

Clemmensen Reduction. Part 6.¹ The Synthesis of Cyclopropane-1,2-diyl Diacetates

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The synthesis of a number of cyclopropane-1,2-diyl diacetates is reported. Non-enolisable 1,3-dicarbonyl compounds are converted to cyclopropane-1,2-diyl diacetates by reduction with amalgamated zinc powder and dry hydrogen chloride in diethyl ether containing acetic anhydride or acetyl chloride. Enolisable 1,3-diketones give cyclic diol diacetates only when the diketo-component of the tautomeric mixture is high, otherwise enol acetates and other compounds are produced. ¹H and ¹³C N.m.r. spectra are reported and discussed.

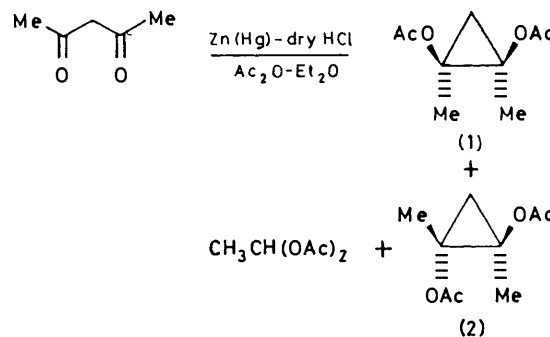
THE intermediacy of cyclopropane-1,2-diols in the Clemmensen reduction of 1,3-diketones was first postulated by Staschewski in 1959² and evidence to support this view was later adduced.^{3,4} In 1969 the isolation of two cyclopropane-1,2-diyl diacetates,⁵ and in one case of a free diol,⁶ from the reduction of 1,3-diketones was reported. The acidolysis of the diols was of interest not only intrinsically, but also because it could provide further insight into the product distribution obtained from the Clemmensen reduction of 1,3-diketones. We therefore synthesised a range of cyclopropane-1,2-diyl diacetates and in a subsequent paper we shall describe their conversion to the free diols and acidolysis of the latter compounds. A number of routes to cyclopropane-1,2-diols and their derivatives have been reported, including carbene addition to ene-diol derivatives,⁷ electrochemical reduction of 1,3-diketones,^{5,8,9} and dissolving-metal reduction of 1,3-dicarbonyl compounds.^{5,7,10,11} In all except one case, the last method was used throughout the present work.

RESULTS AND DISCUSSION

1,3-Dicarbonyl compounds were synthesised either by alkylation of a dicarbonyl compound, or by acylation of a monoketone or of its morpholino-enamine (see Experimental section). The first experiments employing anhydrous conditions for a Clemmensen reduction of a monoketone used acetic anhydride as solvent, and this system was adopted also by Curphey and his co-workers⁵ in their work on 1,3-diketones. However, Yamamura *et al.*^{12,13} later showed that optimum reaction conditions were obtained when diethyl ether was used as solvent with only small amounts of acetic anhydride present, and subsequent work involving trapping of cyclopropanols in the reduction of $\alpha\beta$ -unsaturated ketones has involved this solvent with the addition of small amounts of acetic anhydride.^{14,15} This same system (amalgamated zinc powder, hydrogen chloride, diethyl ether, and acetic anhydride) was employed successfully in our work on 1,3-diketones, with acetyl chloride offering advantage as an alternative trapping agent in the reduction of β -ketoaldehydes. In preliminary experiments, chlorotrimethylsilane was used as trapping agent and the bis-(trimethylsiloxy) ether so obtained was then converted into the diacetate by reaction with acetyl chloride.

However, this extra step was accompanied by insufficient advantage to warrant its subsequent use.

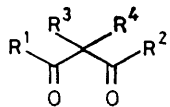
Cyclopropane-1,2-diol derivatives had not been reported from Clemmensen reduction of enolisable 1,3-diketones, but in our hands reaction of pentane-2,4-dione under the modified Clemmensen conditions at -35°C gave a readily separable mixture of the *cis*- and *trans*-diacetates (1) and (2) of 1,2-dimethylcyclopropane-1,2-diol, with the *cis*-isomer predominating (Scheme 1). Also isolated was ethane-1,1-diyl diacetate, which was present in all reductions conducted in the presence of acetic anhydride or acetyl chloride. With several other enolisable 1,3-diketones, however, enol acetate formation



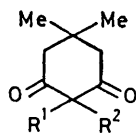
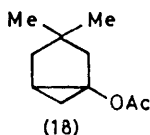
SCHEME 1

and alternative modes of reaction competed with cyclopropanediol formation; 1-phenylbutane-1,3-dione (3), 5,5-dimethylhexane-2,4-dione (4), 5,5-dimethylcyclohexane-1,3-dione (12), 2,5,5-trimethylcyclohexane-1,3-dione (13), 2-acetylcyclohexanone (15), and 2-formylcyclohexanone (16) all gave a complex mixture of products but none of the desired diacetates. Synthesis of cyclopropane-1,2-diyl diacetates by reduction of enolisable 1,3-diketones is thus not a general reaction since either non-enolisable substrates or substrates with a low equilibrium concentration of the enol form are required.

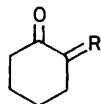
The only product characterised from the reduction of 5,5-dimethylcyclohexane-1,3-dione was the monoacetate (18) identical to that obtained by similar reduction of 5,5-dimethylcyclohexenone, a compound shown by analytical g.l.c. to be present also in the diketone reduction mixture. It was established independently that the enol acetate of the diketone was not involved in the



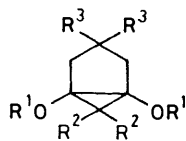
- (3) $R^1 = \text{Ph}, R^2 = \text{Me}, R^3 = R^4 = \text{H}$
 (4) $R^1 = \text{Me}, R^2 = \text{Bu}^t, R^3 = R^4 = \text{H}$
 (5) $R^1 = R^2, R^3 = \text{Me}, R^4 = \text{H}$
 (6) $R^1 = \text{Ph}, R^2 = R^3 = \text{Me}, R^4 = \text{H}$
 (7) $R^1 = R^2 = R^3 = R^4 = \text{Me}$
 (8) $R^1 = \text{Ph}, R^2 = R^3 = R^4 = \text{Me}$
 (9) $R^1 = \text{H}, R^2 = R^3 = R^4 = \text{Me}$
 (10) $R^1 = \text{H}, R^2 = \text{Ph}, R^3 = R^4 = \text{Me}$
 (11) $R^1 = \text{OEt}, R^2 = R^3 = R^4 = \text{Me}$



- (12) $R^1 = R^2 = \text{H}$
 (13) $R^1 = \text{Me}, R^2 = \text{H}$
 (14) $R^1 = R^2 = \text{Me}$



- (15) $R = \text{Ac}, \text{H}$
 (16) $R = \text{CHOH}$
 (17) $R = \text{Me}, \text{CHO}$



- (19) $R^1 = R^2 = \text{H}, R^3 = \text{Me}$
 (20) $R^1 = R^2 = R^3 = \text{H}$
 (21) $R^1 = \text{SiMe}_3, R^2 = R^3 = \text{H}$
 (22) $R^1 = \text{Ac}, R^2 = R^3 = \text{H}$
 (23) $R = \text{Ac}, R = R = \text{Me}$

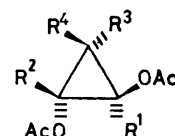
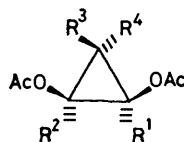
formation of the monoacetate and it is unlikely that the cyclopropanediol (19) is a precursor, since we have shown subsequently that acidolysis of the analogous bicyclic diol (20) gave none of the corresponding cyclohexenone. The bicyclic diol derivative (21) was synthesised by methylene (carbene) addition to 1,2-bis(trimethylsiloxy)cyclopentene; ^{7,16} reaction with acetyl chloride gave the corresponding diacetate (22).

The reduction of 3-methylpentane-2,4-dione (5) afforded all the possible diacetates (24), (25), and (31), while 2-methyl-1-phenylbutane-1,3-dione (6) gave a mixture of two of the four possible products, which were identified (by ¹³C n.m.r. spectroscopy) as the isomers (26) and (32), having the C-3 methyl group *trans* to the phenyl group. At some stage in the reductive cyclisation of the diketone (6) a strong steric interaction must occur between the C-2 methyl and the phenyl, preventing formation of the other two isomers. The phenyldiketone (6) is known to favour the enol tautomer to a much smaller extent than its non-methylated analogue (3),¹⁷ which failed to give any cyclic products on reduction. This result parallels those available from related electrochemical reductions, where cyclopropanediol formation is observed only with substrates existing largely in the

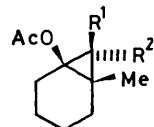
keto-form.^{9,18} As expected, reduction of 3,3-dimethylpentane-2,4-dione (7), 2,2-dimethyl-1-phenylbutane-1,3-dione (8), and 2,2,5,5-tetramethylcyclohexane-1,3-dione (14) under Clemmensen conditions proceeded smoothly to give (27) and (33), (28) and (34), and (23) respectively.

Experiments using three non-enolisable β -keto-aldehydes showed that acetyl chloride was the preferred trapping agent in those cases, since acetic anhydride converted the reactive aldehyde group largely to a *gem*-diacetate or *gem*-chloroacetate; these derivatives were identical with compounds isolated from reaction of the β -keto-aldehyde with acetic anhydride-hydrochloric acid. Thus 2,2-dimethyl-3-oxobutanal (9), 2,2-dimethyl-3-phenyl-3-oxopropanal (10), and 1-methyl-2-oxocyclohexanecarbaldehyde (17) were reduced in the presence of acetyl chloride to give good yields of (29) and (35), (30) and (36), and (37) and (38), respectively.

Neither the ketone nor the ester carbonyl groups of the non-enolisable substrate ethyl 2,2-dimethyl-3-oxobutanoate (11) were reduced under conditions which served to convert β -diketones to cyclopropanediol derivatives. In contrast, the enolisable substrates ethyl 3-oxobutanoate (39) and ethyl 2-methyl-3-oxo-

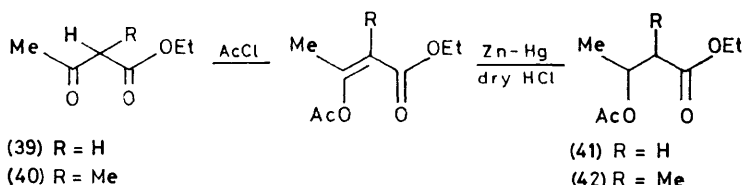


- (24) $R^1 = R^2 = R^3 = \text{Me}, R^4 = \text{H}$
 (25) $R^1 = R^2 = R^4 = \text{Me}, R^3 = \text{H}$
 (26) $R^1 = R^3 = \text{Me}, R^2 = \text{Ph}, R^4 = \text{H}$
 (27) $R^1 = R^2 = R^3 = R^4 = \text{Me}$
 (28) $R^1 = R^3 = R^4 = \text{Me}, R^2 = \text{Ph}$
 (29) $R^1 = R^3 = R^4 = \text{Me}, R^2 = \text{H}$
 (30) $R^1 = \text{Ph}, R^2 = \text{H}, R^3 = R^4 = \text{Me}$
 (31) $R^1 = R^2 = R^3 = \text{Me}, R^4 = \text{H}$
 (32) $R^1 = R^4 = \text{Me}, R^2 = \text{Ph}, R^3 = \text{H}$
 (33) $R^1 = R^2 = R^3 = R^4 = \text{Me}$
 (34) $R^1 = R^3 = R^4 = \text{Me}, R^2 = \text{Ph}$
 (35) $R^1 = R^3 = R^4 = \text{Me}, R^2 = \text{H}$
 (36) $R^1 = \text{Ph}, R^2 = \text{H}, R^3 = R^4 = \text{Me}$



- (37) $R^1 = \text{OAc}, R^2 = \text{H}$
 (38) $R^1 = \text{H}, R^2 = \text{OAc}$

butanoate (40) underwent reduction to give the analogous β -acetoxy-compounds (41) and (42), respectively, which were presumably derived by direct double-bond reduction in the intermediate enol acetates (Scheme 2).



SCHEME 2

Reduction of the ketone carbonyl group to a methylene group was not observed with either substrate.

Analysis of the cyclopropane-1,2-diyl diacetates by both ^1H and ^{13}C n.m.r. spectroscopy resulted in the identification of spectral features which enabled stereochemical assignments to be made on the basis of chemical-shift correlations. For groups on the cyclopropane ring, the chemical shift of their proton resonances was dependent on the nature of the adjacent *cis* substituents. For the protons of methyl or acetate groups there was a monotonic decrease in chemical shift, which may reflect steric interactions, as the adjacent ring-carbon atom substituent was varied from hydrogen to methyl to acetate to phenyl. However, for a proton directly attached to the cyclopropane ring, adjacent methyl groups were found to result in a smaller chemical shift than did contiguous acetate or phenyl groups. This latter result is due presumably to the methyl group having its steric bulk closer to the cyclopropane ring. Stereochemical information was also obtained by correlation of substituent chemical shifts in the ^{13}C n.m.r. spectra, as the resonances of the cyclopropane carbon atoms in the *cis*-isomers (Table 1) always occurred at higher field than in the analogous *trans*-isomers (Table 2). This relationship has been demonstrated previously with 1,2-disubstituted cyclopropanes,^{19,20} including 1,2-diethers.²¹ The carbon resonances of the methyl substituents underwent appreciable upfield shifts on replacement of an adjacent *cis*-cyclopropane proton by a methyl or acetate group, but no such shift was observed for a *cis*-related phenyl group. This latter result may be due to the steric effect being cancelled by an equally strong downfield γ -substituent effect. Upfield shifts caused by interaction with an acetate group were con-

sistently about 1 p.p.m. greater than shifts due to interaction with a methyl group, so from a combination of ring and substituent chemical shifts it was possible to confirm or deduce the stereochemistry of all the cyclopropane-1,2-diyl diacetates from their ^{13}C n.m.r. spectra.

EXPERIMENTAL

M.p.s were determined with a Reichert-Kofler hot-stage apparatus. I.r. spectra were measured with a Perkin-Elmer 237 spectrometer for solutions in carbon tetrachloride or chloroform, ^1H n.m.r. spectra with a Varian T60 spectrometer (solvent CCl_4 or CDCl_3), and ^{13}C n.m.r. spectra with a JEOL JNM-FX60 Fourier-transform spectrometer (solvent CDCl_3). Low-resolution mass spectra were obtained with a Varian MAT CH-7 spectrometer. Microanalyses were performed by Professor A. D. Campbell and associates, University of Otago, New Zealand.

Amalgamated zinc powder was prepared as previously described.¹⁵ The reduction products were separated by p.l.c. and the liquid compounds were further purified by short-path (bulb-to-bulb) distillation on a Kugelrohr distillation apparatus, with the quoted temperature being the oven temperature. Products were identified by both spectral (i.r., ^1H n.m.r., ^{13}C n.m.r., and mass spectrometry) and melting-point analysis where appropriate. Quoted yields are those obtained from p.l.c.

Preparation of 1,3-Dicarbonyl Compounds.—3-Methylpentane-2,4-dione (5). Pentane-2,4-dione was treated with the stoichiometric amount of potassium *t*-butoxide and iodomethane in *t*-butyl alcohol to give the monomethyl diketone (5) in 50% yield, b.p. 168–170°C.

3,3-Dimethylpentane-2,4-dione (7). Treatment of pentane-2,4-dione with an excess of iodomethane and potassium carbonate in aqueous methanol gave the dimethyl diketone (7) in 55% yield, b.p. 172–173°C.

1-Phenylbutane-1,3-dione (3). Acetophenone and ethyl acetate were condensed together using sodium ethoxide in dry ether to give, after hydrolysis, the phenyldiketone (3) in 58% yield, b.p. 138–139°C at 20 mmHg, m.p. 55–56°C (lit.,²² 59–60°C).

2-Methyl-1-phenylbutane-1,3-dione (7). Methylation of the sodium salt of 1-phenylbutane-1,3-dione (3) with iodomethane in acetone gave the monomethyl diketone (7) in 72% yield, b.p. 129–131°C at 6 mmHg (lit.,²³ 115–118°C at 5 mmHg).

2,2-Dimethyl-1-phenylbutane-1,3-dione (8). Reaction of the sodium salt of the monomethyl dione (7) with iodomethane in tetrahydrofuran gave the dimethyl dione (8) in 51% yield, b.p. 120°C at 6 mmHg (lit.,⁹ 84°C at 2 mmHg).

2,2,5,5-Tetramethylcyclohexane-1,3-dione (14).—Methylation of 5,5-dimethylcyclohexane-1,3-dione (12) with an excess of iodomethane and potassium carbonate in aqueous methanol gave 2,2,5,5-tetramethylcyclohexane-1,3-dione (14), m.p. 94–95°C (hexane) (lit.,²⁴ 98°C). Attempted formation of the tetramethyldione (14) using iodomethane and anhydrous potassium carbonate in dry methanol gave methyl 3,3,6-trimethyl-5-oxoheptanoate as the major product, b.p. 84°C at 15 mmHg (Found: C, 66.2; H, 10.0. $\text{C}_{11}\text{H}_{20}\text{O}_3$ requires C, 66.0; H, 10.1%); m/e 200 (M^+ , $\text{C}_{11}\text{H}_{20}\text{O}_3$); ν_{max} 1735 and 1705 cm^{-1} (C=O); δ_{H} 1.05 (6 H, d, J 7 Hz, 6-Me and 7-H₃), 1.08 (6 H, s, 3-Me₂), 2.44 (2 H, s, 2-H₂), 2.54 (1 H, septet, J 7 Hz, 6-H), and 3.58 (3 H, s, OMe);

TABLE 1

^{13}C N.m.r. chemical shifts of cyclopropane-*cis*-1,2-diyl diacetates^a

Compd.	C-1	C-2	C-3	1-Me	2-Me	<i>c</i> -3-Me ^b	<i>t</i> -3-Me ^b
(1)	59.3	59.3	25.1	17.7	17.7		
(24)	60.3	60.3	27.5	18.2	18.2	7.0	
(26)	60.9	65.3	24.7	19.3		6.9	
(27)	62.9	62.9	26.2	16.5	13.6	15.5	17.5
(28)	63.8	66.9	27.9	16.9		15.7	20.6
(29)	61.2	61.2	23.6	16.8		13.9	20.4
(30)	65.8	59.5	25.1			14.0	21.8

^a MeCO_2 , δ 20.4–21.2; MeCO_2 , δ 169.7–171.2. ^b With respect to C-1 and C-2 acetates.

TABLE 2

^{13}C N.m.r. chemical shifts of cyclopropane-*trans*-1,2-diyl diacetates^a

Compd.	C-1	C-2	C-3	1-Me	2-Me	<i>c</i> -3-Me ^b	<i>t</i> -3-Me ^b
(2)	61.3	61.3	25.5	16.7	16.7		
(31)	62.8	62.8	28.0	11.8	17.0	7.9	
(32)	63.5	67.1	26.1	12.2			8.0
(33)	64.4	64.4	27.2	12.7	12.7	16.8	16.8
(34)	66.4	67.2	29.3	13.6		19.5	16.9
(35)	64.0	62.1	25.9	12.5		19.3	14.8
(36)	66.9	63.7	27.1			19.5	17.4

^a MeCO_2 , δ 20.4–21.2; MeCO_2 , δ 169.7–171.2. ^b With respect to C-1 acetate.

δ_C 18.2 (6-Me and C-7), 28.2 (3-Me₂), 32.5 (C-3), 41.8 (C-6), 44.3 (C-2), 49.4 (C-4), 51.0 (OMe), 172.5 (C-1), and 213.6 (C-5).

1-Methyl-2-oxocyclohexanecarbaldehyde (17).—2-Hydroxymethylenecyclohexanone was prepared by the method of Ainsworth²⁵ and methylated with iodomethane and anhydrous potassium carbonate in dry acetone to give the cyclic β -keto-aldehyde (17) in 60% yield, b.p. 115–120 °C at 50 mmHg (lit.,²⁵ 29–31 °C at 1 mmHg).

2,2-Dimethyl-3-oxobutanal (9) and **2,2-dimethyl-3-phenyl-3-oxopropanal (10)** were prepared from the morpholino-enamine of 2-methylpropanal by the method of Inukai and Yoshizawa,²⁶ while ethyl 2-methyl-3-oxobutanoate (40) and ethyl 2,2-dimethyl-3-oxobutanoate (11) were prepared from the appropriate sodium salts by the method of Folkers and Adkins.²⁷

Synthesis of Cyclopropane-1,2-diyl Diacetates.—**General reduction procedure.** Reduction of 1,3-diketones to cyclopropane-1,2-diyl diacetates was achieved using a modification of the procedure of Jefford and Boschung for $\alpha\beta$ -unsaturated ketones.¹⁵ A stirred suspension of the diketone (1 g), acetic anhydride (2 ml), and amalgamated zinc powder (5 g) in dry ether (15 ml) was cooled to –35 °C and anhydrous hydrogen chloride gas was bubbled in slowly for 1 min. The mixture was stirred at –35 °C for 15 min and allowed to warm slowly to room temperature over a further 30 min. After neutralisation with saturated aqueous sodium hydrogencarbonate the reaction was worked up in ether. β -Keto-aldehydes were reduced by a similar procedure, with acetyl chloride being used as the trapping agent instead of acetic anhydride.

Reduction of pentane-2,4-dione. Reduction of pentane-2,4-dione as above gave: (i) 1,2-dimethylcyclopropane-*trans*-1,2-diyl diacetate (2) (4%); (ii) 1,2-dimethylcyclopropane-*cis*-1,2-diyl diacetate (1)²⁸ (12%) as needles, m.p. 42–43.5 °C from pentane; and (iii) ethane-1,1-diyl diacetate, identical with material obtained by acetylation of acetaldehyde with acetic anhydride and concentrated hydrochloric acid.

Reduction of 5,5-dimethylcyclohexane-1,3-dione (12). The cyclic dione (12), dissolved in dry chloroform, was reduced in the presence of acetic anhydride to give a mixture of products from which was isolated 3,3-dimethylbicyclo[3.1.0]hexane-1-yl acetate (18) (33%), b.p. 75 °C at 15 mmHg (Found: C, 71.2; H, 9.8. C₁₀H₁₆O₂ requires C, 71.4; H, 9.6%); *m/e* 168 (M⁺, C₁₀H₁₆O₂); ν_{\max} 1 745 (C=O), 1 315 (CMe₂), and 1 240 cm⁻¹ (C–O); δ_H 0.73 and 0.92 (2 H, 2 d, J 6 Hz, 6-H₂), 0.97 and 1.15 (6 H, 2s, 2-Me₂), 1.94 (3 H, s, OAc), and 1.98 (2 H, br s, 2-H₂); δ_C 21.1 (OAc), 22.9 (C-6), 24.6 (C-5), 30.5 and 32.4 (3-Me₂), 41.4 (C-3), 43.3 (C-4), 47.9 (C-2), 68.2 (C-1), and 171.1 (OAc). This compound was also isolated as the major product (44% yield) when a sample of 5,5-dimethylcyclohex-2-enone was reduced under the same conditions. The formation and reduction of the enol acetate of the diketone (2), under the same conditions, failed to give any of the bicyclic acetate (18).

Bicyclo[3.1.0]hexane-1,5-diyl diacetate (22). 1,2-Bis(trimethylsilyloxy)cyclopentene was prepared by reductive cyclisation of diethyl glutarate using the method of Rühlmann.¹⁶ Reaction with a zinc-copper couple²⁹ and diiodomethane then gave 1,5-bis(trimethylsilyloxy)bicyclo[3.1.0]hexane (21)⁷ which, on treatment with acetyl chloride in ether, gave bicyclo[3.1.0]hexane-1,5-diyl diacetate (22), b.p. 110 °C at 20 mmHg (Found: C, 60.7; H, 7.4. C₁₀H₁₄O₄ requires C, 60.6; H, 7.1%); ν_{\max} 1 750 cm⁻¹

(C=O); δ_H 0.98 and 1.35 (2 H, AB quartet, J 7 Hz, 6-H₂) and 2.00 (6 H, s, OAc).

Reduction of 3-methylpentane-2,4-dione (5). Reduction of the methyl dione (5) gave: (i) 1,2,3-trimethylcyclopropane-*r*-1,2-diyl diacetate (31) (14%) (Found: C, 60.2; H, 8.4. C₁₀H₁₆O₄ requires C, 60.0; H, 8.05%); ν_{\max} 1 750 (C=O), 1 360 (C–Me), and 1 225 cm⁻¹ (C–O); δ_H 0.97 (4 H, s, 3-H and 3-Me), 1.28 (3 H, s, 2-Me), 1.48 (3 H, s, 1-Me), and 1.95 and 2.03 (6 H, 2s, OAc); (ii) 1,2,3-trimethylcyclopropane-*r*-1,2-diyl diacetate (24) (14%), m.p. 43–44.5 °C (pentane) (Found: C, 60.1; H, 8.2. C₁₀H₁₆O₄ requires C, 60.0; H, 8.05%); ν_{\max} 1 750 (C=O), 1 360 (C–Me), and 1 215 and 1 235 cm⁻¹ (C–O); δ_H 0.90 (4 H, apparent br s, 3-H and 3-Me), 1.50 (6 H, s, 1- and 2-Me), and 1.97 (6 H, s, OAc); and (iii) a mixture (4%), the major component being 1,2,3-trimethylcyclopropane-*r*-1,2-diyl diacetate (25); δ_H 0.50 (1 H, q, J 6 Hz, 3-H), 1.02 (3 H, d, J 6 Hz, 3-Me), 1.43 (6 H, s, 1- and 2-Me), and 2.05 (6 H, s, OAc).

Reduction of 2-methyl-1-phenylbutane-1,3-dione (6). Reduction of 2-methyl-1-phenylbutane-1,3-dione (6) gave an approximately 1 : 1 mixture of 1,2,3-trimethylcyclopropane-*r*-1,2-diyl diacetate (26) and 1,2,3-trimethylcyclopropane-*cis*-1,2-diyl diacetate (32) (31%), b.p. 95 °C at 0.2 mmHg (Found: C, 68.6; H, 7.0. Calc. for C₁₅H₁₈O₄: C, 68.7; H, 6.9%); ν_{\max} 1 750 (C=O), 1 360 (C–Me), and 1 220 cm⁻¹ (C–O); δ_H 1.07 (1 H, apparent s, 3-H), 1.20 (3 H, apparent s, 3-Me), 1.52 and 1.55 (3 H, 2 s, 1-Me), 1.83, 1.93, and 2.03 (6 H, 3 s, OAc), and 7.33 (5 H, m, aromatic).

Reduction of 3,3-dimethylpentane-2,4-dione (7). Reduction of 3,3-dimethylpentane-2,4-dione (7) gave: (i) 1,2,3,3-tetramethylcyclopropane-*trans*-1,2-diyl diacetate (33)²⁸ (26%); and (ii) 1,2,3,3-tetramethylcyclopropane-*cis*-1,2-diyl diacetate (27)²⁸ (23%).

Reduction of 2,2-dimethyl-1-phenylbutane-1,3-dione (8). The diketone (8) gave: (i) 1,3,3-trimethyl-2-phenylcyclopropane-*trans*-1,2-diyl diacetate (34) (37%), b.p. 78 °C at 0.1 mmHg (Found: C, 69.7; H, 7.3. C₁₆H₂₀O₄ requires C, 69.5; H, 7.3%); ν_{\max} 1 748 (C=O), 1 360 (C–Me), and 1 215 cm⁻¹ (C–O); δ_H 0.92 (3 H, s, *c*-3-Me), 1.25 (3 H, s, *t*-3-Me), 1.58 (3 H, s, 1-Me), 1.83 and 1.87 (6 H, 2 s, OAc), and 7.33 (5 H, m, aromatic); and (ii) 1,3,3-trimethyl-2-phenylcyclopropane-*cis*-1,2-diyl diacetate (28) (9%), m.p. 81–82 °C (Found: C, 69.9; H, 7.3. C₁₆H₂₀O₄ requires C, 69.5; H, 7.3%); ν_{\max} 1 750 (C=O), 1 360 (C–Me), and 1 215 cm⁻¹ (C–O); δ_H 1.17 (6 H, s, 3-Me₂), 1.32 (3 H, s, 1-Me), 1.87 (3 H, s, 2-OAc), 2.05 (3 H, s, 1-OAc), and 7.33 (5 H, m, aromatic).

Reduction of 2,2,5,5-tetramethylcyclohexane-1,3-dione (14). The diketone (14) gave 3,3,6,6-tetramethylbicyclo[3.1.0]hexane-1,5-diyl diacetate (23) (85%), m.p. 88 °C (hexane) (lit.,¹⁰ 87–89 °C); δ_C 14.9 (*c*-6-Me), 16.2 (*t*-6-Me), 20.5 (OAc), 26.3 (*c*-3-Me), 31.4 (*t*-3-Me), 32.6 (C-6), 42.6 (C-3), 46.1 (C-2 and C-4), 71.5 (C-1 and C-5), and 170.1 (OAc).

Reduction of 2,2-dimethyl-3-oxobutanal (9). The β -keto-aldehyde, on reduction in the presence of acetyl chloride, gave: (i) 1,3,3-trimethylcyclopropane-*trans*-1,2-diyl diacetate (35)²⁸ (13%); ν_{\max} 1 750 cm⁻¹ (C=O); δ_H 1.03 (3 H, s, *t*-3-Me), 1.10 (3 H, s, *c*-3-Me), 1.40 (3 H, s, 1-Me); and (ii) 1,3,3-trimethylcyclopropane-*cis*-1,2-diyl diacetate (29)²⁸ (27%) (Found: C, 60.3; H, 8.2. Calc. for C₁₀H₁₆O₄: C, 60.0; H, 8.05%); ν_{\max} 1 755 cm⁻¹ (C=O); δ_H 0.97 (3 H, s, *c*-3-Me), 1.08 (3 H, s, *t*-3-Me), 1.47 (3 H, s, 1-Me), 2.00 and 2.05 (6 H, 2 s, OAc), and 3.47 (1 H, s, 2-H).

Appreciable amounts of by-products were formed when the above reaction was performed in the presence of acetic anhydride, with the major components being 4-acetoxy-4-chloro-3,3-dimethylbutan-2-one, 4,4-diacetoxy-3,3-dimethylbutan-2-one, and ethane-1,1-diyl diacetate.

Reduction of 2,2-dimethyl-3-oxo-3-phenylpropanal (10). The β -keto-aldehyde (10) gave: (i) 3,3-dimethyl-1-phenylcyclopropane-trans-1,2-diyl diacetate (36) (22%) as needles, m.p. 80–81 °C (pentane) (Found: C, 68.9; H, 7.0. $C_{15}H_{18}O_4$ requires C, 68.7; H, 6.9%); ν_{\max} 1 765 (C=O), 1 380 (CMe₂), and 1 220 cm⁻¹ (C-O); δ_H 0.96 (3 H, s, *t*-3-Me), 1.33 (3 H, s, *c*-3-Me), 1.87 and 1.94 (6 H, 2 s, OAc), 4.07 (1 H, s, 2-H), and 7.30 (5 H, m, aromatic); and (ii) 3,3-dimethyl-1-phenylcyclopropane-cis-1,1-diyl diacetate (30) (34%), b.p. 170 °C at 12 mmHg (Found: C, 68.8; H, 7.0. $C_{15}H_{18}O_4$ requires C, 68.7; H, 6.9%); ν_{\max} 1 765 (C=O), 1 380 (CMe₂), and 1 230 cm⁻¹ (C-O); δ_H 0.90 (3 H, s, *t*-3-Me), 1.22 (3 H, s, *c*-3-Me), 1.90 (3 H, s, 1-OAc), 2.05 (3 H, s, 2-OAc), 4.25 (1 H, s, 2-H), and 7.30 (5 H, m, aromatic).

Reduction of 1-Methyl-2-oxocyclohexanecarbaldehyde (17). The cyclic β -keto-aldehyde (17) gave: (i) 6-methylbicyclo[4.1.0]heptane-trans-1,7-diyl diacetate (38) (15%) (Found: C, 63.7; H, 8.2. $C_{12}H_{18}O_4$ requires C, 63.7; H, 8.0%); ν_{\max} 1 755 and 1 740 (C=O), 1 360 (C-Me), and 1 070 cm⁻¹ (C-O); δ_H 1.09 (3 H, s, 6-Me), 1.98 and 2.05 (6 H, 2 s, OAc), and 3.70 (1 H, s, 7-H); δ_C 19.9 (6-Me), 20.6 and 20.9 (OAc), 21.8 and 22.1 (C-3 and C-4), 25.5 (s, C-6; and t, C-2 or C-5), 27.3 (C-2 or C-5), 62.8 (C-1), 63.4 (C-7), and 170.8 (OAc); and (iii) 6-methylbicyclo[4.1.0]heptane-cis-1,7-diyl diacetate (37) (45%) (Found: C, 63.4; H, 8.2. $C_{12}H_{18}O_4$ requires C, 63.7; H, 8.0%); ν_{\max} 1 740 (C=O), 1 365 (C-Me), and 1 240 cm⁻¹ (C-O); δ_H 0.96 (3 H, s, 6-Me), 2.00 and 2.03 (6 H, 2 s, OAc), and 3.58 (1 H, s, 7-H); δ_C 14.0 (6-Me), 20.4 and 20.7 (OAc), 21.0 and 21.8 (C-3 and C-4), 24.3 (C-6), 29.3 and 30.9 (C-2 and C-5), 59.2 (C-7), 60.6 (C-1), and 170.4 and 171.0 (OAc).

Reduction of ethyl 3-oxobutanoate (39). Reduction of the keto-ester (39) under the same conditions as above gave ethyl 3-acetoxybutanoate (41) (52%) as the only product; ν_{\max} 1 740 (C=O) and 1 240 and 1 190 cm⁻¹ (C-O); δ_H 1.25 (3 H, t, *J* 7 Hz, ethyl Me), 1.27 (3 H, d, *J* 6 Hz, 4-H₃), 2.07 (3 H, s, OAc), 2.42 and 2.53 (2 H, 2 d, *J* 2 Hz, enantiotopic 2-H₂), 4.10 (2 H, q, *J* 7 Hz, ethyl CH₂), and 5.14 (1 H, sextet, *J* 6 Hz, 3-H).

Reduction of ethyl 2-methyl-3-oxobutanoate (40). The keto-ester (40) was treated as above to give a mixture of

starting material and ethyl 3-acetoxy-2-methylbutanoate (42).

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