Polyketo-enols and Chelates. Chemistry of the Formation of Xanthophanic Enol and its Glutaconate and Pyran Intermediates

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The formation mechanism for xanthophanic enol (3) under ' melt ' conditions is clarified by stepwise synthesis *via* 2.4-diacetylglutaconic ester (1) and the anion from methyl 5-acetyl-6-oxo-2-methyl-6*H*-pyran-3-carboxylate (11).

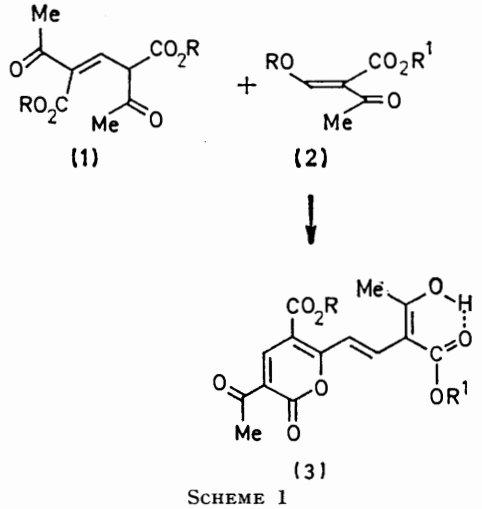
Dimethyl 2.4-diacetylglutaconate exists mainly as the cyclic form (4) in solution. and increasing in solvent polarity. increasing temperature. or catalysis by pyridine. promotes n.m.r. equivalence of the acetyl methyls. In the case of 1.1.3.3-tetra-acetylpropene. first two. and then all four acetyl methyl signals coalesce showing an equilibrating system of cyclic structures involving hemi-acetal and *Z–E* changes. 1.1.3.3-Tetrakismethoxycarbonylpropene has a normal acyclic structure (9).

Glutaconate (1) gives methyl 5-acetyl-6-oxo-2-methyl-6*H*-pyran-3-carboxylate (11) when treated with sodium methoxide (0.5—4.0 mol) : at higher concentrations (12 mol) the aldol product dimethyl 5-hydroxytoluene-2.4-dicarboxylate (15) and its half-ester are formed. With magnesium methoxide as base. 1 mol or less gives the pyran (11), but the compounds with 2 mol and above are the Claisen product methyl 5-acetyl-2.4-dihydroxybenzoate (18) and the aldol product (15). These differing responses to bases are considered. and the effects of magnesium chelation on reactivity are discussed in terms which explain why Claisen condensations are favoured whilst aldol condensations are disfavoured during anion attack on the chelate.

In earlier work it was shown that the structure of xanthophanic enol, formed when an alkoxymethyleneacetoacetate is heated at 100 °C with dry sodio-acetoacetate, (' melt ' procedure), is (3).[1,2] In this paper, the formation of xanthophanic enols in a step-wise fashion is examined: the reactions are considered similar to those of the uncontrolled ' melt ' procedure. As the chemistry of the intermediates is of interest, the opportunity is taken to develop certain aspects.

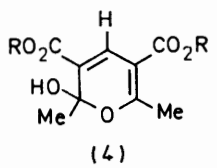
RESULTS AND DISCUSSION

The first postulated intermediate in xanthophanic enol synthesis, a 2,4-diacetylglutaconate (1),[1] is readily isolated when an alkyl sodio-acetoacetate is shaken in ether with an alkoxymethylene acetoacetate. The latter compounds (2), as prepared by the usual reaction between alkyl orthoformate, alkyl acetoacetate, and acetic anhydride,[3] are mixtures of the two geometrical



SCHEME 1

isomers since the n.m.r. spectra show various resonances to be doubled. Treating such a diacetylglutaconate (1) with a further 1 mol of alkoxymethylene acetoacetate in the presence of alkoxide then leads to a xanthophanic



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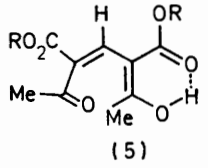

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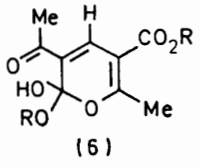

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enol (xanthyrone) [1,4] (Scheme 1). Evidence presented later, however, makes it likely that pyrone formation from (1) occurs first, and that (2) condenses with the substituted 6-methylpyrone anion. Although conveniently written for reaction purposes in acyclic form, spectroscopic examination of dimethyl and diethyl 2,4-diacetylglutaconates shows that they exist in solution predominantly as cyclic forms (4, R = Me or Et).

In 0.01N-acidic ethanol † the dimethyl ester had $\lambda_{max.}$ 249 (ε 9 400) and 317 (7 400) nm, whilst in 0.01N-alkaline ethanol it had $\lambda_{max.}$ 271 (ε 9 800) and 389 (23 300) nm. The i.r. spectrum showed ($CHCl_3$) bands at 1 707 and 1 636 cm^{-1} (unsaturated esters and double bonds) but there was no absorption at 1 665—1 690 cm^{-1} ascribable to an α-unsaturated acetyl or a chelated ester as required by (5 R = Me) or the cyclic form (6 R = Me). The ^1H n.m.r. spectrum ($CDCl_3$) lacked a low-field signal expected for a chelated hydroxy as in (5, R = Me) [*cf.* the chelated proton in dimethylxanthophanic enol (3),[1] τ −4.5]. The hydroxy resonance was located by deuteriation near 4.97. Structure (4), with which other n.m.r. assignments are in agreement (Table 1), thus appears to be the major form in $CDCl_3$.

† In ordinary ethanol there is partial ionisation, as shown by absorption at $\lambda_{max.}$ 389 (s 1 200) nm.

On examining the n.m.r. spectrum of dimethyl diacetylglutaconate in four different solvents it was found that as the polarity increased, the two upfield methyls began to coalesce, and in $(CD_3)_2SO$ the two resonances were broad but just resolved at 21 °C. On

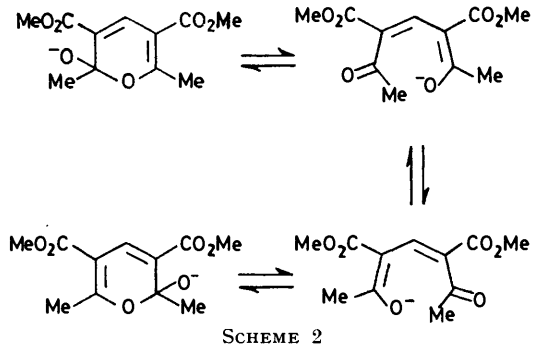
TABLE 1

N.m.r. spectral assignments for dimethyl 2,4-diacetylglutaconate (4, R = Me)

	Assignment				
Solvent [a]	ring CH	OH	$2\times CH_3O$	$CH_3{\cdot}C(O){\cdot}$	$CH_3{\cdot}C(O)_2{\cdot}$
CCl_4	2.46	5.40 [b]	6.25	7.60	8.14
C_6H_6	2.11	5.02 [b]	6.56	7.68	7.98
$CDCl_3$	2.32	4.97 [b]	6.22	7.57	8.07
$(CD_3)_2SO$	2.48	2.57 [b]	6.28	7.75 [b]	8.10 [b]

[a] Temperature 21 °C. [b] Broad.

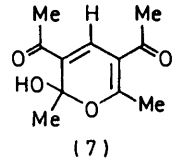
warming to 41.5 °C the two resonances coalesced to a broadened singlet at τ 7.88. The addition of a trace of pyridine to the benzene solution caused the two resonances at τ 7.68 and 7.98 to coalesce to a sharp signal at τ 7.82, but the addition of trifluoroacetic acid did not. These results indicate a base-catalysed exchange process which when rapid leads to time-averaged equivalence of the two methyl signals (Scheme 2). There may also be equilibration with (6) to a minor extent.



SCHEME 2

As a result of these findings we have also investigated 1,1,3,3-tetra-acetylpropene [(8) in the enolised acyclic form],[3] and 1,1,3,3-tetrakismethoxycarbonylpropene (9, R = Me),[3,5] by similar methods.

1,1,3,3-Tetra-acetylpropene had $\lambda_{max.}$ (0.01N ethanolic HCl) 275 (ε 12 000) and 332 (7 500) nm, shifted to $\lambda_{max.}$



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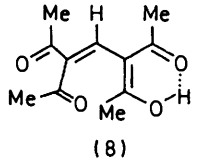

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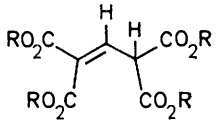


(9)

308 (ε 12 600) and 390 (17 500) nm in 0.01N alkaline ethanol. The i.r. spectrum ($CHCl_3$) showed absorptions at 1 663 and 1 618 cm^{-1} [α-unsaturated ketone and C=C stretch in the cyclic form (7)]. No signal indicating chelated hydroxy was found in the n.m.r. ($CDCl_3$), the resonance of the hydroxy proton being at τ 2.67 [*cf.* the chelated proton in tetra-acetylxanthyrone,[1] τ −7.97]. Other assignments consistent with a cyclic structure (7) are shown in Table 2. Again, as the solvents become

TABLE 2

N.m.r. spectral assignments for 1,1,3,3-tetra-acetylpropene (7)

	Assignment				
Solvent *	ring CH	OH	$2\times CH_3CO$	$CH_3{\cdot}C(O){\cdot}$	$CH_3{\cdot}C(O)_2{\cdot}$
CCl_4	2.68		7.62	7.90	7.97
C_6H_6			7.92	8.12	8.16
$CDCl_3$	2.51	2.67	7.61	7.86	7.86
$(CD_3)_2SO$	2.47	2.57 (broad)	7.78	7.78	7.78

* Temperature 21 °C.

more polar, the two upfield methyl signals coalesce, and they also coalesced on warming the benzene solution to 35 °C. From results in $(CD_3)_2SO$ another point emerges. In this solvent all four methyls have apparently become equivalent at τ 7.78. Supporting this interpretation, addition of a trace of pyridine to the benzene solution caused the signals from the three types of methyl at τ 7.92, 8.12, and 8.16 to coalesce to a single sharp peak at τ 8.01. Without showing all the terms, the equilibrium may be written as in Scheme 3, in which rapid *Z–E* equilibration is involved in addition to keto–hemiacetal equilibria.

In contrast 1,1,3,3-tetrakismethoxycarbonylpropene exists largely in the acyclic glutaconate form (9). In ethanol it had $\lambda_{max.}$ 207 (ε 7 900), 258 (2 300), and 360 (800) nm (partly ionised) [5] and in 0.01N alkaline ethanol $\lambda_{max.}$ 262 (ε 13 900) and 362 (21 850) nm. The i.r. spectrum ($CHCl_3$) showed a broad maximum at 1 745 cm^{-1} (ester). The four ester methyls show a broad multiplet signal near τ 6.20 in the n.m.r. ($CDCl_3$) whilst the two remaining protons form an AB quartet at 2.74 and 5.25 (J 9 Hz) in agreement with structure (9, R = Me). When shaken with D_2O the signal due to the non-olefinic proton at τ 5.25 disappears and the signal at τ 2.74 becomes a singlet.

We then looked at the behaviour of dimethyl 2,4-diacetylglutaconate on treatment with bases.[6] When set aside (24 h) with a solution of sodium, lithium, or

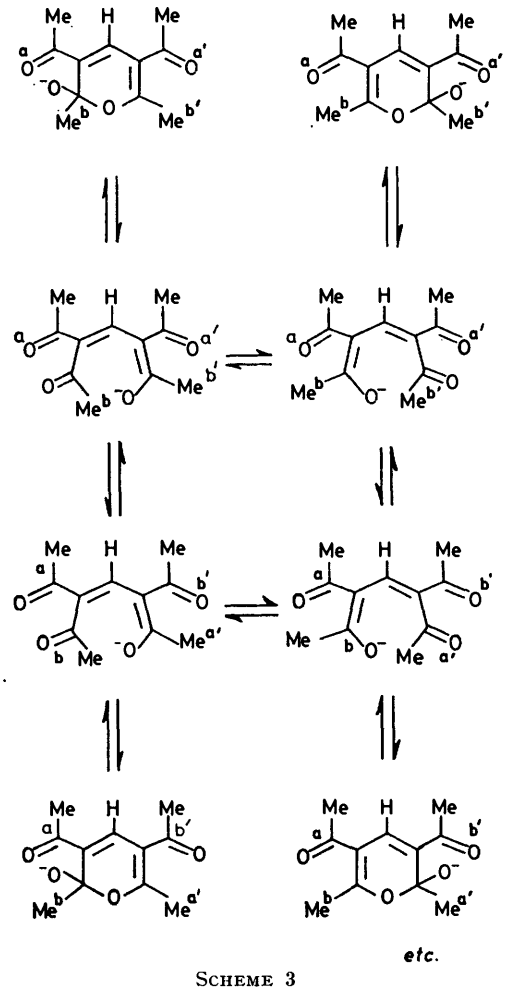
TABLE 3

Yields (%) of (11, R = Me) from dimethyl 2,4-diacetylglutaconate

	Base : ester			
Base	0.5 : 1	1 : 1	2 : 1	4 : 1
NaOMe	43	79	83	77
LiOMe	30	80	79	75
$Ca(OMe)_2$	67	79	81	81

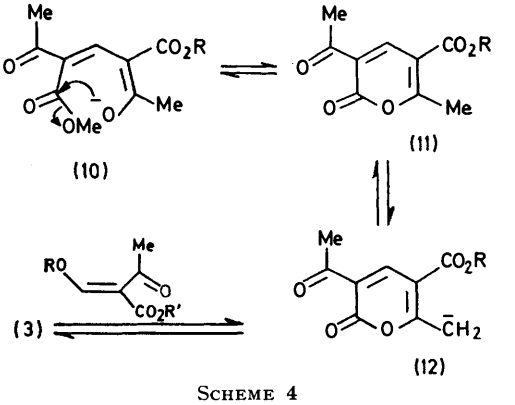
calcium methoxide in methanol–benzene it was converted into methyl 3-acetyl-6-methyl-2-oxo-2*H*-pyran-5-carboxylate (11, R = Me) as indicated in Table 3. The

oxopyrancarboxylate showed carbonyl vibrations (CCl_4) at 1 755 (ring CO), 1 726 (ester), and 1 694 (acetyl) cm^{-1},



SCHEME 3

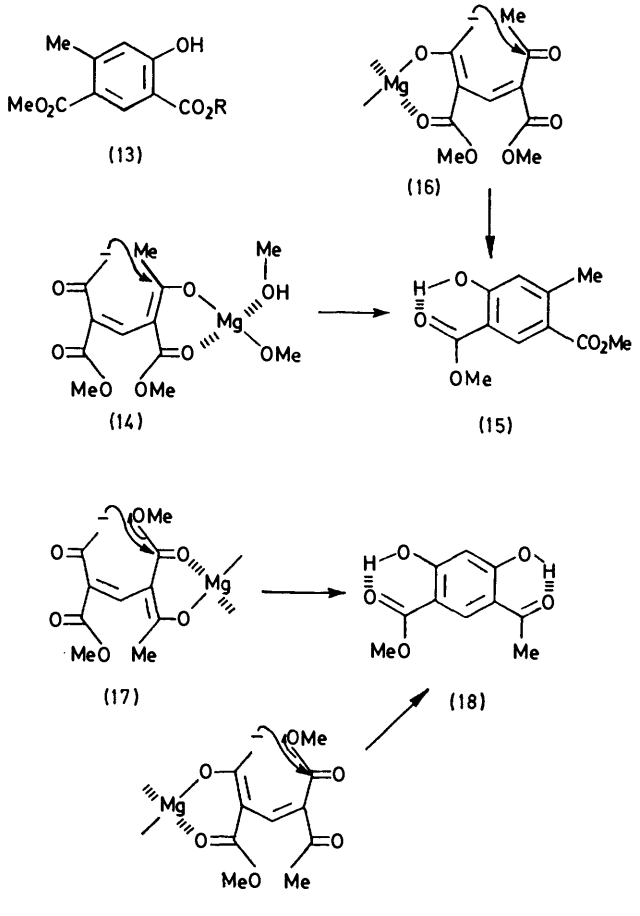
and the n.m.r. spectrum supports the structure indicated. In neutral and acid solution the diacetylglutaconate (4, R = Me) (see above) and the oxopyrancarboxylate (11, R = Me) have rather similar absorption spectra



SCHEME 4

[(11) (0.01N ethanolic HCl) $\lambda_{max.}$ 249 (ε 8 100) and 325 (7 300) nm] but in 0.01N ethanolic potassium hydroxide the shifts are characteristic for the two different ionic species [for the glutaconate see earlier; (11) (0.01N ethanolic KOH) $\lambda_{max.}$ 287 (ε 11 700) and 343 (21 200)]. On acidification, the two alkali-induced absorptions revert to their original values in acid: the two ionic species are thus distinct and there is no interconversion under these mild conditions.

If the sodium methoxide concentration (*cf.* Table 3) was substantially increased in a preparative experiment involving dimethyl 2,4-diacetylglutaconate, aldol cyclisation occurred. Thus, a 12-fold molar excess of methoxide gave a mixture (61%) of the dimethyl isophthalate derivative (15) and the corresponding half-ester (13, R = H) [3] was isolated. Examination of the mother liquors (t.l.c.) showed no Claisen product (18): the half-ester (13, R = H) was the main component together with a compound having the same R_F as the naphthalene (28).



SCHEME 5

When treated with sodium methoxide the oxopyrancarboxylate (11, R = Me) gave anion (12), stabilised by extensive delocalisation, and this could be trapped with 1 mol of methyl alkoxymethyleneacetoacetate as dimethyl xanthophanic enol (3, R = R^1 = Me) (46%), thus reproducing the melt procedure. The new method gives

stepwise control over the formation of xanthophanic enols and is particularly useful for mixed ester types for which the melt procedure is not suitable because of scrambling.

When dimethyl 2,4-diacetylglutaconate is set aside (24 h) with a solution of magnesium methoxide in methanol–benzene, the results (Table 4) contrast with

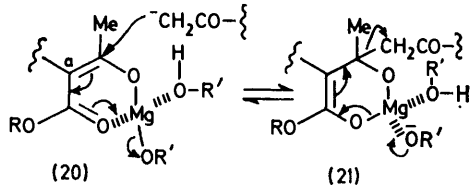
TABLE 4

Products from treatment of dimethyl 2,4-diacetylglutaconate (1, R = Me) with magnesium methoxide (yields in %)

	Base : ester				
Products	0.25 : 1	0.5 : 1	1 : 1	2 : 1	4 : 1
Unchanged (1, R = Me)	53%	0	0	0	0
Pyran (11, R = Me)	47	84	79	0	0
Isophthalate (15)	0	0	trace *	70	75
Resorcinol (18)	0	0	trace *	30	25

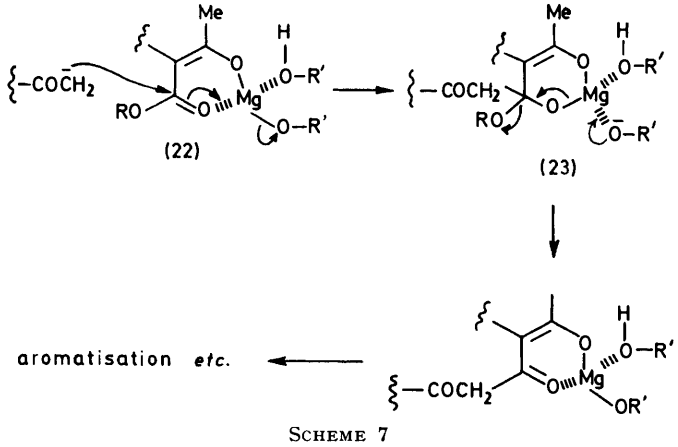
* Detected by t.l.c.

those from the bases of Table 3. At the lower magnesium methoxide : glutaconate ratios the oxopyrancarboxylate (11, R = Me) is again formed. But



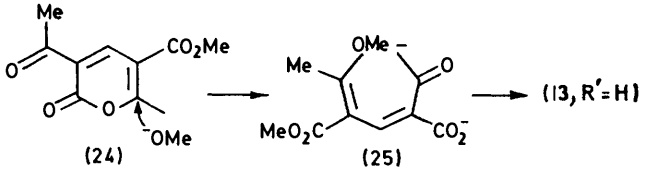
SCHEME 6

beyond a 1 : 1 ratio the product changes, and the aromatic compounds (15) and (18) [2,7] form, no pyran being found. Compound (15), the isophthalate, is the major product and is of the aldol cyclisation type, whilst (18) the acetylresorcinol ester, is of the Claisen cyclisation type.



SCHEME 7

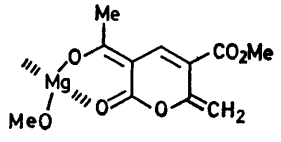
The tendency of excess of magnesium methoxide to favour Claisen, and disfavour aldol, condensation in conditions where a number of other bases including sodium methoxide (or low concentrations of magnesium methoxide) give only aldol products,[1,2,8] may be ascribed to the influence of metal chelation as follows. Michael-aldol type attack on the magnesium complex (20) leads to alkoxide ionisation followed reversibly by regeneration of the starting species with restoration of the chelate ring as in (21) (Scheme 6).



SCHEME 8

The Claisen condensation pathway is shown in Scheme 7. Here, initial attack is on the ester grouping (22). Attack by OR'^- in (23) can reverse the initial process as in the aldol case or, alternatively, eject OR^- as shown and the Claisen condensation and consequent steps then proceed. In more complex systems the geometrical restriction caused by chelate formation, as well as solubility and other factors, also play a part in determining the course of the reaction.

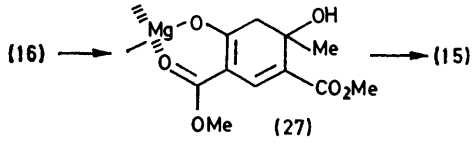
The pattern of base-catalysed reactions of dimethyl 2,4-diacetylglutaconate described above may thus be rationalised as follows. In sodium methoxide solution the anion of diacetylglutaconic ester forms (10, R = Me) and cyclises to the oxopyrancarboxylate (11, R = Me) which can give rise to the anion (12, R = Me) as demonstrated by the trapping as xanthophanic enol. At higher sodium methoxide concentrations the diacetyl-



glutaconate anion, equilibrating with the oxopyrancarboxylate, reacts irreversibly by the aldol pathway to give the isophthalate diester (15). More half-ester is found than diester, however, and this may indicate that there is irreversible attack at the 6-position of the pyran (24) as well as the reversible attack at the 2-position. The product (25) can then cyclise to the half-ester (13, R = H) (Scheme 8). On the other hand, alternative possibilities for the origin of the free carboxylate grouping also require investigation.

Lower concentrations of magnesium methoxide cause cyclisation of dimethyl 2,4-diacetylglutaconate to the pyran (11, R = Me) which may bind magnesium as (26). With larger amounts of magnesium methoxide present, the glutaconic ester will be held in equilibrium as the magnesium chelate and becomes the substrate for the two types of aromatic cyclisation.[6] Claisen cyclisation as in (17) occurs as discussed above, and the reaction may also proceed as in (19). Geometry is assumed to be labile in conjugated anionic systems of this type, and in the alternative geometry, reaction (14) would be disfavoured for reasons given in Scheme 6, although the con-

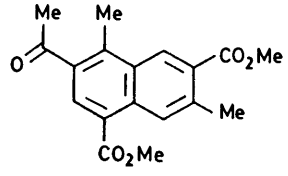
jugated attachment at position ' a ' [*cf.* (20)] may have a modifying influence. However aldol reaction as in anion (16) is a reasonable pathway to account for the formation of the aldol product, the isophthalate diester (15). This latter pathway does not involve destruction of the chelate and leads reversibly to (27), which reacts irreversibly to give (15) (Scheme 9). Destruction of a chelate ring is also not involved in the Claisen process (19)→(18).



SCHEME 9

When one mol of magnesium methoxide is added to the pyran (11, R = Me), it is recovered unchanged after acidification. On adding 2 mol of this reagent, however, the isophthalate (15) and the acetylresorcinol ester (18) are formed. These two compounds are also produced when 1 mol of magnesium methoxide is added to dimethyl 2,4-diacetylglutaconate followed by 1 mol of sodium or calcium methoxide. Aluminium methoxide (8 mol) reacted with dimethyl 2,4-diacetylglutaconate to give only (11, R = Me) (40%) and a similar addition followed by 1 mol of sodium methoxide also gave (11) (48%) but no aromatic compounds. This reagent is thus different from the magnesium reagent in its effects.

Apart from the responses ascribed to magnesium chelation, the products from base-catalysed reactions of dimethyl 2,4-diacetylglutaconates, and other polyketonic systems may depend on the type of base, solvent, and other conditions. Thus, when treated with sodium hydroxide in benzene containing a little methanol, the glutaconate (1, R = Me) gave dimethyl 7-acetyl-3,8-dimethylnaphthalene-2,5-dicarboxylate (28) (46%),



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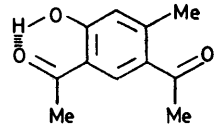

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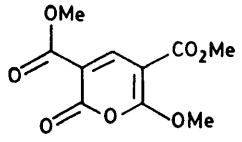

(30)

which was also formed when the pyran (11, R = Me) was treated with piperidine in ethanol. This naphthalene, a consequence of bimolecular condensation, is found as a by-product in the melt reaction leading to xanthophanic enol and has been discussed earlier.[9]

In the case of 1,1,3,3-tetra-acetylpropene, pyran formation and Claisen cyclisation pathways are not available and treatment with 1, 2, or 4 mol of sodium methoxide solution gave the aldol product, the diacetylhydroxytoluene (29):[1] 0.5 mol of the base gave largely unchanged tetra-acetylpropene. Magnesium methoxide at similar concentrations gave analogous results. The tetraester, dimethyl 2,5-dimethoxycarbonyl glutaconate (9) was recovered unchanged when treated with magnesium methoxide (4 mol) or sodium methoxide (4 mol). It has been reported[5] that the methoxypyran (30) is formed on distillation.

EXPERIMENTAL

Unless stated otherwise, i.r. data are for chloroform solutions and u.v. data were determined in ethanol. Ethereal solutions were dried over anhydrous sodium sulphate.

Ethyl Ethoxymethyleneacetoacetate.—Ethyl orthoformate (296 g), ethyl acetoacetate (260 g), and acetic anhydride (408 g) were refluxed together (90 min). Distillation gave ethyl ethoxymethyleneacetoacetate (218 g), b.p. 85 °C at 0·25 mmHg (lit.,[3] b.p. 149—151 °C at 15 mmHg); n_D^{20} 1.475 3; $\nu_{max.}$ (liquid film) 1 731, 1 712, 1 664, 1 635, and 1 593 cm^{-1}; $\lambda_{max.}$ 254 (ε 11 300) nm; n.m.r. (carbon tetrachloride) τ 8.65 (6 H, *J* 7 Hz, 2 × CH_3CH_2O), 7.75 (3 H, CH_3CO), 5.77 (4 H, *J* 7 Hz, 2 × CH_3CH_2O), and 2.48 (1 H, =CH. Signals were split into pairs of closely spaced lines, indicating almost equal amounts of *cis* and *trans* forms.

Methyl Methoxymethyleneacetoacetate.—Methyl orthoformate (525 g), methyl acetoacetate (600 g), and acetic anhydride (1 050 g) reacted as above gave methyl methoxymethyleneacetoacetate (255 g), b.p. 80—84 °C at 0.15 mmHg (lit.,[3] b.p. 150 °C at 16 mmHg), n_D^{17} 1.482 8, m.p. 56—58 °C; $\nu_{max.}$ 1 715 (ester carbonyl), 1 682 (acetyl carbonyl), 1 632, and 1 592 cm^{-1}; $\nu_{max.}$ (liquid film) 1 728, 1 717, 1 683, 1 635, and 1 595 cm^{-1}; $\lambda_{max.}$ 253 (ε 10 250) nm; n.m.r. (carbon tetrachloride) τ 7.74 (3 H, CH_3CO), 6.28 (3 H, ester CH_3O), 5.99 (3 H, CH_3O), and 2.53 (1 H, =CH) (signals were split).

Methoxymethyleneacetylacetone. Methyl orthoformate (106 g), acetylacetone (100 g), and acetic anhydride (200 g) were refluxed together (75 min) to give methoxymethyleneacetylacetone (38 g), b.p. 80 °C at 0.6 mmHg (lit.,[3] b.p. 140 °C at 16 mmHg), n_D^{22} 1.491 2; $\nu_{max.}$ 1 680 (acetyl carbonyl), 1 624, and 1 586 cm^{-1}; $\nu_{max.}$ (liquid film) 1 713w, 1 680, 1 628, and 1 590 cm^{-1}; $\lambda_{max.}$ 262 (ε 9 350) nm; n.m.r. (carbon tetrachloride) τ 7.80 (3 H, CH_3CO), 7.70 (3 H, CH_3CO), 5.91 (3 H, CH_3O), and 2.40 (1 H, =CH).

Dimethyl Methoxymethylenemalonate.—Methyl orthoformate (106 g), dimethyl malonate (132 g), acetic anhydride (225 g), and zinc chloride (7 g) were heated together under reflux (90 min). Methyl acetate was distilled off, maintaining the temperature below 110 °C. The residue was heated under reflux for 2 h, and methyl acetate was again distilled off. This procedure was continued until the total reflux time was 8 h. Zinc chloride was filtered off, and the product distilled to give dimethyl methoxymethylenemalonate (60 g), b.p. 106 °C at 0.7 mmHg (lit.,[3] b.p. 167 °C at 20 mmHg), which crystallised as long needles, m.p. 44—45 °C (lit.,[3] m.p. 46 °C); $\nu_{max.}$ 1 729br (ester carbonyl) and 1 635 cm^{-1}; $\nu_{max.}$ (liquid film) 1 735br and 1 625 cm^{-1}; $\lambda_{max.}$ 242 (ε 11 950) nm; n.m.r. (carbon tetrachloride) τ 6.32 (3 H, ester CH_3O), 6.30 (3 H, ester CH_3O), 6.04 (3 H, CH_3O), and 2.58 (1 H, =CH).

Diethyl 2,4-Diacetylglutaconate (1, R = Et).—Ethyl sodioacetoacetate (15.1 g) and ethyl ethoxymethyleneacetoace-

tate (18.6 g) were shaken in ether (150 ml) for 45 min. The mixture was poured into water (150 ml), acidified with 4N hydrochloric acid, and extracted with ether. Evaporation gave diethyl 2,4-diacetylglutaconate, which was recrystallised from light petroleum (b.p. 60—80 °C), m.p. 94—95 °C (lit.,[3] m.p. 96 °C); $\nu_{max.}$ 1 700br (free ester), 1 635, and 1 568 cm^{-1}; $\nu_{max.}$ (mull) 3 390, 1 726, 1 715, 1 685, 1 635, and 1 570 cm^{-1}; $\lambda_{max.}$ (ethanol) 209 (ε 9 750), 250 (8 400), 311 (6 700), and 388 (4 800) nm; $\lambda_{max.}$ (0.001N ethanolic potassium hydroxide) 212 (ε 19 600), 272 (11 000), and 389 (23 450) nm; $\lambda_{max.}$ (0.01N ethanolic hydrochloric acid) 208 (ε 9 650), 248 (9 950), and 314 (7 850) nm; n.m.r. (carbon tetrachloride) τ 8.67 (6 H, *J* 7 Hz, 2 × CH_3CH_2O), 8.14 [3 H, $CH_3C(O)_2$·], 7.62 [3 H, $CH_3C(O)$·], 5.80 (4 H, *J* 7 Hz, 2 × CH_3CH_2O), 5.03 (1 H, broad, O*H*), and 2.49 (1 H, =CH). The ester gave a green-brown colour with ferric chloride.

Dimethyl 2,4-*Diacetylglutaconate* (1, R = Me).—Methyl sodio-acetoacetate (34.5 g) and methyl methoxymethyleneacetoacetate (39.5 g) gave, as above, dimethyl 2,4-diacetylglutaconate, which crystallised from light petroleum (b.p. 60—80 °C) (33.5 g), m.p. 90 °C (lit.,[4] m.p. 85 °C); $\nu_{max.}$ 1 707br (free ester), 1 636, and 1 568 cm^{-1}; $\nu_{max.}$ (mull) 3 390, 1 730, 1 716, 1 688, 1 684, and 1 536 cm^{-1}; $\lambda_{max.}$ (chloroform) 250 (ε 8 050) and 315 (7 300) nm. It gave a green colour with ferric chloride.

1,1,3,5-*Tetra-acetylpropene* (8).—Sodio-acetylacetone (12.2 g) and methoxymethyleneacetylacetone (14.2 g) were shaken together in ether (150 ml) for 1 h. Work-up as above gave an oil (17.6 g), from which crystallised 1,1,3,3-tetra-acetylpropene, on addition of light petroleum (b.p. 60—80 °C). It was recrystallised from benzene–light petroleum (b.p. 60—80 °C), as pale yellow needles, m.p. 114 °C (lit.,[3] m.p. 117—118 °C); $\nu_{max.}$ 1 663 (free acetyl CO), 1 618, 1 553, and 1 540 cm^{-1}; $\nu_{max.}$ (mull) 3 185, 1 668, 1 658, 1 653, 1 608, and 1 526 cm^{-1}; $\lambda_{max.}$ (chloroform) 277 (ε 11 200) and 334 (6 350) nm. It gave a red colour with ferric chloride.

Dimethyl 2,4-*Dimethoxycarbonylglutaconate* (9, R = Me).—Dimethyl sodio-malonate (7.7 g) and dimethyl methoxymethylenemalonate (8.7 g) were shaken together in ether (125 ml) for 6 h and poured into water. Work-up yielded dimethyl 2,5-dimethoxycarbonylglutaconate (8.4 g), as a pale yellow liquid; *m/e* 274 (M^+); $\nu_{max.}$ 1 745br (free ester), 1 660, 1 650, and 1 603 cm^{-1}; $\nu_{max.}$ (liquid film) 1 742, 1 660, 1 650, and 1 603 cm^{-1}; it gave a deep orange colour with ferric chloride.

Magnesium Methoxide on Dimethyl 2,4-*Diacetylglutaconate* (1).—(*a*) 4 : 1 *Molar ratio*. Dimethyl 2,4-diacetylglutaconate (2 g, 1 mol) in benzene (10 ml) was added to magnesium methoxide solution, prepared from magnesium (0.804 g, 4 g atom) and methanol (30 ml). The solution was set aside (24 h) and a white precipitate formed. Water (40 ml) was added, the solution was acidified with 4N hydrochloric acid, and extracted with benzene (3 × 30 ml). Chromatography on alumina (elution with light petroleum–benzene) gave dimethyl 5-hydroxytoluene-2,4-dicarboxylate (15) (1.18 g, 59%: n.m.r. showed 75% yield) which was recrystallised from light petroleum (b.p. 40—60 °C), m.p. 114—115 °C [2,7] (Found: C, 58.89; H, 5.31. Calc. for $C_{11}H_{12}O_5$: C, 58.92; H, 5.40%); *m/e* 224 (M^+); $\nu_{max.}$ 3 190br (OH), 1 720 (free ester CO), 1 680 (chelated ester CO), 1 622, and 1 575 cm^{-1}; $\nu_{max.}$ (mull) 3 120, 1 723, 1 689, 1 620, and 1 575 cm^{-1}; $\lambda_{max.}$ 230 (ε 21 300), 250 (11 100), and 303 (3 100) nm; n.m.r. (carbon tetrachloride) τ 7.42 (3 H, aryl CH_3), 6.18, 6.05 (6 H 2 × CH_3O), 3.24, 1.64 (2 H aryl), and −0.83 (1 H, chelated OH); it gave a dark red colour with ferric chloride. Further elution (benzene–chloroform) gave methyl 3-acetyl-4,6-dihydroxybenzoate (18) [2,7] (0.32 g, 19%: n.m.r. showed 25% yield), m.p. and mixed m.p. 120—121 °C (from methanol) (Found: C, 57.05; H, 4.75. Calc. for $C_{10}H_{10}O_5$: C, 57.14: H, 4.80%); *m/e* 210 (M^+); $\nu_{max.}$ 3155br (OH), 1 682 (chelated ester CO), 1 645 (chelated acetyl CO), 1 603, and 1 494 cm^{-1}; $\nu_{max.}$ (mull) 1 688, 1 683, 1 645, 1 630, 1 615, and 1 595 cm^{-1}; $\lambda_{max.}$ 243 (ε 39 600), 268 (10 500), and 313 (4 850) nm; n.m.r., τ 7.41 (3 H, CH_3CO), 6.03 (3 H, CH_3O), 3.57, 1.68 (2 H, aryl), and −1.33, −2.85 (2 H, chelated O*H*); it gave a dark red colour with ferric chloride.

(*b*) 2 : 1 *Molar ratio*. Dimethyl 2,4-diacetylglutaconate (2 g, 1 mol), in benzene (10 ml), when treated as above (24 h) with magnesium methoxide solution from magnesium (0.402 g, 2 g atom) and methanol (30 ml), gave a solid (1.81 g) which was chromatographed to give dimethyl 5-hydroxytoluene-2,4-dicarboxylate (1.10 g, 55%: n.m.r. analysis 70% yield), m.p. and mixed m.p. 114—115 °C (n.m.r. and i.r. spectra identical with an authentic sample), together with methyl 3-acetyl-4,6-dihydroxybenzoate (18) (0.45 g, 26%: n.m.r. shows 30% yield), m.p. and mixed m.p. 120—121 °C (i.r. and n.m.r. spectra identical with an authentic sample).

(*c*) 1 : 1 *Molar ratio*. Dimethyl 2,4-diacetylglutaconate (2 g, 1 mol), in benzene (10 ml), when treated (24 h) with magnesium methoxide solution from magnesium (0.201 g, 1 g atom) and methanol (30 ml), gave a yellow gum (1.99 g) which crystallised. T.l.c. indicated only one compound with trace amounts of dimethyl 5-hydroxytoluene-2,4-dicarboxylate and methyl 3-acetyl-4,6-dihydroxybenzoate. The crude material was crystallised from light petroleum (b.p. 40—60 °C) to give colourless needles, m.p. 60—61 °C, of *methyl* 5-*acetyl*-6-*oxo*-2-*methyl*-6H-*pyran*-3-*carboxylate* (11, R = Me) (1.37 g, 79%) (Found: C, 57.15; H, 4.90. $C_{10}H_{10}O_5$ requires C, 57.14; H, 4.80%); *m/e* 210 (M^+); $\nu_{max.}$ 1 755 (ring CO), 1 726 (ester CO), 1 694 (acetyl CO), 1 616, and 1 548 cm^{-1}; $\nu_{max.}$ (mull) 1 755, 1 725, 1 698, 1 690, 1 610, and 1 550 cm^{-1}; n.m.r., τ (carbon tetrachloride) 7.47 (3 H, ring CH_3), 7.27 (3 H, CH_3CO), 6.10 (3 H CH_3O), and 1.54 (1 H ring =CH); it gave a purple colour with ferric chloride.

Treatment of this pyran (1 mol) in benzene with magnesium methoxide (1 mol) solution, as described above, gave unchanged pyran with only trace amounts of dimethyl 5-hydroxytoluene-2,4-dicarboxylate and methyl 3-acetyl-4,6-dihydroxybenzoate, as shown by t.l.c. and i.r. Treatment of the pyran (1 mol) in benzene with magnesium methoxide (2 mol) solution gave some unchanged pyran and substantial amounts of dimethyl 5-hydroxytoluene-2,4-dicarboxylate and methyl 3-acetyl-4,6-dihydroxybenzoate, as shown by t.l.c. and i.r.

(*d*) 1 : 2 *Molar ratio*. Dimethyl 2,4-diacetylglutaconate (2 g, 1 mol) in benzene (10 ml) treated (24 h) with magnesium methoxide solution [from magnesium (0.100 5 g, 0.5 g atom) and methanol (30 ml)] gave a yellow gum (1.89 g). It was crystallised from light petroleum (b.p. 40—60 °C) to give methyl 5-acetyl-6-oxo-2-methyl-6*H*-pyran-3-carboxylate (1.42 g, 84%), m.p. and mixed m.p. 60—61 °C.

(*e*) 1 : 4 *Molar ratio*. Dimethyl 2,4-diacetylglutaconate (2 g, 1 mol) in benzene (10 ml) when treated (24 h) with magnesium methoxide solution [from magnesium (0.050 3 g, 0.25 g atom) and methanol (30 ml)] gave a yellow gum (1.90 g). I.r. and n.m.r. spectra indicated roughly equal

amounts of starting material and pyran (11). Quantitative n.m.r. analysis gave dimethyl 2,4-diacetylglutaconate (53%) and (11) (47%). Another experiment yielded the pyran (11), m.p. and mixed m.p. 58 °C (14%), after trituration with light petroleum (b.p. 40—60 °C).

Sodium Methoxide (12, 4, 2, 1, *and* 0.5 *mol*) *on Dimethyl* 2,4-*Diacetylglutaconate* (1 *mol*).—A solution of sodium methoxide was made from sodium (6.336 g) and methanol (250 ml), and into each of 4 flasks was pipetted 30, 15, 7.5, and 3.75 ml (for 4, 2, 1, and 0.5 mol respectively); each was made up to 30 ml with methanol. To each flask was added dimethyl 2,4-diacetylglutaconate (2 g, 1 mol) in benzene (10 ml). The yellow solutions were set aside at room temperature for 24 h, water (40 ml) was added, the solutions were acidified with 4N hydrochloric acid, and extracted with benzene (3 × 30 ml). The combined benzene extracts were washed with water (2 × 15 ml), dried, and the benzene evaporated off. *Base* : *ester* 4 : 1. This gave a gum (1.89 g) which crystallised, and was shown by t.l.c. to be one compound. It was recrystallised from light petroleum (b.p. 40—60 °C) to give methyl 5-acetyl-6-oxo-2-methyl-6*H*-pyran-3-carboxylate (1.33 g, 77%: another experiment 66%), m.p. 58 °C. Identity was confirmed (and in the cases below) by t.l.c. and i.r. spectral comparison, and a mixed m.p. *Base* : *ester* 2 : 1. A solid (1.96 g) (one compound by t.l.c.) was formed which on crystallisation gave the pyran (11) (1.42 g, 82%: another experiment 81%), m.p. 58 °C. *Base* : *ester* 1 : 1. This gave a solid (1.88 g), shown by t.l.c. (elution with chloroform and with methanol, and examination under u.v. or in iodine vapour) to be one compound with a small trace of dimethyl xanthophanic enol. It was recrystallised to give the pyran (11) (1.37 g, 79%: another experiment 76%), m.p. 58 °C. *Base* : *ester* 0.5 : 1. The solid (1.83 g) crystallised, and was shown by t.l.c. to contain a small trace of dimethyl xanthophanic enol. I.r. and n.m.r. spectra indicated almost equal amounts of unchanged starting material and the pyran (11). Quantitative n.m.r. analysis gave dimethyl-2,5-diacetylglutaconate (43%) and the pyran (11) (56%). Another experiment gave the pyran (11), m.p. 58 °C (44%), after trituration with light petroleum (b.p. 40—60 °C). *Base* : *ester* 12 : 1. The experiment gave a mixture (61%) of dimethyl 5-hydroxytoluene-2,4-dicarboxylate (15) and its half-ester (13, R = H) (mainly the latter) identified by i.r. and t.l.c. The mother liquors contained further (13, R = H), together with small amounts of the naphthalene (28).

Lithium Methoxide (4, 2, 1, and 0.5 *mol*) *on Dimethyl* 2,4-*Diacetylglutaconate* (1 *mol*).—A solution of lithium methoxide was made from lithium (0.5 g) and methanol (100 ml), and into each of the flasks was pipetted 27.75, 13.9, 6.95, and 3.45 ml (for 4, 2, 1, and 0.5 mol respectively). To each of the four flasks was added dimethyl 2,4-diacetylglutaconate (1.21 g, 1 mol) in benzene (10 ml). The yellow solutions were set aside at room temperature for 2 days and worked up as above (1.05, 1.07, 1.09, and 1.11 g, for 4, 2, 1, and 0.5 mol respectively). The products all crystallised and gave the pyran (11), m.p. 59—60 °C, on recrystallisation (0.78, 0.83, 0.84, 0.32 g: 75, 79, 80, and 30% for 4, 2, 1, and 0.5 mol respectively).

Calcium Methoxide (4, 2, 1, *and* 0.5 *mol*) *on Dimethyl* 2,4-*Diacetylglutaconate* (1 *mol*).—Solutions of calcium methoxide were made from calcium (0.8, 0.4, 0.2, and 0.1 g for 4, 2, 1, and 0.5 mol respectively) and methanol (80, 40, 20, and 10 ml for 4, 2, 1, and 0.5 mol respectively). To each of the flasks was added dimethyl 2,4-diacetylglutaconate (1.21 g, 1 mol) in benzene (10 ml). The solutions were set aside for 2 days and worked up to give crystals (1.09, 1.04, 1.03, and 1.09 g for 4, 2, 1, and 0.5 mol respectively). The solids were recrystallised to give the pyran (11) (0.85, 0.85, 0.83, and 0.70 g: 81, 81, 79, and 67% for 4, 2, 1, and 0.5 mol respectively), m.p. 58—59 °C. Identity was confirmed as before.

Magnesium Methoxide (1 *mol*) *followed by Sodium Methoxide* (1 *mol*) *on Dimethyl* 2,4-*Diacetylglutaconate* (1 *mol*).—Dimethyl 2,4-diacetylglutaconate (1.21 g, 1 mol) in benzene (10 ml) was added to magnesium methoxide solution, from magnesium (0.121 5 g, 1 g atom) and methanol (20 ml), and the solution was set aside for 18 h. A small sample was removed, treated in the usual way, and t.l.c. showed it to be the pyran (11) with only trace amounts of dimethyl 5-hydroxytoluene-2,4-dicarboxylate and methyl 3-acetyl-4,6-dihydroxybenzoate. Sodium methoxide solution, from sodium (0.115 g, 1 g atom) and methanol (23 ml) was added and the mixture was set aside for 24 h. T.l.c. then showed substantial formation of dimethyl 5-hydroxytoluene-2,4-dicarboxylate and methyl 3-acetyl-4,6-dihydroxybenzoate, together with some (11). An experiment using 1 mol of calcium methoxide in place of the sodium methoxide gave similar results.

Aluminium Alkoxide (8 *mol*) *on Dimethyl* 2,4-*Diacetylglutaconate* (1 *mol*).—Dimethyl 2,4-diacetylglutaconate (1 g, 1 mol) in benzene (5 ml) was added to a slurry of aluminium isopropoxide (6.744 g, 8 mol) in benzene (20 ml) and methanol (25 ml). The mixture was refluxed for 24 h [setting aside the solution at room temperature gave a mixture of similar amounts of unchanged starting material and the pyran (11) as shown by t.l.c., and i.r. and n.m.r. spectra]. The solution was worked up to give crystals (0.65 g) whose i.r. and n.m.r. spectra were identical with those of the pyran (11), (t.l.c. showed the absence of dimethyl 5-hydroxytoluene-2,4-dicarboxylate and methyl 3-acetyl-4,6-dihydroxybenzoate). The product was crystallised to give the pyran (11) (0.35 g, 40%), m.p. and mixed m.p. 59—60 °C.

Reaction of Methoxymethyleneacetoacetate with Methyl 5-*Acetyl*-6-*oxo*-2-*methyl*-6H-*pyran*-3-*carboxylate*.— Methyl methoxymethyleneacetoacetate (0.158 g, 1 mol) and the pyran (11) (0.210 g, 1 mol) were added to a solution of sodium methoxide [from sodium (0.023 g, 1 g atom) and methanol (5 ml)]. The solution was refluxed for 90 min and became deep red. The methanol was evaporated off and water (20 ml) was added. Acidification at 0 °C with glacial acetic acid–water (1 : 1) gave a red-brown precipitate which was filtered off, washed with water, and dried (0.154 g, 46%), and shown to be dimethyl xanthophanic enol (3, R = R′ = Me). It formed red needles from benzene, m.p. and mixed m.p. 178 °C (lit.,[1] m.p. 179 °C); spectral comparison confirmed its identity.

Reaction of Ethyl Ethoxymethyleneacetoacetate with Methyl 5-*Acetyl*-6-*oxo*-2-*methyl*-6H-*pyran*-3-*carboxylate*.— Ethyl ethoxymethyleneacetoacetate (0.186 g, 1 mol) and the pyran (11) (0.21 g, 1 mol) were added to a solution of sodium methoxide [from sodium (0.023 g, 1 g atom) and methanol (10 ml)] and gave ethyl methyl xanthophanic enol (3, R = Me, R′ = Et) (94 mg, 37%). This formed brown needles, m.p. and mixed m.p. 168 °C, after crystallisation from benzene (lit.,[1] m.p. 168 °C): spectral comparison confirmed its identity.

Magnesium Methoxide (4, 2, 1, *and* 0.5 *mol*) on 1,1,3,3-*Tetra-acetylpropene* (7) *or* (8) (1 *mol*).—1,1,3,3-Tetra-acetylpropene (0.2 g, 1 mol) in benzene (1 ml) was added to

magnesium methoxide solution, prepared from magnesium (0.0927 g, 4 g atom) and methanol (3 ml). This was repeated using varying amounts of magnesium (0.046 4, 0.023 2, and 0.011 6 g for 2, 1, and 0.5 mol respectively). The yellow solutions were set aside for 24 h (little precipitate had formed) and worked up in the usual way. *Base* : *propene* 4 : 1. 2,4-Diacetyl-5-hydroxytoluene (29) (0.188 g, *ca.* 100%) was formed, m.p. 108 °C [from light petroleum (b.p. 60—80 °C)] (lit.,[3] m.p. 112 °C) (Found: C, 68.45; H, 6.05: Calc. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29%); *m/e* 192 (M^+); $\nu_{max.}$ 1 680 (acetyl CO), 1 645 (chelated acetyl CO), and 1 570 cm^{-1}; $\nu_{max.}$ (mull) 1 680, 1 645, 1 598, and 1 564 cm^{-1}; $\lambda_{max.}$ 210 (ε 6 350), 244 (31 100), 262 infl. (9 900), and 320 (2 750) nm; n.m.r., τ 7.43 (3 H, aryl–C*H*$_3$), 7.40, 7.33 (6 H, aryl–C*H*$_3$CO), 3.19, 1.81 (2 H, aryl-H), and −2.57 (1 H, chelated OH); it gave a dark red colour with ferric chloride. *Base* : *propene* 2 : 1. The product was 2,4-diacetyl-5-hydroxytoluene (0.184 g), m.p. 108 °C. Identity was confirmed by t.l.c., i.r. spectral comparison, and a mixed m.p. (similarly in the examples below). *Base* : *propene* 1 : 1. This gave crystals (0.186 g) shown by t.l.c., i.r., and n.m.r. examination to be mainly 2,4-diacetyl-5-hydroxytoluene with some unchanged starting material. Quantitative n.m.r. analysis gave 2,4-diacetyl-5-hydroxytoluene (80%) and 1,1,3,3-tetra-acetylpropene (20%). *Base* : *propene* 0.5 : 1. A gum (0.200 g) was formed, shown by t.l.c. to be starting material with a trace of 2,4-diacetyl-5-hydroxytoluene.

Reaction of Sodium Methoxide (4, 2, 1, and 0.5 *mol*) *with* 1,1,3,3-*Tetra-acetylpropene* (1 *mol*).—A solution of sodium methoxide was made from sodium (1.46 g) and methanol, (50 ml), and into each of four flasks was added 1.5, 0.75, 0.375, and 0.188 ml (for 4, 2, 1, and 0.5 mol) and each made up to 1.5 ml with methanol. To each of the flasks was added 1,1,3,3-tetra-acetylpropene (0.1 g, 1 mol) in benzene (0.5 ml). The yellow solutions were set aside for 24 h and worked up in the usual way. *Base* : *propene* 4 : 1. This gave 2,4-diacetyl-5-hydroxytoluene (0.097 g, *ca.* 100%), m.p. 108 °C. *Base* : *propene* 2 : 1. 2,4-Diacetyl-5-hydroxytoluene formed (0.098 g), m.p. 108 °C. *Base* : *propene* 1 : 1. The solid (0.100 g) was shown by t.l.c. to be 2,4-diacetyl-5-hydroxytoluene with a trace of unchanged starting material. It gave needles, m.p. 107 °C [from light petroleum (b.p. 60—80 °C)]. *Base* : *propene* 0.5 : 1. A gum (0.100 g) which could not be crystallised was formed, and was shown by t.l.c. to be starting material containing a little 2,4-diacetyl-5-hydroxytoluene.

Magnesium Methoxide (4 *mol*) *or Sodium Methoxide* (4 *mol*) *on Dimethyl* 2,4-*Dimethoxycarbonylglutaconate* (1 *mol*).—Dimethyl 2,4-dimethoxycarbonylglutaconate (1 g, 1 mol) in benzene (5 ml) was added to magnesium methoxide solution [from magnesium (0.355 g, 4 g atom) and methanol (15 ml)] and set aside for 24 h. Work-up gave an oil (0.997 g) shown by t.l.c., and i.r. and n.m.r. spectroscopy to be unchanged starting material. The sodium methoxide experiment gave a similar result.

Reaction of Sodium Ethoxide with Diethyl 2,4-*Diacetylglutaconate*.—A solution of diethyl 2,4-diacetylglutaconate (2 g) in ethanol (10 ml) was heated with sodium ethoxide solution [from sodium (1 g) and ethanol (25 ml)], at 85 °C for 4 h in a sealed tube. The slurry was poured into ice–water (100 ml) and acidified with 4N sulphuric acid to give 3-ethoxycarbonyl-4-methyl-6-hydroxybenzoic acid (1.45 g, 88%), m.p. and mixed m.p. 181—182 °C (lit.,[3] m.p. 185—186 °C) from light petroleum (b.p. 100—120 °C); $\nu_{max.}$ 3 120br, 1 714 (free ester CO), 1 682 (chelated acid CO), 1 624, and 1 578 cm^{-1}; $\nu_{max.}$ (mull) 1 715, 1 663, 1 623, and 1 572 cm^{-1}; $\lambda_{max.}$ 229 (ε 19 100), 255 (10 050), and 300 (2 850) nm; n.m.r. [$(CD_3)_2SO$], τ 8.64 (3 H, *J* 7 Hz, C*H*$_3$-CH$_2$O), 7.43 (3 H, aryl–C*H*$_3$), 5.69 (2 H, *J* 7 Hz, CH$_3$C*H*$_2$O), 3.11, 1.62 (2 H, aryl), and 1.62 (2 H, br, CO$_2$*H* and O*H*). 3-Ethoxycarbonyl-4-methyl-6-hydroxybenzoic acid (100 mg) was heated on a steam-bath with 20% aqueous potassium hydroxide for 1 h to give potassium 5-hydroxytoluene-2,4-dicarboxylate (78 mg), m.p. and mixed m.p. 320 °C, after crystallisation from ethanol–water (lit.,[3] m.p. 320 °C); $\nu_{max.}$ (mull) 3 080, 2 620, 1 662 (broad, aryl acid CO), and 1 568 cm^{-1}.

Methanolic Sodium Hydroxide (1 *mol*) *on Dimethyl* 2,4-*Diacetylglutaconate* (1 *mol*).—Dimethyl 2,4-diacetylglutaconate (1.21 g, 1 mol) in benzene (10 ml) was added to sodium hydroxide (0.2 g, 1 mol) in methanol (3 ml). The yellow solution was set aside for four days. Water (15 ml) was added, the solution was acidified with 4N hydrochloric acid, and extracted with benzene. Column chromatography using Grade III Woelm alumina (acid), and eluting with benzene yielded a white solid (0.375 g, 46%) which gave dimethyl 7-acetyl-3,8-dimethylnaphthalene-2,5-dicarboxylate (28), m.p. 130—131 °C (lit.,[9] m.p. 133 °C) from methanol (Found: C, 68.45; H, 5.80. Calc. for $C_{18}H_{18}O_5$: C, 68.78; H, 5.77%); *m/e* 314 (M^+); $\nu_{max.}$ 1 725 (ester), 1 715 (ester), 1 695 (ketone), 1 620 (naphthalene), and 1 563 cm^{-1}; $\nu_{max.}$ (mull) 1 720, 1 685, 1 622, and 1 560 cm^{-1}; $\lambda_{max.}$ 240 (ε 29 700), 260 (49 250), and 310 (5 650) nm; n.m.r., τ 7.32 (3 H, CH$_3$CO), 7.24, 7.17 (6 H, 2 × aryl–C*H*$_3$), 6.00, 5.96 (6 H, 2 × CH$_3$O), and 1.62, 1.20, and 1.16 (3 H, aryl–H). It gave no colouration with ferric chloride. The dimethyl ester (50 mg) was hydrolysed by refluxing with 20% methanolic potassium hydroxide (10 ml) for 10 min. and gave 7-acetyl-3,8-dimethylnaphthalene-2,5-dicarboxylic acid (41 mg), m.p. and mixed m.p. 276—277 °C (lit.,[9] m.p. 284—285 °C), after crystallisation from methanol.

Reaction of Piperidine with Methyl 5-*Acetyl*-6-*oxo*-2-*methyl*-6H-*pyran*-3-*carboxylate* (11).—Piperidine (0.17 g, 1 mol) was added to the pyran (11) (0.42 g, 1 mol) dissolved in ethanol (1 ml) forming a dark red solution, and hydrochloric acid was added. The solution was cooled and filtered to give (28) (0.14 g, 45%), m.p. and mixed m.p. 130—131 °C (Found: C, 68.43; H, 5.61%).

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