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## The Oxidation of Ethyl a-Methylacetoacetate with Lead Dioxide

By R. Brettle\* and D. Seddon, Department of Chemistry, The University, Sheffield S3 7HF

Oxidation of ethyl  $\alpha$ -methylacetoacetate with lead dioxide gives 4.5-diethoxycarbonyl-3,4,5-trimethylcyclopent-2-enone, diethyl  $\alpha\alpha'$ -diacetyl- $\alpha\alpha'$ -dimethylsuccinate, 4-ethoxycarbonyl-3,4-dimethylcyclohex-2-enone and diethyl 2,4,5-trimethyl-3-oxahex-4-enedioate as the major products.

LEAD DIOXIDE effects the oxidative dimerisation of several ketones,<sup>1</sup> e.g. butanone is converted into 3,4-dimethylhexane-2,5-dione, and one example of the oxidative dimerisation of a  $\beta$ -dicarbonyl system, 5-isopropyl-N-methylbarbituric acid, has been reported.<sup>1</sup> In connection with our studies on the anodic oxidation of ethyl  $\alpha$ -methylacetoacetate <sup>2</sup> we have investigated the oxidation of this  $\beta$ -keto-ester with lead dioxide and now report our results in detail.<sup>3</sup>

When ethyl  $\alpha$ -methylacetoacetate was heated with an excess of lead dioxide in refluxing benzene for 55—60 hr. the initially dark brown suspension gradually changed to a pale yellow colour. Filtration, and removal of the benzene led to only a 50—70% recovery of organic material, and it seems probable that a chelated lead derivative is formed. The solid suspension, after thorough washing with both water and organic solvents, showed absorption at 3750, 1570, and 1390 cm.<sup>-1</sup>; the compounds prepared from lead monoxide and a series of  $\beta$ -keto-esters show strong absorption at 1570 and 1385 cm.<sup>-1</sup>.<sup>4</sup>

A 35-40% yield of a mixture of liquid organic products was obtained, and by repeated preparative g.l.c. with the successive use of columns of differing polarities it was possible to isolate pure samples of the four major components. The initial separation, on a Carbowax column, gave four fractions. The material

<sup>1</sup> G.P. 876,237/1953 (Chem. Abs., 1958, 52, 9227).

<sup>2</sup> R. Brettle, J. G. Parkin, and D. Seddon, preceding paper.

with the longest retention time was shown to be 4,5-di-ethoxycarbonyl-3,4,5-trimethylcyclopent-2-enone (I; X = O;  $R^1 = R^2 = EtO_2C$ ) from an accurate mass measurement and from the n.m.r. spectrum, which showed signals at  $\tau 4.04$  and 7.74, with allylic coupling, due to the proton at C-2 and the methyl group at C-3, a singlet at  $\tau 8.56$ , due to the methyl groups at C-4 and C-5 and overlapping  $A_2X_3$  signals due to the two different ester ethyl groups. It was characterised as its 2,4-dinitrophenylhydrazone (I;  $X = N \cdot NH \cdot C_6 H_3(NO_2)_2$ ;  $R^1 = R^2 = EtO_2C$ ). The material with the next longest



retention time was identified as diethyl  $\alpha\alpha'$ -diacetyl- $\alpha\alpha'$ -dimethylsuccinate (II) from the microanalytical figures, the molecular weight determined mass spectro-

<sup>3</sup> Preliminary communication, R. Brettle and D. Seddon, Chem. Comm., 1968, 1546.

<sup>4</sup> S. Tyrlik and R. Marx, Bull. Soc. chim. France, 1967, 9, 3316.

metrically, and the simple n.m.r. spectrum, which showed singlets at  $\tau$  7.82 and 8.42 due to the acetyl groups and the quaternary methyl groups respectively, and at  $\tau 5.79$ and 8.71 (A<sub>2</sub>X<sub>3</sub>) due to the ester ethyl groups. Compound (II) with Brady's reagent gave a bis-2,4-dinitrophenylhydrazone. The third and fourth fractions were both shown to contain two components by analytical g.l.c., but further preparative g.l.c. on these fractions enabled one pure component to be isolated from each fraction. The compound from the third fraction was identified as 4-ethoxycarbonyl-3,4-dimethylcyclohex-2-enone (III; X = O) by its retention time on analytical g.l.c. and by its i.r. and n.m.r. spectra. The fourth fraction gave a compound which was shown by microanalysis and mass spectrometry to have the formula C<sub>12</sub>H<sub>20</sub>O<sub>5</sub>. The i.r. spectrum showed very strong absorption at 1110 cm.<sup>-1</sup> indicative of an ether linkage, and there was an absorption maximum at 246.5 nm. in the u.v. spectrum due to a conjugated carbonyl chromophore. The n.m.r. spectrum showed a six-proton triplet at  $\tau 8.71$ and two two-proton quartets at  $\tau$  5.77 and 5.82 attributable to two different ester ethyl groups, a three-proton doublet at  $\tau$  8.48 due to a saturated methyl group coupled with an adjacent proton absorbing as a quartet centred on  $\tau$  5.29, and two three-proton quartets at  $\tau$ 7.72 and 8.12 (J 1.36 Hz) attributable to methyl groups at adjacent sites on a carbon-carbon double bond showing homoallylic coupling. On the basis of these findings the compound was recognised to be diethyl 2,4,5-trimethyl-3-oxahex-4-enedioate (IV). The structure was confirmed by the ready acid hydrolysis of (IV), expected for an enol-ether, which was shown by analytical g.l.c. to give ethyl lactate and ethyl a-methylacetoacetate. Treatment of (IV) with Brady's reagent gave ethyl  $\alpha$ -methylacetoacetate 2,4-dinitrophenylhydrazone. An alternative approach allowed us to characterise another product and confirm the presence of others. The mixture of oxidation products was partially separated by preparative g.l.c. and each of the fractions was then separately treated with Brady's reagent. The resultant mixtures of 2,4-dinitrophenylhydrazones were then separated by t.l.c. In this way the later fractions gave the 2,4-dinitrophenylhydrazones of (III; X = O), (II), and ethyl  $\alpha$ -methylacetoacetate [derived from (IV)]. The fraction having the shortest retention time gave two 2,4-dinitrophenylhydrazones. The major component was shown by microanalysis and mass spectrometry to have the formula C<sub>17</sub>H<sub>20</sub>N<sub>4</sub>O<sub>6</sub>. The u.v. spectrum showed an absorption maximum at 378 nm., as expected for the 2,4-dinitrophenylhydrazone of an  $\alpha\beta$ -olefinic ketone, and the n.m.r. spectrum showed the expected absorptions for a 2,4-dinitroanilino-residue together with signals at  $\tau$  5.75 and 8.71 (A<sub>2</sub>X<sub>3</sub>) due to an ester ethyl group,  $\tau$  3.53 and 7.91 due to a vinylic proton coupled allylically to a methyl group on a carbon-carbon

double bond,  $\tau$  6.89 due to a single proton coupled to a methyl group absorbing at  $\tau 8.70$ , and at  $\tau 8.69$  due to a quaternary methyl group. These results allow the compound to be formulated as either (I;  $X = N \cdot NH \cdot C_{6}H_{3}(NO_{2})_{2}; R^{1} = CO_{2}Et; R^{2} = H) \text{ or } (I; X = I)$  $N \cdot N H \cdot C_6 H_3 (NO_2)_2; R^1 = H; R^2 = CO_2 Et)$  and we tentatively suggest that the compound is the 2,4-dinitrophenylhydrazone of 4-ethoxycarbonyl-3,4,5-trimethylcyclopent-2-enone (I;  $X = N \cdot NH \cdot C_6 H_3 (NO_2)_2$ ;  $R^1 = CO_2Et$ ;  $R^2 = H$ ) as a result of the following consideration. A comparison of the mass spectra of 6-ethoxycarbonyl-3,6-dimethylcyclohex-2-enone and 4-ethoxycarbonyl-3,4-dimethylcyclohex-2-enone 2,4-dinitrophenylhydrazones {(V;  $X = N \cdot NH \cdot C_6 H_3 (NO_2)_2$  and [III;  $X = N \cdot NH \cdot C_6H_3(NO_2)_2$ ] respectively)} shows that a major difference is in the intensity of the peak at 303  $(M^+ - CO_2Et)$ . In the compound where the guaternary ester group is at the 4-position the intensity of this peak equals that of the parent ion peak, but in the isomer the intensity is only 25% of that of the parent-ion peak. In the case of [I;  $X = N \cdot NH \cdot C_6 H_3(NO_2)_2$ ;  $R^1$  or  $R^2 =$ H and  $CO_2Et$ ] the intensity of this peak is 82% of the intensity of the parent-ion peak, suggesting that the  $\gamma$ -ethoxycarbonyl- $\beta\gamma$ -dimethyl- $\alpha\beta$ -olefinic 2,4-dinitrophenylhydrazone unit present in [III;  $X = N \cdot NH \cdot C_{e}H_{3}$ - $(NO_2)_2$  is also present in the cyclopentenone 2,4-dinitrophenylhydrazone. The samples of 4-ethoxycarbonyl-3,4-dimethylcyclohex-2-enone (III; X = O) and 6-ethoxycarbonyl-3,6-dimethylcyclohex-2-enone (V; X = O) were prepared by the cyclisation of ethyl  $\alpha \gamma$ -diacetyl- $\alpha$ methylbutyrate.<sup>5</sup> Pleininger and Suehiro <sup>5</sup> showed that (III; X = 0) was the major product in basic conditions, but that under acid conditions (V; X = O) predominated, but did not isolate the pure isomers. We find that cyclisation with piperidinium acetate gives (III; X = 0) and (V; X = O) in the ratio 3.5:1 and that cyclisation with phosphoric acid gives (III; X = 0) and (V; X =O) in the ratio 1:8. Both isomers were isolated by preparative g.l.c. and characterised as 2,4-dinitrophenylhydrazones. Compound [V;  $X = N \cdot NH \cdot C_6 H_3 (NO_2)_2$ ] has been prepared previously 6 from material obtained by the bromination-dehydrobromination of 2-ethoxycarbonyl-2,5-dimethylcyclohexanone which, in view of the known 7 equilibrium between 3,4- and 3,6-dimethylcyclohex-2-enones, is likely to have been a mixture of (III; X = O) and (V; X = O).

Other experiments have shown that the relative amounts of the products depend on the molar ratio of ethyl a-methylacetoacetate to lead dioxide. With a twofold molar excess of the ester over the oxidant the only major products were (IV) and (II) which were formed in 32 and 55% yields respectively and could be isolated by fractional distillation.

The nature of the products, and their similarity to those resulting from the electrochemical oxidation of ethyl a-methylacetoacetate<sup>2</sup> suggests that they all arise initially from the radical (VI). Compound (II) is the expected product of  $C \longrightarrow C$  coupling from (VI), and (I; X = O,  $R^1 = R^2 = CO_2Et$ ) is derived from (II) by

<sup>&</sup>lt;sup>6</sup> H. Pleininger and T. Suchiro, Chem. Ber., 1956, 89, 2789.
<sup>6</sup> G. Pyne, R. C. Banerjee, and D. Nasipuri, J. Indian Chem. Soc., 1963, 40, 199 (Chem. Abs., 1963, 59, 7383).
<sup>7</sup> R. N. Lacey, J. Chem. Soc., 1960, 1639.

cyclisation and dehydration. Another example of the cyclisation of a 1,4-diketone, produced by oxidative dimerisation with lead dioxide, to a cyclopentenone is

$$\begin{bmatrix} O & O \\ || & | \\ MeC - \dot{C}Me \cdot CO_2 Et & \longrightarrow MeC = CMe \cdot CO_2 Et \end{bmatrix} (VI)$$
$$\begin{array}{c} MeCO - CH \cdot CH_2 \cdot CMe \cdot COMe \\ | & | \\ CO_2 Et & CO_2 Et \end{bmatrix} (VII)$$

known.<sup>8</sup> Compound [I;  $X = N \cdot NH \cdot C_6 H_3(NO_2)_2$ ;  $R^1 =$  $CO_2Et; R^2 = H$ ] is, in turn, derived from (I; X = O;  $R^1 = R^2 = CO_2Et$ ). Disproportionation of the radical (VI) leads, via ethyl a-methyleneacetoacetate, to diethyl ay-diacetyl-a-methyl-glutarate (VII),<sup>2</sup> cyclisation of which, with loss of an ethoxycarbonyl group, would give predominantly (III; X = O), the isolated product, under the basic conditions. The enol-ether (IV), not detected amongst the electrolysis products,<sup>2</sup> is presumably formed from (VI) by  $C \longrightarrow O$  coupling; intramolecular  $C \longrightarrow O$  coupling has been observed during oxidative phenolic coupling with lead dioxide.9 The unexpected loss of an acetyl group during the formation of (IV) presumably occurs by a subsequent retro-Claisen fission, but the nature of the base remains unclear. Our results provide no information about the heterogeneous oxidation leading to the formation of the radical (VI).

The reaction of ethyl acetoacetate with lead dioxide takes a different course. An exothermic decomposition, of the type observed with pentane-2,4-dione,<sup>3</sup> occurs and the only identifiable products are acetone and ethanol.

## EXPERIMENTAL

For general directions see the preceding paper  $^2$  and references given there.

Ethyl αγ-Diacetyl-α-methylbutyrate.—Addition of ethyl α-methylacetoacetate <sup>2</sup> to methyl vinyl ketone gave ethyl αγ-diacetyl-α-methylbutyrate, b.p. 159—162°/15 mm. (lit., <sup>5</sup> 148—150°/12 mm.),  $\tau$  5·8 (2H, q, J 7 Hz, ester CH<sub>2</sub>), 7·4—8·2 (4H, m, CH<sub>2</sub>–CH<sub>2</sub>), 7·84 (6H, s, MeCO), 8·66 (3H, s, Me) and 8·82 (3H, t, J 7 Hz, ester Me), bis-2,4-dinitrophenylhydrazone, m.p. 182—188° (from CHCl<sub>3</sub>–EtOH),  $\lambda_{max}$ , 357 nm. (log  $\varepsilon$  4·55) (Found: C, 48·3; H, 4·7; N, 19·65. C<sub>23</sub>H<sub>26</sub>N<sub>8</sub>O<sub>10</sub> requires C, 48·1; H, 4·5; N, 19·5%).

Cyclisation of Ethyl  $\alpha\gamma$ -Diacetyl- $\alpha$ -methylbutyrate.—(i) Cyclisation of ethyl  $\alpha\gamma$ -diacetyl- $\alpha$ -methylbutyrate (4.08 g.) with 90% orthophosphoric acid (17 ml.) for 0.75 hr. at 55—65° gave an oil (1.85 g.), b.p. 149—152°/14 mm. shown by g.l.c. (D6, 10% CW, 152°; F and M, 10% A, 195°) to contain (V; X = O), (III; X = O), and starting material in the ratios 16:2:7. Preparative g.l.c. (A, 10% DEGS, 165°) gave 6-ethoxycarbonyl-3,6-dimethylcyclohex-2-enone (V; X = O) (Found: C, 67·2; H, 8·1. C<sub>11</sub>H<sub>16</sub>O<sub>3</sub> requires C, 67·35; H, 8·2%),  $\tau$  4·11 (1H, bs, CH=C), 5·84 (2H, q, J 7 Hz, ester CH<sub>2</sub>), 7·4—8·3 (4H, m, CH<sub>2</sub>-CH<sub>2</sub>), 8·02 (3H, s, Me-C=C), 8·63 (3H, s, Me), and 8·88 (3H, t, J 7 Hz, ester Me), 2,4-dinitrophenylhydrazone, m.p. 149—152° (lit.,<sup>6</sup> 155—156°) (Found: C, 54·6; H, 5·4; N, 15·0. C<sub>17</sub>H<sub>20</sub>N<sub>4</sub>O<sub>6</sub> requires C, 54·3; H, 5·3; N, 14·9%),  $\tau$  3·70 (1H, bs, CH=C),

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5.87 (2H, q, J 7 Hz, ester CH<sub>2</sub>), 7.4-8.3 (4H, m, CH<sub>2</sub>-CH<sub>2</sub>), 7.96 (3H, s, Me-C=C), 8.44 (3H, s, Me) and 8.75 (3H, t, J 7 Hz, ester Me), m/e 376 (M<sup>+</sup>, 100%), 330 (20%), 303 (25%), 285 (20%), 269 (40%), 267 (30%), 223 (20%), 208 (15%), and 194 (25%). Preparative g.l.c. on a different stationary phase (A, 30% AP, 170°) gave 4-ethoxycarbonyl-3,4-dimethylcyclohex-2-enone (III; X = O) (Found: C, 67.7; H, 8·3%)  $\tau$  4·10 (1H, q, J 1·2 Hz, CH=C), 5·50 (2H, q, J 7 Hz, ester CH<sub>2</sub>), 7·4-8·3 (4H, m, CH<sub>2</sub>CH<sub>2</sub>), 8·03 (3H, d, J 1·2 Hz, Me-C=C), 8.55 (3H, s, Me), and 8.72 (3H, t, J 7 Hz, ester Me), 2,4-dinitrophenylhydrazone, m.p. 114° (Found: C, 54.25; H, 5·4; N, 14·8%),  $\tau$  3·79 (1H, q, J 1·0 Hz, CH=C), 5·80 (2H, q, J 7.5 Hz, ester CH<sub>2</sub>), 7.2-8.3 (4H, m, CH<sub>2</sub>CH<sub>2</sub>), 8.01 (3H, d, J 1.0 Hz, Me-C=C), 8.58 (3H, s, Me), and 8.72 (3H, t, J7.5 Hz, ester Me), m/e 376 (M<sup>+</sup> 100%), 303 (100%), 285 (2%), 269 (20%), 267 (1%), 223 (5%), and 194 (2%). (ii) Cyclisation of ethyl  $\alpha \gamma$ -diacetyl- $\alpha$ -methylbutyrate (5.2 g.) with piperidinium acetate (1.68 g.) in ethanol (5 ml.) for 2 hr. at 78° gave an oil (3.65 g.), b.p. 143-150°/11 mm. shown by g.l.c. (as above) to contain (V; X = O), (III; X = O), and starting material in the ratios 11:38:1.

Oxidation of Ethyl a-Methylacetoacetate with Lead Dioxide. --(i) Ethyl α-methylacetoacetate<sup>2</sup> (20 g., 0.14 mole) was heated under reflux with commercial lead dioxide (18 g., 0.075 mole) in benzene (300 ml.) for 55-60 hr. The suspended solid was collected on a filter and washed with a little benzene (the washings being added to the filtrate), chloroform, ethanol, and water and was then dried. The filtrate was dried (CaCl<sub>2</sub>) and distilled to give material (7.7 g.), b.p. 120-165°/15 mm. Analytical g.l.c. (F and M, 10% CW, 190°) before and after the distillation showed that no change in the products occurred during the distillation. The products were examined by two methods: (a) The mixture was separated into four fractions by preparative g.l.c. (A, 30% CW, 190-220°), and each fraction was analysed by g.l.c. on columns of differing polarities. The fraction of longest retention time was 4,5-diethoxycarbonyl-3,4,5-trimethylcyclopent-2-enone (I; X = O;  $R^1 = R^2 =$ CO<sub>2</sub>Et) (Found: M, 268.1325. C<sub>14</sub>H<sub>20</sub>O<sub>5</sub> requires M268.1311),  $v_{max}$  1740, 1710, 1630, and 1095 cm.<sup>-1</sup>, m/e 268, 223, 196, 167, 149, 139, 123, 122 (base peak) and 121. Compound (I; X = O;  $R^1 = R^2 = CO_2Et$ ) gave a mixture of 2,4-dinitrophenylhydrazones (180 mg.) from which 4,5-diethoxycarbonyl-3,4,5-trimethylcyclopent-2-enone 2,4-dinitrophenylhydrazone (12 mg.), m.p. 133—134° (from ethanol) (Found: C, 53.5; H, 5.6; H, 5.6; N, 12.3.  $C_{20}H_{24}N_4O_8$  requires C, 53.6; H, 5.4; N, 12.5%),  $v_{max}$  3300, 1725, 1620, 1590, and 1330 cm.<sup>-1</sup> was isolated by preparative t.l.c.

The fraction of second longest retention time was diethyl  $\alpha \alpha'$ -diacetyl- $\alpha \alpha'$ -dimethylsuccinate (II) (Found: C, 59.0; H, 7.5.  $C_{14}H_{22}O_6$  requires C, 58.7; H, 7.7%),  $v_{max}$  1730, 1720, and 1090 cm.<sup>-1</sup>, m/e 286, 268, 213, 201, 199, 196, 155, 127, 125, and 123 (base peak), bis-2,4-dinitrophenylhydrazone, m.p. 182–183° (from CHCl<sub>3</sub>–EtOH) (Found: C, 48.6; H, 4.8; N, 17.1.  $C_{26}H_{30}N_8O_{12}$  requires C, 48.3; H, 4.6; N, 17.3%),  $\lambda_{max}$  356 nm. (log  $\varepsilon 4.78$ )  $\tau$  –1.03 (2H, bs, NH), 0.85–2.76 [6H, m,  $C_6H_3(NO_2)_2$ ], 5.74 (4H, q, 7 Hz, ester CH<sub>2</sub>), 7.88 (6H, s, Me–C=N), 8.14 (6H, s, Me), and 8.80 (6H, t, J 7 Hz, ester Me).

The third fraction still contained two components (g.l.c.,

<sup>8</sup> R. Brettle and B. Crowther, unpublished data.

<sup>9</sup> C. H. Hassall and J. R. Lewis, *J. Chem. Soc.*, 1961, 2312; D. Taub, C. H. Kuo, H. L. Slates, and N. L. Wendler, *Tetrahedron*, 1963, **19**, 1. F and M, 10% SR, 127°; retention times 5.0 and 6.6 min.) and a trace of a third. The component having a retention time of 5.0 min. was identified as 4-ethoxycarbonyl-3,4-dimethylcyclohex-2-enone (III; X = O) and a sample collected by preparative g.l.c. (A, 30% SR, 180°) was identical (n.m.r., i.r.) with an authentic sample.

The fraction having the shortest retention time was shown (F and M, 10% SR, 127°) to contain one major and one minor component. The major component, purified by preparative g.l.c. (A, 30% SR, 160–170°), was shown to be diethyl 2,4,5-trimethyl-3-oxahex-4-enedioate (Found: C, 58·7; H, 8·5. C<sub>12</sub>H<sub>20</sub>O<sub>5</sub> requires C, 59·0; H, 8·2%)  $n_{\rm D}^{25}$  1·4569,  $\lambda_{\rm max}$  246·5 nm. (log  $\varepsilon$  4·11),  $\nu_{\rm max}$  1760, 1700, 1630, and 1110 cm.<sup>-1</sup>, m/e 244, 199, 198, 171, 127, 126, 125, 123, 98 (base peak), and 97.

(b) The oxidation products were separated into three fractions by preparative g.l.c. (A, 30% SR, 200°) and each fraction was separately converted into a mixture of 2,4-dinitrophenylhydrazones. Preparative t.l.c. on the products from the fraction having the shortest retention time gave 4-ethoxycarbonyl-3,4,5-trimethylcyclopent-2-enone 2,4-dinitrophenylhydrazone (I; X = N·NH·C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>2</sub>; R<sup>1</sup> = CO<sub>2</sub>Et; R<sup>2</sup> = H), m.p. 131-132° (from ethanol) (Found: C, 54·5; H, 5·2; N, 15·1. C<sub>17</sub>H<sub>20</sub>N<sub>4</sub>O<sub>6</sub> requires C, 54·3; H, 5·3; N, 14·9%),  $\lambda_{max}$  378 nm. (log  $\varepsilon$  4·40),  $\nu_{max}$  3300, 1730, 1620, 1590, 1430, and 1097 cm<sup>-1</sup>, m/e 376 (100%), 303 (82%), 205 (2%), 269 (10%), 267 (5%), 223 (4%), and 194 (4%). Later fractions on preparative t.l.c. yielded ethyl  $\alpha$ -methylacetoacetate 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 62°, 4-ethoxycarbonyl-3,4-dimethylcyclohex-2-enone

2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 114°, and diethyl  $\alpha\alpha'$ -diacetyl- $\alpha\alpha$ -dimethylsuccinate bis-2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 179—182°.

(ii) Ethyl  $\alpha$ -methylacetoacetate (24.7 g., 1 mol.) was heated with commercial lead dioxide (21.0 g., 0.5 mol.) in benzene (300 ml.) for 61 hr. under reflux, to give an oil (13.6 g.) which was distilled to give four fractions (i), b.p. 92—93°/0.04 mm. (1.39 g.), (ii) b.p. 100—110°/0.04 mm. (4.13 g.), (iii) b.p. 110—122°/0.04 mm. (2.48 g.), and (iv), b.p. 122—132°/0.04 mm. (1.32 g.). Analytical g.l.c. (F and M, 10% SR, 120°) showed that fraction (i) was 98% diethyl 2,4,5-trimethyl-3-oxahex-4-enedioate and that fraction (iv) was diethyl  $\alpha\alpha'$ -diacetyl- $\alpha\alpha'$ -dimethylsuccinate; fractions (ii) and (iv) were mixtures of these two components.

Reactions of Diethyl 2,4,5-Trimethyl-3-oxahex-4-enedioate. —(a) Diethyl 2,4,5-trimethyl-3-oxahex-4-enedioate (160 mg.) in ethanol (1 ml.) with an excess of 2,4-dinitrophenylhydrazine (140 mg.) in ethanol (10 ml.) containing sulphuric acid (0·3 ml.) gave ethyl  $\alpha$ -methylacetoacetate 2,4-dinitrophenylhydrazone, (72 mg.), m.p. and mixed m.p. 60—61°.

(b) Diethyl 2,4,5-trimethyl-3-oxahex-4-enedioate (100 mg.) was warmed for 10 min. with 2N-hydrochloric acid (0·1 ml.) at 100° and the mixture was then kept at 20° for 5 days. The products, collected in chloroform were shown by analytical g.l.c. (F and M, 10% DEGS, 160°; 10% SR, 120°) to have retention times identical with those of ethyl lactate and ethyl  $\alpha$ -methylacetoacetate.

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