Tetrahedron Vol 32, pp. 65 to 71 Pergamon Press 1976. Printed in Great Britain

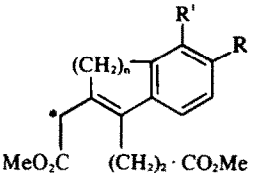
DIECKMANN CYCLISATION OF SOME β,γ-UNSATURATED DIMETHYL ESTERS—I

A. K. SARKAR*, A. CHATTERJEE and B. BANDYOPADHYAY
Department of Chemistry, Jadavpur University, Calcutta-32, India

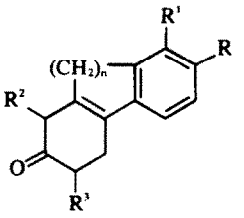
(*Received in the UK 2 June* 1975; *Accepted for publication 8 July* 1975)

Abstract—Dieckmann cyclisation of some β,γ-unsaturated diesters of the indane series gives as major product of the ring closure the compound derived from the more carbanion formed under standardised reaction conditions. The methyl β-(2-methoxycarbonylmethyl-7-methylinden-3-yl)propionate (**2**) on Dieckmann ring closure, gives 1-methoxycarbonyl-2-oxo-1,2,3,4-tetrahydro-8-methylfluorene (**7**) and not the isomeric 3-methoxycarbonyl-2-oxo-1,2,3,4-tetrahydro-8-methylfluorene (**6**) reported earlier.

The recent findings on the course of Dieckmann cyclisations of the unsaturated diesters **1**[1] and **2**[2] with sodium methoxide are contradictory, and we have investigated the course of ring closures of some similar unsaturated diesters. The structure **5** for the unstable β-keto-ester, obtained through cyclisation of **1** with sodium methoxide in benzene, was established[1] through *in situ* methylation and subsequent conversion of the crude methylated product to 1-methyl-7-methoxyphenanthrene. Similar cyclisation of **2** was, however, reported[2] to afford the β-keto-ester **6** in excellent yield. 1,6-Dimethylfluorene, obtained through methylation of **6** and subsequent acid hydrolysis of the methylated product, was claimed[2] to be identical with an authentic sample prepared in an unambiguous way. In the case of the unsaturated ester **2**, one should expect the predominant formation of the isomeric β-keto-ester **7** formed through the carbanion at the methylene group (starred) subject to a carbomethoxylic as well as styryl activation. Detailed studies on the Dieckmann cyclisations of the unsaturated diesters are rare in the literature, and the object of the present investigation is to find out whether there is any relationship between the stability and the reactivity of the carbanions formed during Dieckmann ring closures of some typical unsaturated diesters of the indene series, such as **3**, **4** and **2**. The results clearly demonstrate that the major product is derived from the more stable carbanion formed from each of the unsaturated diesters mentioned above under identical reaction conditions.



	n	R	R'
1:	2	OMe	H
2:	1	H	Me
3:	1	OMe	H
4:	1	H	H

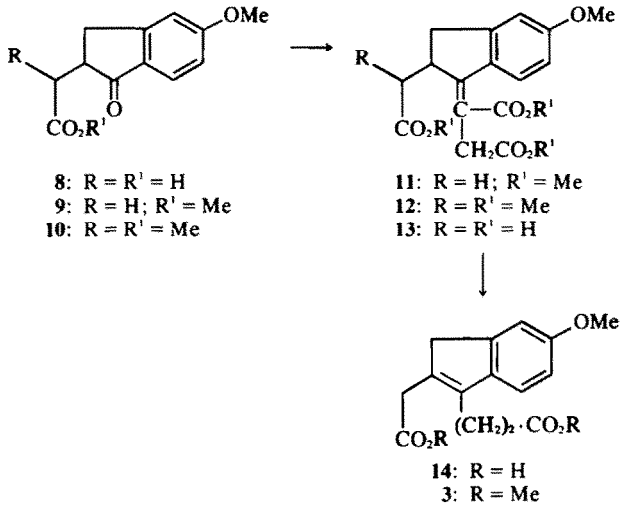


	n	R	R'	R²	R³
5:	2	OMe	H	CO_2Me	H
6:	1	H	Me	H	CO_2Me
7:	1	H	Me	CO_2Me	H
27:	1	H	H	CO_2Me	H

Fig. 1.

The unsaturated ester **3** was prepared from the known keto-acid **8**[3] by esterification to give the crystalline ester **9** and Stobbe condensation with dimethyl succinate under controlled condition to give an acidic material which on esterification with diazomethane provided the unsaturated tri-ester **11**, λ_{max} 288 and 315 nm (log ε 4·11 and 4·22) in 46% yield. It may be mentioned that similar Stobbe condensation of the keto-ester **10** with α-propionic ester side chain gave[4] a better yield (70%) of the corresponding tri-ester **12**. The lower yield of the Stobbe product from **9** is compatible with our earlier observations.[5] Hydrolysis of **11** with ethanolic barium hydroxide gave in excellent yield the crystalline tribasic acid **13**, λ_{max} 288 and 317 nm (log ε 4·12 and 4·24). The position of the double bond in **11** and **13** follows from their ultraviolet spectra. Decarboxylation of **13** with a mixture of pyridine, hydrochloric acid and oxalic acid gave the unsaturated dibasic acid **14**, λ_{max} 267 nm (log ε 4·24) in good yield. Esterification of **14** finally provided the desired unsaturated ester **3**, λ_{max} 267 nm (log ε 4·15). The position of the endo double bond in **3** was finally secured from its NMR spectrum (see Experimental). In another experiment, the crude Stobbe product from **9** on direct hydrolysis, decarboxylation, and subsequent esterification furnished the desired product **3** in 30% overall yield.

The above dimethyl ester **3** readily underwent Dieckmann cyclisation with sodium methoxide under benzene to give a crystalline product with adhering oil. Chromatography of this mixture over silica gel provided a crystalline material, m.p. 160–161° in 56% yield; and this has been assigned structure **15** because (a) it imparted an intense green colouration to alcoholic ferric chloride, and provided expected elemental analysis; (b) the UV spectrum showed the following characteristics: λ_{max} 248 and 277 nm (log ε 4·24 and 4·34), λ_{max}^{EtONa} 248 and 293 nm



8: R = R' = H
9: R = H; R' = Me
10: R = R' = Me

11: R = H; R' = Me
12: R = R' = Me
13: R = R' = H

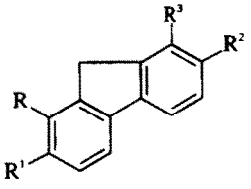
14: R = H
3: R = Me

Fig. 2.

(log ϵ 4·16 and 4·46), (c) the infra-red band at 1670 cm^{-1} showed that the phenolic ester exists completely in the chelated form, (d) the NMR spectrum (see Experimental) is also compatible with the structure assigned. Final confirmation for the above structure **15** was secured through its transformation to the known fluorene derivative **18**, and this will be described later in detail.

serve as a potential intermediate for the synthesis of the phenolic degradation products of hecogenin[9] and jervine.[10]

Lithium aluminium hydride reduction of the above phenolic ester **15** gave in excellent yield the benzyl alcohol **17** which on catalytic hydrogenolysis provided the known 2 - hydroxy - 7 - methoxy - 1 - methylfluorene **18**.[4]



	R	R'	R²	R³		R	R'	R²	R³
15:	CO_2Me	OH	OMe	H	**20**:	CO_2Me	OMe	OMe	H
16:	H	OH	OMe	H	**25**:	Me	H	OMe	H
17:	CH_2OH	OH	OMe	H	**28**:	Me	H	H	H
18:	Me	OH	OMe	H	**29**:	CO_2Me	OH	H	Me
19:	Me	OMe	OMe	H	**30**:	Me	OH	H	Me
					31:	Me	H	H	Me

Fig. 3.

To improve the yield of the phenolic ester **15**, the crude Dieckmann product from **3** was directly dehydrogenated with 10% Pd-C under refluxing xylene. The product thus obtained was chromatographed over silica gel. Elution with ether-light petroleum (1:9) afforded the phenolic ester **15** in slightly better yield (62%). Ether-light petroleum (1:4) eluted another crystalline material, m.p. 187–188°, and this has been characterised as the known 2-hydroxy-7-methoxyfluorene **16**,[6] from its spectral behaviour and elemental analysis. Thermal decarboxylation of β-keto-ester is known in the literature,[7] and the above methoxyfluorenol **16** isolated in low yield, is probably produced through the intermediate unsaturated ketone **21**, formed from the β-keto-ester **22** present in small amount as shown below. The formation of the phenolic ester **15** as the major product from the Dieckmann ring closure of **3** probably takes place through the enol form **23** of the β-keto-ester **22**. The introduction of the third double bond is probably achieved[8] either by aerial oxidation or through disproportionation during the isolation stage. It should be mentioned that the above substituted fluorene **15** may

Methylation of this phenol **18** with methyl iodide in presence of potassium carbonate under acetone gave 1 - methyl - 2,7 - dimethoxyfluorene **19**. The phenolic ester **15** on similar methylation furnished 1 - methoxycarbonyl - 2,7 - dimethoxyfluorene **20**. Reduction of this material **20** with lithium aluminium hydride followed by catalytic hydrogenolysis of the resulting crude benzyl alcohol furnished the same fluorene derivative **19**.

The β-keto-ester enolate formed during ring closure of **3** was trapped through methylation with methyl iodide. The crude methylated product thus obtained was chromatographed over silica gel. Elution of the chromatogram with ether-light petroleum (1:9) afforded the phenolic ester **15** in very low yield. Ether-light petroleum (1:4) eluted an oily material which was further purified by evaporative distillation under vacuum to furnish an oil, λ_{max} 269 nm (log ϵ 4·15). It gave a negative ferric chloride reaction, and analysed correctly for the expected methylated product **24**. The NMR spectrum, however, showed two signals each for the aromatic methoxyl and methoxycarbonyl group, and three sharp

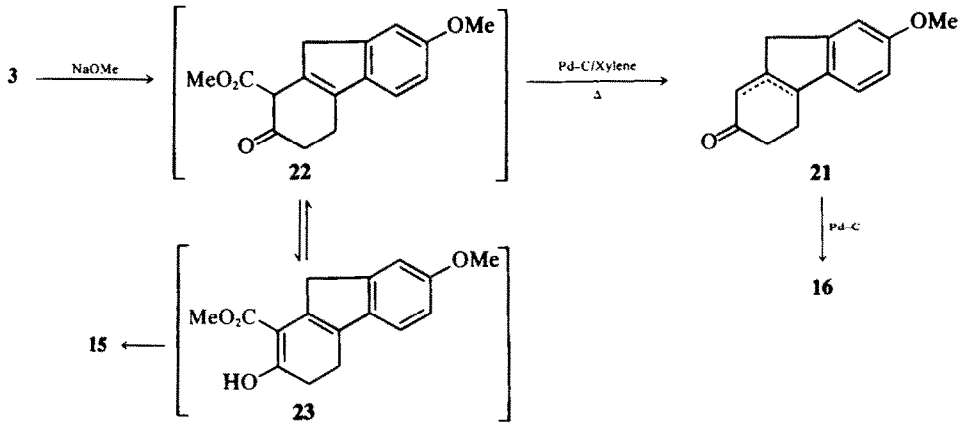


Fig. 4.

signals in the saturated methyl resonance region. This spectral behaviour indicated the product to be a mixture of at least two compounds. Acid hydrolysis of this methylated product, however, gave a neutral product which on chromatography over alumina afforded in 50% yield, 1 - methyl - 7 - methoxyfluorene **25**,[4] as a result of aromatisation with elimination of oxygen. Aromatisation with elimination of oxygen has ample precedents[4,11,12] in the literature. The following mechanism is proposed[13] for the formation of the fluorene derivative **25** through the acid hydrolysis of **24**. Acid hydrolysis of the above methylated product under controlled condition provided a neutral product from which the ketone **26**[4] could be isolated as its 2,4-dinitrophenylhydrazone derivative in poor yield.

agreement with the assigned structure **27**. Further confirmation for this structure was secured from the experiment described below.

The above crystalline β-keto-ester **27** on methylation followed by acid hydrolysis as before gave 1-methylfluorene **28**[12] in good yield. The β-keto-ester enolate derived from **4** was also methylated *in situ* and the resulting methylated product on acid hydrolysis afforded the same fluorene derivative **28** in 50% overall yield.

The course of Dieckmann ring closure of the unsaturated diester **4** is in contradiction to what has been reported[2] for the cyclisation of the similar diester **2** under the same experimental conditions. It was therefore of importance to reinvestigate the Dieckmann ring closure of the diester **2**. The cyclisation of this diester according to

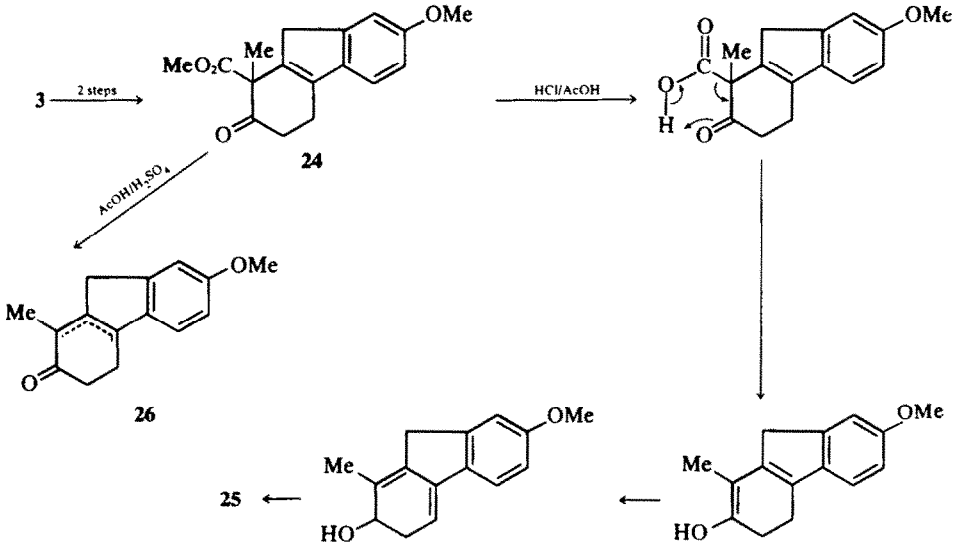
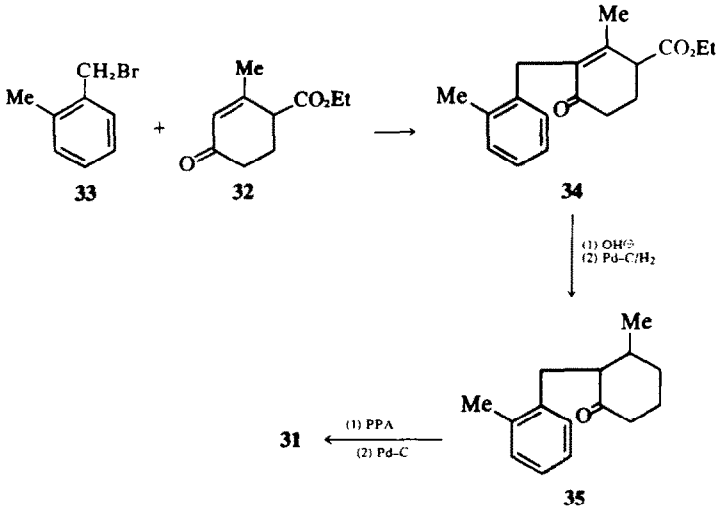


Fig. 5.

Dieckmann cyclisation of the simple unsaturated ester **4** was next investigated. This ester **4** was prepared following the known procedure.[14] The position of the double bond was confirmed from its NMR spectrum. Cyclisation of **4** with sodium methoxide as before afforded an oily-solid material from which the crystalline β-keto-ester **27** could be isolated in 62% yield. The infrared band at 1640 cm^{-1} indicated that the β-keto-ester exists completely in the chelated form. The UV and NMR spectra are quite in the reported[2] procedure furnished a crystalline β-keto-ester in respectable yield. The NMR spectrum (see Experimental) of this product is quite in agreement with the β-keto-ester structure **7** and not **6** assigned previously by Dasgupta.[2] The absence of NMR signal for the allylic methylene group situated α- to the carbonyl clearly ruled out the isomeric structure **6**. The structure **7** was further confirmed by the experiments described below.

The β-keto-ester **7** on treatment with methanol and

hydrochloric acid afforded the phenolic ester **29**. Lithium aluminium hydride reduction of **29** followed by catalytic hydrogenolysis of the crude benzyl alcohol furnished the known[15] 1,8 - dimethyl - 7 - hydroxyfluorene **30** in moderate yield. The β-keto-ester enolate formed during cyclisation of **2** was methylated *in situ* with methyl iodide, and the resulting crude reaction product on acid hydrolysis furnished a fluorene derivative, m.p. 152–154°, which was identical with an authentic sample of 1,8-dimethylfluorene **31** prepared as shown below (Scheme 1).



Scheme 1.

Condensation of Hagemann's ester **32** with o-xylyl bromide **33**[16] in the presence of potassium t-butoxide afforded the desired product **34** in excellent yield. Hydrolysis and decarboxylation of **34** with base provided an α,β-unsaturated ketone which was catalytically reduced to the saturated ketone **35** in good yield. Polyphosphoric acid cyclisation of **35** followed by dehydrogenation afforded 1,8-dimethylfluorene **31**, m.p. 152–154°, in excellent yield.

The melting point of 1,8-dimethylfluorene, thus obtained is similar to that reported by Dasgupta[2] for 1,6-dimethylfluorene. 1,6-Dimethylfluorene is actually known in the literature and has been reported[17] to melt at 117–118°. It is therefore presumed that the above author[2] utilised o-xylyl bromide and not the p-xylyl bromide for the preparation of the authentic sample. The structures for the transformation products derived from **6** (see Ref. 2) should therefore be revised in the light of the corrected structure **7** for the β-ketoester.

EXPERIMENTAL

M.ps (taken in open capillary in H_2SO_4-bath) and b.ps are uncorrected. UV spectra were determined in 95% EtOH on a Unicam SP 500 spectrophotometer and IR spectra were recorded on a Perkin-Elmer Infracord Model 337 in $CHCl_3$ soln. (until otherwise stated). NMR spectra were measured on Varian Associates A 60-D spectrophotometer (using TMS as internal standard). Light petroleum refers to the fraction b.p. 60–80°. Neutral Brockmann alumina (S. Merck and Co.), and silica gel (BDH) were used for column chromatographic experiments. TLC plates were coated with silica gel G (according to Stahl, 200 mesh) having a thickness of about 0·2 mm and the spots were located by exposing the dried plates in I_2 vapour. Extracts were dried over Na_2SO_4.

Methyl (5-methoxy-1-oxoindan-2-yl)-acetate **9**. The known ketoacid[3] **8** (15 g) was heated under reflux with MeOH (90 ml) and H_2SO_4 (9 ml, d 1·84) for 10 h to furnish **9** (14·4 g), m.p. 80–81° (ether-light petroleum); λ_{max} 267 and 286 nm (log ε 4·17 and 4·07); ν_{max} 1702 (s) and 1733 cm^{-1} (s). On TLC it showed a single spot (MeOH-benzene, 20:80). (Found: C, 66·43; H, 5·94. $C_{13}H_{14}O_4$ requires: C, 66·66; H, 6·02%).

Dimethyl α - (2 - methoxycarbonylmethyl - 5 - methoxyindan - 1 - ylidene) - succinate **11**. To an ice-cold soln of potassium t-butoxide prepared from potassium (2 g) in t-BuOH (43 ml) was added dimethylsuccinate (10·1 g). The enolate anion thus obtained was then added dropwise during 3 h to a stirred soln of the ester **9** (5 g) in t-BuOH (15 ml) under dry N_2 at room temp. The reaction mixture was further stirred for a period of 2 h and left for 16 h at room temp. The reaction mixture was then acidified, most of the t-BuOH was removed under reduced pressure, and the brown oil was taken up in ether. The solvent was washed with water and the acidic material was repeatedly extracted with sat aq $NaHCO_3$. The combined alkaline soln was acidified, and the liberated acid was extracted with ether. Evaporation gave a crude acidic material (7·2 g) which was directly esterified with an ethereal soln of diazomethane to furnish **11** (2·80 g; 46%) as a pale yellow oil, b.p. 165° (bath)/0·05 mm; λ_{max} 299 and 315 nm (log ε 4·11 and 4·22); ν_{max} 1732 cm^{-1} (s). (Found: C, 62·93; H, 5·99. $C_{19}H_{22}O_7$ requires: C, 62·98; H, 6·12%).

α - (2 - Carboxymethyl - 5 - methoxyindan - 1 - ylidene) - succinic acid **13**. The above trimethyl ester **11** (2·05 g) was saponified by heating under reflux for 3 h with a mixture of $Ba(OH)_2$, $8H_2O$ (31·5 g), water (182 ml) and EtOH (280 ml). The precipitated barium salt was acidified with conc HCl in the cold, and the liberated acid was extracted with ether-EtOAc mixture. Evaporation of the dry solvent furnished **13** (1·75 g; 96%), m.p. 214–215° (EtOAc-light petroleum); λ_{max} 288 and 317 nm (log ε 4·12 and 4·24). (Found: C, 63·04; H, 5·62. $C_{16}H_{16}O_7$ requires: C, 63·15; H, 5·30%).

β - (2 - Carboxymethyl - 6 - methoxyinden - 3 - yl) - propionic acid **14**. The preceding tribasic acid **13** (9·1 g) was heated under reflux for 2 h with a mixture of pyridine (150 ml), conc. HCl (260 ml) and oxalic acid (90 g). The reaction mixture was diluted with water and the solid that separated was taken up in EtOAc-ether mixture. The organic layer was then repeatedly extracted with NH_4OH soln (1N). The combined alkaline extract was acidified with conc. HCl and the liberated acid was extracted with EtOAc-ether mixture. The solvent was washed, dried and evaporated to furnish **14** (8 g; 97%), m.p. 173° (dil MeOH); λ_{max} 267 nm (log ε 4·24). (Found: C, 64·88; H, 5·67. $C_{15}H_{16}O_5$ requires: C, 65·21; H, 5·84%).

Methyl β - (2 - methoxycarbonylmethyl - 6 - methoxyinden - 3 -

yl) - propionate **3**. The preceding dibasic acid **14** (13·8 g) was heated under reflux with MeOH (100 ml) and H_2SO_4 (10 ml, d 1·84) for 7 h. The reaction mixture after usual processing afforded **3** (13·58 g) as a pale yellow oil, b.p. 170° (bath)/0·2 mm; λ_{max} 267 nm (log ε 4·15); ν_{max} 1715 cm^{-1} (s); NMR τ(CCl_4): 7·53–7·20 (4H, m), 6·67 (2H, s, $-\overset{|}{C}=\overset{|}{C}-CH_2-CO_2R$), 6·58 (2H, s, $-CH_2-Ph$), 6·39 (3H, s, $-CO_2Me$), 6·34 (3H, s, $-CO_2Me$), 6·23 (3H, s, –OMe), 3·40–2·83 (3H, m, ArH). (Found: C, 66·87; H, 6·56. $C_{17}H_{20}O_5$ requires: C, 67·09; H, 6·62%).

Dieckmann cyclisation of methyl β - (2 - methoxycarbonylmethyl - 6 - methoxyinden - 3 - yl) - propionate **3**. *Formation of 1 - methoxycarbonyl - 2 - hydroxy - 7 - methoxyfluorene* **15**. A soln of the unsaturated dimethyl ester **3** (1 g) in dry benzene (6 ml) was added to finely divided sodium (130 mg) suspended in dry benzene (6 ml). The reaction was initiated by the addition of 0·7 ml of dry MeOH and completed by refluxing for 3 h under N_2. Resulting solid cake was cooled in ice and decomposed with dil H_2SO_4. The separated product was extracted with ether. The organic layer was washed with sat $NaHCO_3$ soln and water. The solvent was dried and evaporated to give a solid material (890 mg), m.p. 105–115°, which was chromatographed over silica gel (30 g). Elution with 10% ether-light petroleum furnished 1 - methoxycarbonyl - 2 - hydroxy - 7 - methoxyfluorene **15** (510 mg; 56%), m.p. 160–161° (MeOH); λ_{max} 248 and 277 nm (log ε 4·24 and 4·38); $\lambda_{max}^{EtONa/EtOH}$ 248 and 293 nm (log ε 4·16 and 4·46); ν_{max} 1670 cm^{-1} (s); NMR τ($CDCl_3$): 6·16 (5H, s, $-CO_2Me$ and $-CH_2Ph$), 5·98 (3H, s, –OMe), 3·21–2·32 (5H, m, ArH), −1·40 (1H, s, chelated phenol). On TLC (MeOH-benzene, 20:80) it showed a bright single spot. It gave an intense green colouration with alcoholic $FeCl_3$ (Found: C, 70·94; H, 5·16. $C_{16}H_{14}O_4$ requires: C, 71·10; H, 5·22%).

A soln of this crude Dieckmann product (890 mg) in dry xylene (40 ml) was dehydrogenated with 10% Pd–C (300 mg) by heating under reflux for 3 h under N_2. Usual processing of the reaction mixture gave a yellow solid (840 mg) which was next chromatographed over silica gel (30 g). Elution with 10% ether-light petroleum afforded **15** (560 mg; 61%), m.p. 160–161°. Elution with 20% ether-light petroleum furnished 2 - hydroxy - 7 - methoxyfluorene **16** (40 mg; 5%), m.p. 187–188° (dil MeOH) (reported[6] m.p. 188–189°); λ_{max} 275 nm (log ε 4·37); λ_{max}^{EtONa} 297 nm (log ε 4·42); it produced a green colouration with alcoholic soln of $FeCl_3$ (Found: C, 78·83; H, 6·28. $C_{14}H_{12}O_2$ requires: C, 79·23; H, 5·70%).

1-Hydroxymethyl-2-hydroxy-7-methoxyfluorene **17**. To $LiAlH_4$ (200 mg) in dry THF (10 ml) was added dropwise with stirring, a soln of **15** (100 mg) in dry THF (10 ml). The mixture was stirred for a further period of 3 h and left for 16 h at room temp. The complex was decomposed with ice-cold dil H_2SO_4 and the product was extracted with ether. Evaporation of the dry solvent afforded **17** (81 mg; 91%), m.p. 161–162° (MeOH); λ_{max} 276 and 315 nm (log ε 4·35 and 3·66); $\lambda_{max}^{EtONa/EtOH}$ 297 nm (log ε 4·42); ν_{max} 1595 cm^{-1}; it gave an intense green colouration with alcoholic $FeCl_3$. (Found: C, 74·12; H, 6·06. $C_{15}H_{14}O_3$ requires: C, 74·36; H, 5·82%).

1-Methoxycarbonyl-2,7-dimethoxyfluorene **20**. A soln of the phenolic ester **15** (150 mg) in dry acetone (20 ml) was heated under reflux for 21 h with anhydrous K_2CO_3 (500 mg) and CH_3I (6 ml). Usual work-up of the reaction mixture gave **20** (140 mg; 88%), m.p. 131–132° (MeOH); λ_{max} 247, 276 and 330 nm (log ε 4·00, 4·39 and 3·67); ν_{max} 1720 cm^{-1} (s); NMR τ($CDCl_3$): 6·13 (2H, s, $-CH_2Ph$), 6·08 (3H, s, $-CO_2Me$), 6·00 (6H, s, 2–OMe), 3·19–2·90 (3H, m, ArH), 2·36 (2H, q, J, 6 Hz); it gave negative $FeCl_3$ test. (Found: C, 72·03; H, 6·08. $C_{17}H_{16}O_4$ requires: C, 71·82; H, 6·08%).

1-Methyl-2-hydroxy-7-methoxyfluorene **18**. A soln of **17** (120 mg) in EtOAc (20 ml) was hydrogenated over 10% Pd–C (100 mg). Hydrogen (13 ml) was absorbed at room temp. within 30 min. The catalyst was then filtered off and the solvent was evaporated to give a pale yellow solid which was chromatographed over activated silica gel (6 g). Elution with 10% ether-light petroleum furnished **18** (90 mg; 80%), m.p. and m.m.p. with an authentic sample,[3] 187–188° (benzene); λ_{max} 277 nm (log ε 4·4); λ_{max}^{EtONa} 301 nm (log ε 4·45); it gave no colouration with alcoholic $FeCl_3$. (Found: C, 79·59; H, 6·17. $C_{15}H_{14}O_2$ requires: C, 79·62; H, 6·24%).

1-Methyl-2,7-dimethoxyfluorene **19**. (a) A soln of **18** (80 mg) in dry acetone (20 ml) was heated under reflux for 20 h with anhyd K_2CO_3 and CH_3I (7 ml). Usual work-up of the reaction mixture as before furnished **19** (83 mg; 98%), m.p. 167–168° (ether-light petroleum); λ_{max} 277 and 310 nm (log ε 5·05 and 4·25); it gave a negative $FeCl_3$ reaction. (Found: C, 79·87; H, 6·90. $C_{16}H_{16}O_2$ requires: C, 79·97; H, 6·71%).

(b) To $LiAlH_4$ (100 mg) in dry THF (10 ml) was added dropwise with stirring a soln of **20** (50 mg) in dry THF (10 ml). The mixture was stirred further for 3 h and left for 16 h at room temp. Usual work-up as before gave a yellow solid (40 mg), m.p. 100–105°, which on hydrogenation over 10% Pd–C (50 mg) as before furnished **19** (26 mg; 65%), m.p. 167–168° (ether-light petroleum).

Methylation of the intermediate β-ketoester resulting from the cyclisation of **3**. *Formation of 1 - methyl - 7 - methoxyfluorene* **25** *and 1 - methyl - 2 - oxo - 1,2,3,4 - tetrahydro - 7 - methoxyfluorene* **26**. The diester **3** (2 g) was treated with sodium sand (260 mg) suspended under benzene as described before. The solid cake so formed was cooled, an excess of CH_3I added and the mixture was refluxed for 6 h under N_2. Usual work-up of the mixture as before furnished crude methylated product (1·1 g) (68%), b.p. 140–145° (bath)/0·01 mm, which was chromatographed over silica gel (40 g). Elution with 10% ether-light petroleum afforded the phenolic ester **15** (22 mg), m.p. 160–161°. Elution of the column with 20% ether-light petroleum furnished an oil (1 g) (62%) which gave a negative $FeCl_3$ test and analysed correctly for the expected methylated β-ketoester **24**; λ_{max} 269 nm (log ε 4·15); ν_{max} 1715 cm^{-1}; it showed a bright single spot on TLC (MeOH-benzene, 20:80; EtOAc-light petroleum, 40:60). [(Found: C, 71·53; H, 6·28. $C_{17}H_{18}O_4$ **24** requires: C, 71·31; H, 6·34)]. The NMR spectrum, however, showed that the methylated product is probably a mixture of at least two compounds; τ(CCl_4): 8·70 (s), 8·57 (s), 8·50 (s), 7·60–7·04 (m), 6·71 (s), 6·37 (s), 6·33 (s), 6·22 (s), 6·19 (s), 3·38–2·80 (m).

The above methylated product (300 mg) was heated under reflux with AcOH (3 ml), HCl (1·7 ml) and water (0·5 ml) for 6 h under N_2. It was cooled, diluted with water and extracted with ether. The organic layer was washed with $NaHCO_3$ soln, dried, and evaporated. The residue (205 mg) thus obtained was chromatographed over activated alumina (8 g). Elution with 10% benzene-light petroleum afforded 1 - methyl - 7 - methoxyfluorene **25** (80 mg; 49%), m.p. and m. m.p. with an authentic sample,[3] 111–112° (MeOH); λ_{max} 272, 301 and 310 nm (log ε 4·29, 3·76 and 3·71). (Found: C, 85·66; H, 6·70. $C_{15}H_{14}O$ requires: C, 85·68; H, 6·71%). The methylated product (200 mg) was heated under reflux with a mixture of AcOH (5 ml) and 7·5% H_2SO_4 aq. (1·4 ml) for 3·5 h under N_2. Usual processing of the mixture furnished a liquid product (99 mg), b.p. 160° (bath)/0·5 mm. This oil provided a 2,4-dinitrophenylhydrazone derivative (51%) of the ketone **26**. The derivative melted at 195–196° (d) (MeOH-benzene) and was found to be identical with an authentic sample.[3]

Methyl β - (2 - methoxycarbonylmethyl - inden - 3 - yl) - propionate **4**. The unsaturated diester **4**[12] was prepared following the known procedure.[12] The position of the double bond is supported by the NMR spectrum, τ(CCl_4): 7·64–7·12 (4H, m), 6·59 (2H, s, $-CH_2Ph$), 6·49 (2H*, s), 6·35 (3H, s), 6·30 (3H, s), 2·92–2·51 (4H, m, ArH).

1 - Methoxycarbonyl - 2 - oxo - 1,2,3,4 - tetrahydrofluorene **27**. A soln of the diester **4** (1·5 g) and dry MeOH (0·5 ml) in dry benzene (10 ml) was added with stirring to finely divided sodium suspended in dry benzene (10 ml) under N_2. The reaction mixture was refluxed for 3·5 h under N_2. The mixture was then worked up as before to give a yellow solid (820 mg) (62%), m.p. 120–124°. Two recrystallisations from acetone-light petroleum provided an analytical material of **27**, m.p. 126–127°; λ_{max} 240 and 272 nm (log ε 4·18 and 4·16); $\lambda_{max}^{EtONa/EtOH}$ 304 nm (log ε 4·32); ν_{max} (Nujol) 1640 cm^{-1}; NMR τ($CDCl_3$): 7·40–7·20 (4H, m), 6·36 (2H, s), 6·09 (3H, s), 3·02–2·45 (4H, m); it produced an intense green colouration with alcoholic $FeCl_3$ (Found: C, 74·75; H, 6·32. $C_{15}H_{14}O_3$ requires: C, 74·36; H, 5·82%).

1-Methylfluorene **28**. (a) To sodium dust (50 mg) suspended in dry benzene (20 ml) was added with stirring under N_2 a soln of the β-keto-ester **27** (380 mg) in dry benzene (10 ml). The stirring was continued for 6 h and the mixture was kept for 16 h at room temp. The solid cake thus formed was refluxed with CH_3I (5 ml) for 12 h under N_2. It was cooled, diluted and worked up as before to give a crude methylated β-ketoester (340 mg), m.p. 95–101°, λ_{max} 261 nm

(log ε 4·08); ν_{max} (Nujol) 1710 and 1736 cm^{-1}; it gave a negative $FeCl_3$ test. The above crude methylated β-ketoester (340 mg) was hydrolysed by heating under reflux with a mixture of AcOH (4 ml), conc. HCl (2 ml) and water (0·5 ml) for 8 h under N_2. Usual work-up of the mixture as before gave an oily solid (240 mg) which was chromatographed over alumina (15 g). Elution with light petroleum gave a product which was purified by distillation at 90° (bath)/0·2 mm to furnish **28** (160 mg; 60%), m.p. and m. m.p. with an authentic sample,[12] 84–85° (petroleum ether, 40–60°).

(b) In another experiment the diester **4** (1 g) was treated with finely divided sodium (130 mg) suspended in dry benzene (10 ml). Dry MeOH (0·3 ml) was added and the mixture was refluxed for 3 h under N_2. The solid cake thus formed was cooled, an excess of CH_3I (7 ml) added and the mixture was refluxed for 8 h under N_2. It was worked up as before to give the methylated β-ketoester (700 mg) which gave a negative $FeCl_3$ test. This crude methylated product was subsequently hydrolysed as before by refluxing with a mixture of AcOH (6 ml) conc. HCl (3 ml) and water (0·5 ml) to furnish 1-methylfluorene **28** [330 mg; 50% based on the diester **4** used].

Dieckmann cyclisation of methyl β - (2 - methoxycarbonyl-methyl - 7 - methylinden - 3 - yl) - propionate **2**. The unsaturated dimethyl ester[2] **2** (2 g) in dry benzene (10 ml) was subjected to Dieckmann cyclisation following the known procedure[2] by heating under reflux in an atmosphere of N_2 for 2·5 h with sodium methoxide, prepared from sodium dust (332 mg) and dry MeOH (0·53 ml). The mixture was next cooled and acidified with ice-cold dil H_2SO_4. On usual work-up, a brown-coloured oil was obtained which solidified on trituration with MeOH, m.p. 90–102°. One crystallisation from ether-light petroleum provided the crystalline β-ketoester (880 mg; 49·5%), m.p. 95–104°. Three more recrystallisations from the same solvent mixture afforded an analytical sample of **7**, m.p. 104–105°; λ_{max} 238 and 269 nm (log ε 4·26 and 4·24); $\lambda_{max}^{EtONa/EtOH}$ 300 nm (log ε 4·27); ν_{max} 1640 cm^{-1}; NMR τ(CDCl$_3$): 7·63 (4H, m), 7·30 (3H, s, –CH$_3$), 6·48 (2H, s, –CH$_2$–Ar), 6·10 (3H, s, –CO$_2$Me), 3·06–2·70 (3H, m, ArH), –3·15 (1H, s, chelated enol). It gave an intense green colouration with alcoholic $FeCl_3$ (Found: C, 75·28; H, 6·50. $C_{16}H_{16}O_3$ requires: C, 74·98; H, 6·29%). The oil (500 mg) obtained after separation of the β-ketoester **7** was chromatographed over silica gel (18 g). Elution of the chromatogram with 5% ether-light petroleum provided a solid product (220 mg), m.p. 130° with previous shrinkage at 90°. This nonhomogeneous product is most probably a mixture of the β-ketoester **7** and the phenolic ester **29**.

1 - *Methoxycarbonyl* - 2 - *hydroxy* - 8 - *methylfluorene* **29**. To a soln of the β-ketoester **7** (200 mg) in dry MeOH (12 ml) was added conc. HCl (2–3 drops), and the resulting homogeneous soln was allowed to stand at room temp. for 5 days whereby colourless long needles separated. The mixture was extracted with ether. The ether extract was washed with brine, dried, and evaporated to furnish oily solid (220 mg) which was chromatographed over silica gel (8 g). Elution with 5% ether-light petroleum afforded phenolic ester **29**, (100 mg, 50%), m.p. 141° (MeOH); λ_{max} 240 and 270 nm (log ε 4·18 and 4·21); $\lambda_{max}^{EtONa/EtOH}$ 300 nm (log ε 4·32); ν_{max} 1667 cm^{-1}. It produced an intense green colouration with alcoholic $FeCl_3$ (Found: C, 75·80; H, 5·98. $C_{16}H_{14}O_3$ requires: C, 75·58; H, 5·55%).

1-*Methyl*-2-*hydroxy*-8-*methylfluorene* **30**. To $LiAlH_4$ (500 mg) in THF (25 ml) was added a soln of the crystalline phenolic ester **29** (250 mg) in THF (25 ml). The mixture was worked up as before to give an oily material which produced a green colouration with alcoholic $FeCl_3$ soln. A soln of the above oily product in 95% EtOH (45 ml) was hydrogenated over 10% Pd–C (200 mg) as before. Usual processing of the reaction mixture provided 1 - methyl - 2 - hydroxy - 8 - methylfluorene **30** as colourless needles [70 mg; 33% on the basis of the phenolic ester **29**], m.p. 191–193°. Three recrystallisations from acetone-light petroleum afforded an analytical sample of **30**, m.p. and m. m.p. with an authentic sample[15] 195–197°. (Found C: 85·58; H, 6·56. $C_{15}H_{14}O$ requires: C, 85·68; H, 6·71%).

1,8-*Dimethylfluorene* **31**. The enolate anion, formed during ring closure of the unsaturated diester **2** (500 mg) in dry benzene (20 ml) with sodium methoxide from sodium (83 mg), was methylated with CH_3I (7 ml) as before. Usual work-up of the reaction mixture afforded a dark brown-coloured material (350 mg) which gave no colouration with alcoholic $FeCl_3$ soln. Hydrolysis of this product (350 mg) by refluxing with a mixture of glacial AcOH (4 ml), conc. HCl (2 ml) and water (0·4 ml) gave a neutral product (180 mg) as yellow solid and an acidic material (120 mg). The neutral product was chromatographed over activated alumina (10 g). Elution of the chromatogram with light petroleum afforded 1,8-dimethylfluorene **31** [85 mg; 24% on the basis of the amount consumed of the unsaturated diester **2**], m.p. 152–154° (MeOH). Mixed m.p. with an authentic sample remained undepressed. (Found: C, 92·66; H, 7·31. $C_{15}H_{14}$ requires: C, 92·74; H, 7·26%). The above acidic material (120 mg) failed to give any crystalline product, and this was not investigated further.

Preparation of an authentic sample of 1,8-*dimethylfluorene* **31**. 2 - (*o* - *Methylbenzyl*) - 4 - *ethoxycarbonyl* - 3 - *methyl* - Δ^2 - *cyclohexenone* **34**. To an ice-cold suspension of potassium t-butoxide, prepared from potassium (5 g) and t-BuOH (100 ml), Hagemann's ester **32** (23 g) was added with shaking; *o*-xylylbromide[16] **33** (24 g), b.p. 216–224° was next added in portions and the resulting mixture was heated under reflux for 15 h. The reaction mixture was then acidified with cold dil HCl and the product was extracted with ether. Evaporation of the dry solvent gave **34** (24 g; 67%); b.p. 170°/0·2 mm; λ_{max} 242 nm (log ε 4·08); ν_{max} 1725 and 1665 cm^{-1}. (Found: C, 75·57; H, 8·00. $C_{18}H_{22}O_3$ requires: C, 75·50; H, 7·74%).

2 - (*o* - *Methylbenzyl*) - 3 - *methylcyclohexan* - 1 - *one* **35**. The ketoester **34** (21 g) was hydrolysed and simultaneously decarboxylated by heating under reflux with a soln of KOH (16 g) in water (16 ml) and EtOH (106 ml) for 30 h under N_2. Excess EtOH was removed, residue was acidified with HCl (6*N*) and heated on the steam bath until effervescence of CO_2 ceased. The product was extracted with ether and the extract was washed successively with brine, sat $NaHCO_3$ soln and finally with water. The dry solvent was evaporated to furnish an unsaturated ketone (9·6 g); b.p. 132–135°/0·2 mm; λ_{max} 242 nm (log ε 4·04); ν_{max} 1653 cm^{-1}. This product (5 g) in 95% EtOH (25 ml) was hydrogenated with 10% Pd–C (500 mg). On usual work-up, the reaction mixture furnished **35** (4·5 g; 90%); b.p. 125–128°/0·2 mm; λ_{max} 264 and 271 nm (log ε 2·53 and 2·49); ν_{max} 1700 cm^{-1}. (Found: C, 83·09; H, 9·62. $C_{15}H_{20}O$ requires: C, 83·29; H, 9·32%).

1,8-*Dimethylfluorene* **31**. To well-stirred polyphosphoric acid, prepared from *ortho*-phosphoric acid (18 ml, 89%) and phosphorus pentoxide (30 g), the compound **35** (3 g) was added, and the mixture was heated at 80–90° for 2 h with stirring. The reaction mixture was cooled, decomposed with ice-water and the product was extracted with ether. The ether extract was washed successively with sat $NaHCO_3$ soln, brine, and finally with water. Evaporation of the dry solvent furnished a colourless oil (2·05 g), b.p. 110°/0·2 mm. The above oil (500 mg) was dehydrogenated by heating for 13 h with 10% Pd–C (120 mg) at 180–190° under N_2. The product was thoroughly extracted with ether. Usual processing of the reaction mixture gave 1,8-dimethylfluorene **31** (420 mg; 85%), m.p. 152–154° (MeOH); λ_{max} 266 nm (log ε 4·26). (Found: C, 92·40; H, 7·50. $C_{15}H_{14}$ requires: C, 92·74; H, 7·26%).

Acknowledgements—The authors are indebted to Drs. M. M. Dhar and Nitya Nand for NMR spectra and to Mr. B. B. Bhattacharyya for microanalysis. The authors wish to thank Dr. U. R. Ghatak for helpful discussions.

REFERENCES

[1]D. Nasipuri and K. K. Biswas, *Ind. Chem. Soc.* **45**, 603 (1968).
[2]K. Das Gupta, *Ibid.* **46**, 415 (1969).
[3]D. Mukherjee, Ph.D. Dissertation, Jadavpur University, 1968.
[4]D. Mukherjee, *Ind. J. Chem.* **9**, 628 (1971).
[5]A. Chatterjee, S. Banerjee, A. K. Sarkar and B. G. Hazra, *J. Chem. Soc. (C)* 661 (1971).
[6]N. Ishikawa and M. Okazaki, *Chem. Abstr.* **52**, 18340 (1958).
[7]W. S. Johnson, B. Bannister, R. Pappo and J. E. Pike, *J. Am. Chem. Soc.* **78**, 6354 (1956).
[8]W. Hückel and R. Schewen, *Ber.* **89**, 481 (1956).
[9]W. F. Johns fiand I. Laos *J. Org. Chem.* **30**, 123 (1965).

[10]J. Fried and A. Klingsberg, *J., Am. Chem. Soc.* **75**, 4929 (1953).
[11]P. A. Robins and J. Walker, *J. Chem. Soc.* 3260 (1956); *Ibid.* 177 (1957).
[12]B. K. Bhattacharyya, A. K. Bose, A. Chatterjee and B. P. Sen, *J. Ind. Chem. Soc.* **41**, 479 (1964).
[13]Cf. ref. 12.
[14]B. P. Sen, A. Chatterjee, S. K. Gupta and B. K. Bhattacharyya, *J. Ind. Chem. Soc.* **35**, 751 (1958).
[15]K. Das Gupta, *Science and Culture* **33**, 55 (1967).
[16]A. E. F. Joseph and J. F. Thorpe, *J. Chem. Soc.* **91**, 1695 (1907).
[17]B. Longo and M. Pirona, *Chem. Abstr.* **42**, 544 (1947).