Polyketo-enols and Chelates. Product Control by Magnesium Chelation in the Rearrangement of Dimethyl Xanthophanic Enol and Other Xanthyrones

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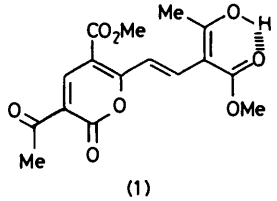
The products formed when dimethyl xanthophanic enol (1) is treated with magnesium methoxide depend strikingly on the molar ratio of the reactants. Up to near a 1 : 1 molar ratio of methoxide to enol, the enol is recovered unchanged. At a 1 : 1 molar ratio the main product is the isophthalate (11) formed by aldol reaction. When the molar ratio is >2 : 1, the main product is the pyran (13) and formation of (11) is much diminished. At a 3 : 1 molar ratio no isophthalate (11) is formed, pyran (13) has diminished in amount, and the resorcylic ester (14), a product of Claisen condensation, is now dominant. At a >6 : 1 molar ratio of magnesium methoxide to enol the resorcylic ester is the sole product, formed in high yield. These results are explained in terms of methoxide-initiated pyran opening and the role of the resulting mono- and bis-magnesium chelated species as substrates for aldol and Claisen rearrangements. The protective action of magnesium complexing on an otherwise base-sensitive chain is also a significant factor. For comparison, the reaction of dimethyl xanthophanic enol is examined using initial sodium methoxide : enol ratios of 1—24 : 1. Only the aldol product, the isophthalate (6, R = H), is formed across the whole concentration range.

The ester-interchange situation, when variously substituted xanthyrones are transformed into resorcylic esters by excess of magnesium methoxide, is studied in support of the proposed mechanisms. The xanthyrones (34)—(36), without a pyrone acetyl and thus incapable of undergoing the resorcylic ester transformation, form substituted pyrans (39)—(41). Sodium methoxide, however, causes chain degradation and cyclisation of the major fragment to dimethyl 4-hydroxyisophthalate, again demonstrating a substantial diversion of reaction pathway resulting from the complexing effect of magnesium methoxide.

It was shown in our earlier work that when treated with sodium methoxide (2 mol) in methanol–benzene, dimethyl xanthophanic enol (1)[1] undergoes pyrone cleavage and recyclisation by aldol condensation to give a substituted isophthalate (6, R = H).[2] Magnesium methoxide (1 mol) under similar conditions gives the closely related isophthalate products (11) and (12, R = Me).[3] Employment of a large excess of magnesium methoxide (12 mol) in the reaction leads, however, to a quite different product, the resorcinol (14), formed by Claisen condensation in excellent yield. No such response to reagent : substrate ratio was found in the case of sodium methoxide and the different behaviour of the excess of magnesium reagent was ascribed to formation and cyclisation of a co-ordinated magnesium species.[2] A closer study of the products formed in reactions involving a range of magnesium methoxide : dimethyl xanthophanic enol ratios is now reported, and reveals an intricate pattern of responses which can be interpreted as base-catalysed reactions of magnesium chelated species.[2]

RESULTS AND DISCUSSION

The reaction of dimethyl xanthophanic enol (1) was studied with 0.5, 0.75, 1, 1.5, 2, 2.5, 3, 6, and 12 mol of



(1)

$Mg(OMe)_2$ in methanol–benzene at 20 °C for 20 h. Initial work was devoted to a search for, and identification of, the products and this was followed by a semi-quantitative study in which the data were built up by crystallisation of the products combined with quantitative t.l.c. of mixed crops and liquors. The results are summarised in Table 1. A total of five crystalline products was found: two of these were the isophthalate-type acetylcoumarin (11) and the substituted resorcylic ester (14), identical with our earlier samples.[2]

TABLE 1

Products from dimethyl xanthophanic enol (1) and magnesium methoxide [a]

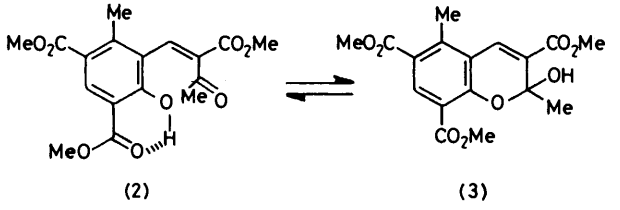
	Base : ester ratio								
Product	0.5 : 1	0.75 : 1	1 : 1	1.5 : 1	2 : 1	2.5 : 1	3 : 1	6 : 1	12 : 1
Starting material	100 [b]	95	5—10	<1	0	0	0	0	0
Isophthalate (11)	0	5	80—85	50	35—40	0	0	0	0
Isophthalate (12, R = H)	0	0	5	10—15	10	trace	0	0	0
Isophthalate (12, R = Me)	0	0	trace	trace	trace	trace	0	0	0
Pyran (13)	0	0	<5	35—45	50—55	65—70	35—40	5	0
Resorcinol (14)	0	0	0	0	0	25—30	60—65	95	100
Crystalline material (%)	92	78	66	59	48	55	49	68	89

[a] See Experimental section for details. [b] % Based on crystalline product.

A yellow compound $C_{17}H_{18}O_8$, m.p. 142—144 °C, was isolated from the reaction with 1.5 mol $Mg(OMe)_2$ and on standing with further reagent was converted into the coumarin (11). In acid solution its u.v. spectrum was very like the acetal (12, R = Me). Examination of the n.m.r. spectrum indicates that it consists of the tautomeric system (2) ⟷ (3). All the expected signals are present but doubled; *e.g.* aromatic methyl τ 7.33, 7.44, olefinic proton τ 2.08, 2.14, and aromatic proton τ 1.54, 1.58. There is a chelated hydroxy resonance as required for (2) at τ −1.63 and the total C–Me to ester O–Me groups integrate in the ratio 2 : 3 also, as required. Integration indicates approximately equal amounts of the two forms in solution.

From reaction of the enol (1) with 2 mol $Mg(OMe)_2$ a new yellow pyran $C_{16}H_{16}O_8$, m.p. 149—150 °C, was isolated and formulated as (13). In the i.r. it had absorptions at 1 749 (ring CO with 3-acyl CO), 1 725 (ester CO), 1 663 (unsaturated ketone), 1 615 (ring C=C), and 1 570 cm^{-1} (chelated CO). N.m.r. examination showed a close resemblance to dimethyl xanthophanic enol. The presence of an enolised acetoacetate residue is confirmed by the enol proton at τ −4.63 (enol Me 7.63, ester OMe 6.05) and an AB quartet is present (2.23, 2.37, *J* 15 Hz) along with an ester methyl, a pyran ring-proton, and a pyran ring-methyl. The structure (13) assigned was of particular interest to us, as in our original work on xanthophanic enol it was a structural contender for formulation of the latter:[1] however, the structure was rejected because it failed to explain the products arising from pyran decarboxylation on heating with water, and on other evidence. This rejection is supported by the u.v. spectra in acid and base which are very different from those of (1). On the other hand the two compounds (34) and (35), carrying two pyran esters and no acetyl, and for which an alternative formulation of the type (13) is therefore impossible, are clearly of the same chromophoric class as xanthophanic enol. As expected from its constitution, when treated with 12 mol $Mg(OMe)_2$ (13) gave the same product (14) as does xanthophanic enol itself.

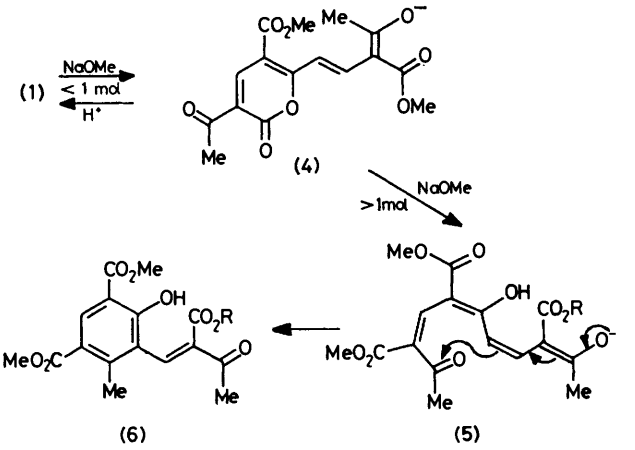
For comparison with the $Mg(OMe)_2$ system, a similar study was made using NaOMe in methanol–benzene. Only one major product, the isophthalate (6, R = H), identical with our earlier specimen,[2] was found across the concentration range 1—24 mol (Table 2). By heating, or



(2) (3)

treatment with acid, it cyclises to (11) and traces of this coumarin were noted in the reaction products. With 1 mol NaOMe or less, the sodium salt of xanthophanic enol is formed and on work-up the starting material is regenerated, but at all the higher sodium methoxide : substrate ratios the pyran is opened and the product undergoes Michael-aldol reaction to form (6, R = H) (Scheme 1).

The subtle response, in terms of product formation, of dimethylxanthophanic enol towards differing ratios of $Mg(OMe)_2$, can be explained in terms of a changing



(6) (5)

SCHEME 1 Influence of sodium methoxide : dimethyl xanthophanic enol ratios on product formation

pattern of reactivity towards methoxide ion of the variously chelated species now acting as substrates. With ⩽1 mol $Mg(OMe)_2$ dimethylxanthophanic enol binds magnesium as a chelate (7) [or (15)] and on work-up the compound is merely recovered (Table 1). At a *ca.* 1 : 1 mol ratio sufficient methoxide ion is available to open the pyran and the mono-magnesium chelate of the new ester, formed by chelate equilibration, is envisaged as (8), cyclising by aldol reaction to give (11) and (12, R = H). [The alternative (16) is less attractive, as the magnesium chelate ring forms a poor electrophilic acceptor because of the reversibility of the aldol system.[4]] The product structures (11) and (12, R = H) are now fixed and addition of excess magnesium methoxide cannot convert them into (13) or (14).

TABLE 2

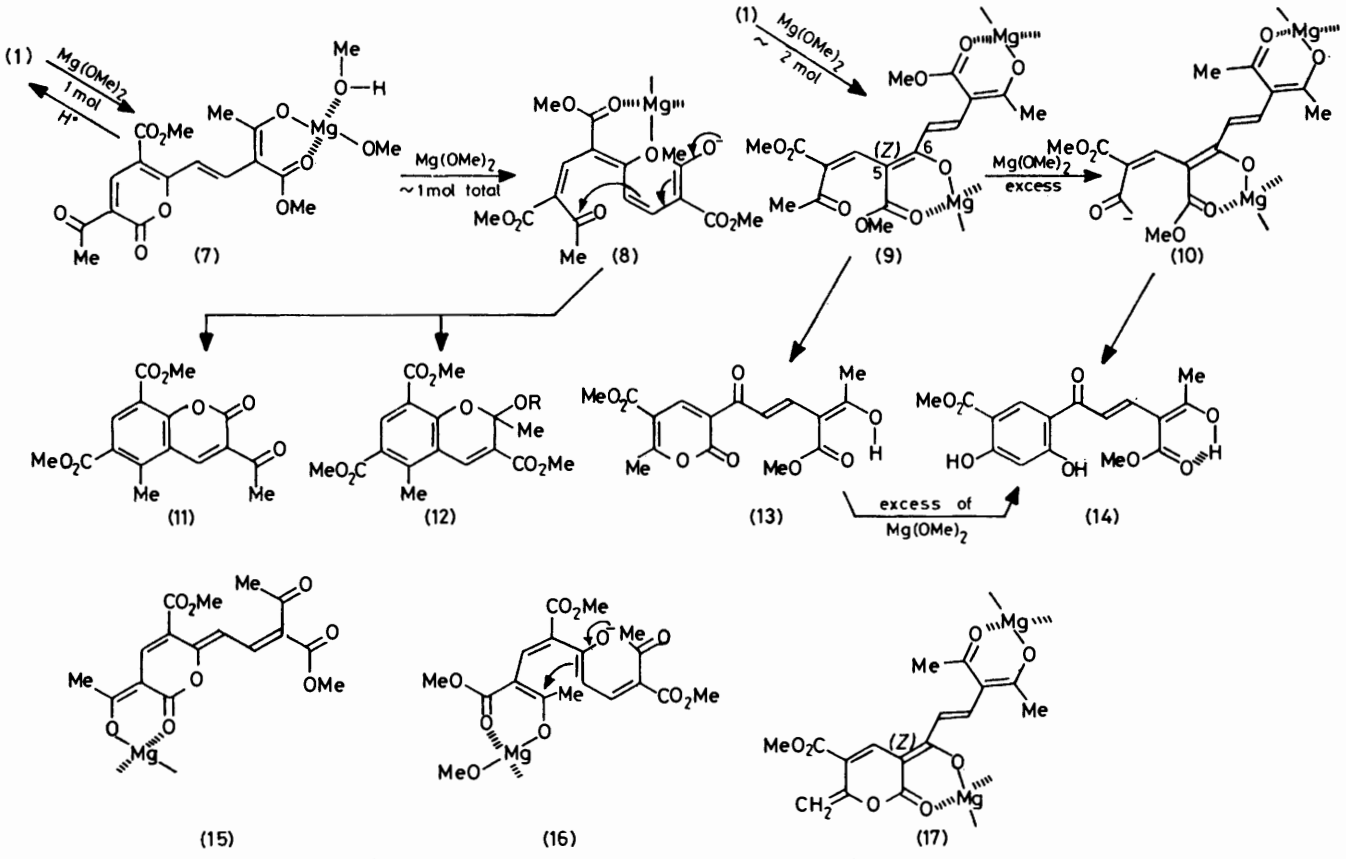
Products from dimethyl xanthophanic enol (1) and sodium methoxide [a]

	Base : ester ratio					
	1 : 1	2 : 1	3 : 1	6 : 1	12 : 1	24 : 1
Product						
Starting material	99 [b]	35—40	20—25	<1	<1	<1
Isophthalate (6, R = H)	<1	60—65	75—80	99	99	99
Isophthalate (11)	trace	trace	trace	trace	trace	trace
Crystalline material (%)	94	47	58	51	56	57

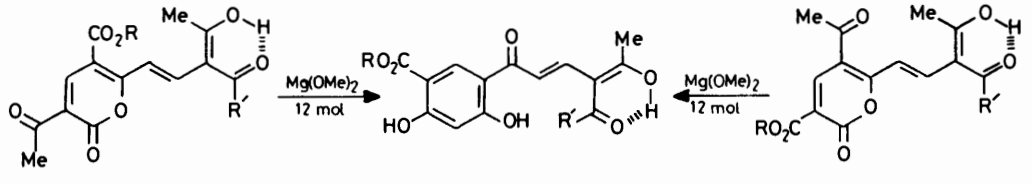
[a] See Experimental section for details. [b] % Based on crystalline product.

As the initial $Mg(OMe)_2$: substrate ratios move through the range 1 : 1 to 2.5 : 1 the yield of (11) falls to zero, and the related products (12, R = H) and (12, R = Me) also disappear in this range. Accompanying these declines (Table 1), is the emergence of the new pyran (13). The suppression of (11) and its relatives, and the formation of (13), can be explained as a consequence of formation of a bis-magnesium chelated

species (9). In this molecule two of the β-keto-esters now have their reactivity extensively modified and new geometrical restrictions are imposed by the stable magnesium-chelated rings. The structure is a less effective candidate for an internal aldol reaction as the initiating anionic centre is chelated, and in this condition the molecule is stabilised in open-chain form by chelate blocking. On work-up and release of the chelation, the chain can be viewed as stabilising itself by pyran formation to give (13). It is of interest that the released chain could also stabilise itself as xanthophanic enol (1) and a factor which may be significant is that the 5,6-double bond in the magnesium chelate is necessarily *Z* as opposed to the *E*-configuration required in structure (1). An alternative modification of the viewpoint above, is that the pyran ring is already formed in the bis-chelate, *i.e.* (17), and that work-up merely involves removal of the magnesium. Such a situation appears feasible, as pyran formation from (9) is the mechanistic analogue of a Claisen-type attack on the magnesium chelate ring which our earlier work indicates is a favoured process. Structures (9) and (17) may thus equilibrate.



SCHEME 2 Influence of magnesium methoxide : dimethyl xanthophanic enol ratios on product formation, showing postulated magnesium-chelated substrates



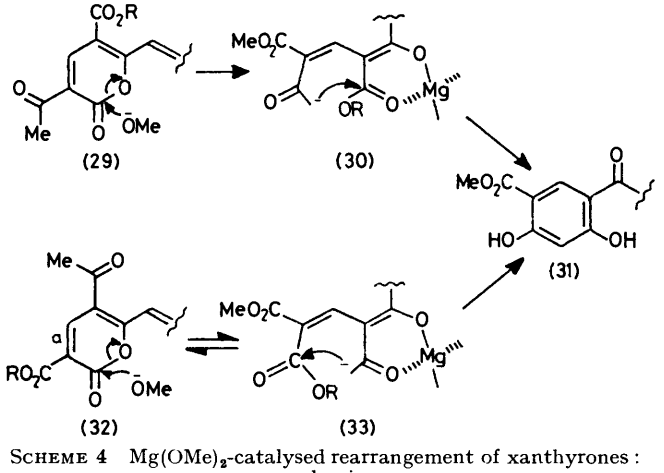
(18) R = Et, R′ = OEt → (22) R = Me, R′ = OEt
(19) R = Me, R′ = OEt → (23) R = Me, R′ = OEt
(20) R = Et, R′ = OMe → (24) R = Me, R′ = OMe
(1) R = Me, R′ = OMe → (14) R = Me, R′ = OMe
(21) R = Me, R′ = Me → (25) R = Me, R′ = Me ← (27) R = Me, R′ = Me
(26) R = Me, R′ = Me ← (28) R = Et, R′ = Me

SCHEME 3 Ester exchanges in the $Mg(OMe)_2$-catalysed rearrangement of xanthyrones

As the ratio of magnesium methoxide to substrate is increased further, the resorcinol (14) becomes the major, and ultimately the exclusive, product formed in high yield. This is conceived as originating from the anion of the bis-metal chelated open-chain species (10). Whereas pyran formation is reversible, the Claisen reaction shown leads to an irreversible outcome and (14) is the ultimate exclusive product. It is presumably held in the reaction mixture as a bis- or tris-magnesium complex, moderating the effects of further base-degradation.

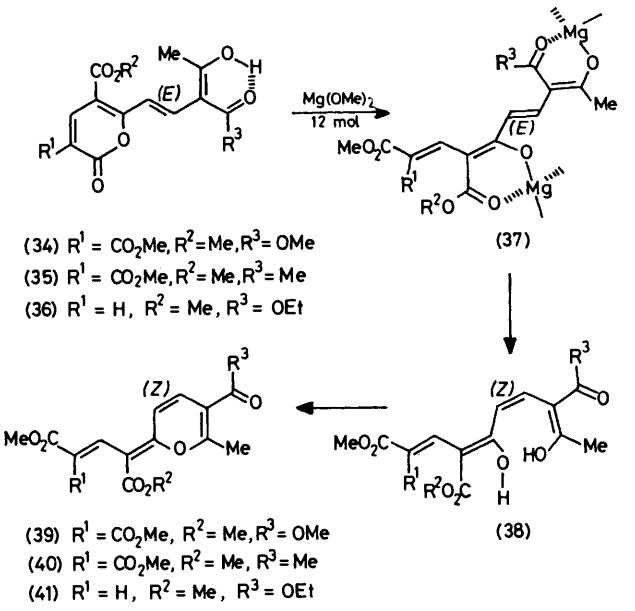
In the course of this work a number of new xanthyrones have been prepared, and the remainder of this paper is devoted to a study of their reactions with excess (12 mol) of $Mg(OMe)_2$. Diethyl xanthophanic enol (18) is known from earlier work [2] to form the resorcylic ester (22) with the aromatic ester group only, exchanged to methyl (Scheme 3). Generalised ester interchange is apparently slow under the conditions used and the single ester interchange can be ascribed to its necessity in the reaction mechanism shown in Scheme 4 [(29)→(30)→(31)]. The five examples in Scheme 3 [(1), (18)—(21)] bear this out convincingly. Xanthyrones with the ester and acetyl pyran substitutes interchanged [(27), (28)] also give resorcylic esters [(25), (26)] with aromatic ester interchange [2] and this is readily explained by reversal of the roles of the acetyl and ester as indicated in Scheme 4 [(32)→(33)→(31)]. Ester interchange occurs in the case of (28) and can be completely accounted for if there is stereomutation of the double bond ' a ' of the delocalised anion formed from (32), along with reversibility in the pyran-opening step.

In view of the mechanisms in Scheme 4 it was of interest to examine the reaction of (34) with excess of $Mg(OMe)_2$. In this example no pyran acetyl is available for the customary resorcylic cyclisation. Instead, an orange compound, $C_{17}H_{18}O_9$, was formed which had $\nu_{max.}$ 1 730 cm^{-1} (esters) and showed signals in the n.m.r. due to



SCHEME 4 $Mg(OMe)_2$-catalysed rearrangement of xanthyrones: mechanism

an unsaturated methyl (τ 7.35), four ester methyls (6.13—6.26), and an AB quartet (2.69 and 2.37, J 10 Hz). The coupling constant indicates a *cis* disposition of these two protons. The remaining olefinic proton, β to three esters, resonates at τ 2.09. This product is thus formulated as (39). A second example (40) was found when the



SCHEME 5 Magnesium methoxide-catalysed rearrangements of xanthyrones which have no acetyl substituent on the pyran ring

xanthyrone (35) having an acetylacetone terminus was treated with 12 mol magnesium methoxide. Finally the xanthyrone (36), carrying only an ester substituent on the pyran ring, when treated with $Mg(OMe)_2$ (5 mol) gave the yellow-orange (41) (two AB quartets in the n.m.r., J 11 and 16 Hz). It will be noted that a new methyl ester is produced in each rearrangement but ester exchange does not occur (see 41).

In this class of rearrangement, pyran opening by methoxide ion with bis-magnesium chelate formation (37) is envisaged. From the earlier discussion re-formation of (34) on work-up could be a possible outcome since formation of (13) or (14) requires R^1 to be COMe. It seems likely that compounds (39)—(41) are therefore formed from an intermediate represented here as (38), on work-up. (*E*)-(*Z*)-Stereomutation, necessary at the 2,3-linkage, would have a low energy barrier in unsaturated enolic systems of this kind. In (39)—(41) the representation of the side-chain geometry is arbitrary as, except for (41), we have no decisive information on this.

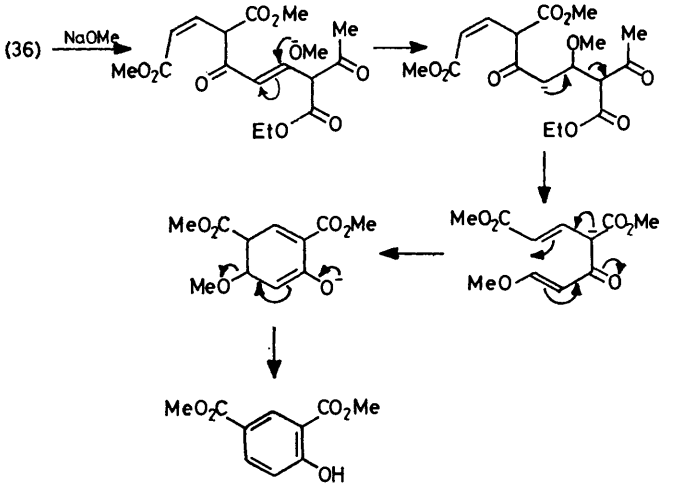
In view of this simple pyran opening–pyran reclosure mechanism proposed it may be questioned whether $Mg(OMe)_2$ has a special role in such transformations. The reaction was therefore performed with sodium methoxide (10 mol) and the main product was found in fact to be dimethyl 4-hydroxyisophthalate (42) formed by chain degradation. It can be accounted for (Scheme 6) by elimination of an ethyl acetoacetate anion from the opened (or intact) pyrone, followed by cyclisation. The magnesium-complexed chain [*cf.* (37)] is protected

from further degradation by methoxide ion, and the reaction has a quite different outcome.

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.

Isolation of Resorcylic Ester (14) *by Treatment of Dimethyl Xanthophanic Enol with Magnesium Methoxide* (12 *mol*).—Magnesium (1.73 g) was refluxed with methanol (anhydrous, 25 ml) in the presence of a trace of iodine until dissolved, and a solution of dimethyl xanthophanic enol (2.0 g) in benzene (25 ml) was added. The solution was set aside at room temperature for 20 h, poured into water (30 ml) and 4N hydrochloric acid (15 ml). The combined benzene extracts were washed, dried, and evaporated to dryness. Addition of ether (15 ml) yielded yellow crystals (1.20 g) of the resorcinol derivative (14), m.p. and mixed m.p. 166—167 °C (lit.,[2]



SCHEME 6 Sodium methoxide-catalysed reaction of xanthyrone (36) having no acetyl substituent on the pyran ring, represented without enolic forms

167—168 °C) (Found: C, 57.00; H, 4.65. Calc. for $C_{16}H_{16}O_8$: C, 57.14; H, 4.80%).

Isolation of Pyran (13) *by Treatment of Dimethyl Xanthophanic Enol with Magnesium Methoxide* (2 *mol*).—Magnesium in anhydrous methanol (25 ml) and the enol (2.0 g) in benzene (25 ml), when treated as above, yielded crystals (635 mg). Recrystallisation from chloroform–ether yielded the yellow *pyran* (13) (243 mg), m.p. 149—150 °C [Found: C, 56.4; H, 4.9%; M^+ 336.084 3 (15). $C_{16}H_{16}O_8$ requires C, 57.1; H, 4.8%; M^+, 336.084 52]; $\nu_{max.}$ 1 749 (pyran ring CO), 1 725 (ester CO), 1 663 (ketone CO), 1 615 (double bond), and 1 570 cm^{-1} (chelated CO); $\nu_{max.}$ (mull) 1 755, 1 729, 1 660, 1 615, and 1 565 cm^{-1}; $\lambda_{max.}$ (0.01N ethanolic sulphuric acid) 258 (ε 6 700) and 372 (14 100) nm; $\lambda_{max.}$ (neutral solution) the same; $\lambda_{max.}$ (0.01N ethanolic potassium hydroxide) 283 (ε 28 100), 320infl. (21 700), 427 (36 900), and 542 (9 600) nm; n.m.r., τ 7.63 (3 H, CH_3CO), 7.25 (3 H, CH_3), 6.08 and 6.05 (6 H, 2 × CH_3O), 2.27 and 2.25 (2 H, *J* 15.3 Hz, *CH*=*CH*), 1.27 (1 H, −*CH*=), and −4.33 (1 H, chelated *OH*).

Comparative spectral data for the isomeric dimethyl xanthophanic enol (1), m.p. 178 °C (from benzene), were $\nu_{max.}$ 1 753 (pyran ring CO), 1 728 (ester CO), 1 688 (ketone CO), 1 648, 1 618 (C=C), and 1 578 (chelated CO) cm^{-1}; $\lambda_{max.}$ (0.01N ethanolic sulphuric acid) 301 (ε 13 100), 437 (19 800), and 530infl. (3 800) nm; $\lambda_{max.}$ (0.01N ethanolic potassium hydroxide) 253 (ε 12 300), 297 (12 000), 320infl. (10 400), 366 (12 000), 498infl. (39 700), and 525 (48 900) nm; τ 7.56 (3 H) and 7.35 (3 H) [CH_3CO and $CH_3C(O)$], 6.13 and 6.03 (2 × ester CH_3CO), 2.23 and 2.07 (*J* 15.0 Hz, CH=CH), 1.31 (pyran −CH=), and −4.61 (chelated OH).

Isolation of Isophthalate (12, R = H) *by Treatment of Dimethyl Xanthophanic Enol with Magnesium Methoxide* (1.5 *mol*).—Magnesium (217 mg) in anhydrous methanol (25 ml) and the enol (2.0 g) in benzene (25 ml) when treated as above yielded five crystal crops [(i) 174 mg, (ii) 1 000 mg, (iii) 84 mg, (iv) 64 mg, and (v) 166 mg]. Crystal crop (i) was recrystallised from chloroform–ether solution and yielded crystals of the pyran (13) (57 mg). Crop (ii) was separated by preparative layer chromatography on silica gel plates using benzene–methanol (95 : 5). This gave the pale yellow *isophthalate* (12, R = H) (120 mg), m.p. 142—144 °C [Found: C, 58.05; H, 5.35%; M^+ (mass spectrum), 350.100 5(16). $C_{17}H_{18}O_8$ requires C, 58.28; H, 5.18%; *M*, 350.100 5]; $\nu_{max.}$ 1 735 (ester CO), 1 690 (ketone CO), 1 635, 1 590, and 1 575 cm^{-1}; $\nu_{max.}$ (mull) 1 735, 1 725, 1 690, 1 630, 1 585, and 1 570 cm^{-1}; $\lambda_{max.}$ (0.01N ethanolic sulphuric acid) 225infl. (ε 17 800), 255 (33 300), 290 (11 000), 300infl. (10 600), and 335 (7 500) nm; $\lambda_{max.}$ (neutral) no change; $\lambda_{max.}$ (0.01N ethanolic potassium hydroxide) 239 (21 800), 286 (24 200), and 402 (6 300) nm; n.m.r., τ 7.94, 7.44, and 7.33 (9 H, CH_3), 7.63 (3 H, CH_3CO), 6.14 and 6.03 (18 H, 6 × CH_3O), 5.21 (1 H, OH), 2.41 and 2.08 (2 H, 2 × −CH=), 1.58 and 1.54 (2 H, aryl-H), and −1.58 (1 H bonded OH). Crystal crops (iii), (iv), and (v) were united and dissolved in methanol; water was added until a precipitate began to form, and the solution was then crystallised at 0 °C. Recrystallisation from aqueous methanol gave the isophthalate (11), m.p. and mixed m.p. 146 °C (lit.,[2] m.p. 148—149 °C) (Found: C, 60.30; H, 4.50. Calc. for $C_{16}H_{14}O_7$: C, 60.40; H, 4.45%), M^+ 318; $\nu_{max.}$ 1 750 (broad, pyran ring CO and aryl ester), 1 625, and 1 590 cm^{-1}; $\nu_{max.}$ (mull) 1 745, 1 690, and 1 581 cm^{-1}; $\lambda_{max.}$ (0.01N ethanolic sulphuric acid) 225 (ε 44 000), 250 (48 600), 303 (25 400), and 335infl. (18 600) nm; $\lambda_{max.}$ (neutral) no change; $\lambda_{max.}$ (0.01N ethanolic potassium hydroxide) 238 (ε 44 000), 286 (46 800), and 440 (12 100) nm; n.m.r., τ 7.28 (3 H, CH_3), 7.15 (3 H, CH_3CO), 6.05 and 5.98 (6 H, 2 × CH_3O), 1.35 (1 H, aryl-H), and 1.14 (1 H, −CH=).

Semi-quantitative Examination of the Products from Treatment of Dimethyl Xanthophanic Enol with 0.5, 0.75, 1, 2, 2.5, 3, 6, *and* 12 *mol of Magnesium Methoxide.*—Solutions of magnesium methoxide in dry methanol (10 ml) were prepared from the appropriate weight of magnesium. Xanthophanic enol (200 mg) in benzene (10 ml) was added and the mixture was set aside at 20 °C for 20 h. After work-up, crystal crops (3—5) were removed, and the components identified. The composition of each crystal crop was estimated semi-quantitatively by t.l.c. using standard solutions prepared from the pure components. Staining was usually with iodine. In appropriate cases the pure components were isolated by crystallisation and the composition of the mother liquors estimated by t.l.c. From these results the data in Table 2 were assembled; the percentages refer to the percentages in the total crystalline material; the total yield of crystalline material is also recorded.

Reactions of the Pyran (13) *and the Isophthalate* (12, R =

H) *with Magnesium Methoxide*.—The pyran (13) (25 mg) in dry benzene (2.5 ml) was added to dry methanol (2.5 ml) containing magnesium methoxide prepared from the amount of magnesium calculated to give 3, 6, and 12 mol and set aside at 20 °C for 20 h. Work-up showed that substantial amounts of the resorcinol (14) were formed in all cases: some pyran (13) remained unreacted (t.l.c.).

A similar experiment using the isophthalate (12, R = H) and 1.5, 3, and 6 mol of magnesium methoxide showed the formation of isophthalate (11), some (12, R = H) remaining unchanged (t.l.c.). Similar treatment of the pure isophthalate (11) showed that it was not further changed.

Semi-quantitative Examination of the Products from Treatment of Dimethyl Xanthophanic Enol with 1, 2, 3, 6, 12, *and* 24 *mol of Sodium Methoxide*.—Solutions of sodium methoxide in dry methanol (10 ml) were prepared from the appropriate weight of sodium. Xanthophanic enol (200 mg) in benzene (10 ml) was added and the mixture was set aside at 20 °C for 20 h. After work-up, crystal crops were collected and their composition examined semi-quantitatively (t.l.c. against standards) with the results shown in Table 2. Examination of the residual gums from which no further crystals could be obtained showed only isophthalate (6, R = H) detectable in those from the 6, 12, and 24 mol reactions. Those from the 2 and 3 mol reactions contained dimethyl xanthophanic enol as well as (6, R = H). That from the 1 mol reaction was dimethylxanthophanic enol containing a trace of (6, R = H).

A specimen of the isophthalate (6, R = H), made by the literature method, had m.p. and mixed m.p. 140 °C (lit.,[2] m.p. 140—141 °C).

Reaction between Magnesium Methoxide (12 *mol*) *and* 3′-*Acetyl*-3,5,3′-*trimethoxycarbonylxanthyrone* (34).—Magnesium methoxide solution [from magnesium (823 mg) and anhydrous methanol (25 ml)] was added to the xanthyrone (1.0 g) in dry benzene (25 ml) and the mixture set aside (7 days). It was then poured into water acidified with hydrochloric acid, extracted with benzene, and evaporated to dryness. P.l.c. silica gel gave bright orange crystals (0.22 g) of the *pyran* (39), m.p. 144 °C [Found: C, 54.62; H, 4.92%; M^+ 366.094 9(15). $C_{17}H_{18}O_9$ requires C, 55.74; H, 4.95%; *M*, 366.095 07]; $\nu_{max.}$ 1 730 (αβ-unsaturated ester), 1 640, 1 605 (C=C), and 1 540 cm^{-1}; $\nu_{max.}$ (mull), 1 725, 1 700, 1 630, 1 590, and 1 530 cm^{-1}; $\lambda_{max.}$ (0.01N ethanolic sulphuric acid) 266 (ε 8 300), 354 (16 600), and 418 (15 000) nm; $\lambda_{max.}$ (neutral) no change; $\lambda_{max.}$ (0.01N ethanolic potassium hydroxide) 275infl. (ε 10 100), 342 (9 500), and 500 (20 200) nm; τ 7.35 (3 H, CH_3), 6.26, 6 24, 6.15 and 6.13 (12 H, 4 × CH_3O), 2.69 and 2.37 (2 H, *J* 10.3 Hz, CH=CH), and 2.08 (1 H, −CH=).

Reaction between Magnesium Methoxide (12 *mol*) *and* 3′,3′-*Diacetyl*-3,5-*dimethoxycarbonylxanthyrone* (35).—Magnesium methoxide solution [from magnesium (867 mg) and anhydrous methanol (25 ml)] was added to the xanthyrone (1.0 g) in dry benzene (25 ml). The product was worked up and purified as above to give orange crystals of the *pyran* (40), m.p. 124 °C [Found: C, 58.45; H, 5.20%; M^+ 350.100 6(17). $C_{17}H_{18}O_8$ requires C, 58.28; H, 5.18%; *M*, 350.100 16]; $\nu_{max.}$ 1 735 (ester CO), 1 700 (ketone CO), 1 620, 1 600 (C=C), and 1 540 cm^{-1}; $\lambda_{max.}$ (0.01N ethanolic sulphuric acid) 268 (ε 6 000), 368 (14 000), and 418infl. (10 600) nm; $\lambda_{max.}$ (neutral) no change; $\lambda_{max.}$ (0.01N ethanolic potassium hydroxide) 273infl. (ε 10 600), 346 (11 300), and 524 (42 300) nm; n.m.r., τ 7.57 (3 H, CH_3CO), 7.41 (3 H, CH_3), 6.30 and 6.15 (9 H, 3 × CH_3O), 2.78 and 2.45 (2 H, *J* 10.3 Hz, C*H*=C*H*), and 2.14 (1 H, −CH=).

Reaction between Magnesium Methoxide (5 *mol*) *and* 3′-*Acetyl*-3′-*ethoxycarbonyl*-5-*methoxycarbonylxanthyrone* (36).—The xanthyrone (36) [5] (308 mg) in methanol (10 ml) was added to a refluxing solution of magnesium (120 mg) dissolved in dry methanol (30 ml). Refluxing was continued for 8 h and the mixture was poured into dilute acid. Extraction with chloroform gave the *pyran* (41) (252 mg), orange needles from chloroform and ether, m.p. 128—129 °C [Found: C, 59.75; H, 5.84%; M^+ 322. $C_{16}H_{18}O_7$ requires C, 59.62; H, 5.63); $\nu_{max.}$ 1 722 and 1 695 (ester); $\lambda_{max.}$ 258, 349, and 410 nm; n.m.r. resonances for one ethyl group, two methyl esters (τ 6.20 and 6.26), an olefin-bonded methyl (τ 7.33) and two AB quartets, the first (τ 2.30 and 2.80, *J* 11 Hz) assigned to the pyran and the second (τ 2.13 and 3.64, *J* 16 Hz) to the side-chain.

Reaction between Sodium Methoxide (10 *mol*) *and* 3′-*Acetyl*-3′-*ethoxycarbonyl*-5-*methoxycarbonylxanthyrone* (36).—The xanthyrone (36) (300 mg) in methanol (10 ml) was refluxed with sodium methoxide (10 mol) in methanol for 8 h and poured into dilute acid. Chromatography on silica gel, eluting with benzene, gave dimethyl 4-hydroxyisophthalate (42), m.p. 95—96 °C, identical (mixed m.p. and spectral comparison) with an authentic specimen.[6]

Reaction of Magnesium Methoxide (12 *mol*) *with* 3′,3′,5-*Triacetyl*-3-*methoxycarbonylxanthyrone* (27).—The xanthyrone (27) (1.0 g) in benzene (25 ml) was treated with magnesium methoxide [from magnesium (907 mg) in dry methanol (25 ml)] at 20 °C for 20 h. Work-up gave the yellow resorcylic ester (25) (650 mg), m.p. and mixed m.p. 136 °C, and spectral comparison (lit.,[2] m.p. 162—163 °C; the original specimen, however, had m.p. 136 °C and retained the value after several crystallisations).

Reaction of Magnesium Methoxide (12 *mol*) *with* 3,3′,3′-*Triacetyl*-5-*methoxycarbonylxanthyrone* (21).—The xanthyrone (21) (1.0 g) in benzene (25 ml) was treated as above to give the resorcylic ester (25), m.p. and mixed m.p. 135 °C, and spectral comparison with the authentic specimen above (Found: C, 60.1; H, 4.85%. Calc. for $C_{16}H_{16}O_7$: C, 60.0; H, 5.1%), M^+ 320.

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