Anodic Oxidation. Part IX.¹ Electrolysis of Ethyl Sodiomethylacetoacetate

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The electrolysis of ethyl sodiomethylacetoacetate in NN-dimethylacetamide at a platinum anode gives diethyl α,α'-diacetyl-α,α'-dimethylsuccinate, 4,5-diethoxycarbonyl-3,4,5-trimethylcyclopent-2-enone and 4-ethoxycarbonyl-3,4-dimethylcyclohex-2-enone. Degradation of these products with aqueous ethanolic alkali gives a mixture of dimethylcyclohexenones and trimethylcyclopentenones; the synthesis of 2,3,4-trimethylcyclopent-2-enone is discussed.

WE have reported ² that electrolysis of diethyl sodiomethylmalonate gives products arising from both the coupling and the disproportionation of the radical $\dot{C}Me(CO_2Et)_2$ formed by the oxidation of the carbanion. We report now on the electrolysis of ethyl sodiomethylacetoacetate.

The electrolysis of ethyl sodiomethylacetoacetate in NN-dimethylacetamide at a platinum anode gave three major products, 4-ethoxycarbonyl-3,4-dimethylcyclohex-2-enone (I; $R = CO_2Et$), 4,5-diethoxycarbonyl-3,4,5-trimethylcyclopent-2-enone (II; $R = CO_2Et$) and diethyl α, α' -diacetyl- α, α' -dimethyl succinate (IIII; $R = CO_2Et$). Samples of (II; $R = CO_2Et$) and (III; $R = CO_2Et$) were obtained by preparative g.l.c. on a Carbowax column and identified by their n.m.r. spectra.³ Compound (I; $R = CO_2Et$) was not separated from two minor components, detected by analytical g.l.c., under these conditions, but a sample having an n.m.r. spectrum identical with an authentic sample³ was obtained by further preparative g.l.c. on a diethyleneglycol succinate column. Diethyl 2,4,5-trimethyl-3-oxahex-4-enedioate, with (III; $R = CO_2Et$) a major product from the oxidation of ethyl α -methylacetoacetate with lead dioxide,^{3,4} was not detected amongst the products by g.l.c.



Compound (III; $R = CO_2Et$) is the expected oxidative dimer, formed by the self-coupling of the radical CMe(COMe)CO₂Et formed in discharge of the carbanion at the anode, and (II; $R = CO_2Et$) is a base-catalysed cyclisation product of (III; $R = CO_2Et$). The ester (I; $R = CO_2Et$) is derived from diethyl $\alpha\alpha'$ -diacetyl- α methylglutarate (IV) by cyclisation and retro-Claisen

¹ Part VIII, R. Brettle and D. Seddon, J. Chem. Soc. (C), paper Org. 9/1950. ² R. Brettle and J. G. Parkin, J. Chem. Soc. (C), 1967, 1352. loss of an ethoxycarbonyl group, and (IV) is the expected product by analogy with the behaviour of the radical $\dot{C}Me(CO_2Et)_2$ if radical disproportionation, followed by Michael addition of the carbanion to the resultant ethyl methyleneacetoacetate, takes place. This second example suggests that such a disproportionation of tertiary radicals formed by the anodic oxidation of carbanions will be general.

In preliminary experiments the combined electrolysis products were degraded with aqueous ethanolic alkali to a mixture of methyl-substituted cyclic $\alpha\beta$ -olefinic ketones. Five compounds were detected by analytical g.l.c. Three of these were recognised as 3,4-dimethylcyclohex-2-enone (I; R = H), 2,3,4-trimethylcyclopent-2-enone (V), and 3,6-dimethylcyclohex-2-enone (VI) by their retention times. One of the two minor products was not identified, but an impure sample of the other was separated by semipreparative g.l.c. and collected in carbon tetrachloride. The n.m.r. spectrum showed the signals expected for 3,4,5-trimethylcyclopent-2-enone (II; R = H) with singlets at $\tau 4.12$ and 7.92, showing allylic coupling, due to the proton at C-2 and the methyl group at C-3 respectively, doublets at τ 8.79 and 8.82 due to the methyl groups at C-4 and C-5, and further absorption in the region τ 7.5–8.5 due to the protons at C-4 and C-5. The i.r. spectrum, obtained by condensing a sample from the chromatograph directly onto a rocksalt plate showed absorption at 1715 (C=O) and 1620 cm.⁻¹ (C=C). 3-Methylcyclopent-2-enone shows signals at τ 4.14 and 7.85 due to the C-2 proton and the C-3 methyl group respectively, and at 1711 and 1674 (C=O) and 1625 cm.⁻¹ (C=C).⁵ A further sample of (II; R = H) was collected in Brady's reagent and gave two 2,4-dinitrophenylhydrazones, (A) and (B) in the ratio 1:4; these were separated by t.l.c. Somewhat greater quantities of hydrazone (B) were isolated by t.l.c. from the mixture of 2,4-dinitrophenylhydrazones obtained by treating the unseparated degradation products with Brady's reagent; this enabled it to be confirmed as the derivative of (II; R = H). Hydrazone (B) gave microanalytical figures in agreement with the proposed structure and showed a parent ion at m/e 304 in the mass spectrum. It absorbed at 382 nm. (log ε 4.30) and had an n.m.r. spectrum similar to that of (II; R = H), the main difference being that the signal for the proton at

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J. Chem. Soc. (C), 1970

C-2 was at τ 3.74. Insufficient hydrazone (A) was available for complete characterisation, but since it had an absorption maximum at 387 nm. and had an i.r. spectrum almost identical with that of hydrazone (B), it presumably differs from hydrazone (B) only in stereochemistry.

Cyclisation of the unsymmetrical 1,5-diketone (IV) can occur in either direction to give a 3,4- or a 3,6-dimethylcyclohex-2-enone derivative, but only the 3,4-dimethyl substituted compound (I; $R = CO_2Et$) is formed in the electrolysis. However, 3,4- and 3,6-dimethylcyclohex-2-enone are readily interconverted ⁶ and this accounts for the presence of both (I; R = H) and (VI) amongst the degradation products. Cyclisation of the symmetrical 1,4-diketone (III; $R = CO_{2}Et$), with concurrent loss of the ethoxycarbonyl groups, would lead initially to (II; R = H), but base-catalysed isomerisation via the unconjugated cyclopentenone would then

(see Experimental section) for comparison with one of the degradation products we took the opportunity to examine its reaction with Brady's reagent, since it has been suggested ¹¹ that the 2,4-dinitrophenylhydrazone can exist in two diastereoisomeric forms, although only one form has previously been adequately characterised.¹² Two 2,4-dinitrophenylhydrazones of 3,6-dimethylcyclohex-2-enone (VI) have been described.¹³ Compound (I; R = H) did give two 2,4-dinitrophenylhydrazones, (C) and (D), in the ratio 19:1, readily separable by t.l.c. Hydrazone (C), m.p. 148-149°, corresponded to the previously reported derivative.¹² Hydrazone (D), m.p. 103-104°, was shown by its analytical figures and its n.m.r. spectrum to be diastereoisomeric with hydrazone (C), and the two derivatives had identical mass spectral fragmentation patterns. The n.m.r. spectra of hydrazones (C) and (D) were similar, but the protons at C-2in hydrazone (C) absorbed at τ 3.91 and the NH proton

TABLE

N.mr. spectra at 60 MHz showing the chemical shifts (τ values) for methyl groups at the positions indicated and for vinylic hydrogen atoms at C-2, and the multiplicities *†

Compound			÷ ,			
	Solvent	C-2	C-3	C-4	C-5	C-6
(V)	CCl4	8.39bs	8.02bs	$8 \cdot 84d$		
DNP of (V)	CDČl ₈	8.06bs	8.14bs	8.80d		
(II; $\mathbf{R} = \mathbf{H}$)	CCl	$4 \cdot 12 bs$	7.92bs	8·82d ±	8·79d 1	
$\dot{D}NP \text{ of } (II; R = H) (B)$	$CDCl_3$	3.74bs	7.92bs	8•68d	8.77d	
DNP (C)	CDCl ₃	3.91bs	8.04bs	8·84d		
DNP (D)	CDCl ₃	3.67bs	7.95bs	8·79d		
DNP of (VI), m.p. 172—173°	CDCl ₃	3.98bs	8.05bs			8·87d
	-					

DNP = 2.4-dinitrophenvlhvdrazone.

* bs = broad singlet, d = doublet, J 6.5 Hz. \dagger All compounds showed complex absorption in the region $\tau 6.8$ —8.5 due to protons at C-4, C-5 (and C-6) and the 2,4-dinitrophenylhydrazones also showed the characteristic absorptions of the 2,4-dinitrophenylhydrazones also showed the characteristic absorptions of the 2,4-dinitrophenylhydrazones also showed the characteristic absorptions of the 2,4-dinitrophenylhydrazones also showed the characteristic absorption for the 2,4-dinitrophenylhydrazones also showed the characteristic absorption of the 2,4-dinitrophenylhydrazones residue. ‡ Assignment between C-4 and C-5 uncertain.

give (V). Other examples of this isomerisation of a 3,4,5-trisubstituted cyclopent-2-enone to the 2,3,4-trisubstituted isomer are known.7 In the present work, compound (V) was obtained by the Nazarov reaction from 5-methylhepta-1,5-dien-3-yne,8 but attempts to prepare (II; R = H) also gave (V). The basecatalysed cyclisation and de-ethoxycarbonylation of ethyl $\alpha\beta$ -diacetyl- α -methylbutyrate (III; R = H), which we prepared by the action of 2-bromobutan-3-one on ethyl sodiomethylacetoacetate, is reported⁹ to give compound (II; R = H), but in our hands gave compound (V). The base-catalysed cyclisation of 3,4-dimethylhexane-2,5-dione,¹⁰ similarly gave compound (V).

Having prepared 3,4-dimethylcyclohex-2-enone (I; R = H) by a minor modification of Lacey's method⁶

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at -1.22, whereas those in hydrazone (D) absorbed at τ 3.67 and -1.47 respectively. In the u.v. spectra hydrazone (C) absorbed at 5 nm. longer wavelength than (D). Hydrazone (C), with dilute acid, gave the equilibrium mixture of both isomers; a similar behaviour is shown by the isomers of 3,6-dimethylcyclohex-2-enone 2,4-dinitrophenylhydrazone.13

EXPERIMENTAL

Details of the electrolysis cell,¹⁴ and of procedures for g.l.c.¹⁵ and other general directions ^{1,2} have been given in earlier parts of this series.

Starting Materials and Reference Compounds.-Ethyl α-methylacetoacetate, b.p. 73-75°/13 mm. (lit.,¹⁶ 75.5-76.5°/12 mm.) was prepared by Robinson's method 17 from ethyl β -diethylaminocrotonate 18 and from ethyl β -pyrrolidinocrotonate; 100 the 2,4-dinitrophenylhydrazone had

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m.p. 62—64° (lit.,¹⁹ 56—57°), λ_{max} 356 nm. (log ε , 4·31) (Found: C, 48·2; H, 4·8; N, 17·6. Calc. for $C_{13}H_{16}N_4O_6$: C, 48.1; H, 5.0; N, 17.3%). 3-Methylpentane-2,4-dione, b.p. 168-172° (lit., 20 170-172°), containing some 3,3-dimethylpentane-2,4-dione,²¹ was prepared by the methylation of pentane-2,4-dione.²⁰ 5-Methylhepta-1,5-dien-3yne, b.p. 32-34°/13 mm., n_p¹³ 1.6068 (lit., 8 41-42°/23 mm., $n_{\rm D}^{15}$ 1.5051) was prepared from acetylene by the sequence p-sulphonate ²³ → butenyne ²³ → 5-methylhept-1-en-3yn-5-ol 8 - 5-methylhepta-1,5-dien-3-yne,8 and on cyclisation gave 2,3,4-trimethylcyclopent-2-enone, b.p. 82-84°/ 13 mm., $n_{\rm p}^{18}$ 1.4835 (lit.,⁸ 89–91°/19 mm., $n_{\rm p}^{20}$ 1.4820), 2,4-dinitrophenylhydrazone, m.p. 177-178° (lit.,²⁴ 173°), $\nu_{\rm max}$ 3400, 2950, 1625, 1600, 1580, and 1530 cm.⁻¹, $\lambda_{\rm max}$ 388 nm. (log ε 4·22). 2-Bromobutan-3-one, b.p. 84—84·5°/120 —128 mm., $n_{\rm p}^{20}$ 1·4574 (lit.,²⁵ 87—88°/150 mm., $n_{\rm p}^{20}$ 1.4571), prepared by the bromination of butanone,²⁵ was fractionated through a 12 in. column packed with Raschig rings until pure by g.l.c. (F and M, 10% CW, 95-165°, programmed at 10°/min.); the n.m.r. spectrum agreed with the published spectrum.²⁶ Oxidation of butanone with lead dioxide ¹⁰ gave a mixture of meso- and (\pm) -3,4-dimethylhexane-2,5-dione, b.p. 86-88°/18 mm.

6-Acetyl-3,6-dimethylcyclohex-2-enone.—3-Methylpentane-2,4-dione (57 g., 0.5 mole), methyl vinyl ketone (30 g., 0.42 mole), sodium methoxide [from sodium (0.37 g.)], and quinol (1 g.) were heated together for 2.5 hr.; water (11 ml.) was distilled off and the temperature of the mixture rose from 120° to 220°. The residue was taken up in ether and the ethereal solution was washed with 10% aqueous sulphuric acid and water, and then dried. Distillation gave 6-acetyl-3,6-dimethylcyclohex-2-enone (14.7 g.), b.p. 120-126°/11 mm. (lit., 6 120°/10 mm.), v_{max} 1713, 1670, and 1639 cm.⁻¹. 3,4- and 3,6-Dimethylcyclohex-2-enones.—Hydrolysis of

6-acetyl-3,6-dimethylcyclohex-2-enone by Lacey's method 6 gave 3,6-dimethylcyclohex-2-enone (VI) and 3,4-dimethylcyclohex-2-enone (I; R = H) in the ratio 7:3, having retention times of 13.6 and 20.2 min. respectively (F and M, DEGS, 105°) which were separated by preparative g.l.c.²⁷ (A, DEGS, 100°) and had n.m.r. spectra in agreement with the published spectra.²⁷ 3,6-Dimethylcyclohex-2-enone gave a mixture of two 2,4-dinitrophenylhydrazones with Brady's reagent ¹³ (t.l.c.) from which the isomer m.p. 172-173° (lit., 13 171-172°) was obtained by fractional crystallisation from ethanol. 3,4-Dimethylcyclohex-2-enone also gave a mixture of two 2,4-dinitrophenylhydrazones, which were separated by preparative t.l.c. Hydrazone (C) ($R_{\rm F}$ 0.5, analytical t.l.c., eluant: benzene) had m.p. 148-149° (lit., 12 149—150°), $\nu_{\rm max}$ 3280, 1620, 1580, 1330, and 1300, $\lambda_{max.}$ 383 nm. (log ϵ 4.45), m/e 304 (100%), 299 (4%), 255 (10%), 149 (15%), and 125 (15%) (Found: C, 55.4; H, 5.1; N, 18.4. Calc. for $C_{14}H_{16}N_4O_4$: C, 55.3; H, 5.3; N, 18.4%). Hydrazone (D) ($R_{\rm F}$ 0.34, above conditions) had m.p. 103-104°, $\nu_{\rm max}$ 3290, 1625, 1575, 1330, 1305, and 1290 cm. $^{-1},$ λ_{max} 378 nm. (log ϵ 4·45), m/e 304 (100%), 299 (5%), 255 (10%), 149 (50%), and 125 (22%) (Found: C, 55.3; H, 5.1; N, 18.7%).

Attempted Preparations of 3,4,5-Trimethylcyclopent-2-en-

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one.—(i) Ethyl α -methylacetoacetate (108 g., 0.75 mole) was added dropwise to a stirred suspension of sodium hydride (18 g., 0.75 mole) in NN-dimethylformamide (200 ml.) cooled to 0° ; the mixture was then heated to 60° during 0.5 hr. 2-Bromobutan-3-one (100 g., 0.67 mole) was then added to the stirred mixture at 60° during 4 hr.; the mixture was then stirred for a further 20 hr. at 50°. Precipitated sodium bromide was filtered off from the resultant solution (pH 10) and washed with ether. The filtrate was poured into water (200 ml.) adjusted to pH 7 with 2n-hydrochloric acid and extracted with ether. The combined ethereal solutions were washed with saturated aqueous sodium hydrogen carbonate and water, and then dried. Distillation gave material b.p. 128-142°/14 mm. (42.7 g.), a part of which (20.9 g.) was then heated under reflux for 8 hr. with a solution of potassium hydroxide (50 g.) in water (450 ml.) and ethanol (25 ml.). The mixture was then adjusted to pH 7 with 10n-hydrochloric acid, saturated with salt, and continuously extracted with ether. The extract was dried and distilled to give 2,3,4-trimethylcyclopent-2-enone (6.45 g.), b.p. 86-87°/13 mm., pure by g.l.c. (F and M, CW, 150°) identified by its i.r. and n.m.r. spectra and by conversion into the 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 177-178°. (ii) 3,4-Dimethylhexane-2,5-dione (5 g.) when heated under reflux for 25 min, with a solution of sodium hydroxide (1 g.) in water (70 ml.) and ethanol (10 ml.) gave 2,3,4-trimethylcyclopent-2-enone (2.6 g.), b.p. 113-115°/50 mm., identified by its n.m.r. spectrum.

Electrolysis of Ethyl Sodiomethylacetoacetate in NN-Dimethylacetamide.---A solution of ethyl sodiomethylacetoacetate [from ethyl a-methylacetoacetate (24.0 g., 1 mol.) and sodium hydride (4.0 g., 1 mol.)] in NN-dimethylacetamide (250 ml.) was electrolysed at 15-40° at a platinum anode and a mercury cathode. The current, initially 3.5A at 100v fell to 0.1A after 3.5 hr. The amalgam was separated and the solution was poured into water (200 ml.), adjusted to pH 3 with 2n-hydrochloric acid, and extracted with ether $(4 \times 100 \text{ ml.})$. The extracts were washed with water (2 \times 100 ml.), dried, and distilled to separate ether and ethyl α -methylacetoacetate (10.4 g.), b.p. 30-40°/0.05 mm. The residue (8.8 g.) was examined in two ways. (a) Preparative g.l.c. (A, CW, 190-220°) gave 4,5-diethoxycarbonyl-3,4,5-trimethylcyclopent-2-enone (II; R = CO_2Et) and diethyl $\alpha\alpha'$ -diacetyl- $\alpha\alpha'$ -dimethylsuccinate (III; $R = CO_2Et$) identified by their n.m.r. spectra ³ and a third fraction, resolved by analytical g.l.c. (F and M, DEGS, 180°) into one major component (retention time 9.0 min.) and two minor components (retention times 5.1 and 6.3 min.). Preparative g.l.c. on this fraction (A, DEGS, 190°) gave the major component 4-ethoxycarbonyl-3,4-dimethylcyclohex-2-enone (I; $R = CO_2Et$), identified by its retention time and its n.m.r. spectrum.³

(b) The residue (7.52 g.) was heated under reflux for 20 min. with a solution of sodium hydroxide (3.7 g.) in water (40 ml.) and ethanol (12 ml.). The mixture was cooled to room temperature and 18N-sulphuric acid (6 ml., excess) was added dropwise, with stirring. The mixture was then

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heated under reflux for a further 15 min., after which it was cooled, diluted with water (250 ml.), and adjusted to pH 7 with solid sodium hydrogen carbonate. Continuous etherextraction of the solution for 48 hr. gave an oil (0.78 g.), b.p. 40-90°/13 mm. shown by g.l.c. (F and M, DEGS, 120°) to contain five components (retention times 2.2, 4.9, 6.3, 7.0, and 10.1 min.). The components having retention times 6.3, 7.0, and 10.1 min. were identified as 2,3,4-trimethylcyclopent-2-enone (V), 3,6-dimethylcyclohex-2-enone (VI), and 3,4-dimethylcyclohex-2-enone (I; R = H) by their retention times under the above conditions and other conditions (F and M, CW, 150°). The material of retention time 4.9 min. was identified as 3,4,5-trimethylcyclopent-2-enone by its i.r. spectrum, v_{max} 1715 and 1620 cm.⁻¹, obtained by condensing a sample from the chromatograph directly onto a rock-salt plate, and by its n.m.r. spectrum (see Table) measured on a solution obtained by the repeated collection of small amounts in carbon tetrachloride. Treatment of the material recovered from this solution with Brady's reagent gave a mixture of two 2,4-dinitrophenylhydrazones [(A) and (B); $R_{\rm F}$ 0.69 and 0.59 respectively, analytical t.l.c.; eluant benzene]; 2,3,4-trimethylcyclopent-2-enone 2,4-dinitrophenylhydrazone ($R_{\rm F}$ 0.80) was not detected. Preparative t.l.c. gave one isomer (A) of 3,4,5-trimethylcyclopent-2-enone 2,4-dinitrophenylhydrazone (1 mg.), m.p. 97—100°, $v_{\rm max}$ 3350, 1630, 1610, 1585, 1330, and 1300 cm.⁻¹, $\lambda_{\rm max}$ 387 nm. A second isomer (B) of 3,4,5-trimethylcyclopent-2-enone 2,4-dinitrophenylhydrazone (4 mg.), m.p. 137—143° (from carbon tetrachloride), $v_{\rm max}$ 3300, 1630, 1620, 1590, 1324, and 1300 cm.⁻¹, $\lambda_{\rm max}$ 382 (log ε 4.30) (Found: C, 55.0; H, 5.2; N, 18.3%; M 304. C₁₄H₁₆N₄O₄ requires C, 55.2(5); H, 5.3; N, 18.5%; M 304) was also isolated from this mixture and in greater quantity by preparative t.l.c. on the mixture of 2,4-dinitrophenylhydrazones obtained by treating the total cyclisation products with Brady's reagent.

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