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ACID-CATALYSED CYCLISATION OF 2-METHYL-2[3-(2,4-DIMETHOXYPHENYL)-5-METHOXYPENT-2-ENYL]-CYCLOPENTANE-1,3-DIONE: STRUCTURE OF A NOVEL PRODUCT

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Abstract—Acid-catalysed reaction of the title compound (**3a**) with boiling ethanolic HCl afforded a complex mixture of compounds from which a crystalline keto alcohol was isolated. On the basis of spectral data (UV, IR, NMR and MS), this keto alcohol was assigned the tricyclodecane structure **7a**. Acetylation of the keto alcohol followed by hydrogenation gave the dihydro keto acetate **8b** which was brominated using dioxane dibromide to give the bromo compound **8c**. X-ray crystal structure analysis of the bromo compound confirmed the structure of this compound as well as the parent keto alcohol **7a**.

During the investigations on the total synthesis of 6- and 11-oxasteroid analogues starting from compounds having a built-in ether linkage, Kasturi *et al.*[1] have observed that the main drawback of this approach was the ether cleavage side reactions resulting in very low yields of the expected intermediates. Alternatively, a B-seco approach based on Torgov's[2] coupling reaction between vinyl carbinols and β-diketones was envisaged for the synthesis of 6-oxasteroid analogues. Examples involving a B-seco approach for the total synthesis of steroids are the syntheses of estrone[3] and the synthesis of steroids without ring B.[4] An advantage of this approach is that the B-seco intermediate that could be obtained from a suitably substituted propiophenone may lead not only to oxasteroids but also to aza- and thiasteroids. We wish to report in this paper the synthesis of a novel type of steroid derivative without ring B. A brief communication of this work has been published earlier.[5]

Grignard reaction of 2',3,4'-trimethoxypropiophenone **1a**[6] with vinyl magnesium bromide afforded the vinyl carbinol **2a** in good yield. Since the isothiouronium salt of this carbinol could not be prepared, the carbinol was condensed with 2-methylcyclopentane-1,3-dione in refluxing xylene in the presence of Triton B. The presence of a 2,2-disubstituted cyclopentane-1,3-dione system[7] and a 2,4-dimethoxystyrene chromophore[8] in this product was evident by its IR (1765 and 1725 cm^{-1}) and UV (λ_{max} 240 and 281 nm) spectra respectively. The NMR spectrum, which showed two singlets at 1·17 and 1·00 δ integrating for a total of three protons for the angular Me group, indicated that the product was a mixture of two compounds in the ratio of about 10:1. These two signals may arise from the Me groups of the *E* **3a** and *Z* **4** forms of the expected seco-dione. These two compounds could be separated by careful preparative layer chromatography and their structures and configurations confirmed by a detailed study of their spectral data.† Both the isomers gave the dihydro derivative **5** on catalytic reduction.

Attempts to effect the cyclodehydration of the seco-dione **3a** to the desired B-secopentaenone **6** under different conditions[9] were unsuccessful. However, refluxing a solution of the seco-dione in 20% ethanolic hydrochloric acid for 1 hr gave a mixture of products (TLC). A crystalline compound was isolated from this reaction mixture in about 20% yield by a series of column chromatography followed by crystallisation. Elemental analysis and mass spectrometry (M^+ 314) supported the formula $C_{19}H_{22}O_4$ to this solid. The IR ($CHCl_3$) spectrum (3610 and 1745 cm^{-1}) indicated the presence of OH and 5-membered CO groups. The presence of a 2,4-dimethoxystyrene system was evident from the UV absorption maxima at 245 (ϵ 9,900) and 284 nm (3800). The presence of one double bond in conjugation with the phenyl ring was confirmed by catalytic hydrogenation of this keto alcohol to a dihydro compound (M^+ 316) which exhibited UV absorption maxima at 227 (ϵ 9,500) and 279 nm (3,500). The NMR spectrum ($CDCl_3$) of the keto alcohol exhibited the following signals: 1·13 (s, 3H, $-CH_3$), 1·04 – 1·30(m, 1 H), 1·70 – 3·20 (complex multiplet, 8 H), 3·79 (s, 6 H, 2 Ar—OCH_3), 5·52 (T, J = 3·5 Hz, 1 H, $=CH-CH_2-$), 6·30 – 6·50 (m, 2 H, Ar—H) and 6·98 δ (d, J = 9 Hz, 1 H, Ar—H). It is clear from the spectral data that the side chain methoxyl group in the seco-dione **3a** is lost during the formation of the keto alcohol. If this

†A detailed study of the NMR spectra of these and similar isomeric seco-diones resulted in the assignment of configurations and will be reported elsewhere.

is so, it is expected that, under similar conditions, the seco-dione **3b** should also give the same keto alcohol. With this in view, a study of the ethanolic hydrochloric acid reaction of the seco-dione **3b** was undertaken.

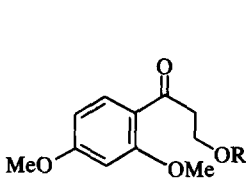
The required seco-dione **3b** was prepared by Grignard reaction of 2′,4′-dimethoxy-3-ethoxy-propiophenone **1b**[9] with vinyl magnesium bromide followed by condensation of the resulting vinyl carbinol **2b** with 2-methylcyclopentane-1,3-dione. Reaction of the seco-dione **3b** with 20% ethanolic hydrochloric acid was carried out as before. From the reaction product, which was found to be a complex mixture similar to the one obtained from the seco-dione **3a** [TLC], only the product which was more polar than the starting material was isolated. This fraction could be readily crystallised from hexane-benzene mixture and was found to be identical with the keto alcohol mentioned earlier.

The hydroxyl group in the aforementioned keto alcohol was found to be tertiary in nature as it did not undergo oxidation. This was confirmed by its NMR spectrum in DMSO-d_6,[10] which exhibited a sharp singlet at 4·94 δ. Further, the NMR spectrum of the corresponding acetate of the keto alcohol showed no signals due to the α-hydrogen of the acetate group in the 4–5 δ region, thus confirming the tertiary nature of the OH group. Hydrolysis of the acetate gave back the original alcohol indicating that no rearrangement occurred during the formation of the acetate.

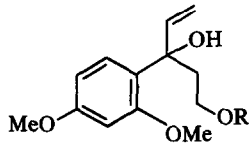
Based on these evidences, the tricyclodecane structure **7a** was tentatively proposed to this keto alcohol. However, several alternate structures* which might account for the aforementioned spectral data, and also be derived mechanistically could not be ruled out. Hence, with a view to establishing the structure and stereochemistry of the keto alcohol, X-ray crystal structure analysis of its bromo derivative was undertaken.

Attempts to prepare the *p*-bromobenzoate **7c**, *p*-iodobenzoate **7d** or bromoacetate **7e** by treating the keto alcohol **7a** eith the respective acid chlorides in pyridine or dimethylaniline[11] were not successful. Similarly, attempts to prepare the bromoacetate **7e**

*For the sake of brevity, these structures are not indicated.



1



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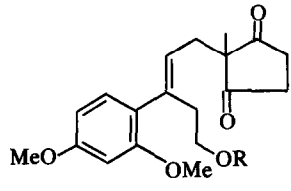
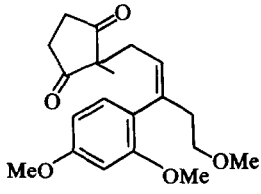


3

a: R = Me b: R = Et



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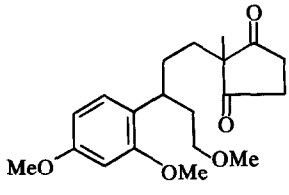

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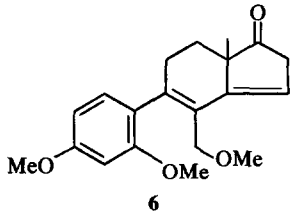

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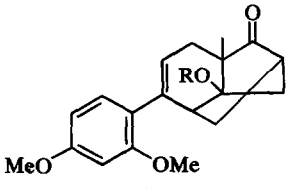
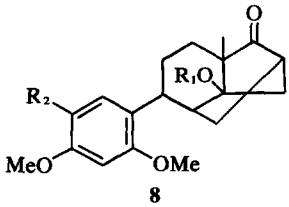


7

a: R = H
b: R = –$COCH_3$
c: R = *p*–BrC_6H_4CO–
d: R = *p*–IC_6H_4CO–
e: R = –$COCH_2Br$



8

a: R_1 = H, R_2 = H
b: R_1 = $COCH_3$, R_2 = H
c: R_1 = $COCH_3$, R_2 = Br

using DCC as the condensing agent[12] were also futile. Steric factors may be responsible for the non-formation of these derivatives. Next, we attempted to prepare a bromo compound of a suitable derivative of this alcohol. For this purpose, the keto acetate **7b** was reduced to the dihydro compound **8b**. Treatment of this dihydro compound with dioxane dibromide[13] in ether at −20° afforded a bromo compound **8c** in good yield. The occurrence of two sharp singlets each of one proton intensity at 6·42 and 7·08 δ in the NMR spectrum of the bromo compound indicated the presence of two aromatic protons in *para* relationship and clearly supported the presence of bromine at *ortho*, *para* positions to the OMe groups. Further, the NMR spectrum of the sample, crystallised from light petroleum-benzene mixture, showed a sharp singlet of 3 proton intensity at 7·34 δ and could be assigned to benzene of crystallisation (0·5 M). This was confirmed by the fact that a sample dried at 100° in vacuum (1-2 mm) for a prolonged period did not show this signal. The benzene of crystallisation could be exchanged to methylene chloride by crystallisation from light petroleum-methylene chloride mixture [NMR: 5·28 δ, 1 H]. Crystals grown from light petroleum-benzene mixture were used for subsequent X-ray crystal structure analysis and the presence of benzene of crystallisation (0·5 M) has been confirmed.[14]

The presence of only one Br atom in the molecule was confirmed from its mass spectrum which showed a molecular ion at *m/e* 436 along with a (M + 2) ion of equal intensity.[15] The presence of ions at *m/e* 333 (9), 307 (10), 255 (11), 229(12) and 199 (13) containing a Br atom, confirms the presence of bromine in the aromatic ring.

The X-ray crystal structure analysis of the bromo compound **8c** established its structure as well as the stereochemistry (Fig 1). It was found that the angular Me group and the acetate groups are in *cis* relationship. Thus, the X-ray analysis of the bromo compound **8c** confirmed the structure assigned to the parent keto alcohol **7a**.

A probable mechanism of formation of the keto alcohol **7a** might involve the intramolecular aldol condensation of the diene **14** that may be formed by acid-catalysed elimination of methanol from the seco-dione **3a** to give the intermediate **16**. Further electrophilic attack of the double bond on the carbonyl in the usual way, results in the product **7a**. The isolation of the diene **14*** in this reaction, and the fact that the diene on further treatment with ethanolic HCl gave the keto alcohol **7a** supports the intermediacy of the diene **14**.

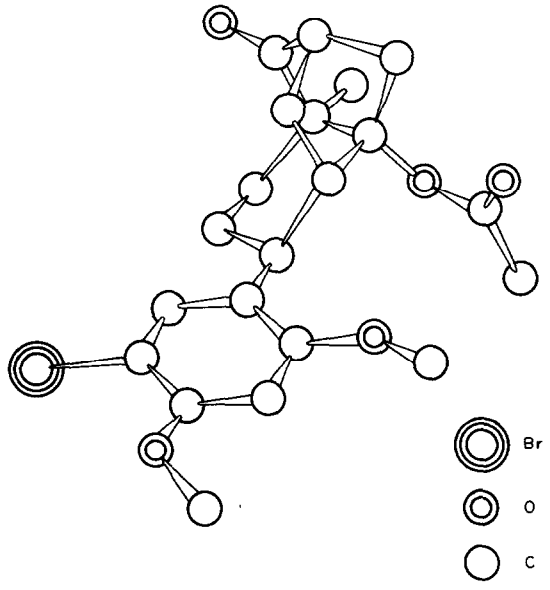
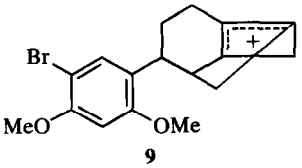


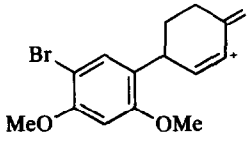
Fig 1. Stereo diagram of the bromo compound **8c**

*The structure of the diene and other compounds isolated in this reaction will be discussed separately.



9

m/e 333, 335



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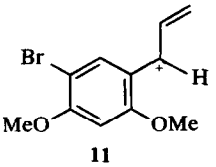
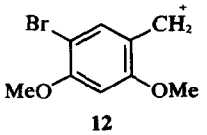
m/e 307, 309



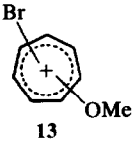
11

m/e 255, 257



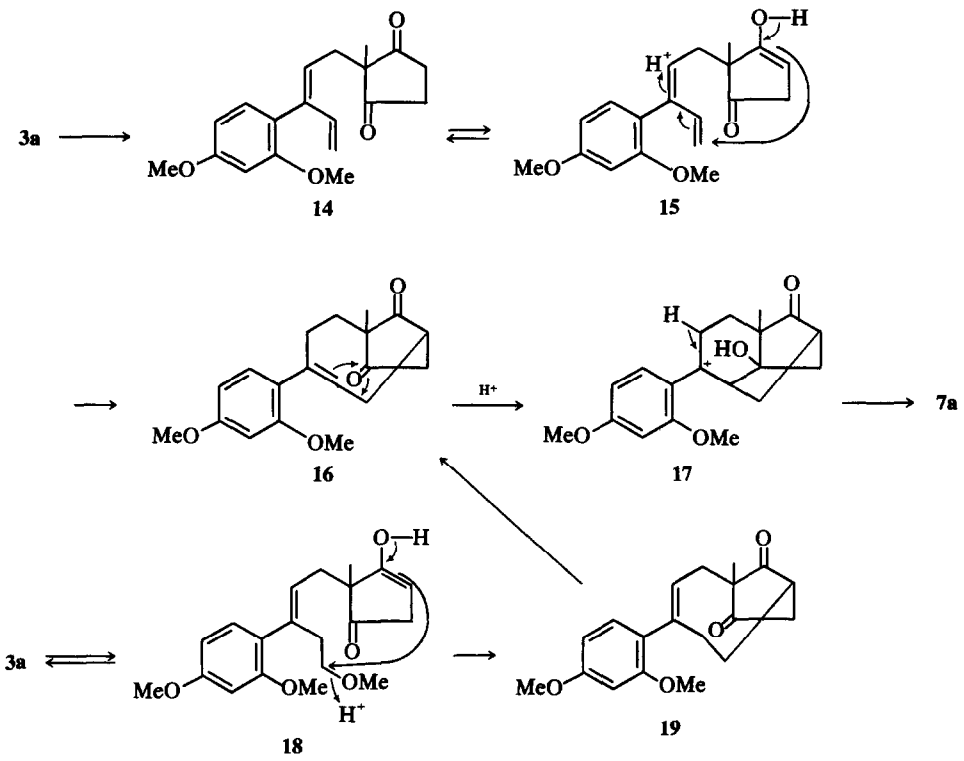
12

m/e 229, 231



13

m/e 199, 201



It is also possible that the intermediate **16** may be formed by the initial displacement of the OMe group with the participation of the enol, as shown in **18**, followed by double bond migration. Instances of displacement and elimination of OMe groups in solvolytic reactions through allylic, homoallylic and neighbouring group participations involving non-classical carbonium ions are known in literature.[16] It is not possible to definitely conclude whether the reaction proceeds by the above stepwise mechanism or by a concerted process.

Similar types of acid as well as base-catalysed enol addition to double bond are known in literature.[17]

EXPERIMENTAL

General. All mps and bps are uncorrected. UV spectra were recorded in 95% EtOH on a Beckmann Unicam SP 700 A spectrophotometer. IR spectra were recorded on a Perkin-Elmer Model 700 spectrophotometer. NMR spectra were recorded on a HA-100D spectrometer using TMS as internal standard. Mass spectra were recorded on an Atlas CH-4 spectrometer equipped with a built-in direct inlet system.

2-Methyl-2 [3-(2,4-dimethoxyphenyl)- 5 -methoxypent- 2 -enyl]-cyclopentane-1,3-dione **3a** and **4**

(*a*) *1-Hydroxy-2', 3, 4'-trimethoxy- 1 -vinyl-propyl benzene* **2a**. A soln of 2',3,4'-trimethoxypropiophenone[6] (7·5 g) in dry THF (50 ml) was added gradually with stirring to vinyl magnesium bromide prepared from Mg (4·5 g) and vinyl bromide (25 ml) in a mixture of dry THF (80 ml) and ether (20 ml) at −20°. After being stirred for 3 hr at the same temp, the suspension was refluxed for 2 hr, cooled and then poured into a mixture of ice and NH_4Cl. The product was extracted with ether and the organic layer was washed several times with water and dried (Na_2SO_4). Removal of solvent yielded **2a** as an oil (8·2 g), IR (Neat): ν_{max} 3600, 1610, 1590, 980 and 920 cm^{-1}.

(*b*) *Condensation of the carbinol* **2a** *with 2-methylcyclopentane-1,3-dione.* A mixture of the carbinol (6 g), 2-methylcyclopentane-1,3-dione (3·5 g), Triton B (1·6 ml) and xylene (40 ml) was refluxed vigorously with stirring for 16 hr and the water formed during the reaction was removed by means of a Dean-Stark apparatus. The cooled mixture was diluted with benzene and washed successively with water, cold 5% KOH aq, water and dried (Na_2SO_4). The solvent was removed and the residual oil (8·5 g) was chromatographed over neutral alumina to afford the seco-dione mixture **3a** and **4** (6·5 g). Preparative layer chromatography of a portion of this mixture using chloroform-ethyl acetate mixture (9:1) afforded two fractions:

Fraction 1. (**3a**, less polar), b.p. 150–160°/1–2 mm (bath temp), IR (Neat): ν_{max} 1765, 1725, 1610 and 1590 cm^{-1}; UV: λ_{max} 240 (ϵ 9,850)and 281 nm (4,200); NMR ($CDCl_3$): 1·17 (s, 3 H), 2·44–2·68 [triplet, (J = 8 Hz) on which a doublet (J = 8 Hz) was superimposed, 4 H], 2·72 (s, 4 H), 3·17 (t, J = 8 Hz, 2 H), 3·22 (s, 3 H), 3·74 (s, 3 H), 3·78 (s, 3 H), 5·22 (t, J = 8 Hz, 1 H), 6·30–6·46 (m, 2 H) and 6·88 δ (d, J = 9 Hz, 1 H); MS: m/e 346 (M^+). (Found: C, 69·23; H, 7·55. $C_{20}H_{26}O_5$ requires: C, 69·36; H, 7·51%).

Fraction 2. (**4**, more polar), b.p. 195–200°/1–2 mm (bath temp); IR (Neat): ν_{max} 1765, 1725, 1610 and 1590 cm^{-1}; UV: λ_{max} 236 (ϵ 7,350) and 281 nm (2,200). NMR ($CDCl_3$): 1·00 (s, 3 H), 2·14 (d, J = 8 Hz, 2 H), 2·50 (t, J = 7 Hz,

2 H), 2·62–2·76 (doublet like multiplet, 4 H) 3·24 (s, 3 H), 3·26 (t, $J = 7$ Hz, 2 H), 3·74 (s, 3 H), 3·80 (s, 3 H), 5·34 (t, $J = 8$ Hz, 1 H), 6·40–6·50 (m, 2 H) and 6·78 δ (d, $J = 9$ Hz, 1 H) (Found: C, 69·02, H, 7·42. $C_{20}H_{26}O_5$ requires: C, 69·36; H, 7·51%).

2-Methyl-2[3-(2,4-dimethoxyphenyl)- 5 -methoxypentyl] -cyclopentane-1,3-dione **5**

A soln of **3a** (0·1 g) in EtOH (20 ml) was stirred with 10% Pd-C catalyst (0·03 g) in an atmosphere of H_2 until no more H_2 was absorbed. The catalyst was filtered and the solvent removed. Chromatography of the residue afforded **5** (0·07 g), b.p. 165–170°/1–2 mm (bath temp); Ir (Neat): ν_{max} 1765, 1725, 1610, 1585 cm^{-1}; UV: λ_{max} 225 (ε 8,700) and 279 nm (2,700); NMR (CCl_4): 0·95 (s, 3 H), 1·00–2·00 (m, 6 H), 2·56 (s, 4 H), 2·70–3·30 (m, 3 H), 3·50 (s, 3 H), 3·74 (s, 3 H), 3·78 (s, 3 H), 6·15–6·55 (m, 2 H) and 6·85 δ (d, $J = 9$ Hz, 1 H); MS: m/e 348 (M^+). (Found: C, 68·78; H, 7·93. $C_{20}H_{28}O_5$ requires: C, 68·96; H, 8·05%).

Treatment of the seco-dione mixture **3a** *and* **4** *with ethanolic hydrochloric acid*

A mixture of **3a** and **4** (6·4 g), conc HCl (80 ml) and EtOH (320 ml) was refluxed on the steam bath for 1 hr. The cooled dark blue soln was diluted with ice-water and extracted several times with ether. The ether extract was washed with water, $NaHCO_3$ aq, water and dried (Na_2SO_4). The gummy residue obtained after removal of the solvent was chromatographed over neutral alumina. Elution with 3:1 hexane-benzene followed by 1:1 hexane-benzene mixture afforded two fractions* (0·9 g and 1·1 g) less polar than the starting material. Further elution with benzene-chloroform (1:1) mixture gave a more polar fraction (2·0 g). Further column chromatography of this fraction followed by crystallization from hexane-benzene yielded **7a** (1·6 g), m.p. 125–126° (Found: C, 72·57; H, 6·89. $C_{19}H_{22}O_4$ requires: C, 72·61; H, 7·00%).

6 - (2,4 - *Dimethoxyphenyl*) - 2 - *keto* - 3 - *methyltricyclo* [5,2,1,$0^{3,8}$]*decan* - 8 *ol* **8a**

Hydrogenation of **7a** (0·2 g) in EtOH (25 ml) with 10% Pd-C catalyst (0·1 g) afforded, after crystallisation from benzene, compound **8a**, m.p. 160–161°; IR (Nujol): ν_{max} 3600, 1735, 1610 and 1585 cm^{-1}; NMR ($CDCl_3$): 1·06 (s, 3 H), 3·80 (s, 3 H), 3·84 (s, 3 H), 6·30–6·50 (m, 2 H) and 6·93 δ(d, $J = 9$ Hz, 1 H). MS: m/e 316 (M^+). (Found: C, 72·45; H, 7·36. $C_{19}H_{24}O_4$ requires: C, 72·15; H, 7·60%).

2-Methyl-2[3-(2, 4-dimethoxyphenyl)- 5 -ethoxypent- 2 -enyl] -cyclopentane-1, 3-dione **3b**

(*a*) *1-Hydroxy-2', 4'-dimethoxy- 3 -ethoxy- 1 -vinyl-propyl benzene* **2b**. Grignard reaction of 2', 4'-dimethoxy-3 -ethoxypropiophenone (2 g) in THF (20 ml) with vinyl magnesium bromide, prepared from Mg (1 g) and vinyl bromide (7 ml) in a mixture of dry THF (15 ml) and ether (15 ml), was carried out as before at −20°. Chromatography of the residue, obtained after the usual work up, gave almost pure **2b** (0·8 g), IR (Neat): ν_{max} 3500, 1600, 1580, 1510, 995 and 910 cm^{-1}.

(*b*) *Condensation of the carbinol* **2b** *with 2-methylcyclopentane-1, 3-dione.* Condensation of the above carbinol (0·8 g) with 2-methylcyclopentane-1,3-dione (0·45 g) in presence of Triton B (0·3 ml) in xylene (10 ml) was carried out as mentioned earlier. The residue, obtained after the usual work up, was purified by column chromatography followed by preparative layer chromatography using hexane-ethyl acetate mixture (3:1) to yield **3b** (0·6 g), b.p. 225-235°/1–2 mm (bath temp.); IR (Neat): ν_{max} 1760, 1720, 1610, 1585 cm^{-1}; UV: λ_{max} 239(ε 8,050) and 279 nm (3,600); NMR ($CDCl_3$): 1·12 (t, $J =$ 7 Hz, 3 H), 1·15 (s, 3 H), 2·40–2·70 (m, 4 H), 2·73 (s, 4 H), 3·10–3·60 (m, 4 H), 3·75 (s, 3 H), 3·80 (s, 3 H), 5·25 (t, $J = 8$ Hz, 1 H), 6·30–6·60 (m, 2 H) and 6·92 δ (d, $J = 9$ Hz, 1 H). (Found C, 70·21; H, 7·85. $C_{21}H_{28}O_5$ requires: C, 69·98; H, 7·83%).

Treatment of the seco-dione **3b** *with ethanolic hydrochloric acid.* A mixture of **3b** (0·4 g), conc HCl (4·8 ml) and EtOH (19·2 ml) was refluxed for 1 hr. The residue, obtained after the work up, was subjected to preparative layer chromatography and the fraction more polar than the starting seco-dione was isolated in the usual way. Crystallisation of this fraction from hexane-benzene mixture gave a keto alcohol (0·04 g) identical with **7a**.

8 - *Acetoxy* - 6 - (2,4 - *dimethoxyphenyl*) - 3 - *methyltri* - *cyclo*[5,2,1·$0^{3,8}$]*dec* - 5 - *en* - 2 - *one* **7b**

Method A. A mixture of **9a** (0·5 g), Ac_2O (5 ml) and pyridine (5 ml) was heated on the steam bath for 6 hr. The cooled mixture was diluted with water and the material extracted with ether. The ether extract was successively washed with dil HCl, water, $NaHCO_3$ aq and water. The residue, obtained after removal of solvent, was chromatographed and crystallized from light petroleum to give **7b** (0·42 g), m.p. 148–150°; IR (Nujol): ν_{max} 1740, 1610, 1585 and 1220 cm^{-1}; UV: λ_{max} 243 (ε 9,400) and 283 nm (3,600); NMR ($CDCl_3$): 1·14 (s, 3 H), 2·10 (s, 3 H), 3·73 (s, 3 H), 3·78 (s, 3 H), 5·59 δ (t, $J = 4$ Hz, 1 H); MS: m/e 356 (M^+). (Found: C, 71·06; H, 6·79. $C_{21}H_{24}O_5$ requires: C, 70·80; H, 6·74).

Method B. A mixture of **7a** (0·1 g) and perchloric acid-acetic anhydride reagent[18] (10^{-3} M in $HClO_4$ and 1 M in Ac_2O) (10 ml) was allowed to stand at room temp for 15 min. The deep brown coloured soln was then washed with $NaHCO_3$ aq, water and dried (Na_2SO_4). Removal of solvent followed by crystallisation from light petroleum afforded **7b** (0·09 g).

Hydrolysis of the keto acetate **7b**. A mixture of **7b** (0·04 g) and 10% HCl (10 ml) was refluxed for 5 hr. The mixture was cooled and extracted with ether. The ether extract was washed with water, $NaHCO_3$ aq water and then dried. Removal of solvent followed by crystallisation of the residue (0·025 g) from hexane-benzene mixture afforded the **7a**, m.p. 125–126°.

8 - *Acetoxy* - 6 - (2,4 - *dimethoxyphenyl*) - 3 - *methyltri* - *cyclo*[5,2,1,$0^{3,8}$]*decan* - 2 - *one* **8b**

Hydrogenation of **7b** (0·4 g) in EtOH (50 ml) using 10% Pd-C catalyst (0·15 g) gave, after crystallisation from hexane containing a few drops of benzene, the acetate **8b**, m.p. 169–170°; IR: ν_{max} 1740, 1615, 1585 and 1510 cm^{-1}; UV: λ_{Max} 226 (ε 9,100), 278 (3,300) and 283 nm (2,900); NMR ($CDCl_3$): 1·06 (s, 3 H), 1·1–2·1 (m, 7 H), 2·16 (s, 3 H), 2·44–2·84 (m, 2 H), 3·0–3·5 (m, 2 H), 3·78 (s, 6 H), 6·3–6·5 (m, 2 H) and 6·9 δ (d, $J = 9$ Hz, 1 H); MS: m/e 358 (M^+). (Found: C, 69·92; H, 7·52. $C_{21}H_{26}O_5$ requires: C, 70·37; H, 7·31%).

Bromination of the dihydro keto acetate **8b**

Preparation of 8-acetoxy- 6 -(2,4-dimethoxy- 5 -bromo-phenyl)- 3,-methyltricyclo [5,2,1,$0^{3,8}$]*decan- 2 -one* **8c**. To

*Isolation and characterisation of compounds in these fractions will be published later.

a cooled (−20°) soln of **8b** (0·175 g) in dry ether, a soln of dioxane dibromide (0·14 g) in dry ether was added dropwise during 30 min. The mixture was kept overnight and washed thoroughly with water and dried. Removal of solvent followed by crystallisation of the residue from a mixture of light petroleum and benzene gave needle shaped crystalline bromo **8c** (0·14 g), m.p. 202–203°; IR (Nujol): ν_{max} 1740, 1610, 1590 cm^{-1}: UV: λ_{max} 230 (ϵ 12,560), 286 (5,280) and 291 nm (4,550); NMR ($CDCl_3$): 1·04 (s, 3 H), 1·06–2·10 (m, 7 H), 2·16 (s, 3 H), 2·4–2·8 (m, 2 H), 3·0–3·4 (m, 2 H), 3·8 (s, 3 H), 3·85 (s, 3 H), 3·85 (s, 3 H), 6·42 (s, 1 H), 7·08 (s, 1 H) and 7·34 δ (s, 3 H). (Found: C, 60·24; H, 6·06; Br, 15·43. $C_{21}H_{25}O_3Br\frac{1}{2}C_6H_6$ requires: C, 60·50; H, 5·88; Br, 16·80%).

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