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STUDIES IN CLAISEN REARRANGEMENT

NOVEL THERMAL TRANSFORMATION OF α-ARYLOXYMETHYLACRYLIC ACIDS AND THEIR DERIVATIVES†

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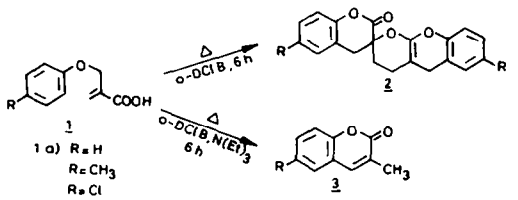
Abstract—α-Aryloxymethylacrylic acids and their derivatives have been found to undergo some novel thermal transformations leading to the formation of 'ene' dimers. The structure of the dimer has been revised on the basis of degradation studies, extensive spectral data and isolation of intermediates.

Ever since the first Claisen rearrangement was reported in 1912[1] there have been innumerable reports on the rearrangement and kinetic studies of allyl aryl ethers and aryl cinnamyl ethers containing various substituents on the aromatic ring,[2] but not many reports on the Claisen rearrangement of allyl aryl ethers bearing functional groups directly on the allylic moiety. A few are on the rearrangement of α- and γ-aryloxy-β-methyl crotonates and α-phenoxy-γ-methyl crotonates,[3] the synthesis of 2-methylbenzo(b)furans and 2-methylbenzo(b)thiophens involving the cyclisation of the corresponding β-chloroallyl phenyl ethers and β-chloroallyl phenyl sulphides respectively, and also the cyclisation of 3-chloro-1-phenoxybut-2-ene thermally to give 4-methyl-2H-chromene.[4]

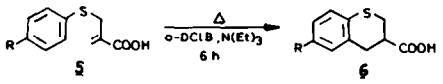
Recent reports on Claisen rearrangement of allyl aryl ethers containing substituents on the allylic moiety includes the syntheses of coumarins via Claisen rearrangement of allylic or propargylic aryl ethers in which the allylic or propargylic α-carbon is further oxygenated.[5] It has further been demonstrated by Box *et al.* that the Claisen rearrangement of 1-(α-naphthoxy)-2-(4-bromophenyl)-3-carbethoxy-2-propene in refluxing N,N-diethyl aniline leads to γ-lactone, while its isomeric compound was relatively inert under those conditions.[6]

In earlier communications we reported the thermal rearrangement of α-aryloxymethylacrylic acid **1** in *o*-dichlorobenzene (*o*-DClB) to produce the dimer **2** for which the structure was assigned.[7] In the presence of an added base like $N(Et)_3$, the acids were found to lead to the respective 3-methyl coumarins **3**[8] (Scheme 1). A



Scheme 1.

† Dedicated to Prof. Swaminathan on the occasion of his 60th birthday.



Scheme 2.

possible product chroman-3-carboxylic acid was not obtained. However, the thio analogue of the acid, **5** behaved differently. On heating in *o*-DClB it did not give the corresponding dimer. In the presence of $N(Et)_3$, the thio acids on heating in *o*-DClB gave the thiochroman-3-carboxylic acid **6** and not the 3-methyl thiocoumarin[9] (Scheme 2).

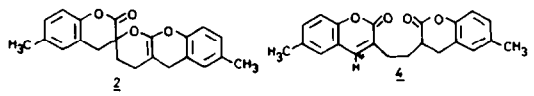
RESULTS AND DISCUSSION

In the present work, extensive study has been undertaken to revise the structure of the dimer **2** based on detailed spectral data (IR, high resolution ^{1}H-NMR and ^{13}C-NMR data).

Heating α-*p*-cresoxymethylacrylic acid **1b** in polyphosphoric acid or in refluxing *o*-DClB afforded a solid which after recrystallisation from ethanol melted at 219–220°. The presence of a molecular ion peak at *m/e* 348 (21%) indicated the compound to have a molecular formula $C_{22}H_{20}O_4$.

IR spectrum of the compound indicated the presence of a δ-lactone carbonyl (1740 cm^{-1}), while its UV spectrum was similar to that of a dihydrocoumarin (λ_{max}^{EtOH} 279 log ε 4.12). Accordingly the dimer was assigned structure **2** (Scheme 3).

However, a study of high resolution IR, ^{1}H-NMR and ^{13}C-NMR revealed a totally different structure, moreso the 270 MHz ^{1}H-NMR spectrum. The high resolution IR showed the presence of two CO's appearing at 1755 cm^{-1} and 1700 cm^{-1} indicating the presence of a saturated lactone CO (1755 cm^{-1}) and a



Scheme 3.

conjugated lactone CO (1700 cm^{-1}). Hence an alternative structure **4** was tentatively assigned for the dimer.

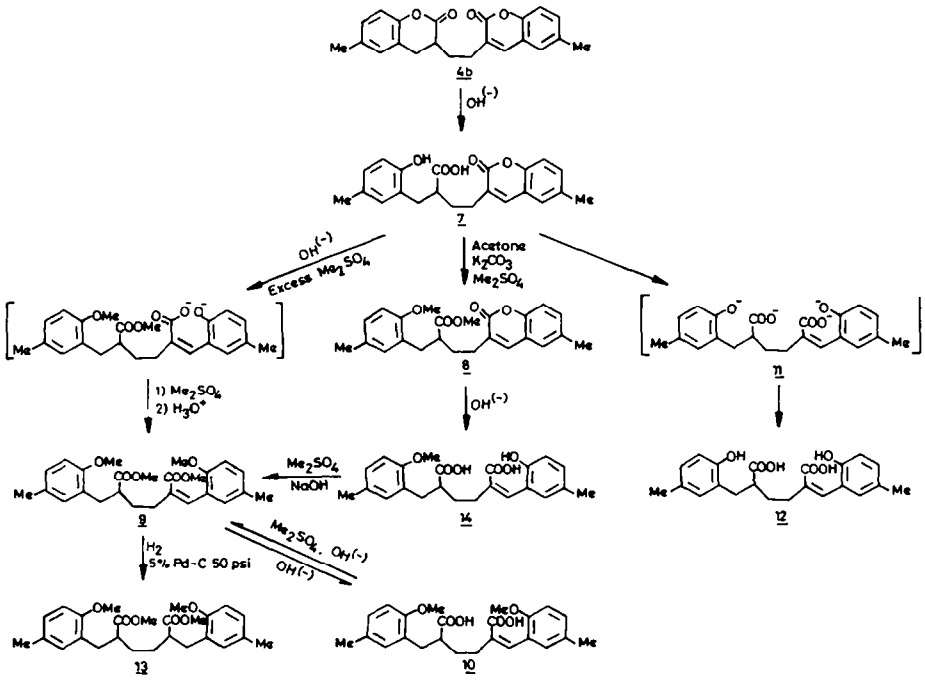
Further, the 270 MHz NMR spectrum showed a signal at 7.64 ppm quite separated from the aromatic region integrating for one proton. The NMR spectrum of 3-methylcoumarin **3** also showed a signal separated from the aromatic region at 7.3 ppm due to the C-4 proton. Thus by comparison it was evident that the dimer should also contain a 3-substituted coumarin unit. The signal at 7.64 ppm was therefore attributed to C-4 proton in the dimer.

Additional evidence in favour of structure **4** was obtained from ^{13}C-NMR data. Both the off-resonance and proton decoupled spectra were studied. The striking difference between structure **2** and **4** is the presence of two CO's in the latter as compared to one carbonyl in the former. In the ^{13}C-NMR spectrum two singlets were observed, one at 170.59 ppm (saturated lactone CO) and another at 161.64 ppm (conjugated lactone CO). Between structures **2** and **4** there is an obvious difference in the number of aliphatic carbons—while structure **2** has five aliphatic carbons, four CH_2 carbons and one quaternary carbon, structure **4** has only four aliphatic carbons, three CH_2 carbons and one CH carbon. In the broad decoupled ^{13}C-NMR spectrum four peaks were observed at 28.22, 28.29, 29.39 and 38.50 of which the peak at 38.50 becomes a doublet in the off-resonance decoupled spectrum. Thus this peak can be assigned to the CH carbon and in turn the dimer should be represented by structure **4** rather than **2**.

While both structures **2** and **4** have sp^2 carbons, the broad band decoupled spectrum showed the presence of a signal at 139.6 ppm which becomes a doublet in the off-resonance decoupled spectrum indicating this signal to be due to the C-4 carbon, being the most deshielded. Further the complete absence of any signal around 70–80 ppm in the ^{13}C-NMR which might correspond to $>$C—O rules out structure **2**. The ^{1}H-NMR showed the following characteristics 1.25 (m, 2H, methylene) 2.76–3.0 (m, 5H, benzylic and allylic protons and methine protons), 7.07 (m, 8H ArH) and 7.65 (m, 1H proton at C-4). The structure of the dimer was further confirmed by degradative studies.

Degradation of dimer: The presence of the δ-lactone system in the molecule offers scope for ring opening and methylation studies. Thus the dimer **4b** was heated with 50% sodium hydroxide solution for 2 hr and the reaction worked up for acidic material. A colourless, crystalline acid was obtained which melted at 167° resolidified and melted again at 219–220°, the m.p. of the dimer. (It is reasonable to assume that the cleaved acid relactonises to furnish the dimer at its m.p. In fact the cleaved acid gave the dimer when refluxed in *o*-dichlorobenzene (b.p. 182°).) The IR spectrum showed absorptions at 3360 cm^{-1} (br, OH), 1695 cm^{-1} (acid CO) and 1690 cm^{-1} (conjugated lactone CO). In the mass spectrum, the molecular ion peak was observed at *m/e* 366. Elemental analysis coupled with the mass spectrum indicated the compound to have a molecular formula of $C_{22}H_{22}O_5$. All these data coupled with the fact that the acid undergoes facile lactonisation to the dimer are in complete accord with the structure **7** assigned to the acid (Scheme 4).

The NMR spectrum of the acid **7** could not be recorded as it was found to be extremely insoluble in the usual NMR solvents. Acid **7** was treated with dimethyl sulphate in refluxing acetone in the presence of anhydrous potassium carbonate to furnish a colourless



Scheme 4.

crystalline solid melting at 91–93°. IR spectrum showed absorptions at 1730 cm^{-1} (ester CO) and 1690 cm^{-1} (conjugated lactone CO). Spectral data (NMR and mass spectrum) coupled with elemental analysis substantiated the structure **8** assigned for the product obtained in this reaction.

The acid **7** on methylation with excess dimethyl sulphate in the presence of sodium hydroxide afforded a neutral material **9** as the major product. A small amount of the acid **10** was also obtained. Once again spectral data lent support for the structures **9** and **10** assigned for the neutral and acidic products respectively.

Acid **10** on methylation with excess dimethyl sulphate in alkaline medium gave the neutral material **9** which on saponification furnished the acid **10**. These interconversions clearly prove the structure of **9** and **10**. The course of the reaction was reversed when the methylation of the acid **7** was carried out under controlled conditions *viz* using calculated amounts of dimethyl sulphate. Under these conditions, the acid **10** was the major product. Products **9** and **10** could be obtained directly from the dimer **4** under these conditions. Heating the dimer **4b** with 50% sodium hydroxide solution and working up for acidic material furnished only the phenolic product **7**. No trace of the acid **12** being formed. This is probably due to the lack of stabilisation of the anionic species **11**. In the presence of dimethyl sulphate, the carboxylic acid gets methylated, and the resulting anion derives stabilisation from the adjacent carbethoxy group.

The presence of an olefinic double bond in the ester **9** was confirmed by catalytic hydrogenation to the dihydro compound **13**. Compound **13** was found to be homogeneous on TLC. Spectral data and elemental analysis provide ample support for the structure **13** assigned for the hydrogenation product.

The diester **9** could also be obtained from the ether ester **8** by initial saponification to the acid **14** followed by methylation in alkaline medium. The acid **14** (m.p. 147–148°) was characterised by spectral data and elemental analysis.

Several α-aryloxymethylacrylic acids **1a–e** furnished the dimers **4a–e** on thermal rearrangement (Tables 1 and 2).

It was also observed that the ester **19** (Table 3) and amide **20** (Table 4) on thermal rearrangement in refluxing *o*-DClB furnished the dimer **4**. However, 3-methyl coumarins **3** were obtained when the rearrangement was performed in the presence of triethylamine (Scheme 5).

A mechanistic rationale for the formation of the dimer **4** can be envisaged via an initial (3,3) sigmatropic rearrangement followed by lactonisation to the

Table 1. α-Aryloxymethylacrylic acids **1**

No.	Phenol used	Yield %	M.p. °C	Analysis: Calculated values	Analysis: Found %
1a	Phenol	75	120–121	C = 67.4; H = 5.66	C = 67.14; H = 5.59
1b	*p*-Cresol	78	121–122	C = 68.74; H = 6.29	C = 68.81; H = 6.45
1c	*o*-Cresol	71	114–115	C = 68.74; H = 6.29	C = 69.10; H = 6.42
1d	*p*-Chlorophenol	76	157–159	C = 56.47; H = 4.23	C = 56.70; H = 4.10
1e	β-Naphthol	67	148–150	C = 73.67; H = 5.3	C = 73.64; H = 5.6

Table 2. Dimers-**4**

No.	Yield %	M.p. °C	Analysis: Calculated values	Analysis: Found %
4a	73	198–199	C = 74.99; H = 5.0	C = 74.66; H = 4.75
4b	82	219–220	C = 75.84; H = 5.79	C = 75.95; H = 6.02
4c	70	213–215	C = 75.84; H = 5.79	C = 75.51; H = 5.62
4d	71	258–259	C = 61.7; H = 3.6	C = 61.36; H = 3.31
4e	60	235–236	C = 79.98; H = 4.79	C = 79.76; H = 5.00

Table 3. Ethyl α-aryloxymethyl acrylates **19**

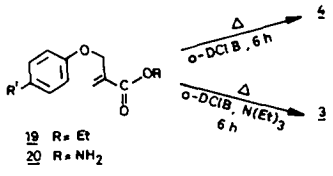
No.	Phenols used	Yield %	B.p. °C	Analysis: Calculated values C%	Analysis: Calculated values H%	Analysis: Found % C%	Analysis: Found % H%
19a	Phenol	97	112–114/2 mm	69.89	6.84	69.52	6.56
19b	*p*-Cresol	84	124–126/2 mm	70.89	7.32	70.58	7.12
19c	*p*-Chlorophenol	94	134–135/4 mm	59.88	5.41	59.42	5.12
19d	β-Naphthol	80	–	74.98	6.29	74.68	6.12

Table 4. α-Aryloxymethyl acrylamides **20**

No.	Yield %	M.p. °C	Analysis: Calculated values C %	Calculated values H %	Found % C %	Found % H %
20a	63	122–124	67.78	6.28	67.62	6.12
20b	83	130–132	69.09	6.85	69.12	6.78
20c	75–76	128–130	56.73	4.72	56.62	4.45

Table 5. Isolation of 3-methylene coumarins **16**

No.	R	Yield %	M.p. °C
a	H	25	66–68
b	CH_3	29	78–80
c	Cl	32	120–122

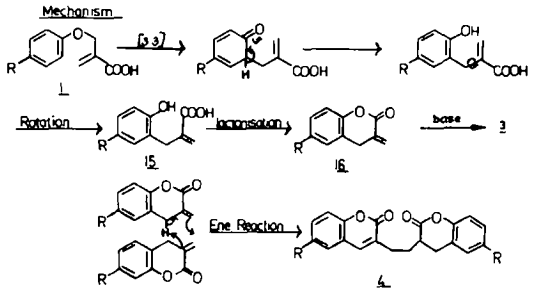


Scheme 5.

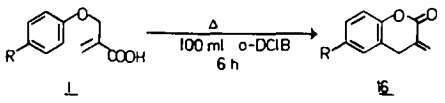
methylene coumarin **16** which then undergoes the 'ene' reaction to furnish the dimer **4** or isomerises in the presence of a base to give the 3-methylcoumarins **3** (Scheme 6).

There is a possibility that the dimer **4** can be obtained by an acid catalysed dimerisation of the intermediate exomethylene coumarin rather than by an 'ene' reaction, since such reactions may be initiated by the glassware (silica) which is acidic enough to catalyse such reactions. However, on carrying out the same reaction in a flask previously washed with boiling 20% NaOH solution and then water, the same dimer (m.p. 219–220°) was obtained.

The intervention of methylenecoumarin intermediate **16** in this transformation has been established by its isolation from the reaction. Thus, refluxing the acrylic acid **1c** in a very large volume of *o*-DCIB (50 times compared to the original concentration) so as to prevent intermolecular reactions, furnished on work-up a compound melting at 120–122°. IR ($CHCl_3$) ν_{max} 1755 cm^{-1} (C=O). NMR spectrum ($CDCl_3$/TMS) showed the following spectral characteristics: 3.8 (t, 2H,



Scheme 6.



Scheme 7.

benzylic protons), 5.7 and 6.4 (t, 2H, exomethylene protons) and 6.9–7.3 (m, 3H, ArH). MS: 194 (M^+) (Table 5) (Scheme 7).

As our work was in progress, a report appeared concerning the syntheses of similar α-methylene-δ-valero lactones.[10] The lactone **17** on storage at room temperature or when heated in the presence of acid was found to give the dimer **18** (Scheme 8).

In order to further establish the reaction sequence leading to the dimer **4** as rationalised in Scheme 6 an attempt was made to isolate the phenolic acid **15**.

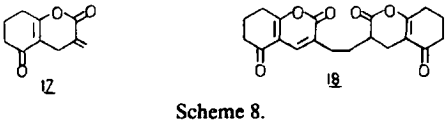
When the methyl α-*p*-chlorophenoxymethylacrylate **19c** was heated in a high boiling solvent like DEA and Ac_2O, the phenolic acid **15** was obtained as the acetate **21** in good yields. It was purified by passing through a silica gel column with hexane as eluent to get crystals m.p. 124–126° and was characterised by IR, ^{1}H-NMR and MS. IR ($CHCl_3$) ν_{max} 1720 cm^{-1} and 1760 cm^{-1} (C=O). NMR ($CDCl_3$/TMS) δ values at 2.3 (s, 3H, $-COCH_3$), 3.6 (s, 2H, benzylic), 3.8 (s, 3H, OCH_3), 5.5 (s, 1H), 6.3 (s, 1H), vinyl protons 7–7.7 (m, ArH) (Scheme 9).

The mass spectra of the acetate **21** did not show any molecular ion peak. It showed a peak at *m/e* 225 corresponding to $[M-COCH_3]^+$ ion.

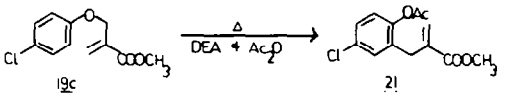
However the reaction of α-*p*-chlorophenoxymethylacrylic acid **1c** on heating in DEA and Ac_2O gave only the 3-methylcoumarin and not the phenolic acetate **21**.

The reaction of α-*p*-chlorophenoxymethylacrylic acid **1c** and the ester **19** on heating in DEA alone gave the methylcoumarins.

Our attempts to induce the Claisen rearrangement of these acrylic acids and esters in trifluoroacetic acid which has been reported[11] to be a unique solvent for Claisen rearrangement proved to be futile. The α-aryloxymethylacrylic acid **1c** on refluxing in TFA for 45 hr gave only the starting material. The α-*p*-chlorophenoxymethylacrylates **19c** also on heating in TFA for 45 hr showed no formation of tangible products. The reaction with TFA and Ac_2O of **1** and **19** also on



Scheme 8.



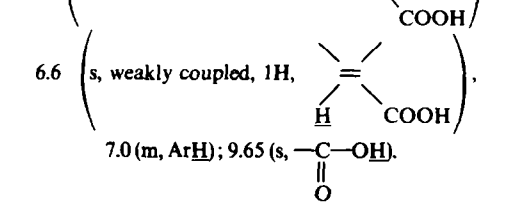
Scheme 9.

heating for 45 hr gave back the starting material effectively.

EXPERIMENTAL

UV spectra were taken in MeOH (spectroscopic grade) using Beckman DU-2 model. IR spectra were recorded on a Beckman IR 20. NMR spectra were taken using a Varian A 60D or EM-390 instrument with $CDCl_3$, CCl_4 and DMSO-D_6 as solvents and TMS as internal standard. The chemical shifts are reported in the δ scale. Mass spectra were taken using a Varian MAT CH 7 Mass spectrometer. TLC analyses were run on glass plates (5 × 20 cm) coated with silica gel-G ACME Sample) of 0.25 mm thickness and visualised using either iodine or short wave UV lamp.

General procedure for the preparation of α-aryloxymethylacrylic acids **1a–e**. In a 250 ml two-necked flask fitted with a reflux condenser and a dropping funnel, a mixture of the phenol (3 mol) and powdered NaOH (3 mol) in EtOH was taken and refluxed till all the NaOH dissolved. To the sodium phenoxide thus formed, a soln of β,β'-dibromisobutyric acid (1 mol) in DMF was added during 1 hr. Heating on a water bath was continued for a further period of 4 hr. The mixture was cooled to room temp and the separated NaBr filtered off, the filtrate concentrated and poured into crushed ice. The aqueous soln was acidified with conc HCl and extracted thoroughly with sat $NaHCO_3$ aq till all the acidic material was extracted. Acidification of the combined bicarbonate washings with ice cold conc HCl afforded the acids **1a–e**. The acids were crystallized from EtOAc–hexane mixture (Table 1). IR ν_{max} ($CHCl_3$) 1690 and 1635 cm^{-1}. NMR ($CDCl_3$/TMS) δ values: 4.7 (t, J = 1.5 Hz, 2H, —O—CH_2—),



7.0 (m, Ar<u>H</u>); 9.65 (s, —C(=O)—O<u>H</u>).

General procedure for the rearrangement of α-aryloxymethylacrylic acids **1a–e**. A soln of **1a–e** (1 part) in *o*-DClB (10 parts by volume) was heated at reflux for 6 hr. At the end of this period the mixture was cooled to room temp. Dilution of this soln with ether furnished **2a–e** in yields ranging from 60–80% (Table 2). The dimers were crystallized from EtOH. All the dimers had satisfactory spectral (IR, NMR characteristics (refer text)).

Degradation products of the dimer **4**

Saponification of the dimer. A soln of **4** (1.16 g, 3 mmol) in 50% NaOH (10 ml) was heated on a water bath for 2 hr. The mixture (homogeneous) was then cooled, acidified with ice-cold conc HCl and extracted with ether (2 × 25 ml). The ether soln was washed with sat $NaHCO_3$ aq. The combined bicarbonate extract was acidified with cold conc HCl and the acidic soln once again extracted with ether (2 × 25 ml). The ether extract was washed with water and dried ($MgSO_4$). Removal of ether by distillation furnished **7** (0.86 g, 73%) as a colourless solid. This solid melted at 167°, solidified and melted again at 218–219° (m.p. of **4**). An analytical sample of **7** prepared from MeOH melted at 168°. IR (KBr) at 3360 (OH), 1695 (C=O) and 1680 (C=O) cm^{-1}. Mass spectrum: *m/e* 366 (M^+). $C_{22}H_{22}O_5$ requires C = 72.12; H = 6.05. Found: C = 71.92; H = 5.94%.

Saponification of the dimer **4** *followed by methylation with excess dimethyl sulphate*. A soln of **4** (0.348 g, 1 mmol) in 50% NaOH aq (10 ml) was heated on a water bath until a clear soln resulted (10 min). Me_2SO_4 (2.52 g, 20 mmol) was added and the heating continued for 30 min longer. The mixture was poured into ice acidified with conc HCl and extracted with ether (2 × 25 ml). The combined ether extract was washed with sat $NaHCO_3$ aq, water and dried ($MgSO_4$). Removal of ether after filtration gave a viscous oil which solidified on cooling in ice to yield as a colourless solid **9** (0.3 g, 68%), m.p. 86–87° (hexane). IR (KBr): 1720 (saturated ester CO) and 1705 (unsaturated ester CO); ^{1}H-NMR (CCl_4/TMS): 1.2–2.0 (broad multiplet, 2H, CH_2), 2.2 (s, 6H, Ar—CH_3), 2.3–3.0 (m, 5H, Ar—<u>CH_2</u>, C=C—<u>CH_2</u>, —<u>CH</u>—COOMe), 3.4 (s, 3H, COO<u>CH_3</u>), 3.5 (s, 3H, —COO<u>CH_3</u>), 3.7 (s, 6H, ArO<u>CH_3</u>) and 6.4–7.0 (m, 6H, —C=<u>CH</u>—Ar and Ar<u>H</u>). MS: *m/e* —440 (M^+). $C_{26}H_{32}O_6$ requires: C = 70.89; H = 7.32. Found: C = 70.62; H = 7.14%.

The sodium bicarbonate extract was acidified with cold conc HCl and the resulting solid filtered, washed with water and dried to yield **10** as a colourless solid (0.1 g, 25%), m.p. 186–187° (MeOH). IR (KBr): 1700 (CO), 1685 (CO) and 1610 cm^{-1} (C=C). MS: *m/e* —412 (M^+). $C_{24}H_{28}O_6$ requires: C = 69.88; H = 6.84. Found: C = 69.72; H = 6.52%.

Methylation of diacid **10** *with dimethyl sulfate in alkaline medium*. To a soln of **10** (0.41 g, 1 mmol) in 50% NaOH aq (5 ml), Me_2SO_4 (1.9 g, 15 mmol) was added and the mixture was heated on a water bath for 1 hr. The cooled mixture was poured onto crushed ice and extracted with ether (2 × 25 ml). The combined ether extract was washed with water and dried ($MgSO_4$). Removal of ether by distillation after filtration afforded a colourless crystalline solid (0.4 g, 90%), m.p. 87–88° (hexane). This solid was identical with **9** (m.p. and mixed m.p.). No acidic material was isolated from the basic aqueous solution.

Saponification of the diester **9**. To a soln of **9** (0.44 g, 1 mmol) in MeOH (10 ml) was added 50% NaOH aq (10 ml) and the reaction mixture was heated on a water bath for 4 hr. The mixture was cooled to room temp, poured into excess ice-water and extracted with ether (25 ml) to remove any unreacted ester. The aqueous soln was acidified with conc HCl. The ppt was filtered off, washed with water and dried to yield a colourless solid (0.35 g, 85%), m.p. 186–188° (MeOH). This compound was identical with **10** (mixed m.p.).

Hydrogenation of the diester **9**. A soln of **9** (0.44 g, 1 mmol) in EtOAc (15 ml) was hydrogenated in Paar Hydrogenator at 50 psi in the presence of 5% Pd–C for 45 min. The catalyst was filtered off and the solvent removed by distillation to yield the symmetrical **13** (0.4 g, 82%), m.p. 96–98° (MeOH). This compound was found to be homogeneous on TLC and different from the starting material. IR (KBr): 1720 cm (CO); ^{1}H-NMR (CCl_4/TMS): 1.2–2.1 (broad multiplet, C<u>H_2</u>), 2.2 (s, 6H, Ar—<u>CH_3</u>), 2.3–2.9 (m, 6H, Ar—<u>CH_2</u>, —<u>CH</u>—COOMe), 3.4 (s, 3H, —COOC<u>H_3</u>), 3.5 (s, 3H, —COOC<u>H_3</u>), 3.7 (s, 6H, Ar—OC<u>H_3</u>) and 6.5–7.0 (m, 6H, Ar<u>H</u>); MS: *m/e* —442 (M^+). $C_{26}H_{34}O_6$ requires: C = 70.56; H = 7.74. Found: C = 70.22; H = 7.36%.

Methylation of phenolic acid **7** *with calculated amount of dimethyl sulfate in alkaline medium*. A soln of **7** (0.37 g, 1 mmol) in 50% NaOH aq (5 ml) was treated with Me_2SO_4 (0.38 g, 3 mmol) and heated on a water bath for 2 hr. The mixture was poured into crushed ice, acidified with conc HCl and extracted with ether (2 × 25 ml). The combined ether extract was washed with sat $NaHCO_3$ aq, water and dried ($MgSO_4$). Removal of ether by distillation gave **9** (50 mg, 11%), m.p. 85–87° (MeOH).

Acidification of the bicarbonate washings furnished **10** (0.25 g, 60%), m.p. 185–187° (no depression admixture with an authentic sample).

Methylation of the acid **7** *with excess dimethyl sulfate in alkaline medium*. The acid **7** (0.36 g, 1 mmol) was heated on a water bath with 50% NaOH aq (10 ml) until a clear soln

resulted (10 min). Me_2SO_4 (2.52 g, 0.2 mol) was added and the mixture was stirred at room temp for 30 min. The mixture was poured onto crushed ice, acidified with conc HCl and extracted with ether (2 × 30 ml). The combined ether extract was washed sequentially with sat $NaHCO_3$ aq, water and dried ($MgSO_4$). Removal of ether by distillation gave a colourless crystalline solid (0.3 g, 68%), m.p. 86–87°. This compound was found to be identical with **9** (m.p. and mixed m.p.). Acidification of the bicarbonate washings gave 50 mg (12%) of **10**; m.p. 186–187°.

Methylation of the acid **7** *with dimethyl sulfate under mild conditions.* A mixture of **7** (0.37 g, 1 mmol), Me_2SO_4 (2.52 g, 20 mmol), anhyd K_2CO_3 (1.38 g, 10 mmol) in dry acetone (20 ml) was refluxed on a water bath for 5 hr. The mixture was cooled, filtered and the solid residue washed with a small amount of acetone. From the filtrate acetone was distilled off and the residue treated with water (25 ml). The aqueous soln was extracted with ether (2 × 30 ml). The combined ether extract was washed with sat $NaHCO_3$ aq, water and dried ($MgSO_4$). Distilling off ether gave a liquid which on trituration with a small amount of MeOH and ice cooling gave **8** (0.3 g, 77%) as a colourless crystalline solid, m.p. 91–93° (MeOH). This ester was found to depress the m.p. of **9**. IR ($CHCl_3$): 1720 (CO) and 1690 cm^{-1} (CO); ^{1}H-NMR ($CDCl_3$/TMS): 1.2–2.2 (m, 2H, $-CH_2-$), 2.4 (s, 3H, Ar—CH_3), 2.5 (s, 3H, Ar—CH_3), 2.6–3.4 (m, 7H, $-CH_2$ and CH), 3.7 (s, 3H, Ar—OCH_3), 3.9 (s, 3H, $COOCH_3$) and 6.7–7.4 (m, 6H, Ar—C<u>H</u>=C— and Ar<u>H</u>); MS: *m/e* −394 (M^+). $C_{24}H_{26}O_6$ requires: C = 73.08; H = 6.64. Found: C = 73.21; H = 6.86%.

Saponification of the ester **8**. A mixture of **8** (0.4 g, 1 mmol), 50% NaOH aq (10 ml) and MeOH (2 ml) was heated on a water bath for 3 hr. The mixture was diluted with water, acidified with ice-cold conc HCl and extracted with ether. The ether extract was washed with sat $NaHCO_3$ aq and with water. The $NaHCO_3$ washing was acidified with ice-cold conc HCl, once again extracted with ether and the ether extract dried ($MgSO_4$). Removal of ether after filtration gave a pale yellow solid **14** (0.2 g, 50%), m.p. 140–144°. This solid when crystallised twice from MeOH gave colourless crystals melting at 147–148°. IR (KBr): 1710 sat acid (CO), 1695 unsat acid (CO) and 1610 cm^{-1} (C=C); MS: *m/e* −398 (M^+). $C_{23}H_{26}O_6$ requires: C = 69.33; H = 6.58. Found: C = 69.22; H = 6.44%.

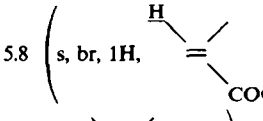
The ether layer left behind after bicarbonate washing on work up gave 100 mg of the starting ester **8** (mixed m.p.).

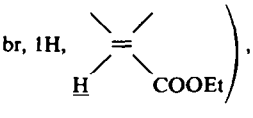
General procedure for the preparation of ethyl-α-aryloxymethyl acrylates **19**. A soln of the phenol (2 mol) in EtOH was treated with powdered NaOH (2 mol) and stirred at room temp till all the NaOH dissolved. A soln of ethyl dibromoisobutyrate (1 mol) in EtOH was added during 15 min. Stirring at room temp was continued for 6 hr. Most of the solvent was removed by distillation under reduced pressure, the residual liquid digested with water (150 ml) and extracted with ether (2 × 75 ml). The combined ether extract was washed with 10% NaOH aq, water and dried ($MgSO_4$). Removal of the solvent by distillation furnished the esters which were distilled under vacuum (Table 3). IR ($CHCl_3$) ν_{max} 1680 (C=O) and 1610 (C=C) cm^{-1}; NMR ($CDCl_3$/TMS) δ values:

1–1.35 (t, 3H, $-\underset{\underset{O}{\|}}{C}-OCH_2C\underline{H}_3$),

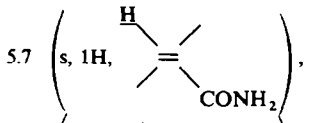
3.9–4.2 (q, 2H, $-\underset{\underset{O}{\|}}{C}-OC\underline{H}_2CH_3$),

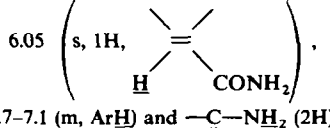
4.55 (s, br, 2H, —O—CH_2—),

5.8 (s, br, 1H, ),

6.2 (s, br, 1H, ), 6.6–7 (m, Ar<u>H</u>).

General procedure for the preparation of α-aryloxymethyl acrylamides **20**. A soln of the α-aryloxymethylacrylic acid (5 or 10 mmol) and $SOCl_2$ (5 or 10 mmol) in dry benzene (10 to 20 ml) was refluxed on a water bath for 1 hr. Benzene was distilled off under reduced pressure. Excess $SOCl_2$ was removed by adding some more dry benzene and distilling off the solvent. The residue was treated with an excess amount of liquor ammonia with ice cooling. The resulting solid amide was filtered, washed with water and dried. The amides were purified by crystallization from MeOH. The yields ranged from 63–83% (Table 4). IR ($CHCl_3$) ν_{max} 3380 cm^{-1} and 3480 cm^{-1} (N—H stretch), 1670 (C=O) and 1625 (C=C) cm^{-1}; NMR ($CDCl_3$/TMS) δ values: 4.7 (s, 2H, Ar—O—C<u>H</u>$_2$),

5.7 (s, 1H, ),

6.05 (s, 1H, ),

6.7–7.1 (m, Ar<u>H</u>) and $-\underset{\underset{O}{\|}}{C}-N\underline{H}_2$ (2H).

Isolation of exomethylene coumarin **16**. 200 mg (0.001 mol) of **1a** in 100 ml of *o*-DClB was refluxed for 6 hr, cooled and *o*-DClB was removed under vacuum. The residue was extracted into ether and washed with sat $NaHCO_3$ aq and water, dried and evaporated to yield 50 mg of **16** (Table 5). Other acids **1b** and **1c** also rearranged in *o*-DClB to give **16b** and **16c**.

Trapping the phenol **15** *as the phenolic acetate* **15a**. A soln of **19** (450 mg, 0.02 mol) was refluxed in DEA and Ac_2O (0.5 ml) in an inert atmosphere for 6 hr. Cooled and the reaction worked up by pouring into water and stirring the soln for some time to remove any excess Ac_2O and then extracting into ether. The ether extract was washed with 2 N HCl and water, dried over Na_2SO_4 and evaporated. The crude residue was purified by passing through a short silica gel column using hexane as eluent.

Rearrangement of **1c** *and* **19c** *in TFA.* Compound **1c** was refluxed in 5 ml of TFA for 45 hr. Cooled and the reaction worked up by pouring into water and extracting into ether. The ether extract washed with sat $NaHCO_3$ aq and then water and dried (Na_2SO_4). NMR showed the presence of only starting material and no rearranged product. Compound **19** was refluxed in 5 ml of TFA for 45 hr and worked up by pouring into water and extracting into ether. Ether extract washed with water and dried (Na_2SO_4). TLC showed the presence of only starting material.

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