone (**60**, 0.232 g, 45%, mp 227-229 °C (dec.)(toluene/CH₃CN)) as yellow crystals; IR (KBr, cm⁻¹) 3440 (broad, OH), 1730 (C=O, s), 1530, 1350 (NO₂, s); NMR (CDCl₃, δ) 8.6-8.46 (m, 2H), 8.20 (d, 1H), 7.76 (d, 1H), 7.32 (s, 5H), 5.26 (s, 1H, OH); m/e calcd for C₁₈H₁₀N₂O₆: 350.05388, obsd: 350.05455. *Anal.* Calcd for C₁₈H₁₀N₂O₆: C, 61.71; H, 2.86; N, 8.00. Found: C, 61.72; H, 3.14; N, 7.95.

Photolysis of 11d in Acetonitrile. Diazoacenaphthenone **11d** (0.4 g, 1.4 mmol) was photolyzed in CH₃CN for 6 h. The solvent was removed at reduced pressure and chromatography of the residue on silica gel (tetrahydrofuran) yielded brown crystals of 8-methyl-(3,4-

dinitroacenaphth)[1,2-*d*]oxazole (**61a**, 0.282 g, 67.4%, mp 275 °C (dec.)(toluene/CH₃CN)); IR (KBr, cm⁻¹) 1530, 1360 (NO₂, s); NMR (CDCl₃ + DMSO-*d*₆, δ) 8.18 (d, 2H), 7.82 (d, 2H), 3.04 (s, 3H); *m/e* calcd for C₁₄H₇N₃O₅: 297.03856, obsd: 297.03907. *Anal.* Calcd for C₁₄H₇N₃O₅: C, 56.56; H, 2.36; N, 14.14. Found: C, 56.73; H, 2.56; N, 13.88.

Photolysis of 11d in Benzonitrile. A solution of **11d** (0.427 g, 1.49 mmol) in benzonitrile was photolyzed 5 h. Upon removing the benzonitrile under vacuum, the residue was chromatographed (silica gel, benzene). 3,4-Dinitro-8-phenylacenaphth[1,2-*d*]oxazole (**61b**, 0.142 g, 26.2%, mp 283-286 °C (dec.)(toluene/CH₃CN)), brown crystals, was the only isolable product; IR (KBr, cm⁻¹) 1530, 1360 (NO₂, s); *m/e* calcd for C₁₉H₉N₃O₅: 359.05421, obsd: 359.05492. *Anal.* Calcd for C₁₉H₉N₃O₅: C, 63.51; H, 2.51; N, 11.70. Found: C, 63.71; H, 2.65; N, 11.92.

Photolysis of 11d in Phenylacetylene. A solution of **11d** (0.5 g, 1.75 mmol) in phenylacetylene was irradiated 2 h and then concentrated under vacuum. Chromatography (silica gel, CHCl₃) of the residue yielded 3,4-dinitro-8-phenylacenaphtho[1,2-*b*]furan (**70b**, 0.3 g, 48%, mp 267-270 °C (ethyl acetate)) as black crystals; IR (KBr, cm⁻¹) 1530, 1360 (NO₂, s); *m/e* calcd for C₂₀H₁₀N₂O₅: 358.05896, obsd: 358.05969. *Anal.* Calcd for C₂₀H₁₀N₂O₅: C, 67.04; H, 2.79; N, 7.82. Found: C, 67.34; H, 2.98; N, 7.76.

Thermolysis of 11d in Dimethyl Acetylenedicarboxylate. A mixture of **11d** (0.163 g, 0.57 mmol) and dimethyl acetylenedicarboxylate (1 mL) in chlorobenzene (20 mL) was refluxed 20 h. Upon removal of the solvents under vacuum, the residue was chromatographed (silica gel, CHCl₃). Dimethyl 3,4-dinitro-7-oxo-7*H*-benzo[*de*]pyrazolo-[5,1-*a*]isoquinoline-10,11-dicarboxylate (**69j**, 0.2 g, 83%, mp 290-293 °C (toluene/CH₃CN)), yellow crystals, was the only isolable product; IR (KBr, cm⁻¹) 1740 (C=O, s), 1550, 1350 (NO₂, s); *m/e* calcd for C₁₈H₁₀N₄O₉: 426.04477, obsd: 426.04537. *Anal.* Calcd for C₁₈H₁₀N₄O₉: C, 50.70; H, 2.35; N, 13.14. Found: C, 51.28; H, 2.29; N, 12.70.

2,7-Dimethoxynaphthalene. Dimethyl sulfate (20 mL) was added slowly to a vigorously stirred

cold solution of 2,7-dihydroxynaphthalene (16.0 g, 0.1 mmol) in 10% aqueous NaOH (90 mL).

The thick yellow-green mixture was stirred for 2 h. After addition of H₂O (200 mL) to the mixture, the gray precipitate that formed was filtered, washed with H₂O until the filtrate was colorless, and dried to give 2,7-dimethoxynaphthalene (18.14 g, 96.5%, mp 134-136 °C (hexane/toluene); lit.³ mp 135 °C).

3,8-Dimethoxyacenaphthenequinone (20). A stirred mixture of 2,7-dimethoxynaphthalene (10.0 g, 53.2 mmol), anhydrous AlCl₃ (10.0 g), and CS₂ (100 mL) was cooled to 0 °C and oxalyl chloride (30 mL) was added keeping the temperature at 0-5 °C. The mixture was then stirred at 25 °C overnight, poured into ice/H₂O, and then heated to remove the CS₂. The orange gummy product which separated on cooling was dissolved in CH₂Cl₂ and washed with H₂O. Evaporation of the solvent and recrystallization from toluene/CH₃CN gave **20** (1.82 g, 14%, mp 278 °C, lit.⁴ mp 279 °C); IR (KBr, cm⁻¹) 1730, 1715 (C=O, s); m/e calcd for C₁₄H₁₀O₄: 242.05790, obsd: 242.05860.

3,8-Dimethoxyacenaphthenequinone 2-*p*-Tosylhydrazone (18). A mixture of **12** (6.14 g, 25.4 mmol) and *p*-tosylhydrazine (5.21 g, 28 mmol) in tetrahydrofuran (60 mL) containing concentrated HCl (3 mL) was refluxed until a clear solution (~ 4 h) was obtained. The mixture was cooled and the yellow crystals were filtered to yield **18** (8.30 g, 80%, mp 173-175 °C (dec.)(tetrahydrofuran)); IR (KBr, cm⁻¹) 3150 (NH, w), 1680 C=O, s), 1360, 1170 (SO₂, s). *Anal.* Calcd for C₂₁H₁₈N₂O₅S: C, 61.46; H, 4.39; N, 6.83; S, 7.80. Found: C, 61.65; H, 4.49; N, 6.82; S, 7.83.

2-Diazo-3,8-dimethoxyacenaphthenone (12). Sodium methoxide (0.6 g, 11.1 mmol) was added to a dry CH₂Cl₂ (100 mL) solution of **18** (3.0 g, 7.3 mmol) and the mixture was stirred overnight. After addition of H₂O, the CH₂Cl₂ layer was separated and dried over CaCl₂. The residue after solvent removal and chromatography (silica gel, benzene/CHCl₃ 1:1) gave orange crystals of **12** (0.924 g, 64%, mp 145-146 °C (toluene)); IR (KBr, cm⁻¹) 2100 (=N₂, s), 1670 (C=O, s); NMR (CDCl₃, δ) 7.87 (d, 1H), 7.56 (d, 1H), 7.07 (d, 2H), 4.14 (s, 3H), 3.95 (s, 3H).

Anal. Calcd for $C_{14}H_{10}N_2O_3$: C, 66.14; H, 3.93; N, 11.02. Found: C, 66.13; H, 4.06; N, 11.30.

Photolysis of 12 in CH_3OH (23a). A solution of **12** (0.4 g, 1.57 mmol) was irradiated in **23a** for 3 h. The residue obtained after removing the **23a** was chromatographed on silica gel ($CHCl_3$) to give 2,3,8-trimethoxyacenaphthenone (**63**, 0.318 g, 78%, mp 130-132 °C (toluene)); IR (KBr, cm^{-1}) 1720 (C=O, s), 1620, 1600 (C=C, s), 1370, 1350, 1330 (CH_3 , m), 1170, 1100, 1050 (C-O, s); NMR ($CDCl_3$, δ) 7.96 (d, 1H), 7.76 (d, 1H), 7.17 (d, 1H), 7.12 (d, 1H), 5.05 (s, 1H), 4.10 (s, 3H), 4.06 (s, 3H), 3.53 (s, 3H); m/e calcd for $C_{15}H_{14}O_4$: 258.08920, obsd: 258.08966. *Anal.* Calcd for $C_{15}H_{14}O_4$: C, 69.76; H, 5.43. Found: C, 69.98; H, 5.22.

Photolysis of 12 in Tetrahydrofuran. Diazoacenaphthenone **12** (0.4 g, 1.57 mmol) was dissolved in tetrahydrofuran and photolyzed for 2.5 h. Removal of solvent and chromatography on silica gel (benzene/ $CHCl_3$ 1:1) yielded spiro[3,8-dimethoxyacenaphthenone-2,2'-tetrahydropyran] (**64**, 0.25 g, 53%, mp 135-138 °C (ethyl ether)) as pale yellow crystals; IR (KBr, cm^{-1}) 1700 (C=O, s), 1350, 1370 (CH_3 , w), 1170, 1050 (C-O, s); NMR ($CDCl_3$, δ) 7.95 (d, 1H), 7.75 (d, 1H), 7.20 (d, 1H), 7.14 (d, 1H), 4.09 (s, 3H), 4.01 (s, 3H), 2.6-1.7 (m, 8H); m/e calcd for $C_{18}H_{18}O_4$: 298.12049, obsd: 298.12116. *Anal.* Calcd for $C_{18}H_{18}O_4$: C, 72.48; H, 6.04. Found: C, 72.26; H, 6.15.

References

1. (a) Clough, R. L.; Mison, P.; Roberts, J. D. *J. Org. Chem.* **1976**, *41*, 2252. (b) Bossenbroek, B.; Sanders, D. C.; Curry, H. M.; Shechter, H. *J. Am. Chem. Soc.* **1969**, *91*, 371. (c) House, H. O.; Koepsell, D.; Cambell, W. J. *J. Org. Chem.* **1972**, *37*, 1003.
2. (a) Ruhemann, S.; *Chem. Ber.* **1920**, *52B*, 287. (b) Rowe, F. M.; Davis, J. H. S. *J. Chem. Soc.* **1920**, 1344.
3. Ullmann, F. *Liebigs Ann. Chem.* **1903**, 327, 117.
4. Staudinger, H.; Goldstein, H.; Schlenker, E. *Helv. Chim. Acta.* **1921**, *4*, 342.