Synthesis of 2,3-Dialkyl-6,7-dichloro- and 2,3-Dialkyl-6,7-dibromo-1,4-naphthoquinones

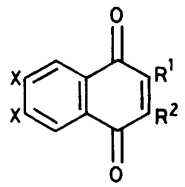
Alamdar Ashnagar, J. Malcolm Bruce,* and Paul Lloyd-Williams
Department of Chemistry, The University, Manchester M13 9PL

Thermal treatment of 1,4-benzoquinone and its 2-methyl and 2,3-dimethyl homologues with 3,4-dichlorothiophene 1,1-dioxide followed by oxidation affords the corresponding 6,7-dichloro-1,4-naphthoquinones; the parent compound and its 2-methyl homologue can be alkylated at the free quinonoid positions using the alkanoic acid–persulphate–silver ion system. Nitration of 2,3-dibromonaphthalene yields 2,3-dibromo-5-nitronaphthalene, which *via* sequential reduction, diazotisation, hydrolysis, and oxidation with Fremy's salt gives 6,7-dibromo-1,4-naphthoquinone, which can be similarly alkylated.

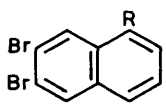
In connection with studies of the reaction centres of photosynthetic bacteria,[1] 2,3-dialkyl-6,7-dichloro- and 2,3-dialkyl-6,7-dibromo-1,4-naphthoquinones were required, particularly those in which one alkyl group is methyl and the other is decyl.

Diels–Alder addition of 3,4-dichlorothiophene 1,1-dioxide to 1,4-benzoquinone with concomitant extrusion of sulphur dioxide followed by oxidation yields[2] 6,7-dichloro-1,4-naphthoquinone (**1**; $R^1 = R^2 = H$; X = Cl). This reaction has now been extended to the methyl homologues (**1**; $R^1 = Me, R^2 = H$; X = Cl) and (**1**; $R^1 = R^2 = Me$; X = Cl), although the addition becomes progressively slower for the series 1,4-benzoquinone, 2-methyl-1,4-benzoquinone, and 2,3-dimethyl-1,4-benzoquinone.

Attempts to convert 3,4-dibromo-2,3,4,5-tetrahydrothiophene 1,1-dioxide[3] into 3,4-dibromothiophene 1,1-dioxide (*cf.* ref. 2) were unsuccessful, and 6,7-dibromo-1,4-naphthoquinone (**1**; $R^1 = R^2 = H$; X = Br) was therefore prepared from 2,3-dibromonaphthalene.[4]



(**1**)



(**2**)

Direct oxidation of 2,3-dibromonaphthalene to the quinone (**1**; $R^1 = R^2 = H$; X = Br) using chromium(III) oxide,[5] hydrogen peroxide,[6] periodic acid,[7] or cerium(IV)–silver nitrate,[8] was unsuccessful. An indirect route to this quinone was therefore used, as follows.

Treatment of 2,3-dibromonaphthalene with nitric–sulphuric acids under conditions[9] appropriate for 1-nitration of naphthalene gave a mixture of di-and tri-nitro compounds. However, this very high reactivity of the dibromonaphthalene allowed the required 2,3-dibromo-5-nitronaphthalene (**2**; R = NO_2) to be obtained by addition of dilute nitric acid to a two-phase dichloromethane–concentrated sulphuric acid system under carefully controlled conditions (see Experimental section); further nitration, giving a mixture of 2,3-dibromo-1,5- and 2,3-dibromo-1,8-dinitronaphthalene, occurred easily.

Reduction of the nitro compound (**2**; R = NO_2) to the corresponding amine (**2**; R = NH_2) was best effect with hydrazine hydrate in the presence of palladium–charcoal,[10] although the conditions had to be carefully defined (see Experimental section) to avoid hydrogenolysis of the bromine substituents. Direct oxidation of the naphthylamine (**2**; R = NH_2) to the corresponding 1,4-naphthoquinone using Fremy's salt was unsuccessful.[11] Attempted conversion of the naphthylamine into the naphthol (**2**; R = OH) by hydrolysis[12] or by the Bucherer reaction[13] was unsuccessful. However, diazotisation[14] followed by hydrolysis yielded the napthol, which upon oxidation with Fremy's salt afforded the quinone (**1**; $R^1 = R^2 = H$; X = Br) in 22% overall yield for 2,3-dibromonaphthalene.

Alkylation of the quinones was effected using the alkanoic acid–ammonium persulphate–silver nitrate system,[15–17] in which the alkyl radical produced by oxidative decarboxylation is scavenged[18] by the quinone. In order to optimise the conditions for monoalkylation of the 6,7-dihalogeno-1,4-naphthoquinones, experiments were initially performed using 1,4-naphthoquinone and its 2-methyl homologue as models.

With 15 mol equiv. of acetic acid under conditions similar to those previously described,[15,16] 1,4-naphthoquinone gave its 2,3-dimethyl homologue in 87% yield. The optimum proportion for monomethylation was 3 mol equiv. of acetic acid, the products then being recovered were quinone (16%), 2-methyl-1,4-naphthoquinone (49%), and 2,3-dimethyl-1,4-naphthoquinone (36%). Similarly, use of 1.5 mol equiv. undecanoic acid gave 2-decyl-[19] and 2,3-didecyl-1,4-naphthoquinone in yields of 28% and 6%, respectively.

The introduction of a second, different, alkyl group was optimised using 2-methyl-1,4-naphthoquinone, which with 2.2—2.4 mol equiv. of propionic, hexanoic, and undecanoic acid afforded 2-ethyl-3-methyl-,[20] 2-methyl-3-pentyl-, and 2-decyl-3-methyl-1,4-naphthoquinone in yields of 55, 74, and 67%, respectively.

Similar treatment of 6,7-dichloro-2-methyl-1,4-naphthoquinone with undecanoic acid gave 6,7-dichloro-2-decyl-3-methyl-1,4-naphthoquinone (**1**; $R^1 = Me, R^2 = decyl$; X = Cl) in 67% yield.

Decylation of 6,7-dibromo-1,4-naphthoquinone gave 32% of the mono- and 41% of the di-decyl homologue, but attempts to methylate the former were not synthetically useful. Methylation of the dibromoquinone gave 32% of the mono- and 16% of the di-methyl homologue, which were separated by p.l.c. Decylation of the former gave 6,7-dibromo-2-decyl-3-methyl-1,4-naphthoquinone (**1**; $R^1 = Me, R^2 = decyl$; X = Br) in 42% yield.

Experimental

6,7-Dichloro-1,4-naphthoquinone.—A mixture of 1,4-benzoquinone (877 mg, 8.12 mmol) and 3,4-dichlorothiophene 1,1-

dioxide[2] (310 mg, 1.66 mmol) in benzene (25 cm^3) was refluxed for 99 h. The solvent was evaporated off to give a dark green solid which was washed with methanol (20 cm^3), and then stirred in methanol (35 cm^3) with 30% hydrogen peroxide (35 cm^3) for 90 min. Crystallisation of the resulting solid from ethanol (charcoal) gave the quinone as yellow plates (148 mg, 39%), m.p. 184—185 °C (lit.,[2] 186—187 °C); $\nu_{max.}(CHCl_2)$ 1 675s, 1 605w, and 1 585m cm^{-1}; δ(60 MHz, $CDCl_3$) 6.95 (s, 2- and 3-H), 8.10 (s, 5- and 8-H); *m/z* 230, 228, and 226 (M^+, 11, 65, and 100%).

6,7-*Dichloro*-2-*methyl*-1,4-*naphthoquinone*.—This *quinone* was obtained from 2-methyl-1,4-benzoquinone using the foregoing procedure, and formed yellow needles (55%), m.p. 182—183 °C (Found: C, 54.7; H, 2.1; Cl, 29.2. $C_{11}H_6Cl_2O_2$ requires C, 54.7; H, 2.2; Cl, 29.5%); $\nu_{max.}(CH_2Cl_2)$ 1 670s, 1 630w, and 1 585m cm^{-1}; δ(60 MHz, $CDCl_3$) 2.18 (d, *J* 2 Hz, Me), 6.18 (q, *J* 2 Hz, 3-H), and 8.08 (s, 5- and 8-H); *m/z* 244, 242, and 240 (M^+, 13, 68, and 100%).

6,7-*Dichloro*-2,3-*dimethyl*-1,4-*naphthoquinone*.—This *quinone* was similarly obtained, from 2,3-dimethyl-1,4-benzoquinone, as pale yellow needles (43%), m.p. 189—191 °C (Found: C, 56.9; H, 3.1; Cl, 27.8. $C_{12}H_8Cl_2O_2$ requires C, 56.5; H, 3.1; Cl, 27.8%); $\nu_{max.}(CH_2Cl_2)$ 1 665s, 1 610w, and 1 590m cm^{-1}; δ (60 MHz, $CDCl_3$) 2.17 (s, 2 × Me) and 8.13 (s, 5- and 8-H); *m/z* 258, 256, and 254 (M^+, 11, 66, and 100%).

2,3-*Dibromo*-5-*nitronaphthalene*.—Concentated sulphuric acid (3 cm^3, 55 mmol) was added to a stirred solution of 2,3-dibromonaphthalene[4] (252 mg, 0.88 mmol) in dichloromethane (12 cm^3) at 0 °C and the two-phase system was further cooled to between −5 and −3 °C. A mixture of nitric acid (*d* 1.42; 1.5 cm^3, 47 mmol) and water (1.5 cm^3) was then added dropwise over 45 min, ensuring that the temperature of the reaction mixture was within the range −5—0 °C. Stirring was then continued for 30 min, within this temperature range. Dichloromethane (15 cm^3) was added, and the organic phase was separated and washed with saturated aqueous sodium hydrogen carbonate, then with water, and dried (Na_2SO_4). The solvent was evaporated off and crystallisation of the residue from acetic acid gave the *nitronaphthalene* (235 mg, 81%) as yellow needles, m.p. 186—187 °C (Found: C, 36.55; H, 1.4; Br, 48.05; N, 4.1. $C_{10}H_5Br_2NO_2$ requires C, 36.25; H, 1.5; Br, 48.3; N, 4.2%); $\nu_{max.}$ 1 580w, 1 525s, and 1 340s cm^{-1}; δ(300 MHz, $CDCl_3$) 7.62 (t, *J* 8 Hz, 7-H), 8.05 (d, *J* 8 Hz, 8-H), 8.27 (s, 1-H), 8.33 (d, *J* 8 Hz, 6-H), and 9.01 (s, 4-H); *m/z* 333, 331, and 329 (M^+, 35, 73, and 36%), and 206 (100).

6,7-*Dibromo*-1-*naphthylamine*.—A mixture of 2,3-dibromo-5-nitronaphthalene (102 mg, 0.31 mmol) and 5% palladium–charcoal (20 mg) in ethanol (15 cm^3) was refluxed for 10 min. Hydrazine hydrate (99—100%; 45 μl, 0.93 mmol) in ethanol (2 cm^3) was added dropwise over 60 min and refluxing was then continued at 15 min. Filtration, evaporation of the solvent, and crystallisation from aqueous ethanol gave the *naphthylamine* as off-white needles (59 mg, 65%), m.p. 123—124 °C (Found: C, 40.3; H, 2.4; Br, 51.8; N, 4.6. $C_{10}H_7Br_2N$ requires C, 39.9; H, 2.3; Br, 53.1; N, 4.7%); $\nu_{max.}(CH_2Cl_2)$ 3 470w, 3 400m, 1 625s, and 1 570s cm^{-1}; δ(300 MHz, CD_2Cl_2) 4.17 (br s, removed by D_2O, NH_2), 6.81 (d, *J* 7.5 Hz, 2-H), 7.18 (d, *J* 7.5 Hz, 4-H), 7.33 (t, *J* 7.5 Hz, 3-H), 8.10 (s, 8-H), and 8.16 (s, 5-H); *m/z* 303, 301, and 299 (M^+, 49, 100, and 51%).

6,7-*Dibromo*-1-*naphthol*.—A solution of 6,7-dibromo-1-naphthylamine (56 mg, 0.18 mmol) in concentrated sulphuric acid (2 cm^3) was added to ice–water (20 cm^3) and the resulting stirred suspension was cooled to 0 °C and treated dropwise over 15 min with sodium nitrite (15 mg, 0.21 mmol) in water (2 cm^3). The solution was allowed to warm to room temperature and then added dropwise over 60 min to boiling 5% sulphuric acid (100 cm^3). The mixture was cooled and extracted with dichloromethane (2 × 50 cm^3). The combined extracts were washed with saturated aqueous sodium hydrogen carbonate, then with water, and dried (Na_2SO_4). The solvent was evaporated off and sublimation of the residue at 100—120 °C/0.1 mmHg gave the *naphthol* as white needles (38 mg, 67%), m.p. 143—144 °C (Found: M^+, 299.8795, 301.8768, and 303.8752. $C_{10}H_6Br_2O$ requires *M*, 299.8786, 301.8767, and 303.8747); $\nu_{max.}(CH_2Cl_2)$ 3 580m, 1 740m, 1 610m, and 1 575s cm^{-1}; δ(300 MHz, $CDCl_3$) 5.26 (br s, removed by D_2O, OH), 6.81 (d, *J* 6.5 Hz, 2-H), 7.30 (m, 3- and 4-H), 8.08 (s, 8-H), and 8.50 (s, 5-H); *m/z* 304, 302, and 300 (M^+, 47, 100, and 50%).

6,7-*Dibromo*-1,4-*naphthoquinone*.—A solution of 6,7-dibromo-1-naphthol (53 mg, 0.18 mmol) in methanol (15 cm^3) was added to a stirred solution of potassium dihydrogen phosphate (250 mg, 1.84 mmol) and potassium nitrosodisulphonate (202 mg, 0.75 mmol) in water (30 cm^3) and stirring was continued for 60 min. The solution was extracted with ether (2 × 50 cm^3), and the combined extracts were washed with water, and dried (Na_2SO_4). The solvent was evaporated off and sublimation of the residue at 100—120 °C/0.1 mmHg gave the *quinone* as yellow–orange needles (31 mg, 56%), m.p. 171—172 °C (Found: M^+, 313.8583, 315.8562, and 317.8545. $C_{10}H_4Br_2O_2$ requires *M*, 313.8579, 315.8559, and 317.8540); $\nu_{max.}(CH_2Cl_2)$ 1 675s, 1 610w, and 1 580m cm^{-1}; δ(60 MHz, $CDCl_3$) 6.96 (s, 2- and 3-H) and 8.29 (s, 5- and 8-H); *m/z* 318, 316, and 314 (M^+, 51, 100, and 51%).

2,3-*Dimethyl*-1,4-*naphthoquinone*.—A solution of 1,4-naphthoquinone (58 mg, 0.37 mmol), silver(I) nitrate (35 mg, 0.21 mmol), and acetic acid (0.26 cm^3, 4.54 mmol) in a mixture of water (3 cm^3) and acetonitrile (4 cm^3) was refluxed and ammonium persulphate (241 mg, 1.06 mmol) in water (3 cm^3) was added over 30 min, and refluxing was then continued for 30 min. The cooled solution was extracted with dichloromethane (2 × 10 cm^3), and the combined extracts were washed with water, and dried (Na_2SO_4). The solvent was evaporated off and sublimation of the residue at 80—100 °C/0.1 mmHg gave the quinone (60 mg, 87%) as yellow needles, m.p. 123—126 °C (lit.,[21] 126—127 °C), identical (m.p. and spectra) with authentic[21] material.

2-*Methyl*-1,4-*naphthoquinone*.—This was prepared using the foregoing method from 1,4-naphthoquinone (17 mg, 0.11 mmol), silver(I) nitrate (9 mg, 0.05 mmol), acetic acid (20 μl, 0.35 mmol), and ammonium persulphate (42 mg, 0.18 mmol). P.l.c. (silica, CH_2Cl_2) of the total organic product gave 2-methyl-1,4-naphthoquinone (9 mg, 47%) as yellow plates, m.p. 104—105 °C (lit.,[22] 106—107 °C).

2-*Decyl*-1,4-*naphthoquinone*.—This was prepared by a similar method using 1,4-naphthoquinone (30 mg, 0.19 mmol), silver(I) nitrate (10 mg, 0.06 mmol), undecanoic acid (56 mg, 0.30 mmol), and ammonium persulphate (61 mg, 0.27 mmol). Column chromatography (silica, CH_2Cl_2) gave (*a*) 2,3-*didecyl*-1,4-*naphthoquinone* (R_F 0.90) (5 mg, 6%), m.p. 40—41 °C (Found: C, 82.0; H, 10.7. $C_{30}H_{46}O_2$ requires C, 82.2; H, 10.5%); $\nu_{max.}(CH_2Cl_2)$ 2 940s, 1 665s, and 1 605m cm^{-1}; δ(60 MHz, $CDCl_3$) 0.67—1.61 (m, 38 H), 2.27—2.77 (m, 4 H), and 7.46—8.09 (m, 4 H); *m/z* 439 [$(M + 1)^+$, 33%], 438 (M^+, 100); (*b*) 2-decyl-1,4-naphthoquinone (R_F 0.72) (16 mg, 28%), m.p. 62—63 °C (lit.,[19] 64—65 °C) (Found: C, 80.7; H, 9.0. Calc. for $C_{20}H_{26}O_2$: C, 80.5; H, 8.7%); $\nu_{max.}(CH_2Cl_2)$ 2 940m, 1 670s, and 1 605w cm^{-1}; δ(60 MHz, $CDCl_3$) 0.74—1.77 (m, 19 H),

2.33—2.69 (m, 2 H), 6.70 (br s, 1 H), 7.50—8.18 (m, 4 H); *m/z* 300 [$(M + 2)^+$, 5%], 298 (M^+, 45), and 173 (100); and (*c*) 1,4-naphthoquinone (16 mg).

2-Ethyl-3-methyl-1,4-naphthoquinone.—This was similarly prepared, from 2-methyl-1,4-naphthoquinone (126 mg, 0.73 mmol), silver(I) nitrate (31 mg, 0.18 mmol), propionic acid (0.123 cm^3, 1.65 mmol), and ammonium persulphate (232 mg, 1.02 mmol), and on sublimation at 60—80 °C/0.1 mmHg formed yellow needles (81 mg, 55%), m.p. 62—63.5 °C (lit.,[20] 67—68 °C) (Found: C, 77.3; H, 6.2. Calc. for $C_{13}H_{12}O_2$: C, 78.0; H, 6.0%); $\nu_{max.}(CH_2Cl_2)$ 2 940w, 1 690w, 1 660s, 1 620w, and 1 600 cm^{-1}; δ(60 MHz, $CDCl_3$) 1.12 (t, *J* 9 Hz, 1′-Me), 2.18 (s, 3-Me), 2.67 (q, *J* 9 Hz, CH_2), and 7.53—8.18 (m, 4 ArH); *m/z* 200 (M^+, 100).

2-Methyl-3-pentyl-1,4-naphthoquinone.—This *quinone* was prepared analogously from 2-methyl-1,4-naphthoquinone (125 mg, 0.70 mmol), silver(I) nitrate (31 mg, 0.18 mmol), hexanoic acid (0.206 cm^3, 1.65 mmol), and ammonium persulphate (231 mg, 1.02 mmol), and was obtained by sublimation at 120—125 °C/0.2 mmHg as yellow needles (129 mg, 74%), m.p. 55—56 °C (Found: C, 79.5; H, 7.6. $C_6H_{18}O_2$ requires C, 79.3; H, 7.4%); $\nu_{max.}(CH_2Cl_2)$ 2 960m, 2 940m, 1 690w, 1 660s, and 1 615m cm^{-1}; δ(60 MHz, $CDCl_3$) 0.91 (t, *J* 6 Hz, 4′-Me), 1.05—1.75 (m, 6 H), 2.17 (s, 2-Me), 2.61 (t, *J* 6 Hz, 3-CH_2), and 7.48—8.23 (m, 4 H); *m/z* 243 [$(M + 1)^+$, 9%], 242 (M^+, 43), and 186 (100).

2-Decyl-3-methyl-1,4-naphthoquinone.—This *quinone* was prepared similarly from 2-methyl-1,4-naphthoquinone (125 mg, 0.73 mmol), silver(I) nitrate (31 mg, 0.18 mmol), undecanoic acid (296 mg, 1.59 mmol), and ammonium persulphate (232 mg, 1.02 mmol) and was obtained by sublimation at 110—120 °C/0.2 mmHg as a yellow waxy solid (150 mg, 67%), m.p. 66—67 °C (Found: C, 80.8; H, 9.4. $C_{21}H_{28}O_2$ requires C, 80.8; H, 9.0%); $\nu_{max.}(CH_2Cl_2)$ 2 930w, 1 700w, 1 665s, 1 625w, and 1 595m cm^{-1}; δ(60 MHz, $CDCl_3$) 0.78—1.90 (m, 19 H), 2.17 (s, 3-Me), 2.45—2.83 (m, 2 H), and 7.53—8.24 (m, 4 H); *m/z* 313 [$(M + 1)^+$, 16%], 312 (M^+, 66), and 186 (100).

6,7-Dichloro-2-decyl-3-methyl-1,4-naphthoquinone.—This *quinone* was prepared analogously from 6,7-dichloro-2-methyl-1,4-naphthoquinone (166 mg, 0.68 mmol), silver(I) nitrate (31 mg, 0.18 mmol), undecanoic acid (220 mg, 1.18 mmol), and ammonium persulphate (235 mg, 1.03 mmol), and was obtained by sublimation at 155—160 °C/0.2 mmHg as yellow plates (176 mg, 67%), m.p. 77—78 °C (Found: C, 65.8; H, 6.9; Cl, 18.9. $C_{21}H_{26}Cl_2O_2$ requires C, 66.1; H, 6.8; Cl, 18.6%); $\nu_{max.}(CH_2Cl_2)$ 2 930m, 2 860m, 1 665s, 1 610w, and 1 585m cm^{-1}; δ(300 MHz, $CDCl_3$) 0.86 (t, *J* 7.3 Hz, 9′-Me), 1.14—1.52 (m, 16 H), 2.17 (s, 3-Me), 2.61 (t, *J* 7.3 Hz, 2-CH_2), and 8.16 (s, 2 H); *m/z* 384, 382, and 380 (M^+, 4, 14, and 17%), and 73 (100).

6,7-Dibromo-2-methyl-1,4-naphthoquinone.—This was obtained from 6,7-dibromo-1,4-naphthoquinone (34 mg, 0.11 mmol), silver(I) nitrate (10 mg, 0.06 mmol), acetic acid (23 μl, 0.40 mmol), and ammonium persulphate (45 mg, 0.20 mmol). P.l.c. (silica, CH_2Cl_2) gave (*a*) 6,7-*dibromo*-2,3-*dimethyl*-1,4-*naphthoquinone* (R_F 0.68) (5.9 mg, 16%), m.p. 191—194 °C (decomp.) (Found: M^+, 345.8861, 343.8873, and 341.8899. $C_{12}H_8Br_2O_2$ requires *M*, 345.8853, 343.8872, and 341.8892); $\nu_{max.}(CH_2Cl_2)$ 2 920m, 1 670s, and 1 625w cm^{-1}; δ(60 MHz, $CDCl_3$) 2.12 (s, 2 × Me) and 8.00 (s, 2 H); *m/z* 346, 344, and 342 (M^+, 49, 100, and 51%); (*b*) 6,7-*dibromo*-2-*methyl*-1,4-*naphthoquinone* (R_F 0.57) (11.6 mg, 32%), m.p. 180—182 °C (Found: M^+, 331.8688, 329.8714, and 327.8733. $C_{11}H_6Br_2O_2$ *M*, 331.8696, 329.8716, and 327.8736); $\nu_{max.}(CH_2Cl_2)$ 3 060w, 1 670s, 1 630w, and 1 590m cm^{-1}; δ(60 MHz, $CDCl_3$) 2.16 (d, *J* 2 Hz, Me), 6.76 (q, *J* 2 Hz, 3-H), 8.00 (s, 1 H), and 8.04 (s, 1 H); *m/z* 332, 330, and 328 (M^+, 14, 49, and 15%), and 74 (100); and (*c*) 6,7-dibromo-1,4-naphthoquinone (R_F 0.47) (4.3 mg).

6,7-Dibromo-2-decyl-3-methyl-1,4-naphthoquinone.—This *quinone* was prepared from 6,7-dibromo-2-methyl-1,4-naphthoquinone (10.5 mg, 0.03 mmol), silver(I) nitrate (2 mg, 0.01 mmol), undecanoic acid (12.2 mg, 0.07 mmol), and ammonium persulphate (12.4 mg, 0.05 mmol) and was obtained after filtration (silica, CH_2Cl_2) as yellow plates (6.1 mg, 41%), m.p. 83—85 °C (Found: M^+, 472.0256, 470.0274, and 468.0287. $C_{21}H_{26}Br_2O_2$ requires *M*, 472.0261, 470.0281, and 468.0300); $\nu_{max.}(CH_2Cl_2)$ 2 930m, 2 860w, 1 700w, 1 665s, 1 620w, and 1 585m cm^{-1}; δ(300 MHz, $CDCl_3$) 0.76—0.93 (m, 9′-Me), 1.06—1.48 (m, 16 H), 2.17 (s, 3-Me), 2.62 (m, 2 H), and 8.32 (s, 2 H); *m/z* 472, 470, and 468 (M^+, 4, 13, and 5%), and 43 (100).

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References

1 M. R. Gunner, D. E. Robertson, and P. L. Dutton, *J. Phys. Chem.*, 1986, **90**, 3783, and references therein.
2 H. Bluestone, R. Bimber, R. Berkey, and Z. Mandel, *J. Org. Chem.*, 1961, **26**, 346.
3 W. J. Bailey and E. W. Cummins, *J. Am. Chem. Soc.*, 1954, **76**, 1932.
4 A. A. Danish, M. Silvermann, and Y. A. Tajima, *J. Am. Chem. Soc.*, 1954, **76**, 6144.
5 H. Pluim and H. Wynberg, *J. Org. Chem.*, 1980, **45**, 2498.
6 R. T. Arnold and R. Larson, *J. Org. Chem.*, 1940, **5**, 250.
7 A. J. Fatiadi, *J. Chem. Soc., Chem. Commun.*, 1967, 1087.
8 J. Skarzenki, *Tetrahedron*, 1984, **40**, 4997.
9 A. I. Vogel, 'Textbook of Practical Organic Chemistry,' 4th Edn., Longmans, London, 1978, p. 625.
10 F. D. Bellamy and K. Ou, *Tetrahedron Lett.*, 1984, 839.
11 H. Zimmer, D. C. Lankin, and S. W. Horgan, *Chem. Rev.*, 1971, **71**, 229.
12 G. Vorozhtsov, *J. Gen. Chem. USSR*, 1935, **5**, 1581 (*Chem. Abstr.*, 1936, **30**, 2189); *Chem.-Ztg.*, 1936, **II**, 2359.
13 H. Seeboth, *Angew. Chem., Int. Ed. Engl.*, 1967, **6**, 307.
14 K. H. Saunders, 'The Aromatic Diazo Compounds and their Technical Applications,' Arnold, London, 1949.
15 N. Jacobsen and K. Torsell, *Justus Liebigs Ann. Chem.*, 1972, **763**, 135.
16 N. Jacobsen and K. Torsell, *Acta Chem. Scand.*, 1973, **27**, 3211.
17 N. Jacobsen, *Org. Synth.*, 1977, **56**, 68.
18 D. Veltwisch and K. D. Asmus, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1147.
19 W. Ziegler, U.S.P. 2 480 072/1949 (*Chem. Abstr.*, 1949, **43**, 9085g).
20 A. Osuka, *J. Org. Chem.*, 1982, **47**, 3131.
21 L. I. Smith and I. M. Webster, *J. Am. Chem. Soc.*, 1937, **59**, 664.
22 R. Gaertner, *J. Am. Chem. Soc.*, 1954, **76**, 6150.

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