# Chemically and Photochemically Induced Radical Couplings of Xanthyrones and Glaucyrones

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3',3'-Diacetyl-3,5-bismethoxycarbonylxanthyrone (1) undergoes dehydrodimerisation leading to racemic and *meso*-products (3) and (6) from 1'[1'] radical coupling, when treated with manganese dioxide. Also formed is a 2,8-dioxabicyclo[3.2.1]oct-3-ene (7) apparently arising by 1'[3'] coupling followed by cyclisation: the structure is established by X-ray diffraction. A similar bicyclo-system (11) is formed from diethyl 2,4-diacetylglutaconate (10). 3,3'-Diacetyl-5,5'-bismethoxycarbonylglaucyrone (2) undergoes 7[7] radical coupling to give (13) either photochemically in the presence of acetone as hydrogen acceptor, or by one-electron oxidation by manganese dioxide.
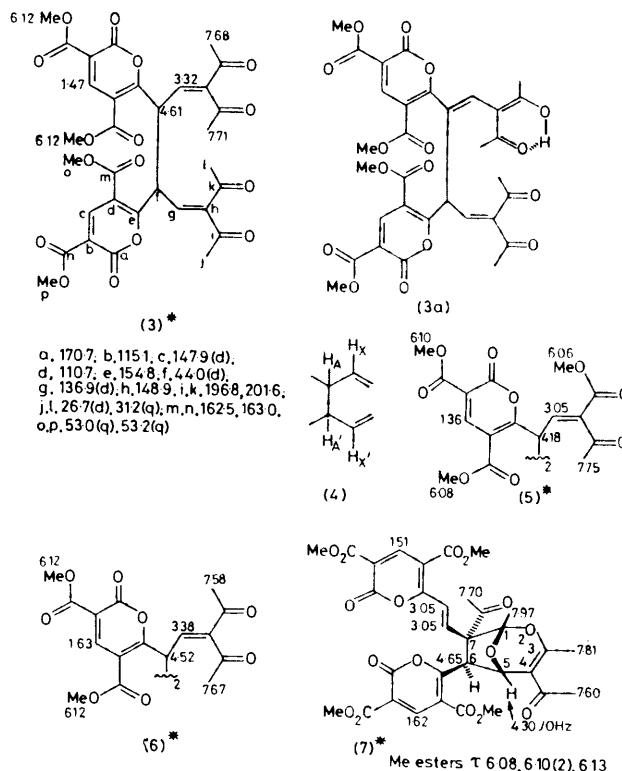
IN previous papers various aspects of the chemistry of xanthyrones and glaucyrones have been considered.[1] It appeared that one-electron transfer reactions might prove of interest and using 3',3'-diacetyl-3,5-bismethoxycarbonylxanthyrone (1) and 3,3'-diacetyl-5,5'-bis-ethoxycarbonylglaucyrone (2) as substrates, we have examined reactions with manganese dioxide in chloroform.

Three compounds A—C were formed from the xanthyrone (1). Compound A, pale yellow, m.p. 195—197 °C, was clearly a dehydro-dimer analysing correctly for $C_{32}H_{30}O_{16}$ and showing an $M - 2H_2O$ peak at 634: the mass spectrum closely resembled that of the substrate

(1)   **(2)**
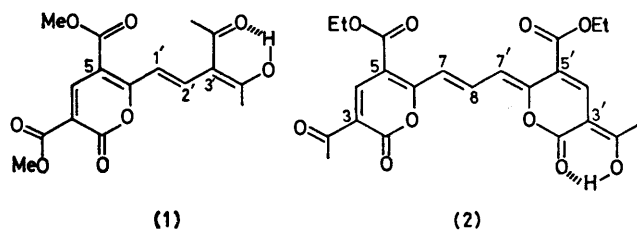
xanthyrone. On prolonged contact with dry silica it decomposed giving (1) together with unstable and unidentified products. I.r. examination confirmed the presence of a substituted 2-pyrone ring, $\nu_{max.}$ 1 770 cm^{-1}, whilst u.v. data, $\lambda_{max.}$ 322 and 243 nm, revealed a less extended chromophore than that of xanthyrone (1). ^{1}H N.m.r. data show that the ' dimer ' A is a symmetrical type containing separate resonances for only half the total number of protons. Further, oxidative coupling does not take place through the 4-position of the pyrone ring in (1) as these signals are still evident. Coupling between 1' and [3'] would not give a symmetrical structure, whilst coupling between 3' and [3'] would necessitate the presence of two identical AB systems in the n.m.r.: these are absent. On the other hand, 1' and [1'] coupling gives a structure (3) which satisfies all the spectral data. Analysis of the multiplets at τ 4.61 and 3.32, treated as an AA'XX' system (4), gave $J_{XX'}$, 0, $J_{AA'}$, 8, J_{AX} 10.44, and $J_{AX'}$, 0.44 Hz, with J_{AX} and $J_{AX'}$ having opposite signs. ^{13}C N.m.r. assignments, appended to (3) are based on our earlier model data [1] and again reveal a symmetrical dehydrodimerisation.

Compound B also formed pale yellow crystals, $C_{32}H_{30}O_{16}$, m.p. 180—183 °C, with u.v. data almost identical with those of A. The i.r. data for A and B are closely similar, differing appreciably only at *ca.* 800 cm^{-1}. ^{1}H

(3) *

a. 170.7; b. 115.1; c. 147.9 (d);
d. 110.7; e. 154.8; f. 440 (d);
g. 136.9 (d); h. 148.9; i,k. 196.8, 201.6;
j,l. 26.7 (d); 312 (q); m,n. 162.5, 163.0;
o,p. 53.0 (q); 53.2 (q)

(4)   **(5) ***

(6) *   **(7) ***

Me esters τ 6.08, 6.10 (2), 6.13

* Close assignments among certain chemically similar groups may be interchanged.

N.m.r. data are given in (6) and it appears that B is a stereoisomer of A: under basic conditions (10% deuterio-pyridine in CDCl$_3$) the two isomers interconvert † and decompose. Analysis of the multiplets at τ 4.52 and 3.31 as an AA'XX' system (4) gave $J_{XX'}$ 0, $J_{AA'}$ 9.5, J_{AX} 11.05, and $J_{AX'}$ 0.55 Hz with J_{AX} and $J_{AX'}$ of opposite

† Spectral examination of (3) and (6) in CDCl$_3$ produced no evidence for enolised forms, *e.g.* (3a): such forms show steric crowding.

sign. Compounds A and B apparently represent racemic and *meso*-forms [2] but assured configurational assignment requires further evidence. Treatment of 3'-acetyl-3,3',5-trismethoxycarbonylxanthyrone with manganese dioxide also effected dehydrodimerisation to compound (5), analogous to (3) and (6), having $J_{AA'}$ 10.0 Hz.

The third compound C obtained by treatment of (1) with manganese dioxide formed crystals, m.p. 138—139 °C, was isomeric with A and B, and appeared to be of particular interest. Although clearly a dehydrodimer of (1) in which evidence for two 3,5-dimethoxycarbonyl-2-pyrone units, two olefinic protons, two acetyls, and two further methyls could be discerned spectroscopically, a structural solution for C could not be obtained with certainty by these means. Structure analysis by single-crystal X-ray direct methods showed that C was the substituted 2,8-dioxabicyclo[3.2.1]oct-3-ene (7) (see Figure 1). ¹H N.m.r. assignments are given on (7) and it is noted that the torsion angle between 5- and 6-H is ca. 90° giving zero coupling and the 1',2'-hydrogens have fortuitously identical chemical shifts, points which caused difficulty in deducing the structure by spectral means.

The Scheme summarises mechanistic proposals for the

On the basis of ¹H and ¹³C comparison with (7) it is formulated as (11) though the stereochemistry of the molecules is not known.

(10)

(11)*   (12)
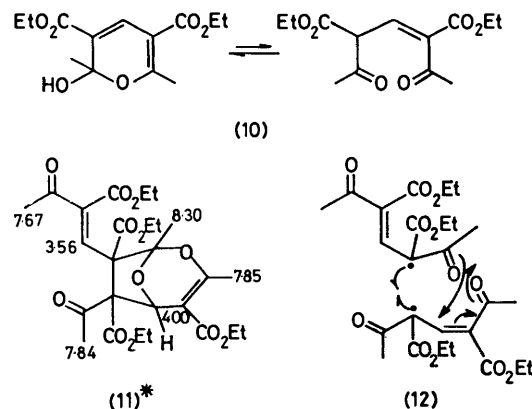
When shaken with manganese dioxide in ethanol-free chloroform 3,3'-diacetyl-5,5'-bisethoxycarbonylglaucyrone (2) initially develops an intense purple colour and after ca. 10 min a didehydro-dimer, m.p. 190—200 °C (decomp.), can be isolated as yellow needles. The same
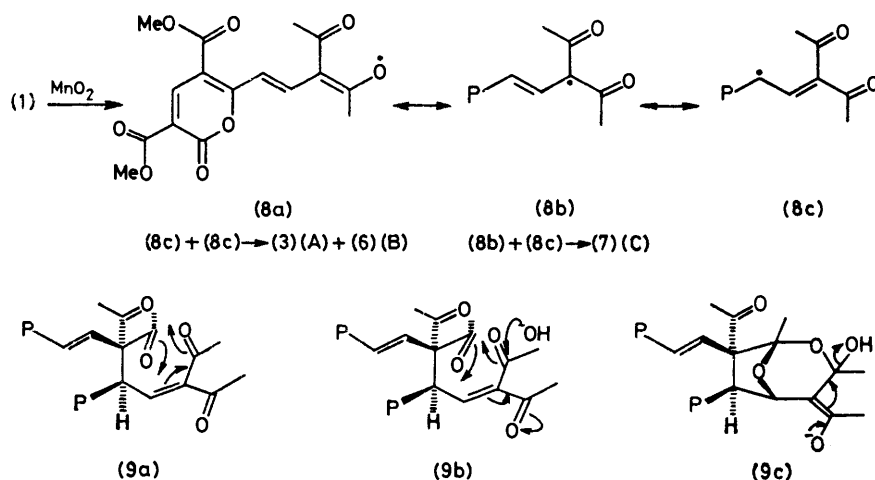
Scheme Formation of dehydro-dimers A–C (P = 3,5-dimethoxycarbonyl-2-pyrone residue)

formation of A—C. The radical generated by one-electron transfer (8a) can be delocalised to 3' (8b) or 1' (8c). Coupling of (8c) with itself gives the racemic and *meso-*' dimers' A and B. Coupling of (8b) and (8c) however leads to compound (9a) which may then undergo cyclisation to give C. This cyclisation may be represented as a rather unusual [2 + 4] electrocyclisation, perhaps metal catalysed with the *cis*-pyrone and styryl-pyrone residues exerting a favourable electronic interaction with each other. Alternatively an ionic process proceeding *via* (9b and c) may be written and this could be initiated by hydroxide ions present on the surface of the manganese dioxide. Diethyl 2,4-diacetylgluta-conate (10) gives a similar dehydro-dimer in low yield when treated with manganese dioxide in chloroform.

' dimer ' can be obtained photochemically by allowing a saturated solution of (2) in acetone to stand in glass apparatus in sunlight for 2—3 days, the initial red colour slowly discharging. Photolysis in oxygen-free dry acetone under nitrogen still produced the dimer but it was not formed in benzene or ethanol until 5% acetone was added as a hydrogen acceptor.

The mass spectral fragmentation of the new ' dimer ', formulated as (13), was very similar to glaucyrone (2) up to 458 a.m.u. but above this, signal intensity fell to ca. 1% of the lower mass fragments. An M^+ ion at ca. 914 was found but could not be accurately measured because of the low intensity: vapour pressure osmometry in chloroform however confirmed that two molecules of (2) were involved in the formation of (13).

Adsorption on silica or heating in ethanol or dioxan caused formation of (2) from (13). I.r. data (KBr) indicated the presence of 2-pyrone (1 750), ester (1 720), and conjugated ketone (1 685 cm^{-1}) as structure elements and the u.v. absorption, $\lambda_{max.}$ (CHCl$_3$) 357 and 250 nm, showed the broken conjugation relative to (2) ($\lambda_{max.}$ 503 nm).

^{1}H N.m.r. assignments (CDCl$_3$) are given on (13) and

(13)*
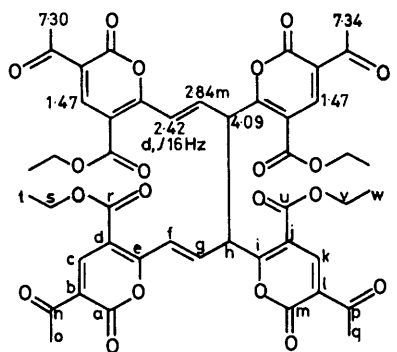
Esters: τ 5·54(q), 5·66(q)
8·50(t), 8·59(t,J8Hz)

a,m,171·0,170·8; b,l,121·6; c,k,147·3(d),147·9(d);
d(d'), j,111·1,111·8,109·7; e,i, 157·5,157·4;
f(f'),125·7(d),126·4(d); g(g'),138·7(d),138·2(d);
h,46·9d; n,p,193·9,193·6; o,q,30·2;
r,u,164·8,162·5; s,v, 62·8(t),62·2(t);
t,w,14·2(q)

have been made using 3-acetyl-5-methoxycarbonyl-6-methyl-2-pyrone and 3-acetyl-3',3',5-trismethoxycarbonylxanthyrone as models.[1] The signal at τ 1.47, integrating for four protons, is assigned to the 4-positions of four similar 2-pyrone rings and rules out radical coupling there. Two types of acetyl and ethyl ester signals in 1 : 1 ratio signify two types of pyrone ring. Because of the molecular symmetry, only coupling from position 7 to [7], equivalent to 7' to [7'] or 7 to [7'], satisfies the spectral data, leading to structure (13), generated via the 7-localised radical [see (14)]
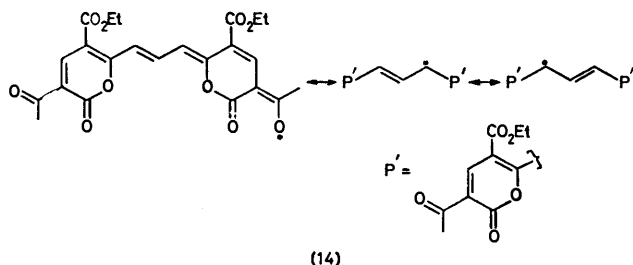
(14)

produced chemically or photochemically. The ^{1}H n.m.r. data indicate a molecule with trans-double bonds (J 16 Hz) and chemical shifts for the two halves about the dimer axis the same. Although apparently a single diastereoisomer, there is not complete symmetry in the ^{13}C spectrum since the olefinic carbons f,[f'] and g,[g'] are doubled. It is suggested, however, that this may be

due to restriction of rotation due to steric effects giving two conformers stable enough for observation, rather than contamination by a second diastereoisomer. This tends to be supported by the observation that crude material from the reaction of (1) with manganese dioxide showed an additional ^{1}H n.m.r. multiplet at
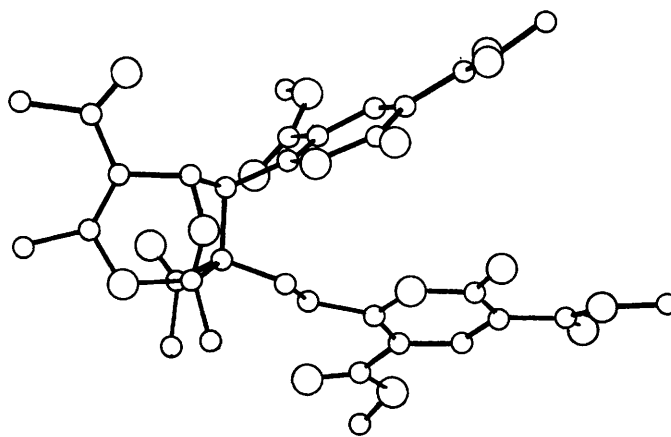
FIGURE 1 X-Ray Structure of ' dimer ' C(7) formed
from (1)

τ 4.13, ca. 20% of the intensity of the multiplet at τ 3.98 in the ' dimer ' above. The additional signal was lost on standing or recrystallisation and this appeared to represent the second diastereoisomer.

X-Ray Examination of ' Dimer' (7).—The crystal structure of the dimer was determined by direct methods from four-circle diffractometer data and refined by
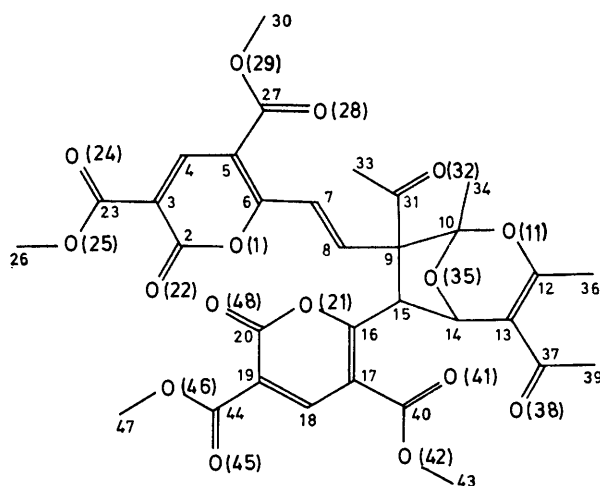
FIGURE 2 ' Dimer ' C(7). Crystallographic numbering

least-squares and difference-Fourier methods to R 10.2%. The poor R value is due to the presence of a disordered chloroform molecule of solvation. The resulting molecular structure is shown in Figure 1 revealing the dimer bridging pattern. For crystallographic purposes the numbering scheme of Figure 2 was adopted and bond lengths and angles are displayed in Figures 3 and 4 together with an indication of their standard deviations.

These adopt broadly expected values although several bond angles at sp^2 hybridised carbons are rather distorted by the close proximity of bulky groups. Both

FIGURE 3 ' Dimer ' C (7). Bond lengths (Å)

pyrone rings are essentially planar although their substituents are rotated slightly out of conjugation for steric reasons as can be seen for the torsion angles (Table 1). The largest twist, about the C(17)—C(40) bond, is

FIGURE 4 ' Dimer ' C (7). Bond angles (°)

27°. In the five-six-fused ring system the five-membered ring adopts the envelope conformation with O(35) out of the plane of the other atoms. The six-membered ring also shows five approximately coplanar atoms with O(35) out of the plane. The resulting torsion angles at the ring junction (Table 1) imply a torsion angle for H(14)—C(14)—C(15)—H(15) of ca. 90° accounting for the absence of coupling between these hydrogens in the n.m.r. (Karplus equation).

TABLE 1

Torsion angles (°) of ' dimer ' C (7)

C(6)—O(1)—C(2)—C(3)	3.2
C(2)—O(1)—C(6)—C(7)	—174.1
C(22)—C(2)—C(3)—C(4)	178.3
C(23)—C(3)—C(4)—C(5)	—177.0
C(4)—C(3)—C(23)—O(24)	11.2
C(3)—C(4)—C(5)—C(27)	—175.6
C(27)—C(5)—C(6)—O(1)	174.2
C(4)—C(5)—C(27)—O(29)	—3.6
O(1)—C(6)—C(7)—C(8)	—18.9
C(7)—C(8)—C(9)—C(10)	145.7
C(8)—C(9)—C(10)—O(11)	—149.6
C(15)—C(9)—C(10)—O(11)	93.8
C(31)—C(9)—C(10)—O(11)	—22.6
C(8)—C(9)—C(15)—C(14)	—124.6
C(10)—C(9)—C(15)—C(16)	116.5
C(8)—C(9)—C(31)—O(32)	—126.7
C(10)—C(9)—C(31)—C(33)	—70.7
C(9)—C(10)—O(11)—C(12)	—77.5
C(9)—C(10)—O(35)—C(14)	46.8
C(10)—O(11)—C(12)—C(13)	—0.7
O(11)—C(12)—C(13)—C(37)	174.3
C(12)—C(13)—C(14)—C(15)	79.4
C(37)—C(13)—C(14)—O(35)	151.4
C(14)—C(13)—C(37)—O(38)	14.2
C(13)—C(14)—C(15)—C(16)	152.9
C(13)—C(14)—O(35)—C(10)	67.3
C(9)—C(15)—C(16)—O(21)	—82.6
C(15)—C(16)—C(17)—C(18)	173.0
O(21)—C(16)—C(17)—C(40)	178.1
C(16)—C(17)—C(18)—C(19)	2.6
C(16)—C(17)—C(40)—O(42)	153.2
C(17)—C(18)—C(19)—C(20)	1.2
C(18)—C(19)—C(20)—O(48)	176.0
C(18)—C(19)—C(44)—O(45)	—8.1
C(20)—C(19)—C(44)—O(46)	—7.6
C(3)—C(23)—O(25)—C(26)	—178.6
O(28)—C(27)—O(29)—C(30)	0.2
C(19)—C(44)—O(46)—C(47)	—174.5
C(6)—O(1)—C(2)—O(22)	—179.2
O(1)—C(2)—C(3)—C(4)	—4.6
O(22)—C(2)—C(3)—C(23)	—3.9
C(2)—C(3)—C(23)—O(24)	—166.6
C(4)—C(3)—C(23)—O(25)	—165.6
C(4)—C(5)—C(6)—O(1)	—6.3
C(27)—C(5)—C(6)—C(7)	—10.1
C(6)—C(5)—C(27)—O(28)	—5.8
C(5)—C(6)—C(7)—C(8)	—165.2
C(7)—C(8)—C(9)—C(15)	—102.8
C(8)—C(9)—C(10)—C(34)	—30.7
C(15)—C(9)—C(10)—C(34)	—147.2
C(31)—C(9)—C(10)—C(34)	96.4
C(8)—C(9)—C(15)—C(16)	—2.7
C(31)—C(9)—C(15)—C(14)	109.8
C(8)—C(9)—C(31)—C(33)	56.1
C(15)—C(9)—C(31)—O(32)	—3.6
C(34)—C(10)—O(11)—C(12)	155.8
O(11)—C(10)—O(35)·C(14)	—70.3
C(10)—O(11)—C(12)—C(36)	176.8
C(36)—C(12)—C(13)—C(14)	—177.4
C(12)—C(13)—C(14)—O(35)	—33.2
C(12)—C(13)—C(37)—O(38)	—160.6
C(14)—C(13)—C(37)—C(39)	—162.9
O(35)—C(14)—C(15)—C(9)	32.3
C(15)—C(14)—O(35)—C(10)	—50.3
C(14)—C(15)—C(16)—C(17)	—143.5
C(15)—C(16)—C(17)—C(40)	—5.0
C(15)—C(16)—O(21)—C(20)	—175.8
C(40)—C(17)—C(18)—C(19)	—179.4
C(18)—C(17)—C(40)—O(41)	153.4
C(17)—C(18)—C(19)—C(44)	—176.9
C(44)—C(19)—C(20)—O(21)	174.6
C(18)—C(19)—C(44)—O(46)	170.3
C(19)—C(20)—O(21)—C(16)	2.1
O(24)—C(23)—O(25)—C(26)	4.6
C(17)—C(40)—O(42)—C(43)	—178.2
O(45)—C(44)—O(46)—C(47)	3.9
C(2)—O(1)—C(6)—C(5)	2.2
O(1)—C(2)—C(3)—C(23)	173.1

TABLE 1 (continued)

C(2)–C(3)–C(4)–C(5)	0.9
C(2)–C(3)–C(23)–O(25)	16.6
C(3)–C(4)–C(5)–C(6)	4.8
C(4)–C(5)–C(6)–C(7)	169.4
C(4)–C(5)–C(27)–O(28)	174.7
C(6)–C(5)–C(27)–O(29)	175.9
C(6)–C(7)–C(8)–C(9)	169.9
C(7)–C(8)–C(9)–C(31)	21.0
C(8)–C(9)–C(10)–O(35)	92.1
C(15)–C(9)–C(10)–O(35)	–24.4
C(31)–C(9)–C(10)–O(35)	–140.8
C(10)–C(9)–C(15)–C(14)	–5.4
C(31)–C(9)–C(15)–C(16)	–128.3
C(10)–C(9)–C(31)–O(32)	106.5
C(15)–C(9)–C(31)–C(33)	179.2
O(35)–C(10)–O(11)–C(12)	37.7
C(34)–C(10)–O(35)–C(14)	174.6
O(11)–C(12)–C(13)–C(14)	–0.4
C(36)–C(12)–C(13)–C(37)	–2.7
C(37)–C(13)–C(14)–C(15)	–96.0
C(12)–C(13)–C(37)–C(39)	22.3
C(13)–C(14)–C(15)–C(9)	–83.5
O(35)–C(14)–C(15)–C(16)	–91.3
C(9)–C(15)–C(16)–C(17)	100.3
C(14)–C(15)–C(16)–O(21)	33.5
O(21)–C(16)–C(17)–C(18)	–3.9
C(17)–C(16)–O(21)–C(20)	1.6
C(16)–C(17)–C(40)–O(41)	–28.6
C(18)–C(17)–C(40)–O(42)	–24.8
C(18)–C(19)–C(20)–O(21)	–3.3
C(44)–C(19)–C(20)–O(48)	–6.1
C(20)–C(19)–C(44)–O(45)	173.9
O(48)–C(20)–O(21)–C(16)	–177.4
C(5)–C(27)–O(29)–C(30)	178.5
O(41)–C(40)–O(42)–C(43)	3.7

EXPERIMENTAL

Oxidation of 3',3'-Diacetyl-3,5-bismethoxycarbonylxanthy-rone (1) *with Manganese Dioxide.*—The xanthyrone (1) (1 g) in ethanol-free chloroform (75 ml) was shaken (3 h) with activated manganese dioxide (18 g). (The latter reagent was prepared in aqueous solution by the potassium per-manganate–manganese sulphate method and baked at 100 °C for at least 3 days).[3] Filtration and evaporation of the chloroform gave a solid which, crystallised three times from chloroform–ether, gave '*dimer A*' (3) (42 mg), m.p. 195—197 °C (Found: C, 57.25; H, 4.8. $C_{32}H_{30}O_{16}$ requires C, 57.3; H, 4.5%), $\nu_{max.}$ (KBr) 1 770, 1 715, 1 665, 1 623, and 1 550 cm^{-1}, $\lambda_{max.}$ (CHCl$_3$) 243 (ε 24 600) and 322 (22 300) nm.

Continued crystallisation of material from the mother liquors gave '*dimer C*' (7) (38 mg), m.p. 138—139 °C (Found: C, 57.3; H, 4.75%), $\nu_{max.}$ (KBr) 1 770, 1 709, 1 630, and 1 555 cm^{-1}, $\lambda_{max.}$ (CHCl$_3$) 252 (ε 22 000), 328 (15 400), and 351infl. (11 000) nm, δ_C 197.8 (s), 193.5 (s), 171.5 (s), 164.7 (s), 162.9 (s), 162.6 (s), 161.9 (s), 148.8 (d), 140.2 (d), 123.8 (d), 116.7 (s), 115.4 (s), 114.6 (s), 111.4 (s), 109.8 (s), 108.3 (s), 78.8 (s), 76.3 (d), 57.1 (d), 52.8 (q), 30.2 (q), 28.2 (q), 21.5 (q), and 19.7 (q) p.p.m.

Further crystallisation gave '*dimer B*' (6) (17 mg), m.p. 180—183 °C (decomp.) (Found: C, 57.3; H, 4.7%), $\nu_{max.}$ (KBr) 1 770, 1 710, 1 665, and 1 550 cm^{-1}; $\lambda_{max.}$ (CHCl$_3$) 243 (ε 24 800) and 322 (22 400) nm.

Oxidation of 3'-Acetyl-3,3',5-trismethoxycarbonylxanthy-rone with Manganese Dioxide.—The xanthyrone (2 g) in chloroform (200 ml) was shaken with activated manganese dioxide (20 g) for 2 h. Filtration and evaporation gave a solid containing a number of compounds of rather similar polarity. Four crystallisations from chloroform–ether

gave the '*dimer*' (5) (42 mg), crystals, m.p. 189—190 °C (Found: C, 54.5; H, 4.35%; M^+, 702. $C_{32}H_{30}O_{18}$ requires C, 54.7; H, 4.25%, M, 702), $\nu_{max.}$ (KBr) 1 775, 1 720, 1 680, 1 630, and 1 560 cm^{-1}, $\lambda_{max.}$ (CHCl$_3$) 243 (ε 19 800) and 328 (17 000) nm.

Oxidation of Diethyl 2,4-Diacetylglutaconate (10) *with Manganese Dioxide.*—The glutaconate (10)[4] (5 g) was shaken in chloroform with active manganese dioxide (50 g) for 3 days. Filtration and evaporation gave an oil which crystallised from ether–n-hexane as needles of '*dimer*' (11) (50 mg), m.p. 146—147 °C (Found: C, 57.9; H, 6.35%; M^+, 538. $C_{26}H_{34}O_{12}$ requires C, 58.0; H, 6.3%; M, 538), $\nu_{max.}$ (KBr) 1 734, 1 724, 1 706, 1 687, and 1 640 cm^{-1}, $\lambda_{max.}$ 239 (ε 12 500) nm. For ¹H n.m.r. data see (11) together with four ester ethyls, τ 8.68, 8.72, 8.76, 8.80 (12 H) and 5.78—5.82 (8 H) (all J 7 Hz). The ¹³C spectrum shows two ketone carbonyls, δ 197.3 (s) and 194.3 (s) p.p.m., four ester carbonyls, δ 167.7 (s), 166.5 (s), 165.1 (s), and 164.3 (s) p.p.m., one olefinic CH, δ 139.9 (d) p.p.m., a further CH, δ 78.3 (d) p.p.m., and a total of eight methyls, δ 29.0, 27.1, 21.1, 18.7, 14.4, 13.9, 13.7, and 13.5 (all q) p.p.m.

Irradiation Experiments using 3,3'-Diacetyl-5,5'-bisethoxy-carbonylglaucyrone (2).—The glaucyrone (2) (2 g) in acetone (400 ml) was exposed to sunlight (3 days) in Pyrex glass apparatus. The initial red colour disappeared and crystals formed. Recrystallisation of the latter from chloroform–ether gave '*dimer*' (13) (450 mg), m.p. 190—200° (decomp.), as yellow needles (Found: C, 60.15; H, 4.7. $C_{46}H_{42}O_{20}$ requires C, 60.35; H, 4.6%), $\nu_{max.}$ (KBr), 1 750, 1 720, and 1 685 cm^{-1}, $\lambda_{max.}$ (CHCl$_3$) 250 (ε 37 000) and 357 (37 400) nm.

Photolysis of (2) (0.2 g) in degassed acetone (40 ml) under nitrogen, as above, gave (13) (41 mg).

Photolysis of (2) (0.2 g) in benzene (50 ml) using a 600-W tungsten-filament quartz-halogen lamp for 12 h produced no apparent reaction. Addition of acetone (2.5 ml) and further photolysis (30 min) gave dimer (13) (32 mg).

Oxidation of 3,3'-Diacetyl-5,5'-bisethoxycarbonylglaucyrone (2) *with Manganese Dioxide.*—The glaucyrone (2) (0.2 g) in chloroform (40 ml) was shaken with active manganese dioxide (2 g) for 30 min as above. The solution turned violet and then pale yellow. Filtration, evaporation, and crystallisation gave the '*dimer*' (13) (136 mg), m.p. and mixed m.p. with the specimen above 192—205 °C: spectral comparison confirmed the identity. ¹H N.m.r. on the fresh crude crystallisation residue showed an additional symmetrical multiplet at τ 4.13 which integrated as 20% of the similarly structured multiplet at τ 3.98: the extra resonance was lost on standing or recrystallisation.

*Degradation of '*Dimer*'* (13) *by Silica.*—A solution of the '*dimer*' (80 mg) in chloroform was absorbed on dry column silica (HF 254) and the excess of solvent was allowed to evaporate. After 2 h, the treated silica was packed on top of a dry column of the same type of silica and eluted with chloroform–acetone–acetic acid (5 : 5 : 0.1). Early frac-tions of unchanged dimer were followed by a blue band of (2) (15 mg), m.p. and mixed m.p. 186—187 °C (lit.,[1] 188—189°), and i.r. comparison with authentic material. There followed a cherry-red band which was unstable: t.l.c. indicated at least three components.

Crystal Structure Determination.—Suitable single crystals were prepared by recrystallisation from chloroform–ether. Unit cell dimensions and space group were established from oscillation and Weissenberg photographs. For intensity measurement a crystal of approximate dimensions 0.2 ×

0.25 × 0.35 mm was mounted on an automatic computer-controlled, four-circle diffractometer. Unit-cell dimensions were refined by a least-squares fit on the positions of 23 peaks found on the diffractometer. Intensity data were collected with Mo-K_α radiation for $2\theta \leqslant 50°$ by use of an ω—2θ scan. Reflections with a net count greater than 3.0σ were considered observed and used in the subsequent structure refinement. A total of 6 419 independent reflections was measured of which 4 106 were considered observed. No absorption corrections were made. Data reduction and subsequent crystallographic calculations were performed using the CRYSTALS system of programs.[5] Atomic scattering factors were taken from ref. 6.

Crystal data. $C_{34}H_{30}O_{14}$,$CHCl_3$, $M = 782.004$. Triclinic, $a = 9.791(2)$, $b = 13.955(3)$, $c = 16.053(4)$ Å, $\alpha = 102.03(2)$, $\beta = 98.57(2)$, $\gamma = 117.73(2)°$, $U = 1 817.15$ Å³, $Z = 2$, $D_c = 1.43$ g cm⁻³, $F(000) = 808$. Space group $P\bar{1}$ assumed and verified by subsequent refinement; Mo-K_α radiation, $\lambda = 0.710 69$ Å, $\mu(\text{Mo-}K_\alpha) = 3.26$ cm⁻¹.

The structure was solved by direct methods using the SHELX program.[7] 563 Reflections with $E > 1.6$ were used and the best set of phases produced were used in an E-map which revealed the positions of 45 of the 48 non-hydrogen atoms in the molecule. The remaining three atoms were readily located in a difference-map following a structure-factor calculation. Four cycles of full-matrix least-squares refinement of atomic positions and isotropic temperature factors only lowered the agreement factor R to 0.237. Another difference map was calculated which revealed the presence of a chloroform molecule of solvation

TABLE 2

' Dimer ' C (7) atomic co-ordinates and their standard deviations

Atom	x/a	y/b	z/c
O(1)	0.335 9(5)	0.266 9(4)	−0.041 3(3)
C(2)	0.422 9(8)	0.257 8(6)	0.032 8(4)
C(3)	0.450 5(7)	0.335 8(5)	0.116 0(4)
C(4)	0.406 4(7)	0.414 6(5)	0.119 5(4)
C(5)	0.328 9(7)	0.423 1(5)	0.041 6(4)
C(6)	0.288 1(7)	0.344 5(5)	−0.037 5(4)
C(7)	0.186 5(8)	0.324 9(5)	−0.123 5(4)
C(8)	0.181 2(7)	0.263 4(5)	−0.199 7(4)
C(9)	0.061 5(7)	0.225 9(5)	−0.286 9(4)
C(10)	0.134 0(8)	0.221 9(5)	−0.367 7(4)
O(11)	0.051 5(6)	0.246 2(4)	−0.435 6(3)
C(12)	−0.098 2(9)	0.159 9(6)	−0.486 8(4)
C(13)	−0.164 0(8)	0.057 4(6)	−0.475 0(4)
C(14)	−0.063 8(7)	0.043 0(5)	−0.403 2(4)
C(15)	−0.071 2(7)	0.095 7(5)	−0.310 6(4)
C(16)	−0.044 0(7)	0.038 9(5)	−0.244 7(4)
C(17)	−0.114 1(8)	0.017 0(5)	−0.180 0(4)
C(18)	−0.084 4(8)	−0.048 5(5)	−0.131 9(4)
C(19)	0.015 3(8)	−0.086 6(5)	−0.145 5(4)
C(20)	0.100 5(8)	−0.057 6(6)	−0.212 0(4)
O(21)	0.060 8(5)	0.003 5(4)	−0.258 9(3)
O(22)	0.454 8(8)	0.185 9(5)	0.015 9(3)
C(23)	0.523 7(9)	0.332 4(6)	0.203 5(4)
O(24)	0.522 6(8)	0.381 8(6)	0.272 4(4)
O(25)	0.596 2(8)	0.273 3(5)	0.195 6(3)
C(26)	0.666 5(15)	0.264 2(9)	0.277 6(6)
C(27)	0.291 4(9)	0.516 4(6)	0.046 4(4)
O(28)	0.236 7(8)	0.534 8(5)	−0.015 5(3)
O(29)	0.331 9(8)	0.577 8(5)	0.129 6(3)
C(30)	0.304 8(15)	0.674 8(9)	0.143 5(6)
C(31)	−0.017 7(8)	0.299 0(5)	−0.289 3(4)
O(32)	−0.159 0(6)	0.257 9(4)	−0.310 9(3)
C(33)	0.090 6(10)	0.426 0(6)	−0.267 2(5)
C(34)	0.311 9(9)	0.306 0(7)	−0.350 6(5)
O(35)	0.102 8(5)	0.111 7(4)	−0.398 5(3)
C(36)	−0.168 9(12)	0.201 6(8)	−0.549 6(5)

TABLE 2 *(continued)*

Atom	x/a	y/b	z/c
C(37)	−0.327 1(9)	−0.040 7(7)	−0.518 4(5)
O(38)	−0.379 6(7)	−0.114 8(6)	−0.483 0(4)
C(39)	−0.433 0(11)	−0.060 6(9)	−0.605 7(6)
C(40)	−0.226 3(9)	0.057 3(6)	−0.160 1(4)
O(41)	−0.220 4(7)	0.140 9(5)	−0.172 3(4)
O(42)	−0.329 1(6)	−0.009 6(4)	−0.125 1(4)
C(43)	−0.448 4(10)	0.016 0(8)	−0.104 7(6)
C(44)	0.029 8(8)	−0.159 8(6)	−0.093 9(5)
O(45)	−0.030 3(7)	−0.175 6(5)	−0.034 8(4)
O(46)	0.111 7(7)	−0.208 1(5)	−0.120 9(4)
C(47)	0.117 6(11)	−0.288 5(7)	−0.079 1(6)
O(48)	0.198 0(7)	−0.077 6(5)	−0.231 0(4)
H(4)	0.4276	0.4684	0.1782
H(7)	0.1127	0.3585	−0.1245
H(8)	0.2654	0.2402	−0.1983
H(4)	−0.0943	−0.0398	−0.4175
H(14)	−0.1807	0.0847	−0.3082
H(15)	−0.1412	−0.0672	−0.0843
H(26A)	0.7198	0.2192	0.2678
H(26B)	0.7463	0.3420	0.3227
H(26C)	0.5774	0.2240	0.3064
H(30A)	0.3345	0.7151	0.2080
H(30B)	0.3605	0.7257	0.1115
H(30C)	0.1810	0.6420	0.1183
H(33A)	0.1798	0.4254	−0.2960
H(33B)	0.1878	0.4726	−0.2218
H(33C)	0.1106	0.4405	−0.3345
H(34A)	0.3425	0.2952	−0.4066
H(34B)	0.3325	0.3863	−0.3290
H(34C)	0.3779	0.2950	−0.3039
H(36A)	−0.1620	0.1801	−0.6041
H(36B)	−0.1373	0.2597	−0.5330
H(36C)	−0.2968	0.1741	−0.5411
H(39A)	−0.3669	−0.0411	−0.6572
H(39B)	−0.4515	−0.0038	−0.5973
H(39C)	−0.6452	−0.1572	−0.6211
H(43A)	−0.5229	−0.0414	−0.0793
H(43B)	−0.5182	0.0132	−0.1602
H(43C)	−0.3968	0.0942	−0.0603
H(47A)	0.1768	−0.3223	−0.1040
H(47B)	0.0006	−0.3548	−0.0899
H(47C)	0.1649	−0.2521	−0.0130
C(51)	0.310(2)	0.433(1)	0.390 0(9)
Cl(52)	0.303(1)	0.502(1)	0.488 4(6)
Cl(53)	0.186(1)	0.430(2)	0.307 2(6)
Cl(54)	0.247(2)	0.292(1)	0.387 5(8)

as weak diffuse peaks suggesting disorder. The chloroform was then included in the least-squares refinement which was later extended to anisotropic vibrations. After apparent convergence with R 0.133 a further difference map was calculated. The major features of this map were peaks in the neighbourhood of the chloroform molecule suggesting alternative orientations of the molecule. Attempts to refine more than one orientation of this molecule with occupation fractions were not successful and were abandoned. The difference-map also revealed the approximate positions of the hydrogen atoms. These positions were then calculated from geometrical considerations and included in subsequent structure-factor calculations without refinement. Further refinement, using a Chebyshev weighting scheme in the last cycles, finally converged when the largest parameter shifts were less than 0.4σ, lowering R to 0.102. A final difference-map was then calculated. This contained several peaks of 1.0 e Å⁻³ in the neighbourhood of the chloroform molecule which also had very high temperature factors. This disordered molecule of solvation accounts for the disappointingly large final R value. The difference map showed no peaks or depressions > 0.3 e Å⁻³ away from this feature. Final atomic co-ordinates are listed in Table 2; temperature factors and observed and calculated structure

factors are listed in Supplementary Publication No. SUP 22877 (48 pp.).*

* For details of Supplementary Publications, see Notice to Authors No. 7 in *J.C.S. Perkin I,* 1979, Index Issue.

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