Tetrahedron Vol. 42, No. 6, pp. 1741 to 1744, 1986
Printed in Great Britain.

0040-4020/86 $3.00+.00

CIS-DIMETHYLDIHYDROPYRENE SYNTHESIS

AN APPROACH UTILIZING A DIELS–ALDER ROUTE TO 1,2,3-TRISUBSTITUTED BENZENES

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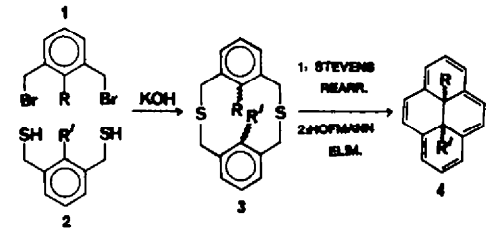
(*Received in USA* 23 *April* 1985)

Abstract—A new route to dihydropyrene precursors, 1,3-bis(bromomethyl)-2-substituted-benzenes, has been found, which starts from the readily available hexachlorocyclopentadiene and 3-substituted acrylic esters. Utilization of an intermediate in this sequence, 1,3-bis(bromomethyl)-4,5-dichlorotoluene, has opened up a route to the relatively inaccessible *cis*-dimethyldihydropyrenes to allow study of their chemistry.

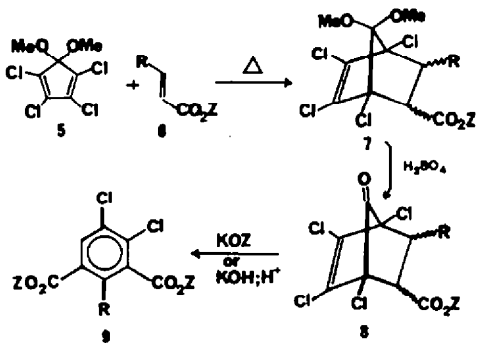
The dithiacyclophane route[1] (Scheme 1) to dihydropyrenes is now well established. It does however have some disadvantages. Firstly, for each new dihydropyrene **4** to be prepared, a different 1,2,3-trisubstituted benzene **1** or **2** is required. Since no general synthesis of these exists, each example of **1** or **2** that has been prepared in the literature has been by a new route.[2] Secondly the cyclization of **1** and **2** to the dithiacyclophane **3** yields mostly anti-isomers, e.g. 7:1 anti:syn for R = R′ = Me in **3**, making the *cis*-dimethyldihydropyrenes very inaccessible.[3]

We have been able to solve both of these problems in part by using an approach to the synthesis of benzenes based on early work by Hoch.[4] In his studies on the Diels–Alder reaction of the dimethoxycyclopentadiene **5** he suggests that the isophthalic acid derivative **9A** (R = H, Z = H) is the end product from reaction with ethyl acrylate in the sequence shown in Scheme 2, using KOH in the final step. His identification of **9A** however was somewhat tenuous, based on the melting point found for **9A** (305–306°) being higher than that normally found for phthalic acids (< 200°), and not the same as that for the known 4,6-dichloroisophthalic acid (286°).

In view of the fact that **5** is readily obtained[5] from the very cheap hexachlorocyclopentadiene, and that with 3-substituted acrylic esters many potential dihydropyrene precursors might become available, we thought it worthwhile to reinvestigate this sequence. Moreover, we have noted[6] that dithiacyclophanes in which one ring has electron-withdrawing substituents, tend to favor the *syn*-isomer in formation. The two chlorine atoms in **9** thus might be able to direct the dihydropyrene synthesis towards the *cis*-isomer, making this series more accessible.



Scheme 1.

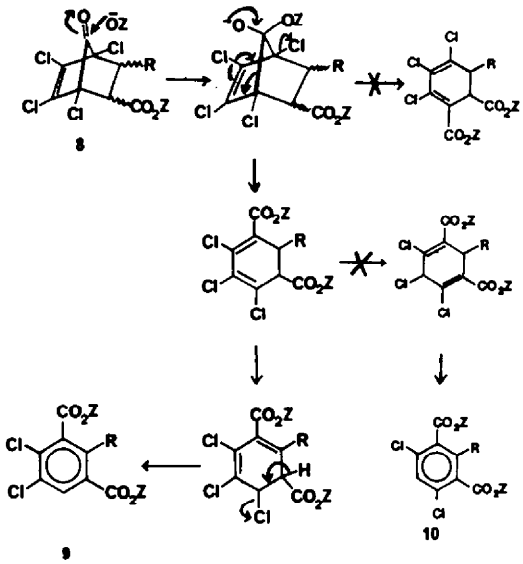


Scheme 2.

RESULTS

Reaction of **5** with methyl crotonoate **6** (R = Z = Me, mostly *trans*-isomer) at 180° proceeded rather slowly, but after 2.5 days gave an essentially quantitative yield of mixed exo–endo isomers of **7** (R = Z = Me). This mixture of isomers was hydrolysed with conc H_2SO_4 to yield about 75% of the ketone **8** (R = Z = Me), again as a mixture of isomers. Neither **7** nor **8** were readily distilled, decomposition resulting. Their structures followed unequivocally however from mass spectral and NMR data, and that they were pure by TLC. Reaction of **8** however with NaOMe in MeOH yielded crystalline **9B** (R = Z = Me), m.p. 74–74.5° in 76% yield, which could be obtained analytically pure. The structure of **9B** was established by ^{13}C-NMR, showing six aromatic carbons and two ester methyl carbons, The isomeric 4,6-dichloro compound **10** (Scheme 3), which might have been formed, is of course symmetrical and would only show four aromatic types of carbon and one type of ester methyl. The corresponding acid **9C** (R = Me, Z = H), obtained from **8** with KOH and then H_2SO_4, also showed six aromatic carbons and two carboxyl carbons in its ^{13}C-NMR, and failed to give a phthalein test,[6] confirming its structure. Reaction of **9B** (R = Z = Me) with W-7 Raney nickel gave an essentially quantitative yield of the known[7] dimethyl 2-methylisophthalate, yielding a useful cheap alternate synthesis.

The synthesis of the *cis*-dihydropyrene **18** (Scheme 4) could now be attempted. Reduction of diester **11A** (≡ **9B**) with di-isobutylaluminum hydride (DIBAL) in

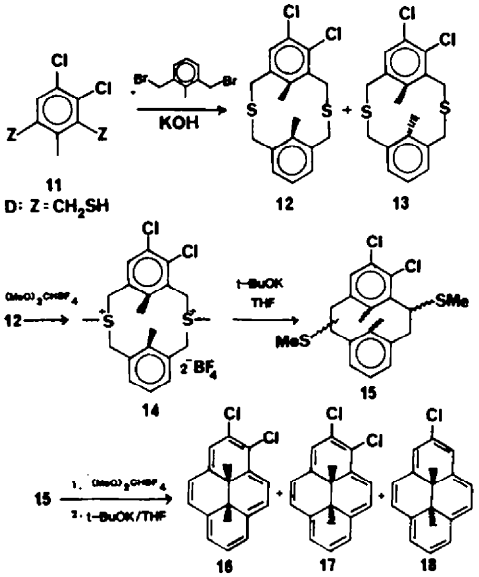


Scheme 3.

benzene gave a quantitative yield of di-alcohol **11B** (Z = CH_2OH), m.p. 180–181°, which with conc HBr gave 98% of dibromide **11C** (Z = CH_2Br), m.p. 106–107°. The latter on reaction with thiourea and then KOH gave the dithiol **11D** (Z = CH_2SH), m.p. 83–84° in 99% yield. The cyclization of dithiol **11D** (Z = CH_2SH) with 2,6-bis(bromomethyl)toluene[1] proceeded in the remarkable yield of 96% and gave 61% of the *syn*-dithiacyclophane **12** and 35% of the *anti*-isomer **13**. The ratio of *syn*-**12**:*ant*-**13** was thus 1.74:1, considerably improved from the 1:7 ratio in the absence of the chloro-substituents. The two dithiacyclophanes **12** and **13** were readily distinguished by their ^{1}H-NMR spectra. The internal methyl protons of *anti*-**13** appear shielded[8] at δ 1.26 and 1.49, whereas those of *syn*-**12** appear normal at δ 2.51 and 2.52. Also the aromatic protons of *syn*-**12** appear shielded at δ 6.91–6.66 while those of *anti*-**13** are normal at δ 7.54–7.08.

Pure *syn*-**12** was then taken through a Stevens rearrangement–Hofmann elimination procedure:[1] methylation of **12** with $(CH_3O)_2CHBF_4$[9] proceeded quantitatively to give **14**, m.p. 205–209° (dec), which with t-BuOK/THF led to the [2.2]cyclophanes **15** as a mixture of isomers in 88% yield. Repeat of this procedure then yielded the dihydropyrenes **16**, m.p. 54–57°, and **17**, m.p. 130–132°, in a 6:4 ratio. The overall yield of *cis*-dihydropyrene **16** is about 30% from **12** which is better than the 8% obtained for *cis*-**4** (R = Me) from *syn*-**3** (R = Me).[1] It is interesting to note however, that even with the additional stabilization afforded the *syn*-cyclophanes by the electron-withdrawing chlorine substituents, substantial isomerization from the *syn* to the *anti* series still[1] occurs during the Stevens rearrangement step, **14** → **15**. As well 2% (from **12**) of the monochlorodihydropyrene **18**, m.p. 132–133°, was also obtained during the sequence, though it is not known how this arose. Like the thiacyclophanes, the two dihydropyrenes **16** and **17** are easily distinguished from their ^{1}H-NMR spectra: the internal methyl protons of *cis*-**16** appear at δ −1.95 and −2.04, while those of the more planar, more diatropic *trans*-**17** appear at δ −4.07.

Thus given that hexachlorocyclopentadiene is available at < U.S. $10/kg and that the overall yield of **16** from this is about 7% over the 12 steps of the synthesis, chlorine substituted *cis*-dihydropyrenes should now be much more accessible for study. Removal of the two chlorine substituents from **16** to yield *cis*-**4** (R = Me) itself has in our hands not yet proved possible (Raney Ni, Li/t-BuOH, Na/NH_3, Li–ultrasound, Bu_3SnH). This is probably due in part to the instability of *cis*-**4**.[3] Removal of the chlorines at an earlier stage, e.g. from **12** is also not feasible, at least with Raney nickel, since the cyclophane is cleaved yielding 4,5-dichloro-1,2,3-trimethylbenzene. However use of (arene)chromium tricarbonyl derivatives of the dithiacyclophanes can overcome this problem[10] and their use with these halogenated cyclophanes will be reported on by us in the future.



Scheme 4.

EXPERIMENTAL

M.ps were determined on a Kofler hot stage and are uncorrected. ^{1}H-NMR spectra were determined in $CDCl_3$ (unless otherwise stated) on a Perkin–Elmer R32 (90 MHz) or Bruker WH-250 (250 MHz) spectrometer. ^{13}C-NMR spectra were recorded on a Nicolet TT-14 (15.1 MHz) spectrometer. All chemical shifts are reported in ppm downfield from TMS as internal standard. Mass spectra were determined on a Finnigan 3300 mass spectrometer at 70 eV (EI) or using methane chemical ionization (CI). Only the molecular ion containing ^{35}Cl is reported, but correct isotope peaks were obtained in all cases. IR spectra were recorded on a Perkin–Elmer 283 IR spectrometer. Microanalyses were carried out by this department or by Canadian Microanalytical Services Ltd. (Vancouver BC). All evaporations were carried out under reduced pressure on a rotary evaporator at about 40°, and all organic layers were washed with water (unless otherwise stated) and dried with anhyd $MgSO_4$.

1,4,5,6 - *Tetrachloro* - 2 - *carbomethoxy* - 3 - *methyl* - 7,7 - *dimethoxybicyclo*[2.2.1]*hept-5-ene* **7** (R = Z = Me). A mixture of **5**[5] (26.4 g, 0.1 mol) and **6** (R = Z = Me) (10.01 g, 0.1 mol) were stirred at 180° for 2.5 days. After cooling, a ^{1}H-NMR spectrum of the crude oil indicated about 98% conversion to **7**. Chromatography on silica gel using CH_2Cl_2 as eluant gave 78% of TLC pure **7**, as a mixture of *exo*- and *endo*-isomers. ^{1}H-

NMR δ (90 MHz) 3.70 (s, 3H, $-CO_2Me$), 3.55 and 3.50 (s, 6H, >—OMe), 3.2–2.0 (m, 2H, CH), and 1.40 and 1.30 (s, 3H, C—Me). IR (film) 1745 ($-CO_2Me$) cm^{-1}. Attempted distillation of this oil resulted in retro-Diels–Alder reactions.

1,4,5,6 - *Tetrachloro* - 2 - *carbomethoxy* - 3 - *methylbicyclo*[2.2.1]*hept* - 5 - *en* - 7 - *one* **8** (R = Z = Me). The ketal **7** (21.84 g, 60 mmol) was stirred at about 20° in conc H_2SO_4 (75 ml) for 18 hr, and then was poured onto ice. The product was extracted into CH_2Cl_2, which was then washed, dried and evaporated, and the residual oil was chromatographed on silica gel using CH_2Cl_2 as eluant to yield 16.4 g (86%) of a mixture of *exo–endo* isomers of **8** as an oil, pure by TLC. ^{1}H-NMR δ (90 MHz) 3.74 (s, 3H, $-CO_2Me$), 3.0–2.4 (m, 2H, CH) and 1.30 and 1.18 (s, 3H, C—Me); IR (film) 1745 ($-CO_2Me$) and 1835 (>C=O) cm^{-1}. Attempted distillation resulted in decomposition.

Dimethyl 4,5-*dichloro*-2-*methylisophthalate* **9B** (R = Z = Me). NaOMe (5.42 g, 0.1 mol) was added with stirring slowly to a soln of **8** (10.0 g, 31.4 mmol) in MeOH (100 ml) at about 20° (caution: reaction is exothermic). After 2 hr, the mixture was poured into CH_2Cl_2, washed well, dried and evaporated. The crude diester was chromatographed over silica gel using CH_2Cl_2–pentane 1:1 as eluant, and the product was recrystallized from aq MeOH to give 6.61 g (76%) of **9B** as white needles, m.p. 74–74.5°. ^{1}H-NMR δ (90 MHz) 8.00 (s, 1H, ArH), 3.95 and 3.89 (s, 3H each, $-CO_2Me$) and 2.48 (s, 3H, ArMe); ^{13}C-NMR (15 MHz) δ 166.5 and 165.6 (C=O), 137.7 and 127.6 (C—Cl), 136.6, 130.6 and 130.1 (ArC—C) and 132.5 (ArCH); IR (KBr) 1740 and 1720 ($-CO_2Me$) cm^{-1}. (Found: C, 47.71; H, 3.57. $C_{11}H_{10}Cl_2O_4$ requires: C, 47.68; H, 3.64%.)

The acid **9C** (R = Me, Z = H) obtained by using KOH in place of NaOMe above was rather insoluble in organic solvents; ^{13}C-NMR (DMSO-D_6) δ 168.2 and 167.9 (C=O), 140.3 and 131.1 (C—Cl), 135.9, 133.4 and 130.4 (ArC—C) and 132.4 (ArCH).

Dimethyl 2-*methylisophthalate*. The ester **9B** (1 g) was refluxed with a slurry of W-7 Raney Ni (10 g) in EtOH–water 1:1 for 3 days. CH_2Cl_2 was added, the solids were removed by filtration and the extract was washed with water, dried and evaporated. The resulting oil was filtered through silica gel using CH_2Cl_2–pentane (1:1) to give the product as an oil (0.75 g, quant.) which gave an identical ^{1}H-NMR spectrum to that of an authentic sample;[7] ^{1}H-NMR (90 MHz) δ 7.8 and 7.2 (A_2B, 3H, ArH), 3.90 (s, 6H, $-CO_2Me$) and 2.70 (s, 3H, ArMe).

3,4-*Dichloro*-2,6-*bis*(*hydroxymethyl*)*toluene* **11B** (Z = CH_2OH). DIBAL (0.127 mol in hexane 120 ml) was added dropwise under N_2 to a stirred soln of **11A** (Z = CO_2Me) (5.8 g, 21 mmol) in benzene (200 ml) at about 20°, and then the mixture was stirred for 14 hr. MeOH, water and then aq HCl were added, and the mixture was then extracted with ether. The extracts were washed, dried and evaporated to yield crude diol 4.6 g (quant.). This was recrystallized from benzene to give **11B** as white needles, m.p. 180–181°. ^{1}H-NMR (DMSO-d_6) δ 7.52 (s, 1H, ArH), 5.31 and 5.07 (t, 1H each, —OH, s after D_2O exchange), 4.68 and 4.48 (d, 2H each, $-CH_2O-$, s after D_2O exchange) and 3.31 (s, 3H, ArMe). (Found: C, 48.76; H, 4.62. $C_9H_{10}Cl_2O_2$ requires: C, 48.90; H, 4.56%.)

2,6 - *Bis*(*bromomethyl*) - 3,4 - *dichlorotoluene* **11C** (Z = CH_2Br). A mixture of **11B** (4.42 g, 20 mmol), 48% aq HBr (200 ml) and conc H_2SO_4 (1 ml) was heated under reflux for 14 hr. After cooling, water was added and the ppt was collected and chromatographed over silica gel using benzene as eluant to give 6.74 g (98%) of **11C**. A portion was recrystallized from hexane as white crystals, m.p. 106–107°. ^{1}H-NMR (90 MHz) δ 7.40 (s, 1H, ArH), 4.66 and 4.39 (s, 3H each, $-CH_2Br$) and 2.42 (s, 3H, ArMe). (Found: C, 31.33; H, 2.56. $C_9H_8Br_2Cl_2$ requires: C, 31.16; H, 2.32%.)

3,4-*Dichloro*-2,6-*bis*(*mercaptomethyl*)*toluene* **11D** (Z = CH_2SH). A mixture of **11C** (8.08 g, 23.3 mmol) and thiourea (3.66 g, 48 mmol) in 95% aq EtOH (45 ml) was refluxed for 3 hr. The solvent was then evaporated and the residue was refluxed under N_2 with a soln of KOH (35 g) in water (75 ml) for 4 hr. The mixture was poured onto ice–aq HCl, and the ppt was collected to yield crude dithiol, 5.83 g (99%). This was recrystallized from hexane–CH_2Cl_2 as white crystals, m.p. 83–84°. ^{1}H-NMR (90 MHz) δ 7.29 (s, 1H, ArH), 3.90 and 3.66 (d, J = 7.5 Hz, 2H each, $-CH_2S-$), 2.37 (s, 3H, ArMe) and 1.88 and 1.68 (t, J = 7.5 Hz, 1H each, —SH). (Found: C, 42.49; H, 3.98. $C_9H_{10}Cl_2S_2$ requires: C, 42.69; H, 3.98%.)

syn- *and* anti - 5,6 - *Dichloro* - 9,18 - *dimethyl* - 2,11 - *dithia*[3.3]*metacyclophanes* **12**, **13**. A soln of 2,6-bis(bromomethyl)toluene[1] (2.78 g, 10 mmol) and **11D** (2.53 g, 10 mmol) in N_2 degassed benzene was added dropwise over 48 hr with vigorous stirring under N_2 to a soln of KOH (1.8 g, 32 mmol) in 95% aq EtOH (800 ml). The mixture was then evaporated to dryness, and water and CH_2Cl_2 were added. The organic layer was washed, dried and evaporated to a crystalline residue which was chromatographed on silica gel using benzene–hexane 1:1 as eluant to yield 3.54 g (96%) of **12** and **13** as a *syn*. *anti* 61:35 mixture of isomers. This was fractionally crystallized from benzene several times, the *anti*-isomer being less soluble, to give pure *anti*-**13**, 1.29 g (35%), m.p. 227–228°; MH^+ (CI) at *m/e* 369; ^{1}H-NMR δ (250 MHz) 7.54 (s, 1H, H-6), 7.44 and 7.21 (d, J = 7.6 Hz, 1H each, H-14, 16), 7.11 (t, J = 7.6 Hz, 1H, H-15), 4.15 and 3.74 (AB, J = 13 Hz, 2H, H-3), 3.84 and 3.77 (AB, J = 13 Hz, 2H, H-10), 3.65 and 3.56, and 3.57 and 3.44 (two AB's, J = 15 Hz, 4H, H-1, 12), 1.49 and 1.26 (s, 3H each, ArMe). (Found: C, 58.40; H, 5.11. $C_{18}H_{18}Cl_2S_2$ requires: C, 58.53; H, 4.91%.)

Recrystallizing the mother liquors also from benzene gave pure *syn*-**12**, 2.25 g (61%), m.p. 224–225°; MH^+ (CI) at *m/e* 369; ^{1}H-NMR δ (250 MHz) 6.91–6.66 (m, 4H, ArH), 4.71 and 3.62 (AB, J = 15 Hz, 2H, H-3), 4.02, 3.97, 3.89 (×2), 3.85 and 3.76 (3AB's, J = 15 Hz, 6H, H-1, 10, 12) and 2.52 and 2.51 (s, 3H each, ArMe). (Found: C, 58.45; H, 5.09. $C_{18}H_{18}Cl_2S_2$ requires: C, 58.53; H, 4.91%.)

Stevens rearrangement–Hofmann elimination of **12**: cis - 1,2 - *dichloro*-10*b*,10*c* - *dimethyl* - 10*b*,10*c* - *dihydropyrene* **16**

Stevens rearrangement. A soln of **12** (1.0 g, 2.7 mmol) in CH_2Cl_2 (40 ml) was added to a stirred suspension of $(CH_3O)_2CHBF_4$[9] (2.0 g, 12 mmol) in CH_2Cl_2 (15 ml) at −30°, under N_2. After stirring without further cooling for 5 hr, EtOAc (40 ml) was added, and stirring continued for 30 min. The insoluble white bis-sulfonium salt, **14**, was then collected and dried to give 1.6 g (98%), m.p. 205–209° (dec). This salt was suspended in dry THF (60 ml) under N_2 and solid t-BuOK (1.2 g, 11 mmol) was added. The mixture was stirred for 20 min and then 2 M aq HCl and CH_2Cl_2 were added. The organic layer was then washed, dried and evaporated. The residual oil was chromatographed on silica gel using CH_2Cl_2–pentane 2:3 as eluant to yield mixed isomers of **15**, 0.86 g (88%) as a light yellow paste, used directly in the next step.

Hofmann elimination. The above paste (0.86 g, 2.33 mmol) dissolved in CH_2Cl_2 (35 ml) was added to a stirred suspension of $(CH_3O)_2CHBF_4$[9] (2.0 g, 12 mmol) in CH_2Cl_2 (15 ml) at −30°, under N_2. After stirring without further cooling for 5 hr, EtOAc (40 ml) was added, and stirring was continued for 2–12 hr to obtain after filtration and drying a light yellow powder, 1.21 g (89%) of mixed sulfonium salts. This was suspended in dry THF (50 ml) under N_2, to which solid t-BuOK (1.4 g, 13 mmol) was then added. The mixture was stirred at about 20° for 2 hr and then 2 M aq HCl and CH_2Cl_2 were added. The organic layer was then washed, dried and evaporated. The residual solid was chromatographed twice over deactivated silica gel using pentane as eluant to yield 202 mg (29%) of *cis*-**16**, 13 mg (2%) of **18** and 135 mg (19%) of *trans*-**17**.

The *cis*-**16**, was obtained as green crystals from MeOH, m.p. 56–58°; ^{1}H-NMR (90 MHz) δ 9.22 (d, J = 8.5 Hz, 1H, H-10), 8.90–8.60 (m, 3H, ArH), 8.35 (s, 1H, H-3), 8.40–8.20 (m, 2H, ArH), 7.60 (t, J = 8 Hz, 1H, H-7), −1.85 and −1.94 (s, 3H each, internal-Me); $M^{+\cdot}$ at *m/e* 300 (10%), 285 (M − Me, 29%), 270 (M − 2Me, 33%), 250 (M − Me, Cl, 100%). (Found: C, 72.01; H, 4.56. $C_{18}H_{14}Cl_2$ requires: C, 71.78; H, 4.68%.)

The *trans*-**17**, was obtained as green crystals from pentane,

m.p. 130–132°; ^{1}H-NMR (90 MHz) δ 8.95 (d, J = 7 Hz, 1H, H-10), 8.8–8.4 (m, 6H, ArH), 8.09 (t, J = 7.5 Hz, 1H, H-7) and −3.96 (s, 6H, internal-Me); $M^{+\cdot}$ at *m/e* 300 (28%), 285 (M − Me, 29%), 270 (M − 2Me, 33%), 250 (M − Me, Cl, 100%). (Found: C, 71.88; H, 4.37. $C_{18}H_{14}Cl_2$ requires: C, 71.78; H, 4.68%.)

The monochloro-**18**, was obtained as green crystals from EtOH, m.p. 132–133°; ^{1}H-NMR (90 MHz) δ 8.54 (s, 2H, H-1, 3), 8.65–8.50 (m, 5H, ArH), 8.08 (t, J = 7.8 Hz, 1H, H-7) and −4.13 and −4.16 (s, 3H each, internal-Me); $M^{+\cdot}$ at *m/e* 266 (16%), 251 (M − Me, 23%) and 216 (M − Me, Cl, 100%).

Acknowledgement—We thank the Natural Sciences and Engineering Research Council of Canada and the University of Victoria for financial support of this work.

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