Tetrahedron, Vol. 37, Supplement No 1, pp. 387 to 391, 1981
Printed in Great Britain

0040-4020/81/Suppl. 1-0387-05 $02.00/0
Pergamon Press Ltd

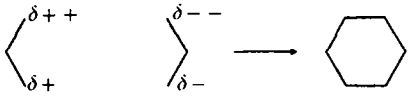
REGIO-CONTROLLED SYNTHESIS OF SUBSTITUTED PHENOLS[1]

T. H. CHAN* and P. BROWNBRIDGE,
Department of Chemistry, McGill University, Montreal, Quebec, Canada H3A 2K6

(*Received in USA* 16 *July* 1980)

Abstract—2,4-Bis(trimethylsiloxy)-penta-1,3-diene (**2**) condenses with various equivalents of β-dicarbonyl compounds and titanium tetrachloride to give substituted *o*-acetylphenols in a regio-controlled manner. Replacing **2** with 2,4-bis (trimethylsiloxy)-1-methoxypenta-1,3-diene (**10**) in the condensation reaction gives substituted methyl salicylates. The salicylates can be converted to phenols by decarboxylation. Condensation of 1,3-bis(trimethylsiloxy)-1-methoxy-2-methylpenta-1,3-diene (**19**) with β-carbonyl equivalents gives cyclisation products which can be aromatised by decarboxylation.

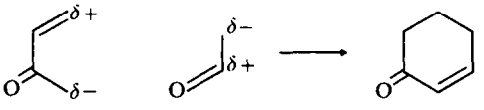
There are no well-established methods for the synthesis of benzeneoid compounds from acyclic precursors. Recently, we described[2] a novel cycloaromatisation reaction involving the condensation of two 3-carbon units, one with two nucleophilic sites and the other containing two electrophilic sites, as in eqn (1). The regiochemistry of



(1)

the reaction is controlled by the differential reactivities of these sites. 1,3-Bis-(trimethylsiloxy)-1-methoxybuta-1,3-diene (**1**) constitutes the 3-carbon fragments with two nucleophilic sites. Condensation of **1** with various equivalents of β-dicarbonyl compounds and titanium tetrachloride gave substituted methyl salicylates. The regiochemistry is controlled by the order of reactivity of the electrophilic sites, which is conjugate position of enone > ketone > monothioacetal, acetal.

This method of construction of 6-membered rings is different conceptually from the classical methods such as Diels–Alder reaction or Robinson annelation which consist of the union of two fragments, one with two C atoms and the other with four carbons. Furthermore, regiochemistry in these reactions is essentially controlled by the direction of polarization within each fragment as represented schematically in eqn (2) for the Robinson annelation.



(2)

In this paper, we wish to extend the generality of eqn (1) to other 3-carbon nucleophilic fragments. We have established as well the reaction as a general synthesis of substituted phenols.

2,4-*Bis(trimethylsiloxy)-penta*-1,3-*diene* (**2**). We are interested to see if eqn (1) can be used for the synthesis of substituted *o*-acetylphenols. For this purpose, compound **2**, the dianion equivalent of acetylacetone, is required. Compound **2** was prepared[3] from 4-trimethylsiloxypent-3-en-2-one (**3**)[2] by Danishefsky's method[4] in 96% yield, as a 1:1 mixture of geometric isomers. It was pure by ^{1}H NMR and gc, and was used without distillation.

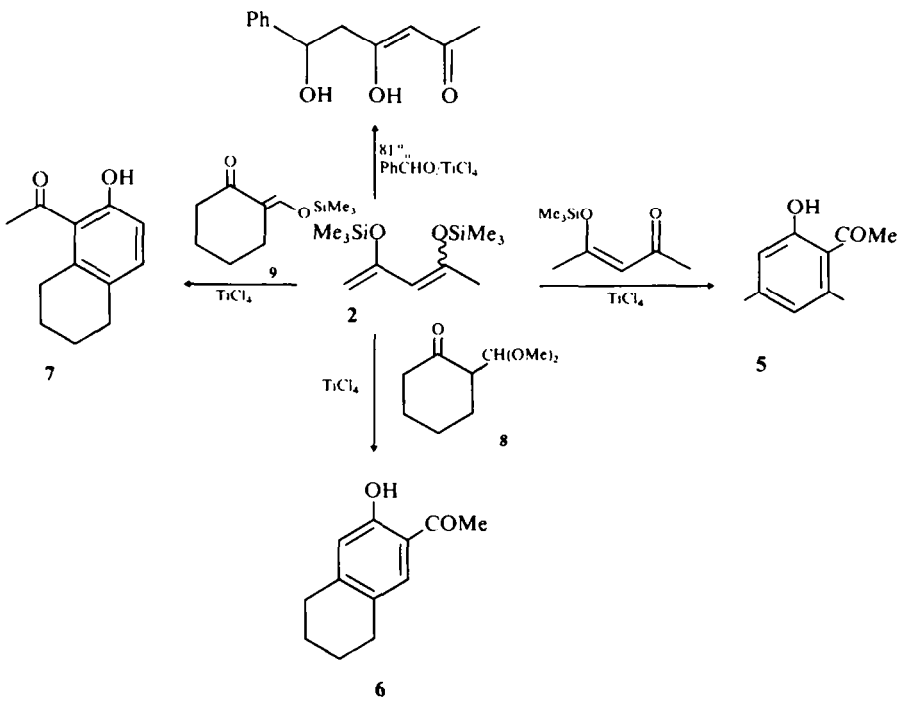
Compound **2** reacts with benzaldehyde in the presence of titanium tetrachloride to give 6-hydroxy-6-phenylhexane-2,4-dione (**4** in enol form) in good yield (Scheme 1). This reaction establishes that, of the two nucleophilic sites in **2**, carbon-1 is the more reactive. Condensation of **2** and **3** with titanium tetrachloride gave compound **5** as product.

It is clear that by using **2** as the nucleophilic component, synthesis of *o*-acetylphenol according to eqn (1) is indeed viable. The control of regiochemistry of the reaction can be demonstrated by the preparation of the regio-isomers **6** and **7**. Using β-oxo acetal **8** as the electrophile[2] in condensation with **2**, compound **6** was obtained exclusively. The regiochemistry of **6** is in accordance with the reactivity order of ketone > acetal. On the other hand, with β-siloxyenone **9** as the electrophile, the isomeric compound **7** was produced without a trace of presence of **6**, again, in agreement with prediction from the reactivity order of the electrophilic sites (Scheme 1).

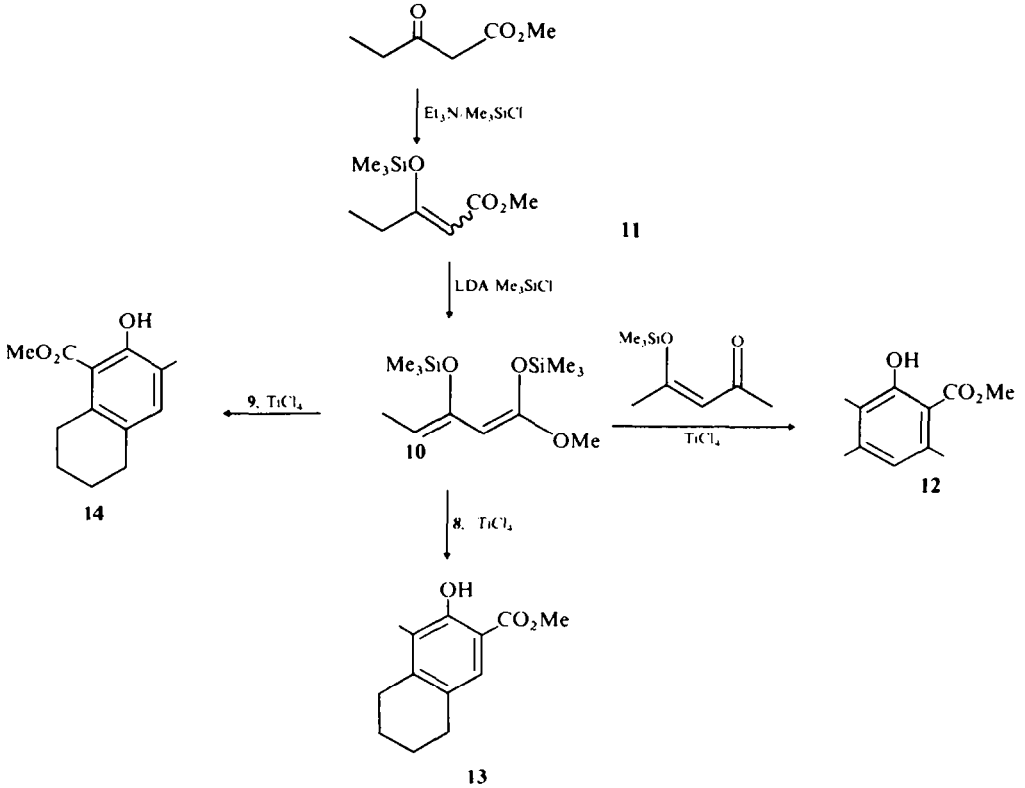
1,3-*Bis*(*trimethylsiloxy*)-1-*methoxypenta*-1,3-*diene* (**10**). So far, of all the salicylates[2] and *o*-acetylphenols prepared according to eqn (1), they are unsubstituted at the *o'*-position. This is a consequence of the structure of the nucleophilic components used. Both **1** and **2** are unsubstituted at the more reactive site. We are interested in examining the effect of substitution on the order of nucleophilic reactivity.

Methyl 3-trimethylsiloxypent-2-enoate (**11**) was prepared from methyl 3-oxovalerate in 95% yield as a 7:2 mixture of *E* and *Z* isomers. Reaction of **11** with lithium di-isopropylamide followed by quenching with trimethylchlorosilane gave compound **10**, a yellowish oil, in 95% yield. Judging from ^{1}H NMR, we tentatively assigned it to be a 5:1 mixture of 1*E*, 3*Z* and 1*E*, 3*E* isomers.

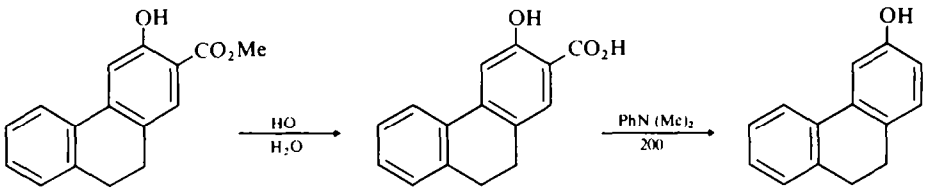
Condensation of **10** with 3-trimethylsiloxybut-3-en-2-one (**3**) and titanium tetrachloride gave methyl 3,4,6-trimethylsalicylate (**12**). The regiospecific nature of the reaction is again demonstrated by the condensation of **10** with either **8** or **9** to give the regioisomeric tetralin derivatives **13** and **14** respectively. The structures of the products establish that the nucleophilic reactivity



Scheme 1.



Scheme 2.



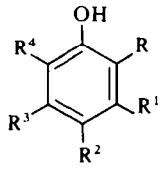
15 17 16

order in **10** is not changed with respect to **1** because of the presence of the extra Me group.

Conversion of salicylates into phenols. It is obvious that by using **1** or **10** as the nucleophilic components in eqn (1), the products derived must have the substituted salicylate structure. The reaction represents nevertheless a general synthesis of substituted phenol because of the ease of removal of the carboxyl group.

This is demonstrated by the conversion of methyl 2-hydroxy-9,10-dihydrophenanthrene-3-carboxylate[2] (**15**) into 9,10-dihydrophenanthen-2-ol (**16**). Alkaline hydrolysis of **15** gave the carboxylic acid **17** in essentially quantitative yield. Decarboxylation of **17** in a solution of N,N-dimethylaniline at 200° gave the phenol **16** in 92% yield.

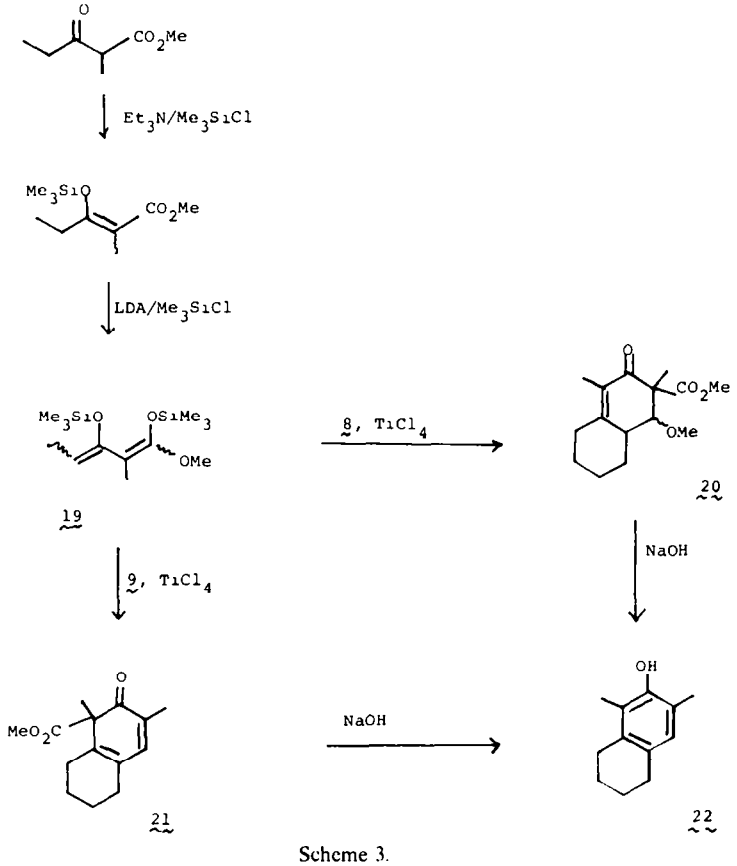
The cycloaromatisation reaction can thus be used for the regiocontrolled synthesis of substituted phenols of general structure **18** where R can be $-CO_2Me$, CO_2H, COMe or H. It remains to be seen whether the reaction can be used for the synthesis of *o,o'*-disubstituted phenols (i.e. R and R^4 both alkyl).



18

1,3-*Bis*(*trimethylsiloxy*)-1-*methoxy*-2-*methylpenta*-1,3-*diene* (**19**). To answer this point, we prepared compound **19** and examined its suitability as the nucleophilic component in eqn (1). Methyl 2-methyl-3-oxopentanoate was converted first to methyl 2-methyl-3-trimethylsiloxypent-2-enoate and thence to compound **19** according to standard procedures (Scheme 3).

Reaction of **19** with compound **8** and titanium tetrachloride gave as product compound **20**. It is clear that cyclisation according to eqn (1) has taken place,



Scheme 3.

but because of the gem-disubstitution at one of the ring carbon, aromatisation could not occur.

The structure of **20** is evident from its spectroscopic data, particularly from its mass spectra (EI-MS, $M^+ = 266$, CI-MS, $MH^+ = 267$). On the other hand, reaction of **19** with compound **9** and titanium tetrachloride gave the cyclohexadienone **21** as product (Scheme 3). The cyclohexadienone structure is consistent with its UV spectrum (λ_{max} (CH_3OH) = 326 nm).

Hydrolysis of either of the foregoing β-ketoesters (**20** or **21**) with hot aqueous sodium hydroxide caused decarboxylation and aromatisation to give 1,3-dimethyl-5,6,7,8-tetrahydronaphthalen-2-ol in 89% yield.

The above sequence of reactions indicates that the cycloaromatisation reaction can be used for a general synthesis of substituted phenols with diverse substitution patterns and functionalities. Since many natural occurring compounds have the phenolic structure, we are confident that the method described here will find application in the synthesis of some of these compounds.

EXPERIMENTAL

General. M. and b.ps are uncorrected. IR spectra were obtained from films on NaCl plates for liquids and from solns in 0.1-mm NaCl cell for solids, using a Perkin-Elmer 297 spectrophotometer. ^1H NMR spectra were recorded on Varian T-60 and T-60A instruments, with Me_4Si as internal standard. Mass spectra were obtained on a Hewlett–Packard 5984A or an LKB 9000 machine operating at 70 eV. Column chromatography was performed on silica gel 60 (Merck). Et_3N, i-Pr_2NH, and TMEDA were dried by distillation from CaH_2; hexane, CCl_4, and benzene from P_2O_5; CH_2Cl_2 from P_2O_5 and then from CaH_2. THF was distilled under N_2 from sodium-benzophenone directly into the reaction vessel. Microanalyses were performed by Guelph Chemical Laboratories Ltd.

2,4-*Bis*(*trimethylsiloxy*)-*penta*-1,3-*diene* (**2**)[3] was prepared from **3**[2] by Danishefsky's method[4] in 96% yield as a 1:1 mixture of geometrical isomers. It was pure by ^1H NMR and gc and was used without distillation. ^1H NMR ($CDCl_3$): δ 0.19 and 0.20 (each s, 4.5 H, Me_3Si), 0.22 (s, 9 H, Me_3Si), 1.83 and 1.99 (each s, 1.5 H, MeC=), 4.04, 4.09, 4.27 br, 4.67, 4.70 br and 5.15 (each s, 0.5 H, HC=); IR (film): 1653, 846 cm^{-1}.

Reaction of **2** *with benzaldehyde.* $TiCl_4$ (0.55 ml, 5 mmol) was added to a mixture of **2** (1.09 g, 4.5 mmol) and benzaldehyde (0.53 g, 5 mmol) in dry CH_2Cl_2 (5 ml) under N_2 at −78°. The dark red soln was stirred at −78° for 3 hr, then allowed to warm to 0°, added to $NaHCO_3$aq and extracted with ether. The extracts were dried ($MgSO_4$) and evaporated to give a yellowish oil (0.88 g) which was substantially pure 6-hydroxy-6-phenylhexane-2,4-dione. Column chromatography caused partial dehydration of this alcohol to *E*-6-phenylhex-5-ene-2,4-dione. The *benzylic alcohol* (0.62 g, 68%) was a colourless oil, R_f 0.47 (CH_2Cl_2), ^1H NMR ($CDCl_3$): δ 2.01 (s, 3 H, MeC=), 2.55 and 2.65 (ABX system, 2 H, J_{AB} 16.5, J_{AX} 5.5, J_{BX} 11.5 Hz, CH_2^*CH), 5.23 (dd, 1 H, J 5.5, 11.5 Hz, $PhCH^*CH_2^*$), 5.28 (s, 1 H, HOC=CHCO), 7.20 (s, 5 H, Ph); IR (film 3420 br, 1666, 1609 cm^{-1} (entirely in the enol form). The *styrene derivative* (0.11 g, 13%) was colourless needles m.p. 83-4° (from cyclohexane), R_f 0.63 (CH_2Cl_2), ^1H NMR ($CDCl_3$) δ 2.08 (s, 3 H, MeC=), 5.46 (s, 1 H, HOC=CHCO), 6.23 and 7.36 (each d, 1 H, J 15 Hz, *trans*-HC=CH), 7.0–7.4 (m, 5 H, Ph); IR ($CHCl_3$) 3500 br, 1638, 1583 cm^{-1} (entirely in the end form); MS *m/e* 188 (M^+, 89%), 145 (100), 131 (91) 103 (64).

1-(4,6-*Dimethyl*-2-*hydroxyphenyl*)*ethanone* (**5**) was prepared as above from **2**, **3** and $TiCl_4$ in 44% yield after column chromatography eluted with CH_2Cl_2. It was colourless needles m.p. 57.5–58° (from water) (lit.[5] 58°), R_f 0.62, ^1H NMR ($CDCl_3$): δ 2.23 (s, 3 H, 4-Me), 2.51 (s, 3 H, 6-Me), 5.28 (s, 3 H, MeCO), 6.42 and 6.51 (each brs, 1 H, Ar), 12.52 (s, 1 H, OH).

1-(2-*Hydroxy*-5,6,7,8-*tetrahydronaphth*-1-*yl*)*ethanone* (**7**) was prepared similarly [using 2-(trimethylsiloxymethylene) cyclohexanone],[2] in 40% yield. It was colourless needles, m.p. 110–112° (lit.[6] 112–3°). R_f 0.54, ^1H NMR ($CDCl_3$) δ 1.6–1.9 (m, 4 H, β-CH_2), 2.56 (s, 3 H, MeCO), 2.6–3.0 (m, 4 H, α-CH_2), 6.60 (d, 1 H, J 8 Hz, H-3), 6.95 (d, 1 H, J 8 Hz, H-4), 10.2 (brs, 1 H, OH). No isomeric products were observed.

1-(3-*Hydroxy*-5,6,7,8-*tetrahydronaphth*-2-*yl*)*ethanone* (**6**). Cyclohexanone silyl enol ether (0.85 g, 5 mmol) was added to a well-stirred mixture of trimethyl orthoformate (0.53 g, 5 mmol) and $TiCl_4$ (0.55 ml, 5 mmol) in dry CH_2Cl_2 (5 ml) under N_2 at −78°. After 1 hr, **2** (1.09 g, 4.5 mmol) in dry CH_2Cl_2 (5 ml), and $TiCl_4$ (0.55 ml) were added. The dark red soln was stirred at −78° for a further 3 hr, then allowed to warm to 0°, poured into $NaHCO_3$aq and extracted with ether. The extracts were dried ($MgSO_4$), evaporated and the residual oil (0.86 g) purified by column chromatography (eluant CH_2Cl_2) to give the acetyl tetralin derivative **6** as cream needles, (0.39 g, 45%), m.p. 71–2° (from EtOH) (lit.[6] m.p. 72-3°), R_f 0.61, ^1H NMR ($CDCl_3$): δ 1.6–1.9 (m, 4 H, β-CH_2), 2.48 (s, 3 H, MeCO), 2.5–2.8 (m, 4 H, α-CH_2), 6.45 (s, 1 H, H-4), 7.17 (s, 1 H, H-1), 11.08 (s, 1 H, OH). No isomerise products were observed.

Methyl 3-*trimethylsiloxypent*-2-*enoate* (**11**) was prepared from methyl 3-oxovalerate by Danishefsky's method[4] in 95% yield. It had b.p. 65–69° (1.4 mm), ^1H NMR ($CDCl_3$); (a 7:2 mixture *E* and *Z* of isomers) δ 0.27 (s, 9 H, Me_3Si), 1.07 (t, 3 H, J 7.5 Hz, $MeCH_2$), 2.12 ^{Z} and 2.69 ^{E} (2 H, each q, J 7.5 Hz, $MeC\underline{H}_2$), 3.61 (s, 3 H, CO_2Me), and 5.02 ^{E} and 5.09 ^{Z} (1 H, each s, HC=); IR (film) 1720, 1622 cm^{-1}; MS *m/e* 202 (M^+, 4%), 187 (100), 89 (92) and 73 (92).

1,3-*Bis*(*trimethylsiloxy*)-1-*methoxypenta*-1,3-*diene* (**10**) was prepared from **3**, **10** and $TiCl_4$ as described for **5**. After preparation of **1**.[2] It was a yellowish oil (91–98% yield). Its ^1H NMR shows a single isomer about C1–2, and a *ca* 5:1 mixture isomers about C3–4: δ ($CDCl_3$) 0.18 and 0.22 (each s, 9 H, Me_3Si), 1.51 ^{E} and 1.58 ^{Z} (3 H, each d, J 7 Hz, MeCH=), 3.49 (s, 3 H, MeO), 3.88 (s, 1 H, HC=), 4.21 ^{E} and 4.87 ^{Z} (1 H, each q, J 7 Hz, MeCH=); IR (film): 1657, 1622 cm^{-1}; MS: *m/e* 274 (M^+, 4%), 259 (2), 245 (4), 170 (19), 73 (100).

Methyl 2-*hydroxy*-3,4,6-*trimethylbenzoate* (**12**) was prepared from **3**, **10** and $TiCl_4$ as described for **5**. After purification and recrystallization from hexane, **12** was obtained as colourless plates (70% yield), m.p. 68–68.5°; ^1H NMR ($CDCl_3$) δ 2.12 (s, 3 H, 4-Me), 2.21 (s, 3 H, 3-Me), 2.43 (s, 3 H, 6-Me), 3.87 (s, 3 H, CO_2Me), 6.42 (s, 1 H, Ar), 11.62 (s, 1 H, OH); IR ($CHCl_3$) 3100 br, 1660, 1616 cm^{-1}; MS *m/e* 194 (M^+, 61%), 162 (100), 134 (85).

Methyl 2-*hydroxy*-3-*methyl*-5,6,7,8-*tetrahydronaphthalene*-1-*carboxylate* (**14**) [from 2-(trimethylsilylmethylene)cyclohexanone, **10** and $TiCl_4$] was purified by elution with CCl_4 through a bed of Fluorisil and recrystallization from MeOH: colourless needles (58% yield), m.p. 59–60°; ^1H NMR ($CDCl_3$) δ 1.5–1.9 (m, 4 H, β-CH_2), 2.19 (s, 3 H, 3-Me), 2.5–3.1 (m, 4 H, α-CH_2), 3.93 (s, 3 H, CO_2Me), 6.98 (s, 1 H, Ar), 11.11 (s, 1 H, OH); IR ($CHCl_3$) 3100 br, 1662, 1618, 1590 cm^{-1}; MS *m/e* 220 (M^+, 51%), 188 (100), 160 (53). No isomeric products were observed. (Found: C, 70.73; H, 7.18. Calc. for $C_{13}H_{16}O_3$: C, 70.89, H, 7.32%).

Methyl 3-*hydroxy*-4-*methyl*-5,6,7,8-*tetrahydronaphthalene*-2-*carboxylate* (**13**) was prepared from trimethyl orthoformate, cyclohexanone trimethylsilyl enol ether, $TiCl_4$ and **10** as described previously for **6**. It was purified by column chromatography eluted with CH_2Cl_2 (41% yield), and had m.p. 59.5–60° (from methanol); R_f 0.63; ^1H NMR ($CDCl_3$): δ 1.6–2.0 (m, 4 H, β-CH_2), 2.09 (s, 3 H, 4-Me), 2.4–2.8 (m, 4 H, α-CH_2), 3.86 (s, 3 H, CO_2Me), 7.33 (s, 1 H, Ar), 10.77 (s, 1 H, OH); IR ($CHCl_3$) 3200 br, 1670, 1619 cm^{-1}; MS *m/e* 220 (M^+, 100%), 188 (94), 160 (74). No isomeric products were observed. (Found: C, 70.60; H, 7.33. Calc. for $C_{13}H_{16}O_3$: C,

70.89; H, 7.32%). The identify of this compound was confirmed by hydrolysis to the known acid: 3-hydroxy-3-methyl-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid (98%), m.p. 238–238.5° (from MeOH) [lit.[7] 237–8] ^{1}H NMR (1:1 $CDCl_3$–CD_3OD) δ 1.6–1.9 (m, 4 H, β-CH_2), 2.14 (s, 3 H, Me), 2.5–2.9 (m, 4 H, α-CH_2), 4.3 (brs, 2 H, OH), 7.43 (s, 1 H, Ar).

9,10-Dihydrophenanthren-2-ol (**16**). Compound **17**[2] (0.12 g, 0.5 mmol) was heated at 200° in N,N-dimethylaniline (5 ml)[8] under N_2 for 3 hr. Colourless crystals were deposited. The mixture was cooled, acidified with 5 M HCl and extracted with ether. The extracts were dried ($MgSO_4$) and evaporated to give colourless needles of 9,10-dihydrophenanthren-2-ol (0.09 g, 92%), m.p. 110–111° after one recrystallization from CCl_4 (lit.[9] 111.5–113°), ^{1}H NMR ($CDCl_3$) δ 2.76 (s, 4 H, CH_2), 5.5 (brs, 1 H, OH), 6.66 (brs, 1 H, H-1), 6.72 (brd, 1 H, *J* 7 Hz, H-3), 7.0–7.3 (m, 3 H, H-6, 7, 8), 7.4–7.7 (m, 2 H, H-4, 5).

Methyl 2-methyl-3-trimethylsiloxypent-2-enoate. Methyl 2-methyl-3-oxopentanoate was prepared by the method of McElvain.[10] It was silylated directly by Danishefsky's method[4] to give methyl 2-methyl-3-trimethylsiloxypent-2-enoate (51.8 g, 48% overall), a colourless oil, b.p. 71–3° (0.7 mm); ^{1}H NMR ($CDCl_3$) (a 5:1 mixture of *E* and *Z* isomers) δ 0.25 (s, 9 H, Me_3Si), 1.10 (t, *J* 7.5 Hz, $MeCH_2$), 1.77 ^{E} and 1.82 ^{Z} (3 H, each s, MeC=), 2.22 ^{Z} and 2.64 ^{E} (2 H, each q, *J* 7.5 Hz, $MeC\underline{H}_2$), 3.68 (s, 3 H, CO_2Me); IR (film) 1714, 1620 cm^{-1}; MS *m/e* 216 (M^+, 7%), 201 (21), 198 (26), 160 (17), 94 (81), 73 (100), 66 (89).

1,3-Bis(trimethylsiloxy)-1-methoxy-2-methylpenta-1,3-diene (**19**) was prepared from methyl 2-methyl-3-trimethylsiloxypent-2-enoate as described previously for compound **1**.[2] It was an orangish oil (84% yield), whose NMR showed a single isomer: δ ($CDCl_3$) 0.15 and 0.20 (each s, 9 H, Me_3Si), 1.57 (d, 3 H, *J* 7 Hz, MeCH=), 1.65 (s, 3 H MeC=), 3.53 (s, 3 H, MeO), 4.73 (q, 1 H, *J* 7 Hz, MeCH=); IR (film) 1667 cm^{-1}, MS *m/e* 288 (M^+, 9%), 273 (6), 259 (23), 184 (20), 73 (100).

Methyl 2,4-dimethyl-1-methoxy-3-oxo-1,2,3,5,6,7,8,8a-octohydronaphthalene-2-carboxylate (**20**) was prepared from trimethyl orthoformate, cyclohexanone trimethylsilyl enol ether, $TiCl_4$ and **19** as described previously for **6**. Purification by column chromatography eluted with CH_2Cl_2 gave **20** as a colourless oil (40%), R_f 0.54, ^{1}H NMR ($CDCl_3$) δ 1.0–2.6 (m, 8 H, CH_2), 1.19 (s, 3 H, Me), 1.73 (s, 3 H, MeC=), 2.7–3.0 (m, 1 H, H-8a), 3.32 (s, 3 H, MeO), 3.6–3.9 (m, 1 H, H-1), 3.70 (s, 3 H, CO_2Me); IR (film) 1745, 1664, 1618 cm^{-1}, UV (CH_3OH) 252.5 nm; MS *m/e* 266 (M^+, 1%), 234 (2), 175 (19), 136 (100); CI-MS (isobutane) 267 (MH^+, 100%), 235 (52), 136 (23).

Methyl 1,3-dimethyl-2-oxo-1,2,5,6,7,8-hexahydronaphthalene-1-carboxylate (**21**) was prepared from **19**, 2-(trimethylsiloxymethylene)cyclohexanone[2] and $TiCl_4$ as described previously for **7**. It was purified by column chromatography eluted with CH_2Cl_2, giving a colourless oil (40%), R_f 0.58, ^{1}H NMR ($CDCl_3$) δ 1.45 (s, 3 H, Me), 1.5–1.8 (m, 4 H, β-CH_2), 1.90 (s, 3 H, MeC=), 2.0–2.4 (m, 4 H, α-CH_2), 3.68 (s, 3 H, CO_2Me), 6.66 (s, 1 H, HC=); IR (film) 1748, 1669, 1648, 1595 cm^{-1}; UV (CH_3OH) 326 nm; MS *m/e* 234 (M^+, 8%), 175 (100); CI-MS (isobutane) 235 (MH^+, 100), 203 (4), 175 (14).

1,3-Dimethyl-5,6,7,8-tetrahydronaphthalen-2-ol (**22**). Hydrolysis of either of the foregoing β-ketoesters (**20** or **21**) with hot NaOHaq causes decarboxylation and aromatization to give 1,3-dimethyl-5,6,7,8-tetrahydronaphthalen-2-ol (89% in each case), colourless needles from methanol, m.p. 97–8° (lit.[11] 97.5–98°), ^{1}H NMR ($CDCl_3$) δ 1.6–2.0 (m, 4 H, β-CH_2), 2.10 and 2.19 (each s, 3 H, Me), 2.4–2.8 (m, 4 H, α-CH_2), 4.4 (brs, 1 H, OH), 6.66 (s, 1 H, Ar).

Acknowledgement—We thank the NSERC of Canada and the Ministry of Education, Government of Quebec, for financial support of this research.

REFERENCES

[1]Part III of the series on A Novel Cycloaromatisation Reaction. For Part II, see T. H. Chan and P. Brownbridge, submitted for publication.
[2]T. H. Chan and P. Brownbridge, *J. Am. Chem. Soc.* **102**, 3534 (1980).
[3]T. Ibuka, Y. Ito, Y. Mori, T. Hoyama and Y. Inubushi, *Syn. Commun.* **7**, 131 (1977).
[4]S. Danishefsky and T. Kitahara, *J. Am. Chem. Soc.* **96**, 7807 (1974).
[5]A. Heikel, *Suomen Kemistilehti* **8B**, 33 (1935); *Chem. Abstr.* **30**, 438[2] (1936).
[6]M. P. O'Farrell, D. M. S. Wheeler, M. M. Wheeler and T. S. Wheeler, *J. Chem. Soc.* 3986 (1955).
[7]H. Mori, V. S. Ghandi and E. Schwenk, *Chem. Pharm. Bull.* **12**, 112 (1964).
[8]D. S. Tarbell, J. Wilson and P. E. Fanta, *Org. Syn. Coll.* vol. III 267.
[9]A. Burger and E. Mosettig, *J. Am. Chem. Soc.* **59**, 1302 (1937).
[10]S. M. McElvain, *Ibid.* **51**, 3124 (1929).
[11]W. Cocker, *J. Chem. Soc.* 36 (1946).