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SELFCONDENSATION OF SOME γ-KETO ACIDS IN SULPHURIC ACID

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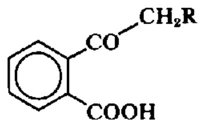
Abstract—A novel type of selfcondensation of some aliphatic and aromatic γ-keto acids (capable of forming γ-lactols) in concentrated sulphuric acid is described. A mechanism for the reaction is proposed, where the key intermediates are the carbonium ion formed by loss of the OH group in the γ-lactols and the α,β-unsaturated γ-lactone with an exocyclic double bond in γ-position formed by loss of one molecule of water from the γ-lactols. The proposal is supported by deuteration experiments. Structure determinations are based on IR, PMR and MS.

2-Acetyl-5-methoxyisophthalic acid (**1**), the methyl ether of a product from the alkaline degradation of the condensation product of acetopyruvic esters,[1] on treatment with conc sulphuric acid and shortly afterwards dilution with water gave a compound $C_{22}H_{18}O_{10}$ (later on proven to have structure (**2**)) indicating that a selfcondensation had taken place. It was therefore decided to investigate this reaction more closely.

As a model substance, 2-acetyl benzoic acid (**3a**) was treated likewise. A crystalline precipitate in good yield was obtained which by fractional crystallization yielded two compounds. They were called the primary (**5a** or **6a**) and secondary products (**4a**), respectively. Similarly, from 2-propionyl benzoic acid (**3b**) two products were obtained (**4b** and **5b** (or **6b**)). The primary products (**5** or **6**) could be titrated as monobasic acids, while the secondary products (**4**) were neutral. On renewed treatment of the primary products with conc sulphuric acid they were partly transformed into the secondary products. Dissolving the secondary products in aqueous alkali followed by acidification yielded the primary products in pure state.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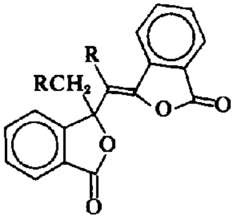
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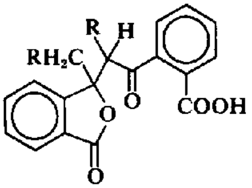
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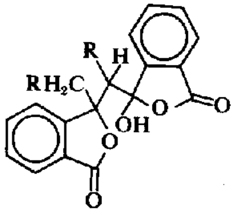
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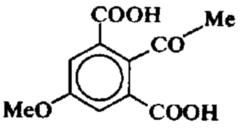
a: R = H
b: R = Me

Structure determination of the condensation products was based mainly on spectroscopic methods. The discussion is in the following concentrated on the products from 2-acetyl benzoic acid (**3a**). Mass spectrometry of the secondary product (**4a**) gave a molecular ion (*m/e* 292) corresponding to a molecular formula of $C_{18}H_{12}O_4$ (by high resolution technique). This means that a condensation has taken place with loss of two molecules of water. Further fragmentation of the secondary products will be dealt with in a separate paper.[2]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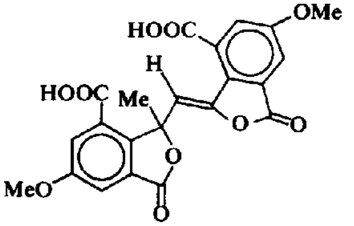
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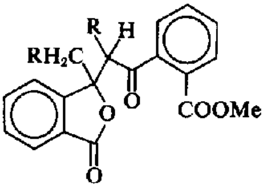
PMR of **4a** revealed the presence of eight aromatic protons in a complex multiplet at $\tau \sim 2{\cdot}2$–$2{\cdot}3$, one single proton at $\tau = 4{\cdot}10$ (olefinic region) and a three-proton singlet at $\tau = 7{\cdot}88$ (Me group). IR spectroscopy (KBr) showed the presence of two CO groups, one at 1760 cm^{-1} probably arising from an α,β-unsaturated γ-lactone, and one at 1775 cm^{-1} probably due to an α,β-unsaturated lactone with an exocyclic double bond in γ-position. (3-Methylenephthalide absorbs at 1780 cm^{-1}.[3]) A rather strong absorption at 1680 cm^{-1} may be assigned to the C=C double bond.

The primary product (**5a** or **6a**) gave a molecular ion at *m/e* 310 corresponding to $C_{18}H_{14}O_5$. PMR indicates, besides the presence of eight aromatic protons ($\tau \sim 2{\cdot}4$) and one Me group ($\tau = 8{\cdot}21$, s), the existence of a slow ring-chain tautomerism. At 40° the spectrum shows the presence of both the open keto-form (**5a**) and the cyclic lactol (**6a**), while at higher temperature only the time averaged signals are observed. The IR spectrum (KBr) indicates that the equilibrium in solid state lies almost completely on the lactol side, with a rather sharp OH-frequency at 3390 cm^{-1} and CO stretching frequencies at 1730 cm^{-1} and 1760 cm^{-1} for the lactol and lactone group, respectively.



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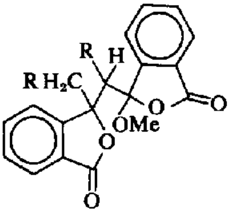

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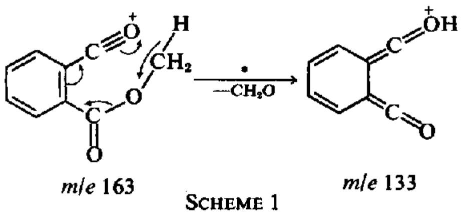
When the primary product (**5a** or **6a**) was treated with diazomethane an ester (*m/e* 324–$C_{19}H_{16}O_5$) was formed, which by spectroscopy was shown to have the open structure (**7**). Thus the mass spectrum showed prominent peaks at *m/e* 163 (100%) and *m/e* 147 (~ 25%). The base peak (*m/e* 163) is the same as found for methyl phthalate[4] and supports the open structure for **7**. It further loses carbon monoxide (to *m/e* 135) or formaldehyde (giving *m/e* 133) as proved by the presence of the proper metastables. The splitting off of formaldehyde may be formulated as in Scheme 1:



Scheme 1

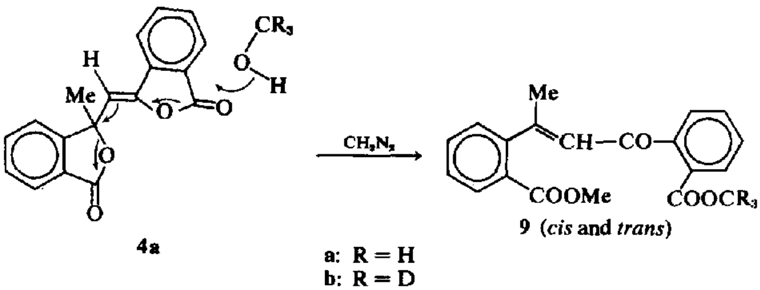
PMR of **7** gave the expected signals for the aromatic protons ($\tau \sim 2{\cdot}1$–$2{\cdot}9$), ester Me protons at $\tau = 6{\cdot}20$ (s), Me protons at sp^3-carbon ($\tau = 8{\cdot}17$ (s)). The methylene protons are now magnetic nonequivalent, giving an almost collapsing AB-quartet ($\tau = 6{\cdot}42$ and $6{\cdot}55$, $J_{AB} = 16{\cdot}5$ Hz). The IR spectrum (CCl$_4$) shows two bands at 1775 cm^{-1} (γ-lactone) and 1725 cm^{-1} (aryl ester) and a weak shoulder at about 1705 cm^{-1} (aryl ketone).

When the secondary product **4a** (or the primary product **5a** (**6a**)) was treated with methanol in presence of mineral acid, PMR showed that together with about 80% of the open ester **7** the two possible diastereoisomeric pseudoesters **8** derived from the lactol form **6** were obtained, and as described in the Experimental partial separation of the three esters could be obtained by column chromatography. The high yield of the open ester **7** from **4a** indicates that the γ-lactone having exocyclic double bond in γ-position is very susceptible for ring opening. This is not surprising since such a lactone may be considered as isoelectronic with phthalic anhydride.

An interesting esterification with rearrangement took place when the secondary product **4a** was treated with methanol and etheral diazomethane to give the ester **9a**. This ester was obtained as a mixture of the two stereoisomers which could not be separated. The PMR spectrum showed the expected signals for the two isomers, *viz* 2 doublets at $\tau = 7{\cdot}77$ ($J = 1{\cdot}5$ Hz) and $7{\cdot}53$ ($J = 1{\cdot}5$ Hz), ($=\overset{|}{C}$—CH$_3$ groups), 2 singlets at $6{\cdot}14$ and $6{\cdot}11$ (methoxy-carbonyl groups), 2 vinyl signals at $3{\cdot}62$ and $3{\cdot}47$ (quartets with $J = 1{\cdot}5$ Hz) and 8 aromatic protons at $2{\cdot}1$–$2{\cdot}9$. The isomer ratio is approximately 3 : 1. The mass spectrum is rather interesting. No molecular ion is present, but the fragmentation indicates a molecular weight of 338. The M-1 peak is present (~ 1%). This is found in benzalacetophenones and interpreted as formation of pyrylium cations.[5] The M-59 peak (~ 20%) is probably also due to formation of a pyrylium cation by expelling a methoxy-carbonyl radical. The base peak is at *m/e* = 175, most likely the styryl-cation while *m/e* = 163 (~ 30%) is the same fragment as found in **7** (*o*-methoxy-carbonyl benzoyl cation).

When the reaction is carried out in trideuteromethanol (CD$_3$OH) and nondeuterated diazomethane the corresponding isomeric deuterated esters **9b** were obtained. In the PMR of **9b** only one methoxy carbonyl group is observed and the mass spectrum confirmed the reaction route outlined in Scheme 2. The M-59 peak is now observed three mass units higher strengthening the proposal of a pyrylium cation. The base peak is still at *m/e* 175 (styryl cation) while the *o*-methoxy-carbonyl benzoyl cation now is observed at *m/e* = 166, thus containing the deuterated ester group.

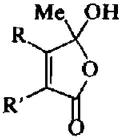
Two aliphatic α,β-unsaturated γ-keto acids (**10a** and **10b**) also gave dimeric lactones (**11**) when



SCHEME 2

treated with sulphuric acid. The PMR data are entered in Table 1.

The fragmentation of **11** in the mass spectrometer is reported on separately.[6]



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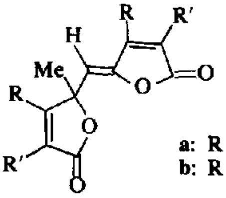


11

a: R = H, R′ = Me
b: R = R′ = Me

As mentioned above, the condensation of 2-propionyl benzoic acid (**3b**) proceeded analogous to that of 2-acetyl benzoic acid (**3a**). However, a few per cent of a byproduct, m.p. 240°, (Experimental) was formed in this case. Higher yields could be obtained when the secondary product **4b** was treated with sulphuric acid. PMR showed two uncoupled Me groups at $\tau = 8{\cdot}25$ and $7{\cdot}40$, one proton singlet at $\tau = 5{\cdot}16$ and seven aromatic protons at $\tau = 1{\cdot}9$–$2{\cdot}7$. High resolution mass spectrometry gave a molecular ion at $m/e = 302$ ($C_{20}H_{14}O_3$). Oxidation (chromium trioxide or ozone) gave a monobasic acid $C_{18}H_{12}O_4$ (high resolution MS), which could be resolved in optically active components. PMR showed one Me group (singlet) at $\tau = 8{\cdot}18$, one protonsinglet at $\tau = 5{\cdot}12$, one mobile proton and seven aromatic protons at $\tau = 1{\cdot}2$–$2{\cdot}7$ ppm. In Scheme 3 is outlined a tentative mechanism for the formation of the byproduct **12** and its oxidation product **13**.

Treatment of **4b** with deuterosulphuric acid gave the byproduct in which the protonsinglet at $\tau = 5{\cdot}16$ in the PMR spectrum was greatly reduced due to isotope substitution.

As seen in Scheme 3 the protonation of **4b** is proposed to take place in such a way that a tertiary carbonium ion is formed at the C atom linking the two lactone rings (alternative to the main reaction course outlined below in Scheme 4). The absence of a similar byproduct from **4a** supports this idea, since the corresponding carbonium ion would then be secondary in nature.

Treatment of oxidation product **13** with excess of alkali led to a dibasic carboxylic acid $C_{18}H_{14}O_5$ (MS) for which the formula **14** was suggested, based on its PMR spectrum and its fragmentation in the mass spectrometer.

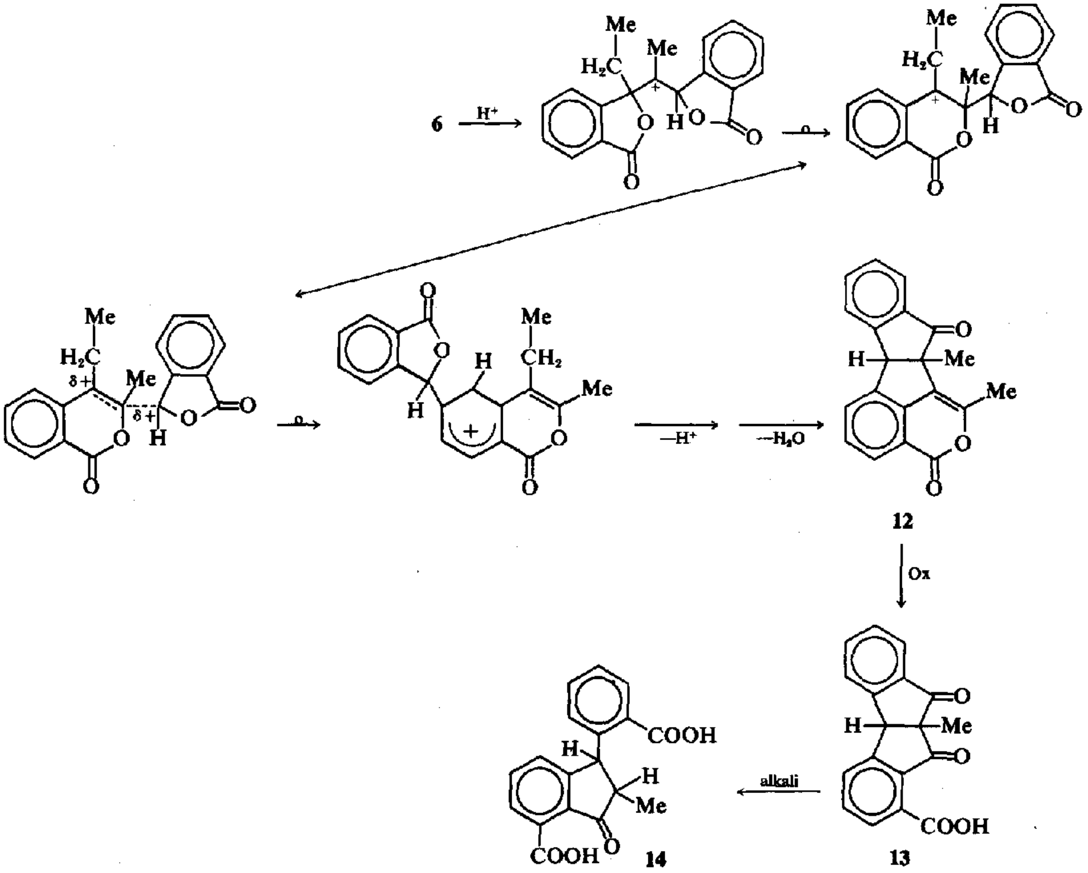
Mechanism of condensation reaction. The key intermediates in the reaction must be the carbonium ion **15** and the alkylidene phthalide **16**. In fact, when the condensation reaction was interrupted at an early stage, varying amounts of the latter intermediate could be isolated. The presence of aryl-conjugated carbonium ions is indicated by the strong coloration of the reaction mixture. The main step is the coupling of the two intermediates which is nothing but an electrophilic addition to a double bond to form the carbonium ion **17**. The proposed mechanism as outlined in Scheme 4 is supported by the following observations.

1. When either the primary products **5** (**6**), the secondary products **4**, or the alkylidene phthalides **16** were subjected to the reaction conditions, the

Table 1[a]

	=C—R	=C—H	=C—R′	—C—Me
11a	2·59 (1H), q (J = 1·5) 2·82 (1H), q (J = 1·5)	4·59 (1H) s	7·99 (3H), d (J = 1·5) 8·11 (3H), d (J = 1·5)	8·30 (3H) s
11b	8·08 (3H), q (J = 1·1) 8·20 (3H), q (J = 1·1)	5·20 (1H) s	7·98 (3H), q (J = 1·1) 8·08 (3H), q (J = 1·1)	8·25 (3H) s

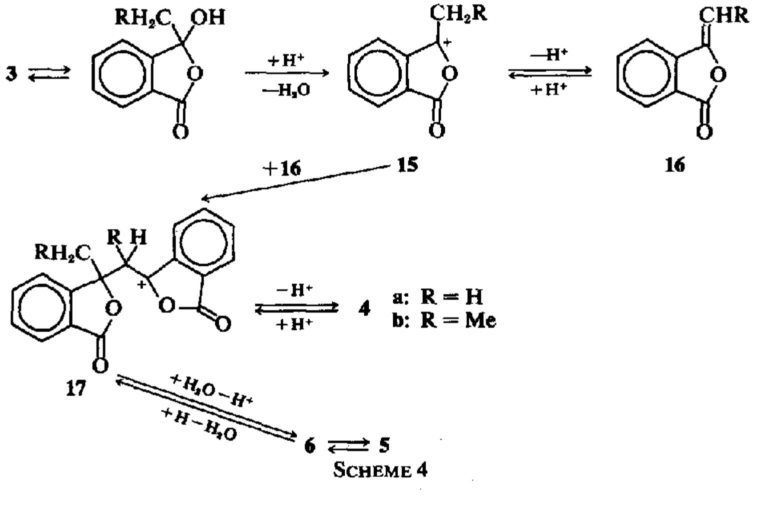
[a] Chemical shift (τ) in ppm relative to TMS, coupling constants in Hz.



SCHEME 3

primary and secondary products were obtained in essentially the same proportions (PMR on crude products).

2. When the aliphatic analogue of **3**, α-methyl-β-acetyl acrylic acid (**10a**), was treated with deuterosulphuric acid a deuterated compound with about 70% isotopic purity was formed, having deuterium in the Me group at the only sp^3-hybridized carbon and at the double bond linking the two lactone units in **11a**. The equilibrium **15** $\rightleftarrows$ **16** must therefore be faster than the reaction **15**+**16**$\rightarrow$**17**. When the aromatic keto acids were treated in the



a: R = H
b: R = Me

SCHEME 4

same way a partial deuteration of the aromatic nucleus takes places along with the abovementioned deuteration.

3. When the condensation products **4** or **11** were treated with deuterosulphuric acid, only the protons at the C atom linking the lactone units were exchanged (about 80%). This excludes any appreciable reversibility in the coupling reaction $\mathbf{15}+\mathbf{16}\rightarrow\mathbf{17}$.

4. When equimolar amounts of **3a** and **3b** were treated with sulphuric acid, only the crossproduct **18** was obtained. Moreover, the reaction time in this case was shorter than for the selfcondensation of **3a** and **3b** separately. The important conclusions, though not unexpected, of these observations are summarized in the energy diagram in Fig 1.

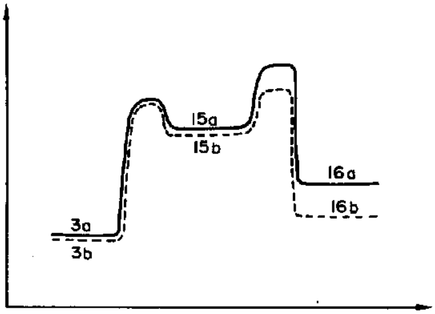
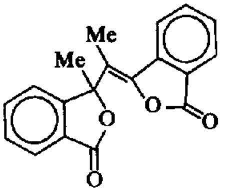


Fig 1.

The equilibrium $\mathbf{15a}\rightleftarrows\mathbf{16a}$ is shifted more to the left side relatively to the equilibrium $\mathbf{15b}\rightleftarrows\mathbf{16b}$. This may largely be due to the higher alkylation of **16b**. The selfcondensation of **3b** is by far the slowest reaction, indicating that the effective concentration of **15b** is low. Also, in the latter case the highest yield of alkylidene phthalide was obtained when the reaction was stopped at an early stage.



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EXPERIMENTAL

General. IR spectra were recorded on a Perkin-Elmer model 457 grating spectrometer. PMR spectra were recorded on a Varian A60A instrument using deuterochloroform as solvent and TMS as internal reference. Mass spectra were obtained on a AEI MS902 spectrometer. M.ps are not corrected.

Condensation of 2-acetyl benzoic acid (**3a**). 2-acetyl benzoic acid (10 g) was dissolved in conc H_2SO_4 (30 ml) with a slight increase in temp (10°) and a colour change from yellow to brown. After 30 min the soln was poured into ice-water giving a white amorphous ppt which turned partly crystalline on scratching. After washing with water and drying, it weighed 8·7 g and was shown by PMR to be a mixture of about equal quantities of **4a** and **5a** (or **6a**). Separation was affected by grinding the ppt with acetone which left **4a** undissolved. Crystallized from EtOAc, m.p. 219°. (Found: C, 73·74; H, 4·24. Calc. for $C_{18}H_{12}O_4$: C, 73·96; H, 4·14%).

The acetone soln contained **5a** (or **6a**) in an impure state. Purification was achieved by dissolving in alkali and adding mineral acid. The ppt, being the primary product **5a** (or **6a**), was recrystallized from aqueous EtOH, m.p. 142°. (Found: C, 70·00; H, 4·60. Calc. for $C_{18}H_{14}O_5$: C, 69·67; H, 4·55%). In analogous way **4a** could be almost quantitatively converted to **5a** (or **6a**).

Esterification of the condensation products from 2-acetyl benzoic acid. The primary product **5a** (or **6a**) gave on treatment with ethereal diazomethane the open ester **7**, m.p. 80°. (Found: C, 70·90; H, 5·01. Calc. for $C_{19}H_{16}O_5$: C, 70·36, H, 4·97%). When either **5a** (**6a**) or the secondary product **4a** was heated in MeOH containing 5% H_2SO_4 a mixture of esters was obtained. By column chromatography on neutral aluminium oxide, using chloroform as eluant, a partial separation was achieved. The first fraction gave one of the diastereoisomeric pseudoesters **8** in pure state, (yield: *ca* 10%) m.p. 163° (Found: C, 69·84, H, 5·18. Calc. for $C_{19}H_{16}O_5$: C, 70·36, H, 4·97%). The next fractions consisted of mixtures of the two possible diastereoisomers **8** (10% in total). Finally, when a mixture of chloroform and methanol was used as eluant, the ester **7** was obtained in about 75% yield. The PMR data of **8** are summarized in Table 2.

Condensation of 2-propionyl benzoic acid (**3b**). 2-Propionyl benzoic acid (prepared from 3-ethylidene phthalide according to Gottlieb,[7] m.p. 96°) (10 g) was dissolved in conc H_2SO_4 (40 ml) with a slight increase in temp and a colour change from yellow to greenish brown. After 2 hr the soln was poured into ice-water. A yellow mass precipitated which after decantation of the aqueous soln followed by maceration with EtOH, became crystalline, weight 2·5 g. After dissolving in EtOH and cooling a voluminous substance separated first (from the lukewarm soln) which constitutes the byproduct **12** (see below). On further cooling the filtrate gave crystals of **4b**, m.p. 156°. (Found: C, 74·90; H, 5·03. Calc. for $C_{20}H_{16}$-

Table 2[a]

	m.p.	Arom. H's	—OMe	$-\mathrm{C}{<}^{\mathrm{H_A}}_{\mathrm{H_B}}$	$>\mathrm{C}-\mathrm{Me}$
8 Diastereomer a	163°	2·1–2·7, m, (8H)	7·13, s (3H)	6·97, s (2H)	8·33, s (3H)
8 Diastereomer b	[b]	2·1–2·7, m, (8H)	7·18, s (3H)	6·91 and 7·07, 2d, (2H) J = 11 Hz	8·32, s (3H)

[a] Chemical shift (τ) in ppm. [b] Obtained as a mixture with diastereomer *a*.

O_4: C, 74·99, H, 5·03%). **4b** could be transformed to **5b** (or **6b**) in the same way as for **4a** → **5a** (or **6a**). **5b** (or **6b**) was a glassy substance. (Found: C, 70·39, H, 5·50. Calc. for $C_{20}H_{18}O_5$: C, 70·99, H, 5·36%).

The byproduct **12** was obtained in a few per cent yield starting with the keto acid **13b**. Better yield (15%) was achieved when starting with **4b**. Even treatment of 3-ethylidene phthalide with conc H_2SO_4 gave some **12**. Recrystallized from EtOH, m.p. 240°. (Found: C, 79·20, H, 4·65. Calc. for $C_{20}H_{14}O_3$: C, 79·45; H, 4·67%).

Oxidation of 12

(a) *With chromium trioxide*. To **12** (1·0 g) were added AcOH (50 ml) and in portions CrO_3 (0·5 g) dissolved in AcOH and a few drops water. On stirring at room temp **12** dissolved and the colour changed to green. The temp was kept at 50° for some time and finally heated on a steam bath for 0·5 hr. After dilution with water and 2N H_2SO_4 (10 ml) the green soln was extracted with ether. Evaporation of the ether soln and washing with EtOAc gave **13** (0·3 g).

(b) *With ozone*. **12** (0·9 g–3 millimoles) were dissolved in MeOH (25 ml) and CH_2Cl_2 (50 ml) and ozonized at −78°. Quantitative absorption of O_3 (3 millimoles). Triphenyl phosphine (0·8 g–3 millimoles) was added and the soln was warmed up to room temp. Gas chromatography showed the presence of ample amounts of AcOMe. The soln was evaporated leaving a yellow oil which was heated with EtOH (20 ml) yielding a crystalline ppt of **13** (0·55 g) m.p. 212°. (Found: C, 74·01; H, 4·21. Calc. for $C_{18}H_{12}O_4$: C, 73·96; H, 4·14%). Methyl ester was prepared with diazomethane, m.p. 174°; MS (high resolution): $C_{19}H_{14}O_4$; PMR: singlets at $\tau = 8{\cdot}32$ (3H), 6·08 (3H) and 5·23 (1H), and 7 aromatic protons at $\tau = 2{\cdot}0$–$2{\cdot}8$.

Optical resolution of **13**. A soln of **13** (0·72 g) and strychnine (0·82 g) in EtOH was left at room temp for a couple of days. A solid crust appeared and on stirring crystallization took place. The crystals (0·72 g) were shaken with HCl and ether (in which **13** is only slightly soluble). The acid (0·32 g) obtained from the ethereal soln was recrystallized from dil EtOH, m.p. 221°. $[\alpha]_D^{20} = +72{\cdot}5°$ (EtOH). The filtrate from the strychnine salt on evaporation left a viscous mass from which on grinding with HCl the levorotatory acid crystallized and was extracted with ether, m.p. 219°, $[\alpha]_D^{20} = -73{\cdot}2°$ (EtOH).

Treatment of **13** *with alkali*. **13** (0·35 g) was dissolved in 0·2 N NaOH (20 ml) and heated for ½ hr on a steam-bath. On acidifying a yellow viscous mass (0·4 g) separated which solidified and was recrystallized twice from MeOH, m.p. 201°. (Found: C, 69·71, H, 4·49. Calc. for $C_{18}H_{14}O_5$: C, 69·67; H, 4·55%). Treatment with diazomethane gave the methyl ester of **14** as a colourless oil; MS: *m/e* 338 (M^+), *m/e* 306 (M-CH_3OH), *m/e* 274 (M-$2CH_3OH$); PMR: doublet at $\tau = 8{\cdot}64$ (3H, $J = 7{\cdot}4$ Hz), multiplet around 7·3 (1H), two singlets at 6·14 and 6·00 (3H in each), doublet at 4·87 (1H, $J = 4{\cdot}9$ Hz) and multiplets at 2·0–3·1 (7H).

Condensation of 2-acetyl-5-methoxy-isophthalic acid (**1**). The corresponding hydroxy acid was prepared according to Berner and Kolsaker[1] by degradation of the so-called Me product. By methylation with dimethyl sulphate the methoxy derivative (**1**) was prepared, m.p. 182°. This acid (1·0 g) was added to conc H_2SO_4 (4 ml). After 10 min the yellow to green soln was poured into ice-water. The crystalline compound (**2**–0·84 g) thus obtained could be recrystallized from aqueous EtOH, m.p. 294. (Found: C, 59·84; H, 3·89; MeO, 14·90. Calc. for $C_{22}H_{16}O_{10}$: C, 60·00; H, 3·66; MeO, 14·09) MS: $m/e = 440$ (M^+). On treatment a soln of **2** in MeOH with diazomethane a product was obtained, which after repeated crystallization from EtOH had m.p. 200°. (Found: C, 61·85; H, 4·37; MeO, 27·00. Calc. for $C_{24}H_{20}O_{10}$: C, 61·54; H, 4·34; MeO, 26·50) MS (high resolution): *m/e* 468–$C_{24}H_{20}O_{10}$, *m/e* 235–$C_{12}H_{11}O_5$, *m/e* 233–$C_{12}H_9O_5$. These peaks support the structure given for **2**;[2] PMR: singlets at $\tau = 7{\cdot}93$ (3H), 6·11 (3H), 6·09 (3H), 6·07 (3H), 5·99 (3H), 2·81 (1H) and doublets at $\tau = 2{\cdot}58$ (1H, $J = 2{\cdot}6$ Hz), 2·40 (1H, $J = 2{\cdot}4$ Hz) 2·18 (1H, $J = 2{\cdot}4$ Hz) and 2·13 (1H, $J = 2{\cdot}6$ Hz).

Condensation of α-methyl-β-acetyl acrylic acid (**10a**). The acid (**10a**) was prepared according to Buchta and Satzinger,[8] m.p. 101°. **10a** (0·2 g) was dissolved in conc H_2SO_4. After 10 min the brown soln was poured into ice-water. The ppt (**11a**) which became crystalline on stirring, could be recrystallized from MeOH/water, m.p. 86°. (Found: C, 65·79; H, 5·45. Calc. for $C_{12}H_{12}O_4$: C, 65·44; H, 5·49%). Condensation of **10a** in deuterosulphuric acid following the same procedure gave about 70% deuteration, while treatment of the condensation product **11a** with deuterosulphuric acid in analogous way gave about 80% deuteration, the points of isotopic substitution being discussed above.

Condensation of α,β-dimethyl-β-acetyl acrylic acid (**10b**). The acid (**10b**) was prepared according to Piskov,[9] m.p. 65°. Condensation reaction was carried out as for **10a**. **11b** had m.p. 135°. (Found: C, 67·63, H, 6·47. Calc. for $C_{14}H_{16}O_4$: C, 70·57; H, 6·77%).

Crosscondensation of **3a** and **3b**. 2-acetyl benzoic acid (3·1 g–18·9 millimoles) and 2-propionyl benzoic acid (3·3 g–18·5 millimoles) was thoroughly mixed and dissolved in conc H_2SO_4 (20 ml) and after 15 min the soln was poured into ice-water. The crystalline product (5·2 g) could be recrystallized from EtOH (**18**), m.p. 166° (Found: C, 74·79; H, 4·79. Calc. for $C_{19}H_{14}O_4$: C, 74·50; H, 4·61%); PMR: singlets at $\tau = 7{\cdot}92$ (3H), 7·82 (3H), multiplett at 1·9–2·6 (8H); MS reported on elsewhere.[2]

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