Intramolecular Oxidative Coupling in Methylene-bis-1,3-cyclohexanediones with Iron(III)hexacyanoferrate(III) *

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Methylene-bis-dimedone (Ia) on treatment with a solution containing equimolar proportions of iron(III) chloride and potassium hexacyanoferrate(III) undergoes intramolecular oxidative carbon-oxygen coupling with formation of the previously described spirane enol ether IIIa. On similar treatment, methylene-bis-1,3-cyclohexanedione (Ib) undergoes both carbon-oxygen and carbon-carbon coupling, giving a mixture of the enol ether IIIb and the isomeric dispiro-cyclopropane derivative IIb which was isolated as the cyclic hydrate IVa (or Va), characterised as the dimethoxy compound IVb. The reaction products formed from IVa by thermal decomposition (IIb, VI) have been studied.

It has long been recognised that both inter- and intramolecular carbon-carbon and carbon-oxygen coupling of phenols can occur on treatment with one-electron acceptors such as iron(III) chloride, potassium hexacyanoferrate(III), or manganese(IV) oxide. In the last decades, these reactions have received renewed attention both from biogenetic and synthetic viewpoints, and several comprehensive reviews [2-5] have been published. Resonance stabilised phenol radicals are generally postulated as intermediates.

Analogous oxidative couplings of β-dicarbonyl compounds have been discussed [2,6] and recent literature gives only rare examples of successful coupling reactions of compounds of this and related types. The dimer of the reactive 2-phenyl-1,3-indandione has been obtained by Behringer, Galton and Huang [7] using potassium hexacyanoferrate(III) and by Becker [8] using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as electron acceptors, evidently by one-electron transfer reactions. Johnston and Stride [9] claim to have obtained dimers of several cyclic β-diketones by means of anodic oxidation in aqueous or aqueous-methanolic sodium hydroxide solutions. However, Åkermark [10] who studied the behaviour of dimedone under Kolbe conditions reports the isolation only of a mixture of trimeric products and of substantial amounts of methylene-bis-dimedone.

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* Preliminary communication: Ref. 1.

It appears however that the oxidants commonly used in phenol chemistry are of little value as electron acceptors for most enolisable β-dicarbonyl compounds.

The present studies were initiated following an observation that an aqueous solution containing equimolar proportions of iron(III) chloride and potassium hexacyanoferrate(III) is rapidly reduced by various enolisable β-dicarbonyl compounds which fail to react with either component alone. Such a solution has been recommended as a spraying reagent for reducing compounds in paper chromatography.[11] It seems reasonable to assume that its pronounced oxidising properties are due to the formation in the solution of the red-brown iron(III) hexacyanoferrate(III) as a neutral, soluble and highly reactive complex. The existence and properties of this complex have recently been discussed by de Wet and Rolle.[12] It readily undergoes one-electron transfer reaction with formation of "Berlin Blue", $Fe^{III}K[Fe^{II}(CN)_6]$. Even bromide in neutral solution may serve as an electron donor in the reduction of the complex.

In the present investigation, methylene-bis-dimedone (Ia) and its lower homologue, methylene-bis-1,3-cyclohexanedione (Ib), were chosen as simple model compounds. Fairly dilute solutions (*ca.* 0.005 M) of both enols have been used in order to avoid complications due to intermolecular coupling reactions. By analogy with mechanisms suggested for similar oxidations of phenols [2-5] and enols,[6-8] Ia and Ib should react *via* short-lived resonance stabilised diradicals which undergo carbon-carbon or carbon-oxygen intramolecular coupling with formation of a cyclopropane derivative (II) or of a spiro-type cyclic enol ether (III) as shown in Scheme 1.
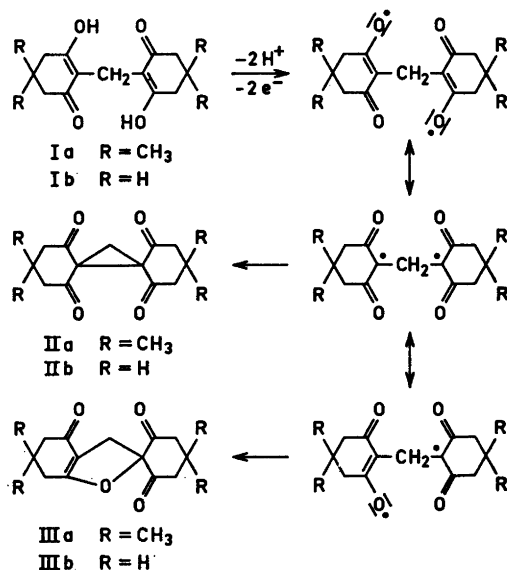
Scheme 1.

Methylene-bis-dimedone (Ia) when treated for 6 h in aqueous acetic acid solution with a moderate excess of the iron(III) hexacyanoferrate(III) reagent gave a single product, $C_{17}H_{22}O_4$, m.p. 214—215°C, in 28 % yield. This compound is obviously identical with a compound m.p. 211—212°C synthesised by Radulescu and Georgescu [13] from the disodium salt of Ia and iodine and erroneously formulated as a cyclopropane derivative (IIa). Recently, Kondrat'eva, Kogan and Zav'yalov [14] obtained the same compound by treatment of Ia with bromine in chloroform and ascribed structure IIIa to it on the basis of UV and IR spectra. The compound exhibits two IR-bands in the region around 1700 cm^{-1} typical for many 2,2-substituted 1,3-cyclo-hexanediones [14,15] (see Table 1).

Additional evidence for structure IIIa is given by the NMR spectrum. The bridge methylene protons at τ 6.83 (2H) appear as a triplet ($J = 1.6$ cps) due to homoallylic coupling to the methylene protons which in turn give a triplet ($J = 1.6$ cps) at τ 7.52 (2H). The singlets at τ 7.23 (4H, broadened) and τ 8.88 (6H) are assigned to the methylene and the gem-dimethyl protons of the cyclohexanedione ring, respectively, which excludes a rigid ring structure but does not allow a choice between a rapid chair-chair equilibrium or an intermediate "flexible" form (cf. Ref. 15). The cyclohexenone ring, however, would be expected to exist preferentially in a single stable conformation with different shielding of the two methyl groups and these appear as singlets at τ 8.84 (3H) and τ 9.01 (3H), respectively. The remaining methylene protons appear at τ 7.77 (2H, singlet).
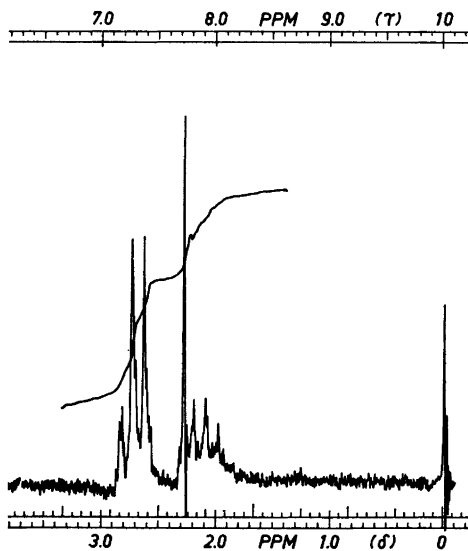

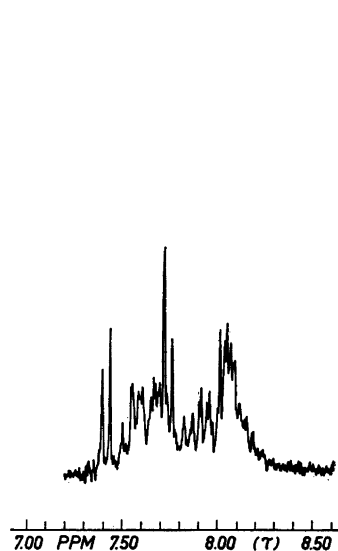Fig. 1. Nuclear magnetic resonance spectrum at 60 Mc of the dispiro-tetraketone IIb.

Fig. 2. Nuclear magnetic resonance spectrum at 100 Mc of the cyclic ketal IVb.

A somewhat different result was obtained with methylene-bis-1,3-cyclo-hexanedione (Ib). On treatment with the iron(III) hexacyanoferrate(III) reagent in aqueous ethanol this afforded two neutral substances, A (28 %) $C_{14}H_{18}O_5$ (266.3), m.p. 133—153°C, crystallised from methanol-isopropanol, and B (22 %), $C_{13}H_{16}O_5$ (252.3), m.p. ca. 150°C (decomp.). The mass spectra of both A and B gave peaks of highest mass at $m/e = 234$, indicating that 32 and 18 m.u., respectively, are easily lost. A detailed discussion of the fragmentation patterns given by the mass spectra of these and other compounds described here will be presented elsewhere.[16]

Substance A on sublimation in vacuo gave a compound $C_{13}H_{14}O_4$ (234.3) formulated as a spiro-type enol ether (IIIb) on the basis of its IR absorption spectrum (1750, 1720, 1640, 1230 cm^{-1}; see Table 1) which shows striking similarities to that of the homologue IIIa. The structure IIIb is supported by the UV (λ_{max} 267 nm, ε 14 000) and NMR spectra. The bridge methylene protons appear as a triplet ($J = 1.8$ cps) at τ 6.81 (2H), close to the corresponding peaks for the homologue IIIa and other related compounds, e.g. methylene-bis-dimedone (Ia) (Table 2). The multiplet centered at τ 7.33 can be assigned to the allylic protons of the cyclohexenone ring.

The substance A shows IR-absorption around 3200 cm^{-1} (OH) and at 2840 cm^{-1} (OCH$_3$) as expected for a semiketal of IIIb with methanol, and loses one mole of methanol on melting. The UV spectra of A and of the parent ketone IIIb are essentially similar but the IR spectrum of A shows only a single band at 1725 cm^{-1}. Hence, one of the unconjugated carbonyl groups of IIIb has been ketalised but obviously two diastereomeric ketals could exist with the methoxyl protons in different environments. The NMR spectrum of A (dimethyl sulphoxide-d$_6$, 20°C) which shows two sharp singlets at τ 6.76 (1.9 H) and τ 6.36 (1.1 H), respectively, assigned to the methoxyl protons, indicates that both isomers are present.

Compound B was almost insoluble in most common solvents but could be crystallised from dimethyl sulphoxide-chloroform. It did not lose water on extended drying in vacuo but on careful, short-path distillation (1.5 × 10^{-4} mm, 135—145°C) gave an oil which in addition to some unchanged B contained two new ketonic compounds, C and D.

The ketone D, $C_{13}H_{14}O_4$, m.p. 97—99°C (decomp.), gave a mass spectrum almost identical with that of B and was converted back to B when crystallized from aqueous acetonitrile. The analytical and spectral values for ketone D are in full accordance with the dispiro-cyclopropane structure IIb discussed above as a possible reaction product from Ib (Scheme 1). The IR spectrum shows a sharp band at 3081 cm^{-1}. As shown by Norin,[17] a band in the range 3050—3090 cm^{-1}, at least in the absence of interfering groups, gives clear evidence for the presence of a cyclopropane ring with a CH$_2$-group. A band at 1020 cm^{-1} when accompanying a band near 3100 cm^{-1} gives further evidence for a cyclopropane ring structure.[18] The tetraketone, as expected, exhibits two bands in the carbonyl region at 1748 and 1715 cm^{-1} (Table 1).

The UV spectrum of D, in agreement with those of compounds containing a cyclopropane ring conjugated with a carbonyl group, shows a weak, broad maximum at 275 nm. The cyclopropane methylene protons which should be in identical environments due to the symmetry of the molecule, can be clearly

Table 1.

Compound	C=O stretching frequency, cm^{-1}		$\varepsilon_1/\varepsilon_2$	Ref.
	1	2		
2,2-Dibenzyl-1,3-cyclohexanedione	1695	1729	2.1	a
2,2-Dibenzyldimedone	1692	1727	2.2	a
2,2-Dimethyl-1,3-cyclohexanedione	1702	1732	3.0	14
2,2-Dimethyldimedone	1702	1732	2.5	14
2,2-Dimethyldimedone	1698	1730	2.0	a
2,2-Dibromo-1,3-cyclohexanedione	1730	1745	2.6	14
2,2-Dibromodimedone	1730	1743	2.6	14
2-Bromo-2-methyl-1,3-cyclohexanedione	1713	1734	1.6	14
2-Bromo-2-methyldimedone	1713	1730	0.9	14
IIIa	1728	1750	2.3	14
IIIa	1722	1750	2.1	a
IIIb	1720	1750	2.1	a
IIb	1715	1748	1.8	a

a This work.

distinguished in the NMR spectrum (Fig. 1) as a sharp signal at τ 7.71 (2H). This is in good agreement with the expected chemical shift for corresponding protons when several electron-withdrawing substituents are attached to the cyclopropane ring.[19] The methylene protons in the α- and β-positions to the carbonyl groups, respectively, give rise to an $A_2B_2A_2$ spectrum (Fig. 1).

The primary reaction product B, $C_{13}H_{16}O_5$, should also contain a cyclopropane ring since its IR spectrum shows a well-defined band at 3098 cm^{-1} in addition to the strong and sharp hydroxyl band at 3435 cm^{-1}. The presence of the cyclopropane ring in B is further confirmed by a near infra-red band at 1617 nm (dimethyl sulphoxide). Cyclopropanes with at least two methylene hydrogens usually absorb in the region 1625—1650 nm (CCl$_4$); with electron-withdrawing substituents the band appears in the lower part of the range.[20,21] These results and especially the difficulty of removing water can be interpreted by formulating compound B as a hydrate of IIb with the structure IVa. The presence of a cyclic ether structure in B is supported also by a strong IR-band at 1050 cm^{-1}. A fused cyclic ether would be expected to be more highly strained than normal tetrahydrofuran rings which absorb in the region 1059—1098 cm^{-1} whereas trimethylene oxides absorb at 971—980 cm^{-1}. Moreover, contrary to the tetraketone IIb the hydrate exhibits only a single band at 1700 cm^{-1} in the carbonyl region. The NMR spectrum of B in dimethyl sulphoxide was poorly resolved and could not be easily interpreted.

IVa R = H
IVb R = CH$_3$

Va R = H
Vb R = CH$_3$
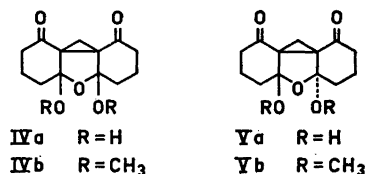
Preliminary experiments have shown that compound B on treatment with nucleophilic reagents readily undergoes ring-opening reactions even under mild conditions.[22] However, brief treatment of B at room temperature with methanol containing traces of hydrochloric acid yielded a compound E, $C_{13}H_{14}O_3(OCH_3)_2$. The UV spectrum (λ_{max} 292 nm, ε 70) and the IR spectrum (ν_{max}^{KBr} 3110 cm^{-1}) of E indicated the presence of a cyclopropane ring. Furthermore, the cyclopropane protons, which are not equivalent, give rise to an AB pattern with proton A centered at τ 7.42 and proton B at τ 7.73 ($J_{AB} = 4$ cps, Fig. 2).

By analogy with the hydrate B compound E is formulated as the corresponding cyclic ketal. From the Dreiding models this could exist either in *cis* (IVb) or in *trans* (Vb) form. A cyclic structure for the ketal is also supported by the IR spectrum which shows only a single band at 1705 cm^{-1} in the carbonyl region and by the NMR spectrum (Fig. 2) which shows no signs of the $A_2B_2A_2$ (or $A_2X_2A_2$) spectrum observed in the case of the tetraketone IIb (Fig. 1) and related 2,2-spirane derivatives of 1,3-cyclohexanedione studied by De Jongh and Wynberg.[15]

The occurrence of a sharp singlet at τ 6.63 (6H) in the NMR spectrum of compound E taken at 100 Mc gives evidence in favour of a *cis* configuration (IVb) of this ketal.

As mentioned above, experiments aiming at the dehydration of compound B always gave a product C and under certain conditions vigorous evolution of gas occurred and C, $C_{12}H_{14}O_3$, was the main reaction product. The chemical and spectral properties of C are in complete accordance with structure VI which can be derived from IIb by loss of carbon monoxide and subsequent isomerisation, e.g. as indicated in Scheme 2.

Scheme 2.
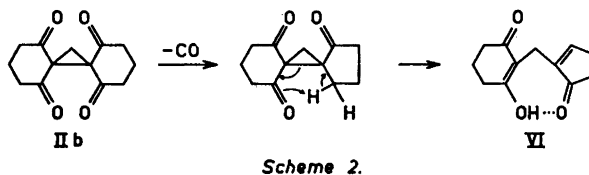
The UV maximum at 259 nm (ε 14 000) in acidic ethanol, shifting to 289 nm (ε 28 000) in alkaline solution, is attributed to the enolised 1,3-cyclohexanedione system. A second maximum at 232 nm, essentially unaffected by the addition of alkali, indicates the presence of an isolated 2-substituted cyclopent-2-enone ring. Two related cyclopentenones, 2,5-dimethyl-5-isopropylcyclopent-2-enone and 2,4-dimethyl-4-isopropylcyclopent-2-enone, show maxima at 228 nm (ε 9700) and 230 nm (ε 11 200), respectively.[23]

The IR spectrum of C shows a strong band at 1675 cm^{-1} which is assigned to a cyclopentenone carbonyl group, the frequency being shifted from the normal value around 1705 cm^{-1} by hydrogen bonding with the enolic hydroxyl group. This hydroxyl group also appears at a low IR frequency, 3135 cm^{-1} and gives an NMR signal at τ −0.11, which agrees with the correla-

tions obtained by Forsén and Åkermark [24] between ν_{OH}, ν_{CO}, and τ_{OH} for hydrogen bonded enols and phenols.

The IR-bands given by compound C at 1638 and 1610 cm^{-1} can be attributed to the enolised 1,3-cyclohexanedione system and the cyclopentenone C=C stretching frequency, respectively. The NMR spectrum shows a vinyl proton signal at τ 2.29 (1H, triplet, $J = 2.5$ cps) and a signal from the bridge methylene protons (Table 2) as a singlet at τ 6.85 (2H).

Table 2. Chemical shifts and spin-spin coupling constants for bridge methylene protons.

Compound	τ CH$_2$	J, cps
Methylene-bis-dimedone (Ia)	6.83	0
IIIa	6.83	1.6
IIIb	6.81	1.8
IIIb, semiketal with methanol	6.88	1.8
VI	6.85	0

The high reactivity of the tricyclic dispiro tetraketone IIb is noteworthy and this cyclopropane derivative and its hydrate (presumably IVa) will be subject to further investigations.[22] Especially the thermally induced decarbonylation of IIb appears to have few counterparts among the β-diketones.

The results presented indicate that certain β-dicarbonyl compounds containing two enolate systems can undergo oxidative cyclisations with carbon-carbon or carbon-oxygen coupling under mild conditions using a reactive one-electron acceptor. So far, no attempts have been made to study the influence of the reaction conditions on the course of reaction. It cannot be excluded that carbon-carbon coupling also occurs in the case of methylene-bis-dimedone (Ia) although a postulated primary reaction product IIa might undergo rapid secondary changes in the acetic acid system used as a solvent in this case.

Some biogenetic implications of these results have been mentioned earlier.[1]

EXPERIMENTAL

Melting points were determined on a Kofler micro hot stage. IR spectra were recorded on a Perkin-Elmer No. 221 or on an Infracord instrument. UV spectra were measured in 99.5 % ethanol with a Beckman DK 2 spectrophotometer. The NMR spectra were obtained on a Varian A-60 spectrometer using 10 % CDCl$_3$ solutions with tetramethylsilane as internal standard unless otherwise stated. Chemical shifts are given in τ units. The mass spectra were recorded on a LKB 9000 instrument at room temperature or on an instrument with an all-glass heated inlet system at 140—150°C. The microanalyses were made by Dr. A. Bernhardt, Mülheim, Ruhr, West Germany.

Chromatographic investigations. All reactions were followed by TLC on polyamide (Merck) plates with 1,2-dichloroethane-methanol (98:2) or methanol-isopropyl ether (1:1) as solvents. The spots were detected by examining the plates under UV and by spraying with 2,4-dinitrophenyl hydrazine (0.25 M) in 85 % phosphoric acid-ethanol (3:2) or with iron(III) chloride and potassium hexacyanoferrate(III) in water-methanol (3:2).

Oxidative coupling of methylene-bis-dimedone. To a solution of methylene-bis-dimedone (2.34 g, 8 mmole) in 50 % aqueous acetic acid (3000 ml) was added dropwise and with stirring an aqueous solution containing iron(III) hexacyanoferrate(III) freshly made from iron(III) chloride (100 ml, 0.36 M) and potassium hexacyanoferrate(III) (100 ml,

0.36 M). After 6 h the mixture was extracted with chloroform (10 × 125 ml). The extract was dried, the solvent was evaporated under reduced pressure and the residue was crystallised by dissolving it in chloroform and then adding isopropyl ether. To prevent contamination by methylene-bis-dimedone which is sparingly soluble in isopropyl ether this was added in portions. Two fractions were collected, the product IIIa (385 mg), and a mixture of IIIa and starting material (360 mg). Repeated crystallisation of the combined fractions gave IIIa (520 mg, 28 %) as needles, m.p. 214−215°C (lit.[13] 211−212°C), λ_{max} 267 nm (ε 11 900) (lit.[14] λ_{max} 266 nm, ε 10 000), $\nu_{max}^{CHCl_3}$ 1750, 1722, 1645(s), 1230 cm^{-1}. (Found: C 70.0; H 7.71; O 22.1. $C_{17}H_{22}O_4$ (290.36) requires C 70.3; H 7.61; O 22.0).

Methylene-bis-1,3-cyclohexanedione (Ib). The enol was prepared as described in the literature[25] and crystallised from isopropanol, m.p. 130−132°C.

Dispiro[5.0.5.1]-trideca-1,5,8,12-tetraone, monohydrate (IVa or Va). To a stirred solution of methylene-bis-1,3-cyclohexanedione (Ib) (7.08 g, 30 mmole) in 50 % aqueous ethanol (4000 ml) was added dropwise over 15 min a freshly made mixture of aqueous solutions of iron(III) chloride (250 ml, 0.36 M) and potassium hexacyanoferrate(III) (250 ml, 0.36 M). The reaction mixture was stirred at room temperature for 3 h and then extracted with chloroform (10 × 200 ml). The extract was dried (magnesium sulphate), filtered and the solvent was evaporated under reduced pressure. Addition of acetonitrile to the remaining oil yielded crystals (IVa) (1.53 g, 22 %). These were dissolved in dimethyl sulphoxide, an undissolved residue was removed by filtration and chloroform was added to the filtrate. The crystals of IVa were collected, thoroughly washed with ethanol and dried *in vacuo*, m.p. *ca.* 150°C (decomp.), λ_{max} 275 nm (ε 300),* ν_{max}^{KBr} 3435(s), 3098, 2990, 1700(s), 1050(s), 1017 cm^{-1}. (Found: C 61.9; H 6.43; O 31.7. $C_{13}H_{16}O_5$ (252.27) requires C 61.9; H 6.39; O 31.7).

4,5,6,7-Tetrahydro-spiro[benzofuran-2(3H),1'-cyclohexane]-2',4,6'-trione(IIIb). The acetonitrile mother liquor from the isolation of IVa was evaporated to dryness *in vacuo*. Addition of isopropanol-methanol (1:1) (30 ml) to the residue yielded a crystalline product (2.09 g, 28 %) which was recrystallised from acetonitrile and dried *in vacuo* at 70°C, giving substance A, m.p. 133−153°C, λ_{max} 266 nm (ε 13 000), ν_{max}^{KBr} 3220 (br), 2840, 1725, 1625(s), 1261, 1135, 1082 cm^{-1}. (Found: C 63.0; H 6.71; O 30.3. $C_{14}H_{18}O_5$ (266.30) requires C 63.2; H 6.81; O 30.0).

Substance A was sublimed (10^{-3} mm, 130°C) to give IIIb, m.p. 138−139°C (85 % yield), λ_{max} 267 nm (ε 14 000), $\nu_{max}^{CHCl_3}$ 1750, 1720, 1640(s), 1230 cm^{-1}, mass spectrum M$^+$ = 234 m.u. (Found: C 66.5; H 6.08; O 27.7. $C_{13}H_{14}O_4$ (234.26) requires C 66.7; H 6.02; O 27.3).

Dispiro[5.0.5.1]-trideca-1,5,8,12-tetraone (IIb). The hydrate (IVa) (100 mg) was distilled in an all-glass system at 1.5 × 10^{-4} mm, 135−145°C (bath temperature). The resulting viscous oil, which contained starting material and two new ketonic compounds, was dissolved in chloroform and filtered. Addition of hexane gave the main product IIb as plates (25 mg), m.p. 97−99°C (decomp.), λ_{max} 275 nm (ε 500),* ν_{max}^{KBr} 3081, 2997, 1748, 1715(s), 1020 cm^{-1}, mass spectrum M$^+$ = 234 m.u. (Found: C 66.5; H 6.16; O 27.3. $C_{13}H_{14}O_4$ (234.26) requires C 66.7; H 6.02; O 27.3). The second ketonic compound (VI) is described below.

Acid-catalysed ketalisation of the hydrate (IVa) with methanol. The hydrate (IVa) (252 mg) was dissolved in methanol (10 ml) containing conc. hydrochloric acid (0.06 ml) and kept at room temperature for 25 min. The clear solution was diluted with water (25 ml) and extracted with ether (4 × 25 ml). The extract was dried and filtered and the solvent was evaporated. The residue was crystallised from ethyl acetate to give the ketal IVb (145 mg), m.p. 160.5−161°C, λ_{max} 290 nm (ε 70), ν_{max}^{KBr} 3110, 2835, 1705(s), 1280, 1075(s), 1020 cm^{-1}, mass spectrum M$^+$ = 280. (Found: C 64.3; H 7.25. $C_{15}H_{20}O_5$ (280.31) requires C 64.3; H 7.19).

Thermal decomposition of the hydrate IVa. The hydrate IVa (100 mg) was distilled at 10^{-3} mm, 150°C. After 10−30 min intense evolution of gas suddenly occurred from

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* *Added in proof.* Recent experiments[22] have shown that compound IIb and IVa undergo ring-opening reactions in ethanol rapidly enough even at room temperature to give unreliable values especially for the molar extinction coefficients.

the material in the distillation tube as well as from the distillate. After a further 20 min the distillate was completely crystalline and the evolution of gas ceased. Crystallisation from acetone gave 2′[(1-oxo-cyclopent-2-en-2-yl)-methyl]-1′,3′-cyclohexanedione (VI) (20 mg) as plates, m.p. 152—153°C, in acid ethanol solution λ_{max} 232 nm (ε 12 000), 259 nm (ε 14 000), in basic ethanol solution λ_{max} 232 nm (ε 9800), 289 nm (ε 28 000), $\nu_{max}^{CHCl_3}$ 3135 (br), 1675 (s), 1638, 1610 (s) cm^{-1}. Mass spectrum M$^+$ = 206; high resolution mass spectrum M$^+$ = 206.0944. $C_{12}H_{14}O_3$ (206.24) requires 206.09430.

2,2-Dibenzyl-1,3-cyclohexanedione. The ketone was prepared according to Stetter and Klauke [26] and showed m.p. 132—134°C (lit.[26] m.p. 137°C).

2,2-Dibenzyldimedone. The ketone was synthesised by the same method as its homologue, m.p. 134—135°C (lit.[27] m.p. 135—136°C).

2,2-Dimethyldimedone. The ketone was prepared as described by Hassal and Thomas [28] and had m.p. 95—96°C (lit.[28] m.p. 98°C).

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