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A REINVESTIGATION OF THE CLAISEN REARRANGEMENT OF METHYL γ-ARYLOXYCROTONATES A CONVENIENT SYNTHESIS OF 3-ETHYLIDENEBENZOFURAN-2(3H)-ONES

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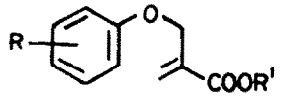
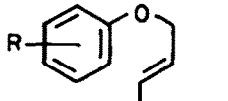
Abstract - The synthesis and Claisen rearrangement of methyl γ-aryloxycrotonates have been reinvestigated. A number of methyl γ-aryloxycrotonates have been prepared and sucessfully rearranged to a mixture of Z and E 3-ethylidenebenzofuran-2(3H)ones in refluxing ethylene glycol.

As part of a general study of exploring the scope and synthetic utility of Claisen rearrangement of allyl aryl ethers bearing carboxyl or carboethoxy substituents on the allyl chain, we took up a study of Claisen rearrangement of α-aryloxymethylacrylic acids, their esters and that of methyl γ-aryloxycrotonates i.e., allyl aryl ethers bearing carboxyl functionalities at the β and γ positions of the allyl chain. It was hoped that the transformation in each case would lead to benzo-fused oxygen heterocycles proceeding via a Claisen rearrangement[1].



1 $R' = H$
2 $R' = CH_3$



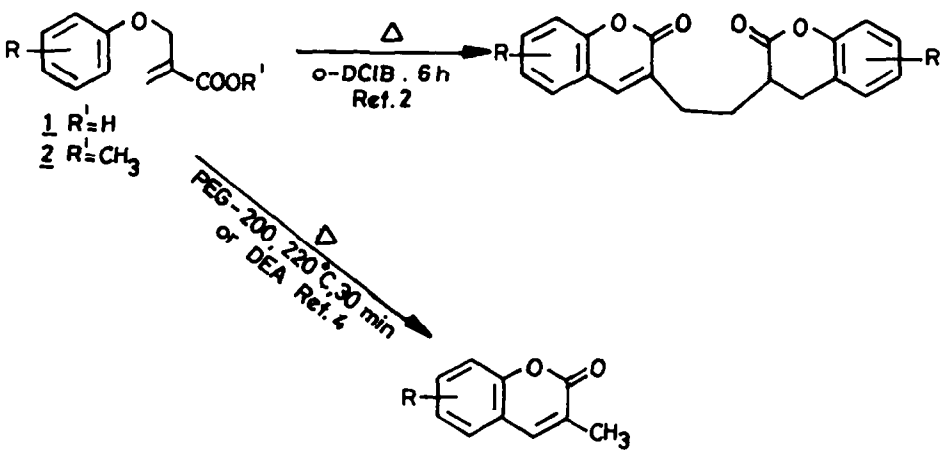
3

The interesting transformations undergone by 1 and 2 leading to various 3-methylcoumarins and coumarins functionally substituted at the 3-methyl group via sequential Claisen rearrangement-lactonisation-ene reactions have been the subject of our recent publications[2-5](Scheme-1).

In contrast the isomeric system viz., methyl γ-phenoxycrotonate was reported by Sultanbawa *et al* to be quite stable[6]. They had observed that it failed to rearrange under different conditions.

In view of this, we took up a detailed reinvestigation on the syntheses and Claisen rearrangement of methyl γ-aryloxycrotonates from both mechanistic and synthetic considerations. Mechanistically it was felt worthwhile to examine the feasibility of such a transformation keeping in mind the deconjugative stabilisation in the transition state[7] that would ensue upon the Claisen rearrangement of 3. The synthetic aspect of this transformation was that it could lead to a convenient entry to 3-ethylidenebenzofuran-2(3H)-ones of which there is only a vague report in the literature and that too not of any preparative significance[8].

Scheme 1

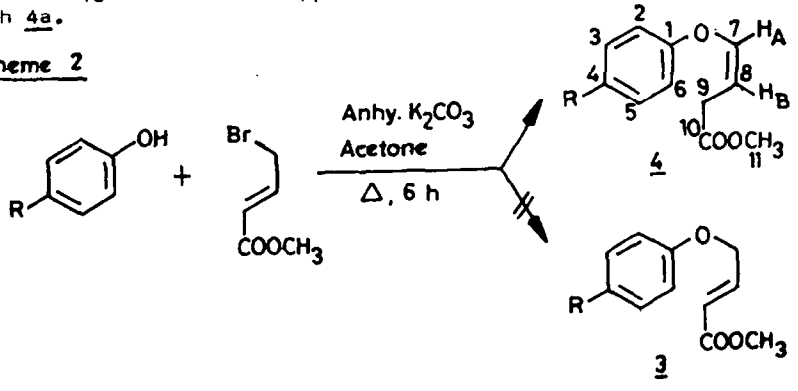


o-DCIB - o-Dichlorobenzene
PEG - Polyethylene glycol - 200
DEA - Diethylaniline

Results and Discussion

Our investigation commenced with the synthesis of methyl γ-aryloxycrotonates. Three reports were available in the literature on its synthesis[6,9,10]. We started our investigation with the preparation of methyl γ-phenoxycrotonate 3a using virtually the same conditions as reported by the earlier workers viz., refluxing a mixture of phenol (5.25g 56 mmol), methyl γ-bromocrotonate (10g 56 mmol) and potassium carbonate (15.45g 112 mmol) in 100 ml of acetone for 6h. This procedure however failed to yield the desired crotonate 3a; instead it afforded the β,γ-isomer 4a as a distillable liquid (b.p. 124°/1 mm in 78% yield). Its mass spectrum showed a molecular ion peak at m/z 192, while its IR spectrum showed bands at 1720 cm^{-1} and 1650 cm^{-1}. NMR spectrum of this compound showed signals at δ 3.1 ppm (d,2H) δ 3.5 ppm(s,3H), δ 4.8 ppm(dt,1H,H_B), δ 6.1 ppm(d,1H,H_A J=8 hz), δ 6.4-6.9 ppm(m,5H,ArH). From the NMR spectral data (90 Mhz) and careful integration of the recorded peaks, it was clear that the product obtained under the reaction conditions employed, was only the β,γ-unsaturated derivative 4a and not the required methyl γ-phenoxy-crotonate 3a (Scheme 2). The cis-stereochemistry for 4a was established from the coupling constant for H_A and H_B, $J_{H_AH_B}$=8 hz. The broad band noise decoupled ^{13}C-NMR spectrum of this compound showed 11 lines. A tentative assignment for the chemical shifts and multiplicities for every carbon are - C_1-157 ppm(s), C_2/C_6-116 ppm(d), C_3/C_5-129 ppm(d), C_4-122 ppm(d), C_7-142 ppm(d), C_8-103 ppm(d), C_9-29 ppm(t), C_{10}-171 ppm(s), C_{11}-51 ppm(q). The ^{13}C-NMR spectral features are consistent with 4a.

Scheme 2



Several other phenols also reacted in a similar manner affording the respective β,γ-unsaturated esters 4a-d as shown in Table 1. There was no trace of the desired crotonate 3 under these conditions. All the esters 4a-d were completely characterised by spectral data (UV,IR, NMR and MS, see experimental)[11].

Table 1 Synthesis of 4a-d

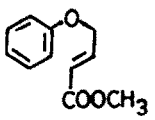
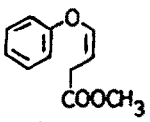
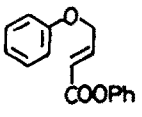
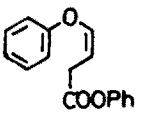
No	R	b.p	yield %
1	a=H	124°/1mm	78
2	b=CH_3	140°/1mm	80
3	c=Cl	155°/1mm	80
4	d=OCH_3	142°/1mm	82

Our attempts to isomerise the β,γ-unsaturated derivative 4a to the α,β-unsaturated isomer 3a under a few acidic and basic conditions proved abortive.

Synthesis of Methyl γ-aryloxycrotonates

We next focussed our attention to synthesise the required crotonates 3 by adopting conditions which have been sucessfully employed in our laboratory as well as elsewhere for the synthesis of many substituted aryl propargyl ethers and aryl allyl ethers. The various conditions tried and the results obtained from these studies are summarised in Table 2. Again in none of the cases, could we obtain the desired crotonates 3 free from the contamination of the β,γ-isomer 4.

Table 2

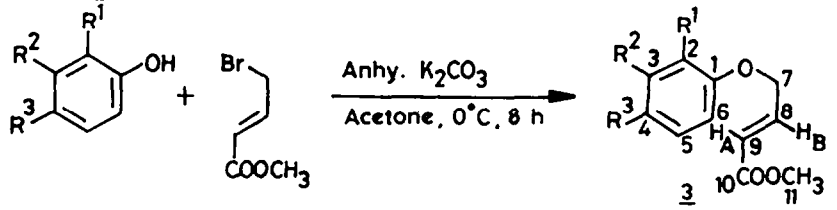
	Reaction condition	 3a	 4a	 5a	 6a
1	$NaOCH_3$/DMF RT 8 h		+		+
2	NaOH/MeOH RT 8h phenol (2eq)	+		+	+
3	NaOH/MeOH RT 8 h phenol (1eq)	+	+		
4	K_2CO_3/DMF RT 8 h	+	+	+	+
5	K_2CO_3/Acetone RT 8 h	+	+		
6	K_2CO_3/Acetone/KI 0° 8 h	+			

\+ Formation of the indicated product

After considerable experimentation, it was observed that by carrying out the above reaction at 0°C, the desired crotonate 3a free from 4a could be obtained as a distillable liquid in 72% yield. Its mass spectrum showed a molecular ion peak at m/z 192 while its IR spectrum showed bands at 1710 cm^{-1} and 1650 cm^{-1}. NMR spectrum of this compound showed signals at δ 3.5 ppm(s,3H), δ 4.4 ppm(m,2H,-OCH_2), δ 5.9 ppm(d,1H,J=18 hz,H_A), and δ6.5-7.0 ppm(m,5H, ArH+H_B). The broad band noise decoupled ^{13}C-NMR of 3c exhibited 9 lines. A tentative assignment for the chemical shifts and multiplicities for every carbon are C_1-156.66 ppm(s),C_2/C_6-

116.02 ppm(d), C_3/C_5-129.45 ppm(d), C_4-126.36 ppm(s), C_7-61.77 ppm(t), C_8-142.19 ppm(d),C_9-121.87 ppm(d), C_{10}-166.32 ppm(s), C_{11}-51.67 ppm(q). The ^{13}C-NMR spectral features are consistent with the assigned structure. Several other methyl γ-aryloxycrotonates 3a-h could also be prepared using the above procedure Table 3[12]. All the esters were completely characterised by spectral data (UV,IR,NMR and MS, see experimental).

Table 3



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No	Compound No.	R^1	R^2	R^3	m.p/b.p °C	yield %
1	3a	H	H	H	150°/2 mm	72
2	3b	H	H	CH_3	46-47	75
3	3c	H	H	Cl	40-42	70
4	3d	H	H	OCH_3	43-45	78
5	3e	H	-CH=CH-CH=CH-		49-50	76
6	3f	OCH_3	H	H	45-46	65
7	3g	CH_3	H	H	182°/2 mm	60
8	3h	Cl	H	Cl	78-79	70

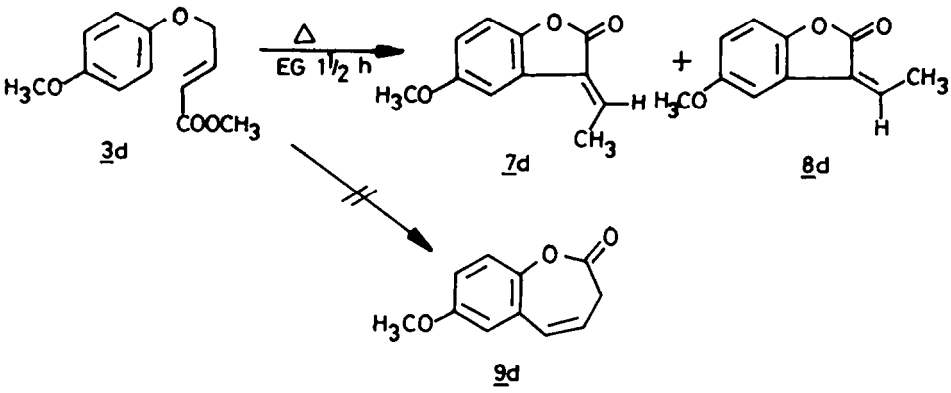
Having obtained the desired methyl γ-aryloxycrotonates, it was of interest to investigate the cause of isomerisation of 3 to 4 that was observed when we tried the conditions reported by Sultanbawa et al and Harding et al for the preparation of 3. It was obvious that either the phenol, potassium carbonate or the temperature or all these factors might have been responsible in bringing about the isomerisation of 3. Refluxing 3a (192 mg 1 eq.) in the presence of phenol(1 eq.) alone in acetone for 8h did not result in any isomerisation neither did refluxing 3a(1 eq.) with potassium carbonate (1 eq.) alone in acetone for 4h lead to any isomerisation. Interestingly when 3a was refluxed in the presence of phenol(1 eq.) and potassium carbonate(1 eq.) in acetone for 4h, a clean isomerisation of 3a to 4a was observed.

Rearrangement studies

The thermal rearrangement of methyl γ-aryloxycrotonates was investigated in various high boiling solvents viz., o-dichlorobenzene(o-DClB b.p.178°C), N,N-diethylaniline(DEA b.p.218°C) decalin(b.p. 195°C), polyethylene glycol-200(PEG-200 b.p.270°C), diethylene glycol(DEG b.p.220°C) and ethylene glycol(EG b.p.198°C) Among all the solvents tried, ethylene glycol appeared to be the best solvent for the rearrangement of 3.

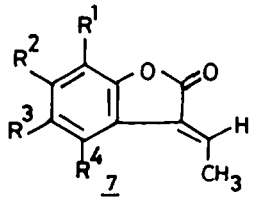
Heating 3d(900 mg 4 mmol) in ethylene glycol(20 ml) at refluxing temperature for 2 1/2 h followed by aqueous workup and extraction with hexane afforded a semi-solid(yield 85%) which proved to be a mixture of two products by TLC. Infra red spectrum showed bands at 1770 cm^{-1} and 1790 cm^{-1}, while its NMR spectrum showed two pairs of doublets centred at δ 2.2 ppm and δ2.35 ppm with a coupling constant of 7.5 hz and a multiplet at δ6.5-7.0 ppm thereby indicating the crude product to be a mixture of 3-ethylidenebenzofuran-2(3H)ones 7d and 8d (Scheme 3). Structure 9d was eliminated on the basis of Infra red and NMR spectral data.

Scheme 3



The crude mixture of E and Z isomers could not be separated by column chromatography or preparative TLC. However fractional crystallisation of the semi-solid in hexane furnished the major isomer 7d as a yellow solid(m.p. 99-100°C) in 30% yield. The E isomer 7d showed a carbonyl band at 1770 cm^{-1}while the Z isomer exhibited the band due to carbonyl at 1790 cm^{-1}. Several other methyl γ-aryloxycrotonates 3a-g were also converted to the respective 3-ethylidenebenzofuran-2(3H)-ones 7a-g and 8a-g in 75-80% yield. Fractional crystallisation in each case afforded the respective pure 7 in 30-40% yield. Table 4. The benzofuranones 7a-g were completely characterised by spectral data (UV,IR,NMR and MS, see Experimental).

Table 4

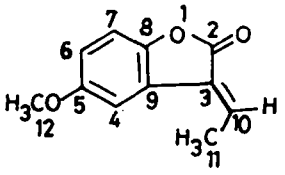


7

No.	Compound No.	R^1	R^2	R^3	R^4	m.p	yield %
1	7a	H	H	H	H	55-57	32
2	7b	H	H	CH_3	H	78-79	34
3	7c	H	H	Cl	H	119-120	33
4	7d	H	H	OCH_3	H	99-100	30
5	7e	H	H	-CH=CH-CH=CH-		110-112	40
6	7f	CH_3	H	H	H	99-100	35
7	7g	OCH_3	H	H	H	109-110	38

The assignment of structure 7 for the major product was based on NMR spectral data and literature analogies. The high resolution NMR spectrum (250 Mhz) of 7d showed the following characteristics: δ 2.2 ppm(d,3H,J=7.5 hz), δ 3.7 ppm(s,3H,-OCH_3), δ 6.83 ppm(dd, 1H), δ 7.03 ppm(d,1H), δ 7.14 ppm(d,1H), δ 7.19 ppm(q,1H, olefinic proton). The assignment of structure 7 for the major isomer was supported by

comparison of the chemical shifts of the $-CH_3$ protons of 7d (δ_{CH_3}=2.2 ppm) and 8d(δ_{CH_3}=2.35 ppm) with those reported in literature for methyl cis crotonate (δ_{CH_3}=2.14 ppm), methyl trans crotonate(δ_{CH_3}=1.88 ppm) and trans-crotonic acid (δ_{CH_3}=1.90 ppm). Further, irradiation of the methyl signal of 7d at δ2.2 ppm resulted in slight increase in part of the aromatic multiplet, while irradiation of part of the multiplet in the region δ6.5-7.0 ppm resulted in noticeable increase in the intensity of the $-CH_3$ doublet in the differential NOE spectrum. The broad band noise decoupled ^{13}C-NMR spectrum of 7d consisted of 11 lines. A tentative assignment for the chemical shifts and multiplicities for every carbon are: C_2-156.29 ppm(s), C_3-124.93 ppm(s),C_4-114.74 ppm(d), C_5-149.15 ppm(s), C_6-109.83 ppm(d),C_7 -111.25 ppm(d),C_8-148.04 ppm(s),C_9-123.50 ppm(s), C_{10}- 140.83 ppm (d), C_{11}-17.15 ppm(q),C_{12}-55.15 ppm(q).



7d

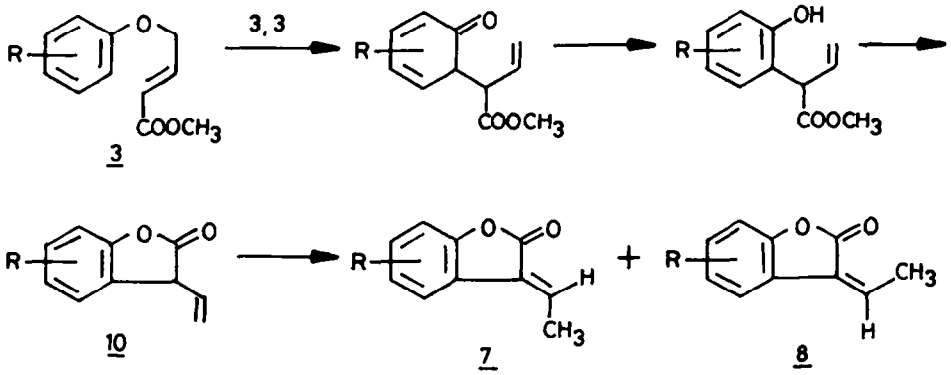
In assigning the E stereochemistry for 7, it is assumed that the effect of carbonyl is far more dominant than that of phenyl ring.

Some efforts were made to find out whether the mixture of benzofuranones 7 and 8 could be converted completely to either of the isomers. Refluxing the mixture in the case of 7d and 8d in dry chloroform containing p-toluenesulphonic acid for 6h however failed to alter the composition of the mixture. Irradiation of the crude mixture in methanol at 257 nm also failed to alter the composition. Irradiation of pure 7d for shorter duration resulted in no change while at longer hours (72h) resulted in 4:1 mixture of 7d and 8d. This composition remained unaltered even on prolonged irradiation viz., 10 days.

Mechanism

The mechanism of the transformation is most likely to involve an initial 3,3-shift followed by aromatisation and lactonisation to the 3-vinylbenzofuranone 10 which further undergoes isomerisation to 7 and 8 (Scheme 4).

Scheme 4



3 10 7 8

In none of the experiments performed, was the intermediate 10 isolated or observed, indicating the isomerisation to be a faster reaction.

There appeared to be only one vague report in the literature on 3-ethylidene benzofuran-2(3H)-ones[8]. The two benzofuranones 7a and 8a were reported to have been formed in minor amounts in addition to 9a when 2H-chromene was reacted with magnesium and the insitu generated cyclic allylmagnesium phenoxide was carboxylated with CO_2 and acidified. The relative ratio of 9a:7a:8a was found to be 66:25:9. While the authors were able to separate 9a from this mixture and characterise it, no mention has been made about the separation of 7a and 8a and about their characterisation. Although the authors have given the spectral data for these benzofuranones, it is not clear from the paper whether the data were taken on the mixture or on pure compounds. No other characterisation excepting the NMR data could be found in the paper.

Rearrangement of 3 in other solvents

The reaction of 3a(200 mg) in refluxing DEA(3 ml) for 4h resulted in clean isomerisation to 4a. It is clear from our observation that what Sultanbawa et al had prepared and tried to rearrange was not the required methyl γ-phenoxycrotonate 3a but the isomeric 4a . The esters 3b,3c and 3d were also isomerised to 4b,4c and 4d in refluxing DEA.

The rearrangement of 3d in refluxing o-DClB for 20h was found to be very sluggish bringing about little change in starting material while in refluxing decalin, a mixture of 7d and 8d was obtained as a gummy material after 5h. This behaviour is in remarkable contrast to that of methyl α-aryloxymethylacrylates 2(see Scheme 1). This brings out clearly the importance of conjugation factor in deciding the ease of Claisen rearrangement. The rearrangement of 3d in PEG-200 or DEG furnished 7d and 8d in very low yield, while charge induced conditions like anhydrous $AlCl_3$ or trifluoroacetic acid failed to bring about any change in the starting material. This is again in contrast to the behaviour of methyl α-aryloxymethylacrylates(See Scheme 1).

In conclusion, the Claisen rearrangement of methyl γ-aryloxycrotonates in ethylene glycol has led to a convenient and easy entry to 3-ethylidenebenzofuran-2(3H)-ones, for which no synthesis has been described in the literature so far[8], though quite a few methods are available for the synthesis of 3-alkylidenebenzofuran-2(3H)-ones[13].

EXPERIMENTAL

1. General Considerations: Melting points and boiling points are uncorrected. Infra red spectra were recorded on Perkin-Elmer(PE-1310) instrument. NMR spectra were recorded on Varian EM-390 or Varian XL-100 instruments with $CDCl_3$ as solvent and tetramethylsilane(TMS) as the internal standard. The chemical shifts reported are in δ scale. UV spectra were taken in methanol(Spectroscopic grade) using Shimadzu 240 instrument. Mass spectra were taken using a Varian Mat CH7 mass spectrometer. All the solvents employed in the present study were purified using literature reported procedures.

2. Synthesis of 4: General procedure: A mixture of phenol(5.25g 56 mmol), methyl γ-bromocrotonate (56 mmol) and anhydrous potassium carbonate (112 mmol) in 100 ml of dry acetone was heated at reflux for 4h. The reaction mixture was cooled and the inorganic salts were filtered. Concentration of the solution gave a brown liquid which was taken up in ether. The ethereal layer was washed with 2N NaOH (3x30 ml) until the aqueous layer was neutral. The solution was dried over anhydrous Na_2SO_4. Evaporation of the solvent gave a liquid which was homogeneous on TLC. The boiling points and yields are shown in Table 1. The esters were characterised by complete spectral data, see Table 5.

Table 5

No.	Compound	UV(MeOH) λmax nm	IR($CHCl_3$) ν_{max} cm^{-1}	NMR($CDCl_3$/TMS)	MS m/z
1.	4a	230 nm (2640) 272 nm (2400)	1720, 1650	δ3.1(d,2H,J=8hz), δ3.5(s,3H,-OCH_3) δ4.8(dt,1H,H_B), δ6.2(d,1H,J=8hz,H_A) δ6.7-7.1(m,5H,ArH)	192 (60.7%)
2.	4b	230 nm (2560) 278 nm (2200)	1720, 1660	δ2.2(s,3H,ArCH_3), δ3.3(d,2H,J=8hz) δ3.7(s,3H,-OCH_3), δ4.8(dt,1H,H_B), δ6.3(d,1H,J=8hz), δ6.5-7.0(m,4H, ArH).	206 (60%)
3.	4c	230 nm (2040) 275 nm (2040)	1720, 1650	δ3.2(d,2H,J=8hz), δ3.5(s,3H,OCH_3) δ4.8(dt,1H,H_B), δ6.2(d,1H,J=8hz) δ6.5-7.1(m,4H,ArH)	226 (60%) 228 (20%)
4.	4d	230 nm (2640) 280 nm (2400)	1720, 1680	δ3.2(d,2H,J=8hz), δ3.6(s,6H,-OCH_3) δ4.9(dt,1H,H_B), δ6.3(d,1H,J=8hz), δ6.7-7.1(m,4H, ArH).	222 (60%)

3. Attempted preparation of methyl γ-phenoxycrotonate 3a:
a. Using NaOMe/DMF: Powdered NaOH(0.8g 20 mmol) in methanol (30 ml) was heated until it dissolved. The methanol was removed completely. To the NaOMe thus formed, phenol(1.8g 20 mmol), methyl γ-bromocrotonate(3.58g 20 mmol) and DMF(40 ml) was added and stirred at room temperature for 8h. The reaction mixture was poured into 100 ml of water and the aqueous layer extracted with ether. The ether extract was washed with 2N NaOH several times, water and dried over anhydrous Na_2SO_4. Removal of solvent furnished an oil. NMR($CDCl_3$/TMS) showed signals at δ3.1 ppm, δ3.5 ppm, δ4.8 ppm, δ6.2 ppm and between δ6.7-7.1 ppm. From the integration of the peaks, the ratio of 4a and 6a was found to be 1:1.
b. Using NaOH/MeOH): A mixture of phenol(1.8g 20 mmol), methyl γ-bromocrotonate (3.58g 20 mmol), NaOH(0.8g 20 mmol) in methanol(50 ml) was stirred at room temperature for 8h. Methanol was distilled off and the residue treated with water. The aqueous layer was extracted with ether. Removal of the solvent gave a liquid, the NMR spectrum of which showed the presence of 5a, 6a, and 3a in a ratio of 2:1:4.
c. Using K_2CO_3/DMF: A mixture of 1.8g(20 mmol) of phenol, 3.5g(20 mmol) of methyl γ-bromocrotonate, 2.6g(20 mmol) of K_2CO_3 in DMF(50 ml) was stirred at room temperature for 8h. The reaction mixture was poured into water and the aqueous layer extracted with ether. The ether layer washed with 2N NaOH, water and dried over anhydrous Na_2SO_4. Removal of solvent afforded a dark liquid, the NMR spectrum of which showed the presence of 3a, 4a, 5a and 6a.
d. Using K_2CO_3/Acetone at room temperature : A mixture of phenol(1.8g 20 mmol), methyl γ-bromocrotonate(3.58g 20 mmol), K_2CO_3(2.6g 20 mmol) in 50 ml of acetone was stirred at room temperature for 8h. The inorganic salts were filtered and the solvent distilled off. The residue was taken up in ether. Workup as usual afforded a liquid which showed the presence of 3a and 4a in a ratio of 1:1 by NMR analysis
4. Preparation of Methyl γ-aryloxycrotonates 3:
General procedure: A mixture of phenol(20mmol) and anhydrous K_2CO_3 (20 mmol) in dry acetone(50 ml) was stirred at 0°C for 15 min. To this mixture, was added a solution of methyl γ-bromocrotonate(20 mmol) in acetone(30 ml) drop by drop over a period of 1h, the reaction mixture being maintained at 0°C during the addition. After the addition was over, the reaction mixture was continued to stir at 0°C for 2h and slowly allowed to come to room temperature. The stirring was allowed to continue for another period of 4h. After this period, the inorganic aalts were filtered and the acetone distilled off. The residue was taken up in ether. The ether extract was washed with 2N NaOH and water and dried over anhydrous Na_2SO_4. Evaporation of ether gave a liquid, homogeneous on TLC. The boiling points and yields of 3a-h are shown in Table 3. The methyl γ-aryloxycrotonates were completely characterised by spectral data, see Table 6.

Table 6

No.	Compound	UV(MeOH) λmax nm	IR($CHCl_3$) ν_{max} cm^{-1}	NMR($CDCl_3$/TMS)	MS m/z
1.	3a	240(2400) 275(2400)	1710,1650	δ3.5(s,3H,-OCH_3), δ4.4(m,2H,-OCH_2) δ5.9(d,1H,J=18hz,H_A)δ6.5-7.0(m,5H ArH +H_B)	192(34.9%)
2.	3b	235(2560) 285(2560)	1710,1650	δ2.2(s,3H,ArCH_3), δ3.6(s,3H,-OCH_3) δ4.4(m,2H,-OCH_2), δ5.9(d,1H,J=18hz H_A),δ6.5-7.0(m,4H,ArH +H_B).	206(40%)

Table 6 (contd.)

No.	Compound	UV(MeOH) λmax nm	IR($CHCl_3$) ν_{max} cm^{-1}	NMR($CDCl_3$/TMS)	MS m/z
3.	3c	240(2280) 280(2040)	1710,1650	δ3.6(s,3H,$-OCH_3$)δ4.4(m,2H,$-OCH_2$), δ5.9(d,1H,J=8Hz,H_A)δ6.4-7.0(m,5H, ArH+H_B)	226(41%) 228(18%)
4.	3d	232(2480) 285(2480)	1710,1650	δ3.6(s,6H,$-OCH_3$),δ4.4(m,2H,$-OCH_2$), δ5.9(d,1H,J=8Hz,H_A)δ6.5-7.0(m,5H ArH+H_B)	222(38%)
5.	3e	245(2460) 280(2220)	1705,1650	δ3.6(s,3H,$-OCH_3$)δ4.6(m,2H,OCH_2), δ6.0(d,1H,J=8Hz,H_A)δ6.7-7.6(m,8H, ArH+H_B)	242(45%)
6.	3f	240(2720) 275(2640)	1710,1650	δ3.6(s,6H,$-OCH_3$)δ4.4(m,2H,$-OCH_2$), δ5.9(d,1H,J=8Hz,H_A)δ6.5-7.0(m,5H, ArH+H_B)	222(39%)
7.	3g	230(2560) 270(1760)	1710,1650	δ2.1(s,3H,$ArCH_3$),δ3.5(s,3H-OCH_3), δ4.4(m,2H,$-OCH_2$),δ5.9(d,1H,J=8Hz, H_A)δ6.3-6.8(m,5H,ArH +H_B)	206(32%)
8.	3h	240(2490) 280(2140)	1710,1650	δ3.6(s,3H,$-OCH_3$),δ4.4(m,2H,$-OCH_2$), δ6.0(d,1H,J=10Hz)δ6.4-7.1(m,4H,ArH +H_B).	260(42%)

5. Rearrangement of methyl γ-aryloxycrotonates 3: General procedure: Rearrangement of 3 in ethylene glycol: Methyl γ-aryloxycrotonate 3(4 mmol)was refluxed in ethylene glycol(20 ml) for for 2 1/2h. The reaction mixture was cooled and poured into water. The aqueous layer was extracted with hexane. The hexane extract was washed with 2N NaOH solution and water and dried over anhydrous Na_2SO_4. Removal of solvent furnished a semisolid(85%). TLC of this showed two spots.The semisolid was dissolved in hexane(50 ml) and concentrated to 10 ml and left overnight. The compound 7 separated out from the solution as yellow crystals. The m.pts and yields of 7a-g are shown in Table 4. The benzofuranones were completely characterised by spectral data, see Table 7.

Table 7

No.	Compound	UV(MeOH) λmax nm	IR($CHCl_3$) ν_{max} cm^{-1}	NMR($CDCl_3$/TMS)	MS m/z
1.	7a	235(2720) 278(2640)	1770,1650	δ2.2(d,3H,J=7.5hz),δ6.8-7.1 (m,5H,ArH+olefinic H)	160(100%)
2.	7b	240(2720) 280(2640)	1770,1650	δ2.2(d,3H,J=7.5hz),δ2.4(s,3H $ArCH_3$),δ6.5-7.0(m,4H,ArH + olefinic H)	174(100%)
3.	7c	240(2650) 279(2480)	1770,1650	δ2.2(d,3H,J=7.5hz),δ6.7-7.4 (m,4H,ArH +olefinic H)	204(100%) 206(33%)
4.	7d	242(2160) 280(2000)	1770,1650	δ2.2(d,3H,J=7.5hz),δ3.7(s,3H $-OCH_3$)δ6.5-7.0(m,4H,ArH + olefinic H)	190(100%)
5.	7e	242(2360) 270(1650)	1770,1650	δ2.2(d,3H,J=7.5hz),δ6.8-7.6 (m,7H,ArH +olefinic H)	220(100%)
6.	7f	225(2760) 290(2160)	1770,1650	δ2.2(d,3H,J=7.5hz),δ3.7(s,3H $-OCH_3$),δ6.5-6.9(m,4H,ArH + olefinic H)	190(100%)
7.	7g	240(2640) 282(2240)	1770,1650	δ2.2(d,3H,J=7.5hz),δ2.38(s,3H $ArCH_3$),δ6.6-7.3(m,4H,ArH + olefinic H)	174(100%)

6. Reaction of the mixture 7d and 8d in PTS/$CHCl_3$: A mixture of 7d and 8d (100 mg) was refluxed in dry $CHCl_3$(10 ml) in the presence of PTS(15 mg) for 6h. Removal of solvent gave a residue which was treated with water. The aqueous layer was extracted with ether and the ether extract washed with water and dried over anhydrous Na_2SO_4. Removal of ether furnished a solid which on NMR spectral analysis indicated no change in the ratio of the benzofuranones 7d and 8d.

7. Rearrangement of 3a in DEA: The compound 3a(200 mg 1 mmol) was refluxed in DEA (3 ml) for 6h. The reaction mixture was cooled and poured into water acidified with concentrated HCl. The solution was extracted with ether. The ether extract was washed thoroughly with 2N HCl, 2N NaOH and water and dried over anhydrous Na_2SO_4. Evaporation of the ether furnished a reddish brown oil(350 mg) which was homogeneous by TLC. Comparison and mixed TLC with 4a indicated definite formation of 4a. NMR spectrum showed signals at δ 3.1 ppm(d,2H),3,5(s,3H),δ4.8(dt,1H),δ6.2 (d,1H) andδ6.7-7.1(m5H).The esters 3b-d were also converted to 4b-d in DEA.
8. Rearrangement of 3d in o-DClB: The compound 3d(450 mg 2 mmol) was refluxed in o-DClB(5 ml) for a period of 6h. The reaction was monitored by TLC. TLC indicated no change in starting material after 6h. It was further refluxed for 14h and o-DClB removed under vacuum. Workup of the residue in the usual manner and analysis by TLC showed only the presence of starting material. NMR spectrum indicated the presence of 3d mostly, and a few signals in the region 2-3.5 ppm.
9. Rearrangement of 3d in polyethylene glycol: 3d(450 mg 2 mmol) was heated at 220°C for 2h in PEG-200. The reaction mixture was poured into water and further extracted with hexane. The hexane extract was washed with 2N NaOH solution, water and dried over anhydrous Na_2SO_4. Removal of solvent afforded a gum(250 mg). TLC showed spots at Rf 0.7 and 0.65(benzene:hexane 1:1) corresponding to 7d and 8d.

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11. To our knowledge, there are no reports on the synthesis of these esters. The above method could be regarded as a convenient method for the preparation of this class of compounds.
12. It was observed that in the case of 3c and 3h, there was a slight tendency for isomerisation to take place if the temperature of the reaction was not maintained at 0°C.
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