Diels–Alder Reactions of Ethyl [10-(Methoxyimino)phenanthren-9-ylidene]acetate with Dienophiles. Synthesis of Dibenzo[*f,h*]quinoline and Dibenzo[*a,c*]acridine Derivatives

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[10-(Methoxyimino)phenanthren-9-ylidene]acetates **3(I,II)**, prepared by Wittig olefination of 10-(methoxyimino)phenanthren-9-one (**1**) with ylide **2**, were transformed by means of a [4 + 2] cycloaddition and methanol elimination to stable spiro-compound **5**. In addition, the use of compounds **3** as heterodienes in Diels–Alder reactions with various electron-deficient dienophiles **6a,b**, **10a–c**, and **14** led to the synthesis of nitrogen-containing polycycles **8a,b**, **11a–c**, **12b,c**, **13b,c**, and **16**.

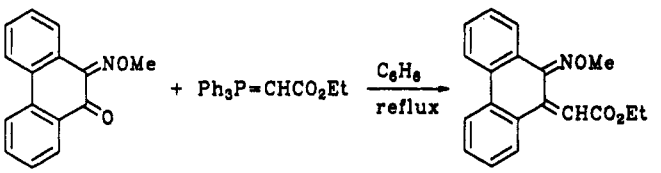
Diels–Alder cycloadditions of *o*-quinone methide imines provide a convenient method for the synthesis of nitrogen-containing polycycles.[1–10] These 1-aza-1,3-butadiene derivatives are generally unstable intermediates and are formed in situ by photolysis, pyrolysis, or thermolysis of various heterocycles such as *N*-phenyloxindole,[1] 2,1-benzisothiazoline 2,2-dioxides,[2,3] *o*-(hydroxymethyl)anilines,[4] dihydrobenzoxazinones[5–7] and also by treatment of *o*-[*N*-alkyl-*N*-(trimethylsilyl)amino]benzyltrimethylammonium salts with CsF.[8–10] In the absence of trapping agents, the azabutadiene derivatives are converted to benzazetidines[1,2] and/or to dimeric spirotetrahydroquinoline derivatives.[1,8]

Although 1-aza-1,3-butadienes with an oxime group in the conjugated system are well known, only in a few cases have the Diels–Alder reactions of these electron-rich dienes with either electron-deficient[11,12] or electron-rich[13] dienophiles been attempted. A few successful reactions with mainly *N*-methoxy derivatives of *o*-benzoquinone methide imines have also been reported.[14,15]

The work detailed here involves the preparation of ethyl [10-(methoxyimino)phenanthren-9-ylidene]acetates **3** via a Wittig olefination of compound **1** with [(ethoxycarbonyl)-methylene] (triphenyl)phosphorane (**2**), the thermal dimerization of **3**, and the reactions of **3** with several electron-deficient dienophiles.

Treatment of known[15] 10-(methoxyimino)phenanthren-9-one **1** with equimolar phosphorous ylide **2** (Scheme 1)

Scheme 1



1 **2** **3(I+II)**

afforded two isomeric ethyl [10-(methoxyimino)phenanthren-9-ylidene]acetates **3(I)** and **3(II)** in 32 and 30% yield, respectively. The configurations of the isomers cannot be assigned with certainty.

Prolonged heating at their melting points transformed both stable isomers **3** to stable spiro-derivative **5**. The formation of **5** most probably involves the intermediacy of [4 + 2] cycloadduct spiro-dimer **4**; elimination of methanol from **4** leads to **5**. Analogous dimerizations were also observed for some unstable *o*-quinone methide imines.[1,8,16] The formation of the other possible intermediate, regio-dimer **4'** was excluded because the intermediacy of **4'** cannot explain the presence of the NH function in final spiro-product **5** (Scheme 2). In contrast to other spiro-dimers, which decompose on standing[8] or are converted to isomeric aniline derivatives,[16] spiro-compound **5** is very stable, possibly because the presence of the olefinic double bond prevents a retro Diels–Alder opening of the N-heterocycle.

Treatment of compound **3(I)** with 1,4-naphthoquinone **6a** gave ethyl 9,10,15,16-tetrahydro-10,15-dioxotribenzo-[*a,c,i*]acridine-16-carboxylate (**8a**) in 65% yield, most probably by means of the elimination of methanol from initially formed Diels–Alder cycloproduct **7a** (Scheme 3). Similarly, the reaction of isomer **3(II)** with **6a** afforded compound **8a** in 66% yield. In an analogous reaction of a mixture of isomers **3(I)** and **3(II)** with 1,4-benzoquinone, ethyl 9,10,13,14-tetrahydro-10,13-dioxodibenzo[*a,c*]acridine-14-carboxylate (**8b**) was obtained in 28% yield. When **8a** was treated with NBS, derivative **9a** (98%) was isolated (Scheme 3).

Next, the reaction of compound **3(II)** with maleic anhydride (**10a**) was studied (Scheme 4). 4-(Ethoxycarbonyl)-1*H*,4*H*-dibenzo[*f,h*]quinoline-2,3-dicarboxylic acid

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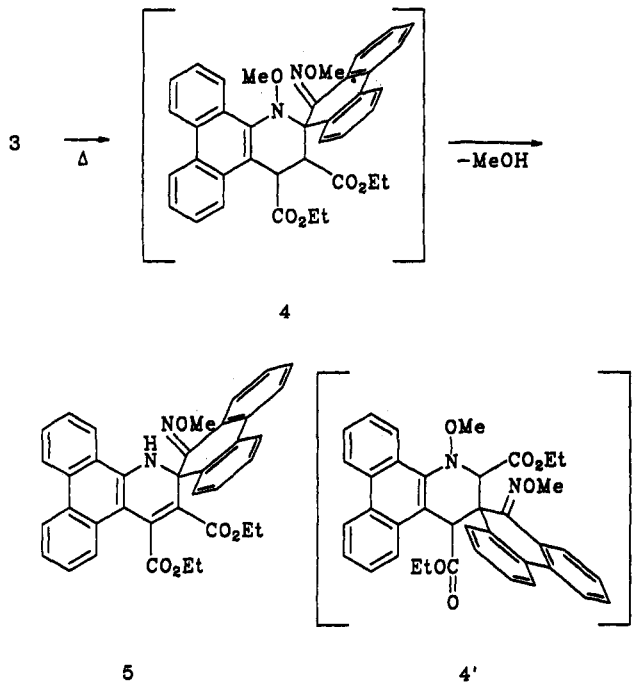
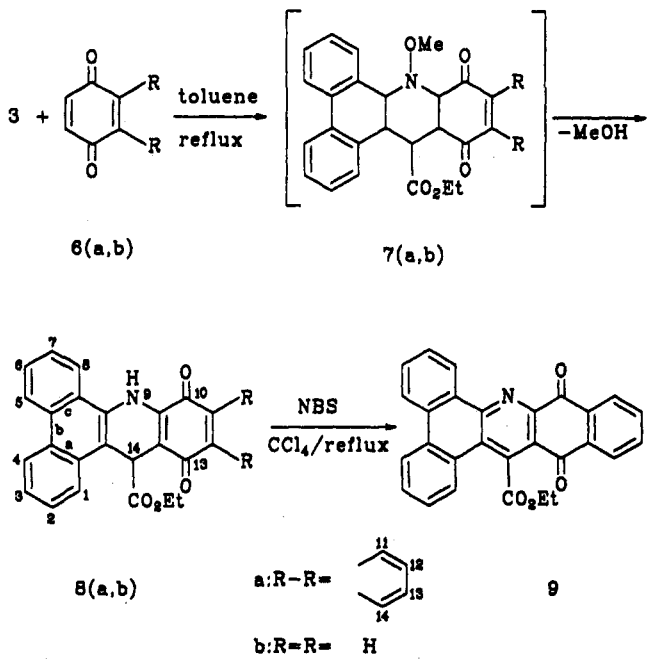
Scheme 2

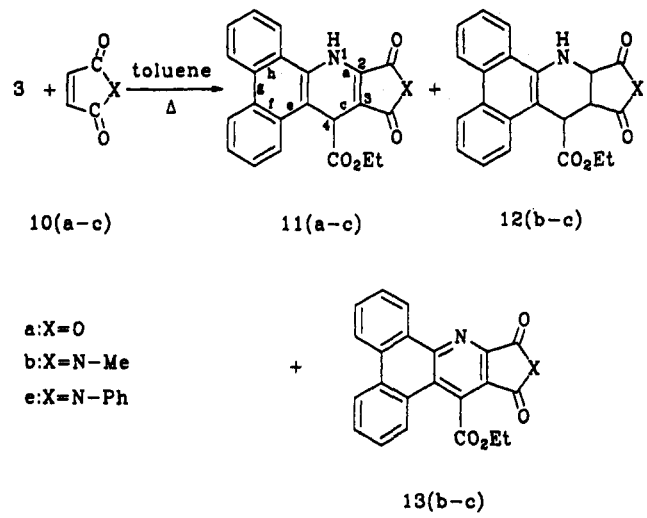


Scheme 3

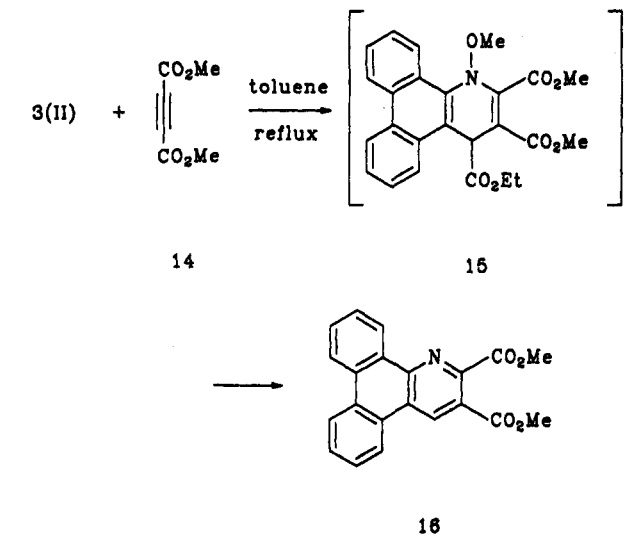


anhydride (**11a**) was isolated in 62% yield. When **3(II)** was treated with *N*-methylmaleimide (**10b**) (Scheme 4), compound **12b** was obtained as the main reaction product in 77% yield, along with expected product **11b** (5%) and fully aromatic derivative **13b** (13%). Similarly, isomer **3(I)** afforded with **10b**, compounds **11b** (4%), **12b** (78%), and **13b** (7%). In an analogous reaction of a mixture of **3(I)** and **3(II)** with *N*-phenylmaleimide (**10c**), only **11c** (5%) and **12c** (45%) were obtained. Compounds **11a–c** are most probably formed via elimination of methanol from the initially formed Diels–Alder cycloproducts, and compound **13b** is formed by air-oxidation of **11b**. Treatment of **12b** with NBS afforded **13b** in 46% yield. A similar treatment of **11c** afforded **13c** in 58% yield. More information is necessary to explain the unexpected formation of compounds **12b,c**. The formation of **12b,c** by further reduction of **11b,c** could be excluded because when

Scheme 4



Scheme 5



the reactions between **3** and **10b,c** were followed by TLC, the formation of compounds **12** was detected before the appearance of **11**. In addition, in a control experiment, compound **12b** could not be converted to **11b** and/or **13b** even by prolonged heating. The above observations could be explained by assuming that a substitution of the methoxy group in compounds **3** with a hydrogen probably proceeds before the reaction of **3** with **10b,c**.

In order to exclude the participation of the solvent in the formation of products **12**, we repeated the reactions of compounds **3(I)** and **3(II)** with **10b** in refluxing dry benzene. In addition, the reactions of **3(I)** and **3(II)** with **10c** were carried out without solvent, by heating the mixture of compounds at 120 °C. TLC examination of the above reaction mixtures showed in all cases mainly the presence of tetrahydro-derivative **12b**.

Furthermore, treatment of **3(II)** with dimethyl acetylenedicarboxylate (**14**) (Scheme 5) resulted in the formation of unexpected dimethyl dibenzo[*f,h*]quinoline-2,3-dicarboxylate **16** in 52% yield, most probably by methanol elimination and decarboethoxylation[17] of initially formed cycloproduct **15**.

In conclusion, stable and easily prepared *N*-methoxy-*o*-quinone methide imines **3** can be successfully used as 1-aza-1,3-dienes in Diels–Alder reactions with electron-

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deficient dienophiles for the preparation of the title compounds. In addition, the easy methanol elimination from the initially formed cycloadducts favors their further transformation to more unsaturated systems.

Experimental Section

All melting points are uncorrected. NMR spectra were obtained in $CDCl_3$. Chemical shifts are given in ppm from Me_4Si. Mass spectra were recorded at 70 eV.

10-(Methoxyimino)phenanthren-9-one was prepared as described.[18]

Ethyl [10-(Methoxyimino)phenanthren-9-ylidene]acetate (3). A solution of 10-(methoxyimino)phenanthrene-9-one (1) (2.37 g, 0.01 mol) and ylide 2 (3.47 g, 0.01 mol) was refluxed in benzene (85 mL) for 72 h. The solvent was evaporated, and the residue was chromatographed (silica gel, CH_2Cl_2). Ethyl [10-(methoxyimino)phenanthen-9-ylidene]acetate [3(I)] was eluted first (982 mg, 32%): mp 117–118 °C (from *n*-hexane/ethyl acetate); IR (Nujol) 1700 cm^{-1}; ^1H NMR δ 1.26 (t, 3H, J = 7 Hz), 4.08 (s, 3H), 4.23 (q, 2H, J = 7 Hz), 6.37 (s, 1H), 7.15–8.07 (m, 7H), 8.33–8.47 (m, 1H); mass spectrum m/z (rel inten) 307 (M^+, 22), 292 (55), 262 (39), 246 (100), 219 (64), 203 (61), 190 (64), 176 (45). Anal. Calcd for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.58; N, 4.56. Found: C, 74.40; H, 5.46; N, 4.59. Isomer 3(II) was eluted second (921 mg, 30%): mp 130–131 °C (from *n*-hexane/ethyl acetate); IR (Nujol) 1710 cm^{-1}; ^1H NMR δ 1.33 (t, 3H, J = 7 Hz), 4.01 (s, 3H), 4.27 (q, 2H, J = 7 Hz), 6.37 (s, 1H), 7.23–8.07 (m, 7H), 8.30–8.44 (m, 1H); mass spectrum m/z (rel inten) 307 (M^+, 36), 292 (60), 264 (25), 262 (43), 246 (100), 219 (59), 203 (61), 190 (53), 176 (37). Anal. Calcd for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.58; N, 4.56. Found: C, 74.40; H, 5.46; N, 4.59.

Cyclodimerization of 3(I). A sample of 3(I) (102 mg, 0.33 mmol) was heated in an oil bath at 140 °C for 18 h. The reaction mixture was separated by preparative TLC (silica gel, 5:1 *n*-hexane/ethyl acetate) to give spiro-compound 5 (50 mg, 50%): mp 201–203 °C (from ether); IR (Nujol) 3380, 1735, 1720 cm^{-1}; ^1H NMR δ 0.89 (t, 3H, J = 7 Hz), 0.96 (t, 3H, J = 7 Hz), 3.36 (q, 2H, J = 7 Hz), 3.83 (q, 2H, J = 7 Hz), 4.04 (s, 3H), 4.55 (br s, 1H), 6.60–8.32 (m, 14H), 8.55–8.87 (m, 2H); mass spectrum m/z (rel inten) 582 (M^+, 100), 550 (35), 535 (8), 507 (16), 477 (99), 432 (86), 190 (53), 176 (17). Anal. Calcd for $C_{37}H_{30}N_2O_5$: C, 76.27; H, 5.19; N, 4.82. Found: C, 76.06; H, 5.12; N, 4.64.

Cyclodimerization of 3(II). The reaction of 3(II) was carried out as described above for 3(I). Spiro-dimer 5 was again isolated in 50% yield.

Reaction of 3(I) with 1,4-Naphthoquinone (6a). A solution of 3(I) (307 mg, 1 mmol) and 1,4-naphthoquinone (158 mg, 1 mmol) in toluene (4 mL) was refluxed for 6 h. The solvent was evaporated, and the residue was chromatographed (silica gel, *n*-hexane/ethyl acetate [1:1 to 1:2]) to give purple crystals of **ethyl 9,10,15,16-tetrahydro-10,15-dioxotribenzo[*a,c,i*]acridine-16-carboxylate (8a)** (281 mg, 65%): mp 245–247 °C (from CH_2Cl_2/*n*-hexane); IR (Nujol) 3390, 1750, 1660 cm^{-1}; ^1H NMR δ 1.04 (t, 3H, J = 7 Hz), 3.99 (q, 2H, J = 7 Hz), 5.69 (s, 1H), 7.12–8.89 (m, 12H); mass spectrum m/z (rel inten) 433 (M^+, 15), 432 (20), 431 (10), 403 (7), 386 (18), 358 (44), 302 (100). Anal. Calcd for $C_{28}H_{19}NO_4$: C, 77.58; H, 4.42; N, 3.23. Found: C, 77.67; H, 4.38; N, 3.30.

Reaction of 3(II) with 6a. The reaction of 3(II) was carried out as described above for 3(I). Ester 8a was again isolated in 66% yield.

Ethyl 10,15-Dihydro-10,15-dioxotribenzo[*a,c,i*]acridine-16-carboxylate (9a). NBS (18 mg, 0.1 mmol) and benzoyl peroxide (2.4 mg, 0.01 mmol) were added to a solution of ester 8a (43 mg, 0.1 mmol) in 10 mL of dry CCl_4. The mixture was heated under reflux for 2 h and filtered while hot. Evaporation of the solvent left an oil, which was chromatographed (silica gel, 2:1 *n*-hexane/ethyl acetate) to give 9a (42 mg, 98%): mp 216–218 °C (from benzene/*n*-hexane); IR (Nujol) 1725, 1680 cm^{-1}; ^1H NMR δ 1.47 (t, 3H, J = 7 Hz), 4.73 (q, 2H, J = 7 Hz), 7.32–8.12 (m, 6H), 8.18–8.81 (m, 5H), 9.35–9.68 (m, 1H); mass spectrum m/z (rel inten) 431 (M^+, 100), 402 (30), 386 (87), 359 (55), 331 (17), 301 (51). Anal. Calcd for $C_{28}H_{17}NO_4$: C, 77.95; H, 3.97; N, 3.25. Found: C, 78.00; H, 4.00; N, 3.34.

Reaction of 3(I,II) with 1,4-Benzoquinone (6b). A solution of a mixture of isomers 3(I) and 3(II) (307 mg, 1 mmol) and 1,2-benzoquinone (540 mg, 5 mmol) in toluene (7 mL) was refluxed for 3 h. The solvent was evaporated, and the residue was chromatographed (silica gel, CH_2Cl_2) to give ethyl **9,10,13,14-tetrahydro-10,13-dioxodibenzo[*a,c*]acridine-14-carboxylate (8b)**, (107 mg, 28%): mp 194–196 °C (from CH_2Cl_2/*n*-hexane); IR (Nujol) 3360, 1720, 1660 cm^{-1}; ^1H NMR δ 1.07 (t, 3H, J = 7 Hz), 1.56 (brs, 1H, D_2O exchangeable), 4.03 (q, 2H, J = 7 Hz), 5.71 (s, 1H), 6.74 (s, 2H), 7.20–9.10 (m, 8H); mass spectrum m/z (rel inten) 383 (M^+, 2), 337 (37), 312 (100). Anal. Calcd for $C_{24}H_{17}NO_4$: C, 75.18; H, 4.47; N, 3.65. Found: C, 75.48; H, 4.49; N, 3.65.

Reaction of 3(II) with Maleic Anhydride (10a). A solution of 3(II) (61 mg, 0.2 mmol) and maleic anhydride (10a) (40 mg, 0.4 mmol) in toluene (10 mL) was refluxed for 48 h. When the reaction mixture cooled, white crystals of product 11a precipitated (40 mg, 62%): mp 279–282 °C; IR (Nujol) 3290, 1840, 1780, 1770, 1720 cm^{-1}; ^1H NMR δ 1.10 (t, 3H, J = 7 Hz), 4.13 (q, 2H, J = 7 Hz), 5.53 (s, 1H), 7.33–9.08 (m, 8H), 9.85 (brs, 1H); mass spectrum m/z (rel inten) 373 (M^+, 22), 301 (67), 300 (100), 272 (25), 256 (19), 228 (72). Anal. Calcd for $C_{22}H_{15}NO_5$: C, 70.77; H, 4.05; N, 3.75. Found: C, 71.01; H, 4.17; N, 3.72.

Reaction of 3(I) with *N*-Methylmaleimide (10b). A solution of 3(I) (307 mg, 1 mmol) and *N*-methylmaleimide (111 mg, 1 mmol) in toluene (2 mL) was refluxed for 28 h. The solvent was evaporated, and the residue was chromatographed (silica gel, 3:1 CH_2Cl_2/*n*-hexane). **4-(Ethoxycarbonyl)dibenzo[*f,h*]quinoline-2,3-dicarboxylic acid *N*-methylimide (13b)** was eluted first (27 mg, 7%): mp 266–268 °C (from *n*-hexane/CH_2Cl_2); IR 1770, 1720 cm^{-1}; ^1H NMR δ 1.51 (t, 3H, J = 7 Hz), 3.34 (s, 3H), 4.72 (q, 2H, J = 7 Hz), 7.51–7.94 (m, 4H), 8.32–8.80 (m, 3H), 9.33–9.61 (m, 1H); mass spectrum m/z (rel inten) 384 (M^+, 100), 355 (44), 339 (35), 312 (90), 254 (45), 227 (74). Anal. Calcd for $C_{23}H_{16}N_2O_4$: C, 71.87; H, 4.20; N, 7.29. Found: C, 71.68; H, 4.08; N, 7.08. Then **4-(ethoxycarbonyl)-1,2,3,4-tetrahydrodibenzo[*f,h*]quinoline-2,3-dicarboxylic acid *N*-methylimide (12b)** and **4-(ethoxycarbonyl)-1*H*,4*H*-dibenzo[*f,h*]quinoline-2,3-dicarboxylic acid *N*-methylimide (11b)** were eluted as a mixture and were separated by a second column chromatography (silica gel, 1:1 *n*-hexane/ethyl acetate). Compound 11b was eluted first (15 mg, 4%): mp 242–245 °C; IR (Nujol) 3390, 1785, 1705 cm^{-1}; ^1H NMR δ 1.21 (t, 3H, J = 7 Hz), 1.53 (brs, 1H), 3.07 (s, 3H), 4.16 (q, 2H, J = 7 Hz), 5.59 (s, 1H), 7.30–8.17 (m, 5H), 8.50–8.80 (m, 3H); mass spectrum m/z (rel inten) 386 (M^+, 5), 384 (2), 355 (1), 339 (1), 313 (100), 254 (7), 228 (30). Anal. Calcd for $C_{23}H_{18}N_2O_4$: C, 71.49; H, 4.70; N, 7.25. Found: C, 71.22; H, 4.84; N, 7.36. Compound 12b was eluted second (303 mg, 78%): mp 115–117 °C (from *n*-hexane/ethyl acetate); IR (Nujol) 3380, 1780, 1700 cm^{-1}; ^1H NMR δ 1.01 (t, 3H, J = 7 Hz), 2.73 (s, 3H), 4.08 (q, 2H, J = 7 Hz), 4.28 (d, 1H, J = 10 Hz), 4.60 (dd, 1H, J = 10 and 1 Hz), 5.13 (d, 1H, J = 1 Hz), 5.31 (brs, 1H, D_2O exchangeable), 7.09–8.34 (m, 6H), 8.38–8.87 (m, 2H); mass spectrum m/z (rel inten), 388 (M^+, 53), 315 (75), 230 (100). Anal. Calcd for $C_{23}H_{20}N_2O_4$: C, 71.12; H, 5.19; N, 7.21. Found: C, 71.06; H, 5.18; N, 7.07.

When the reaction of 3(I) was repeated with two equivalents of *N*-methylmaleimide (10b) under otherwise identical reaction conditions, products 11b, 12b, and 13b were again isolated in 4, 76, and 8% yields, respectively.

Reaction of 3(II) with *N*-Methylmaleimide (10b). The reaction of 3(II) was carried out as described above for 3(I). Products 11b, 12b, and 13b were again isolated in 5, 77, and 13% yields, respectively.

Reaction of 12b with NBS. The reaction was carried out as described above for 9a by heating 12b with NBS for 12 h to give compound 13b in 46% yield.

Reaction of a Mixture of 3(I) and 3(II) with *N*-Phenylmaleimide (10c). A solution of a mixture of 3(I) and 3(II) (307 mg, 1 mmol) and *N*-phenylmaleimide (173 mg, 1 mmol) in toluene (10 mL) was refluxed for 14 h. The solvent was evaporated, and the residue was chromatographed (silica gel, 3:1 CH_2Cl_2/*n*-hexane). **4-(Ethoxycarbonyl)-1*H*,4*H*-dibenzo[*f,h*]quinoline-2,3-dicarboxylic acid *N*-phenylimide (11c)** was eluted first (23 mg, 5%): mp 246–249 °C (from ethyl acetate); IR (Nujol)

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3380, 1770, 1720, 1680 cm^{-1}; ^{1}H NMR δ 1.22 (t, 3H, J = 7 Hz), 1.59 (brs, 1H), 4.19 (q, 2H, J = 7 Hz), 5.63 (s, 1H), 7.43 (s, 5H), 7.58–8.19 (m, 6H), 8.60–8.35 (m, 2H); mass spectrum m/z (rel inten) 448 (M$^+$, <0.5), 375 (M$^+$ – 73, 100), 331 (10), 228 (12). Anal. Calcd for $C_{28}H_{20}N_2O_4$: C, 74.99; H, 4.50; N, 6.25. Found: C, 74.88; H, 4.40; N, 6.08. **4-(Ethoxycarbonyl)-1,2,3,4-tetrahydrodibenzo[*f,h*]quinoline-2,3-dicarboxylic acid *N*-phenylimide (12c)** was eluted second (203 mg, 45%): mp 107–109 °C (from ethanol/ethyl acetate); IR (Nujol) 3390; ^{1}H NMR δ 1.00 (t, 3H, J = 7 Hz), 4.09 (q, 2H, J = 7 Hz), 4.44 (d, 1H, J = 8.8 Hz), 4.76 (dd, 1H, J = 8.8 and 1 Hz), 5.23 (d, 1H, J = 1 Hz), 5.50 (br s, 1H, D_2O exchangeable), 6.70–8.25 (m, 11H), 8.45–8.79 (m, 2H); mass spectrum m/z (rel inten) 450 (M$^+$, 52), 337 (58), 230 (100). Anal. Calcd for $C_{28}H_{22}N_2O_4$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.61; H, 5.00; N, 6.14.

4-(Ethoxycarbonyl)dibenzo[*f,h*]quinoline-2,3-dicarboxylic Acid *N*-Phenylimide (13c). The reaction was carried out, as described above for **9a**, by adding NBS and benzoyl peroxide to compound **11c** in CCl_4 and heating for 1 h. Product **13c** was isolated after chromatography (silica gel, 3:1 CH_2Cl_2/*n*-hexane) in 58% yield; mp 289–290 °C (from CH_2Cl_2); IR (Nujol) 1780, 1725 cm^{-1}; ^{1}H NMR 1.60 (t, 3H, J = 8 Hz), 4.73 (q, 2H, J = 8 Hz), 7.54 (s, 5H), 7.68–8.21 (m, 4H), 8.31–8.94 (m, 3H), 9.42–9.80 (m, 1H); mass spectrum m/z (rel inten) 446 (M$^+$, 100), 417 (8), 401 (5), 373 (15), 299 (3), 227 (8). Anal. Calcd for $C_{28}H_{18}N_2O_4$: C, 75.32; H, 4.06; N, 6.28. Found: C, 75.33; H, 4.24; N, 6.08.

Reaction of 3(II) with Dimethyl Acetylenedicarboxylate (14). A solution of **3(II)** (61 mg, 0.2 mmol) and DMAD (50 mg, 0.35 mmol) in toluene (5 mL) was refluxed for 120 h. The solvent was evaporated, and the residue was chromatographed by preparative TLC (silica gel, 7:1 *n*-hexane/ethyl acetate) to give **dimethyl dibenzo[*f,h*]quinoline-2,3-dicarboxylate (16)** (35 mg, 52% yield): mp 174–176 °C; IR (Nujol) 1735, 1720 cm^{-1}; ^{1}H NMR δ 4.03 (s, 3H), 4.11 (s, 3H), 7.48–7.82 (m, 4H), 8.28–8.68 (m, 3H), 9.12–9.42 (m, 2H); mass spectrum m/z (rel inten) 345 (M$^+$, 100), 314 (11), 286 (14), 256 (14), 229 (98). Anal. Calcd for $C_{21}H_{15}NO_4$: C, 73.03; H, 4.38; N, 4.06. Found: C, 72.92; H, 4.27; N, 4.13.