**891.** *Investigations on the Synthesis of 2-Acetylcyclohex-2-en-1-one.
Part I.*

By (Miss) M. E. McEntee and A. R. Pinder.

Reduction of *o*-anisic acid by sodium and ammonia yielded mainly 1 : 4-
dihydro-*o*-anisic acid, but attempts to convert this into 2-acetyl*cyclo*hex-2-
enone were unsuccessful.   Chlorination and dehydrochlorination of 2-acetyl-
*cyclo*hexanone gave a liquid (probably 2-acetyl*cyclo*hex-3-en-1-one) and a
crystalline product $C_{16}H_{20}O_4$.

THE possible use of 2-acetyl*cyclo*hex-2-en-1-one (I) as intermediate in steroid synthesis [1]
has led to several attempts to synthesise it.[2]   The present communication is an account
of further unsuccessful experiments with this aim.
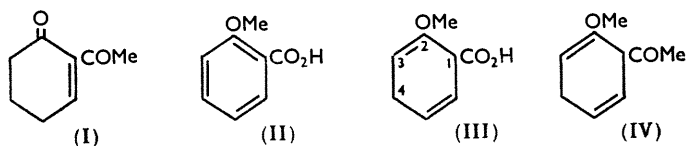
Pinder and Smith [2] found that reduction of suitable aromatic precursors, *e.g. o*-meth-
oxyacetophenone, by sodium and liquid ammonia led to hydrogenolysis.   In reducing
aromatic carboxylic acids, Birch [3] found that in general the aromatic ring was reduced
in the expected manner, and the carboxyl group remained intact, being protected as its
anion against hydrogenolysis.   In later investigations on the reductions of substituted

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* The authors are indebted to a Referee for suggesting this structure, as well as structure (IV) and the
nature of the impurity in the acid (III).

[1] Cf. Peak and Robinson, *J.*, 1937, 759, 1581.
[2] Smith, *J.*, 1953, 803; Pinder and Smith, *J.*, 1954, 113; Jaeger and Smith, *Chem. and Ind.*, 1954,
1106; *J.*, 1955, 160, 646; McEntee, Pinder, Smith, and Thornton, *J.*, 1956, 4699.
[3] Birch, *J.*, 1944, 430; 1950, 1551.

o-anisic acids,[4] although the carboxyl group was not hydrogenolysed, decarboxylation occurred immediately on hydrolysis of the dihydro-acids, and there was evidence of partial hydrogenolysis of the methoxyl group. Nevertheless, if *o*-anisic acid (II) could be reduced to the dihydro-acid (III), the latter could probably be converted into the ketone (IV) and thence, under mild conditions, into (I).

Reduction of *o*-anisic acid with sodium and methanol in liquid ammonia gave an acidic syrup which could not be purified satisfactorily owing to the ease with which it lost carbon dioxide, though it was characterised as *p*-bromophenacyl ester and *S*-benzylthiuronium salt. The compound absorbed maximally in the ultraviolet region at 240 mμ, on acid hydrolysis gave *cyclo*hex-2-enone, with elimination of carbon dioxide, and with chromic acid afforded *o*-anisic acid in high yield. These observations suggest that the product is mainly 1 : 4-dihydro-*o*-anisic acid (III).* A homoannular conjugated diene system is not present, since according to Woodward's rules such systems show maximal absorption above 253 mμ.[5a] Formulation of the acid as a βγ- rather than an αβ-unsaturated acid is further supported by the ease of decarboxylation. The observed ultraviolet maximum may be due to the presence of some 6-oxo*cyclo*hex-1-enecarboxylic acid, arising from the enol ether (III) by hydrolysis during working-up : this keto-acid might be expected to show a maximum at a relatively high wavelength for an αβ-unsaturated acid because of strain in the *cyclo*hexene ring.[5b]

At room temperature the syrupy acid gradually lost carbon dioxide and crystals separated in small yield. The new compound had a molecular weight about twice that of the syrupy acid, was enolic, and still contained a methoxyl group. The structure (V) has been tentatively assigned to it; it would be obtained by Michael addition of 6-oxo*cyclo*-hex-2-enecarboxylic acid, an intermediate hydrolysis product of (III), to the enol ether double bond of (III).

When treated with an excess of diazomethane, the syrupy acid afforded an ester with a terpene-like odour, which showed no strong ultraviolet absorption and appeared to be saturated. Its analysis supported the molecular formula $C_9H_{10}O(OMe)_2$, indicating that simultaneously with esterification of the carboxyl group, two methylene groups had been added to the molecule. Further, the original methoxyl group was no longer hydrolysable to a ketone, and an infrared band at 1010 cm.$^{-1}$ suggested the presence of a *cyclo*propane ring.[6] The structure (VI) is proposed for the ester.

(V)   (VI)   (VII)   (VIII)
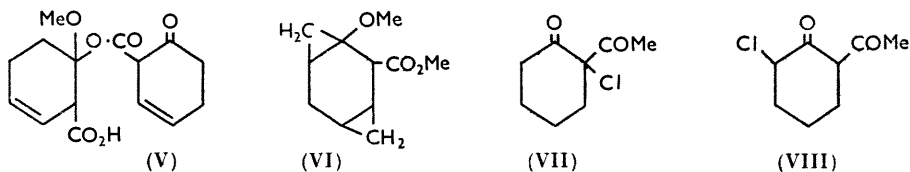
Attempts to convert the syrupy acid into the ketone (IV) by the action of methyl-lithium [7] gave, after hydrolysis, mainly *cyclo*hex-2-enone, with some 1-acetyl*cyclo*hexene, the latter presumably arising from the presence of a little 1 : 2 : 3 : 4-tetrahydrobenzoic acid in the syrupy acid.

Whilst these investigations were in progress, Birch, Hextall, and Sternhell [8] reported some further experiments on the reduction of anisic acids. With *m*-anisic acid and *N*-methylanthranilic acid their ultimate products were respectively 3-oxo*cyclo*hexane-carboxylic acid and *cyclo*hexanone. We have not detected *cyclo*hexanone in our reduction

[4] Birch, Murray, and Smith, *J.*, 1951, 1945.
[5] (*a*) Woodward, *J. Amer. Chem. Soc.*, 1942, **64**, 72, 76; (*b*) Jones, Mansfield, and Whiting, *J.*, 1956, 4073, and references there cited.
[6] Bellamy, " The Infrared Spectra of Complex Molecules," Methuen, London, 1954, pp. 13, 27.
[7] Cf. van Dorp and Arens, *Rec. Trav. chim.*, 1946, **65**, 344; Gilman, Zoellner, and Selby, *J. Amer. Chem. Soc.*, 1933, **55**, 1252.
[8] Birch, Hextall, and Sternhell, *Austral. J. Chem.*, 1954, **7**, 256.

of *o*-anisic acid, which suggests that in the acid (III) conjugation of the double bonds does not occur readily.
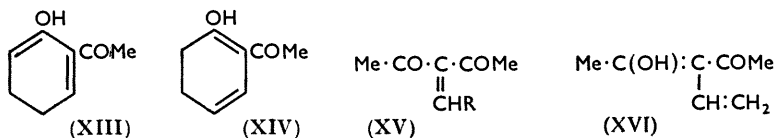
Turning to 2-acetyl*cyclo*hexanone, we found that its treatment with bromine or *N*-bromosuccinimide gave polybromo-ketones which readily decomposed, as in Acheson's work with 2-acetyl*cyclo*pentanone.[9] Warnhoff and Johnson[10] used sulphuryl chloride for the formation of a tertiary α-chloro-ketone: with this reagent in carbon tetrachloride 2-acetyl*cyclo*hexanone afforded 2-acetyl-2-chloro*cyclo*hexanone (VII) in high yield. This compound was insoluble in cold, dilute alkali, gave no colour with alcoholic ferric chloride, and did not form a copper complex; its infrared absorption spectrum was not of the conjugate chelate type,[11] but was that of a non-enolisable diketone, so that possible alternative structures such as (VIII) and (IX) were eliminated.

CO·CH₂Cl structure (IX)   COMe structure (X)   COMe structure (XI)   COMe structure (XII)

(IX)   (X)   (XI)   (XII)
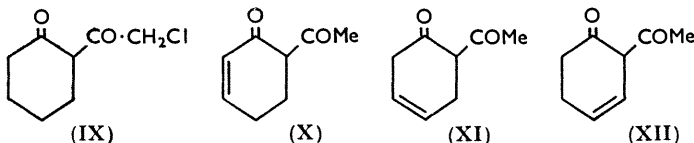
Dehydrochlorination of the chloro-ketone by collidine or by lithium chloride in dimethylformamide[12] gave two products in each case, namely, a liquid, $C_8H_{10}O_2$, and a crystalline compound, m. p. 136°, which appeared to be a dimer of the liquid.

The liquid was typically enolic in its chemical properties, being readily soluble in cold, aqueous alkali, giving a deep purple ferric test, and forming a crystalline copper complex, by means of which it could be purified. Its infrared absorption (liquid film) was of the conjugate chelate type;[11] it showed ultraviolet maxima at 240 mμ (ε 6640) and 325 mμ (ε 2600) (in MeOH), and at 238 mμ (ε 6500) and 322 mμ (ε 3300) (*cyclo*hexane). On catalytic hydrogenation it absorbed one mol. of hydrogen with the formation of 2-acetyl-*cyclo*hexanone, and on catalytic dehydrogenation or mild oxidation it yielded *o*-hydroxy-acetophenone very readily. On this evidence the compound is certainly an acetyl*cyclo*hexenone, of structure (I), (X), (XI), or (XII), the last three being formed by double-bond migration following dehydrochlorination of (VII). The diketone[13] (X) differs in physical and chemical properties from our product. We are grateful to Dr. C. W. Smith, and the Shell Development Co., New York, for supplying unpublished additional information about the compound, which we have attempted unsuccessfully to synthesise by the reaction of *cyclo*hex-2-enone with acetyl chloride in the presence of sodamide,[14] and with acetic anhydride in the presence of boron trifluoride.[15]

The compound $C_8H_{10}O_2$, on oxidation with potassium permanganate in acetone, gave succinic acid as sole crystalline product. This eliminates structure (XI), leaving structures (I) and (XII) to be considered. It is difficult to explain the enolic behaviour of the product on the basis of formula (I). Such a compound could in theory enolise to (XIII),

OH COMe structure (XIII)   OH COMe structure (XIV)   Me·CO·C·COMe ‖ CHR (XV)   Me·C(OH):C·COMe │ CH:CH₂ (XVI)

(XIII)   (XIV)   (XV)   (XVI)

but such an enolisation would in fact require additional activation of the hydrogen atoms at $C_{(6)}$ in (I), and, further, such an enol cannot be stabilised by resonance between

[9] Acheson, *J.*, 1956, 4232.
[10] Warnhoff and Johnson, *J. Amer. Chem. Soc.*, 1953, **75**, 494.
[11] Bellamy, ref. 6, p. 123.
[12] Cf. Holysz, *J. Amer. Chem. Soc.*, 1953, **75**, 4432.
[13] Smith, U.S.P. 2,516,729; *Chem. Abs.*, 1951, **45**, 6217.
[14] Cf. Conia, *Bull. Soc. chim. France*, 1954, 690, 943; 1955, 301.
[15] Hauser, Swamer, and Adams, " Organic Reactions," Vol. VIII, Chapter 3.

zwitterionic forms (cf. Smith [2]). We therefore propose structure (XII), the double bond having taken up a position of non-conjugation with both carbonyl groups. This formulation appears to explain the properties of the product satisfactorily, for enolisation would yield (XIV); spectral measurements indicate that it exists almost wholly as this form in the liquid state and in solution. The peaks at 325 mμ (in MeOH) and 322 mμ (in *cyclo*-hexane) are presumably due to the enol (XIV), in which there is a homoannular conjugated diene system, with a hydroxyl substituent exerting a strong bathochromic effect (compare the enolic form of 2-acetyl*cyclo*hexanone, $\lambda_{max.}$ 290 mμ; Smith [2]).[5,16] The maxima in the 240 mμ region may probably be due to the αβ-unsaturated ketone system which is also present.[5,16]

In an attempt to support this formulation we examined the properties of several compounds based on structure (I). Condensing benzaldehyde with acetylacetone [17] gave 3-benzylideneacetylacetone (XV; R = Ph), which showed no enolic properties. Similar condensation of acetaldehyde and acetylacetone [17] afforded 3-ethylideneacetylacetone (XV; R = Me): this compound, purified, by fractionation, from unchanged acetyl-acetone, showed infrared absorption (liquid film) characteristic of a non-enolised β-di-ketone; the curves of (XV; R = Ph and Me) were indeed closely similar. However the compound gave a purplish-red colour with alcoholic ferric chloride, and dissolved slowly in aqueous alkali: shaking it with cupric acetate solution caused no immediate reaction, but the copper complex of acetylacetone was slowly obtained in high yield, owing to hydrolytic cleavage. It appears that in the liquid state the compound (XV; R = Me) exists wholly as the diketo-form, but in solution in certain solvents may enolise to a small extent to (XVI). The ultraviolet absorption in methanol solution supports this view [$\lambda_{max.}$ 220 (ε 10,600) and 285 mμ (ε 665) ; the latter peak is probably due to the presence of the enol form (XVI)]. It is unlikely that these properties could be due to the presence of acetylacetone as impurity, because the ferric colour is purplish-red, whereas acetyl-acetone gives a wine-red colour. The former colour is characteristic of enolised −CO·CHR·CO− systems, where R is alkyl.[18] Secondly, acetylacetone reacts immediately with cupric acetate, even in very low concentration; and, thirdly, acetylacetone has $\lambda_{max.}$ 272·5 mμ (in EtOH).[19] In *cyclo*hexane solution the compound (XV; R = Me) showed only a single maximum at 218 mμ (ε 12,600), so that in this solvent no appreciable enolisation occurred.

In contrast condensation of propionaldehyde and acetylacetone yields a compound $C_8H_{12}O_2$ which is completely enolic [cf. (XVIII)]. It has a typical conjugate chelate infrared spectrum, readily forms a crystalline copper complex, and gives a deep purple ferric colour. It has ultraviolet maxima at 222 (ε 15,200) and 290 mμ (ε 11,200) in methanol; in *cyclo*hexane the positions are 220 (ε 15,000) and 290 mμ (ε 11,500). These values correspond very well with those of the product $C_8H_{10}O_2$, the longer wavelengths of the maxima in the case of this compound being accounted for by the presence of a cyclic structure.

The chemical properties of the compound (XVII) resemble very closely those of one obtained by Tiemann and Krüger [20] from *iso*valeraldehyde and acetylacetone, to which they assigned structure (XVIII).

An account of investigations on the constitution of the crystalline dimer $C_{16}H_{20}O_4$, m. p. 136°, is reserved for a later communication. In our view this compound is probably a dimer of the structure (I), and its formation accounts in part for the failure to isolate the ketone (I) by the procedure described. Jones and Koch [21] have shown that 1-acetyl*cyclo*hexene dimerises to a compound (XIX); the analogous structure for the

[16] Woodward, *J. Amer. Chem. Soc.*, 1941, **63**, 1123.
[17] Knoevenagel and Ruschhaupt, *Ber.*, 1898, **31**, 1026; Knoevenagel and Faber, *ibid.*, p. 2775.
[18] Henecka, *Chem. Ber.*, 1948, **81**, 179.
[19] Grossmann, *Z. phys. Chem.*, 1924, **109**, 305.
[20] Tiemann and Krüger, *Ber.*, 1895, **28**, 2121.
[21] Jones and Koch, *J.*, 1942, 393.

dimer of 2-acetyl*cyclo*hex-2-enone (I) would be (XX). This, however, cannot represent the dimer, m. p. 136°, since the infrared spectrum of the compound shows the complete absence of a non-enolisable carbonyl group, such as is present in (XX).

Similar studies in the *cyclo*pentane field are being pursued.

(XVII)   (XVIII)   (XIX)   (XX)
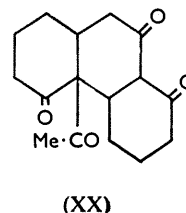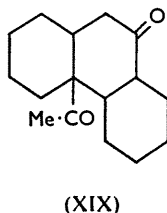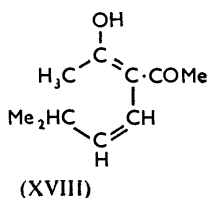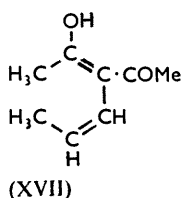
Experimental

Ultraviolet absorption measurements refer to MeOH solutions unless otherwise stated.

o-Anisic Acid.—Methylation of salicylic acid with methyl sulphate and alkali [22] gave a product contaminated with salicylic acid (even when a large excess of methyl sulphate was employed), which could not be removed by fractional crystallisation. Methyl salicylate was therefore methylated by the same procedure,[23] unchanged phenolic material being removed with alkali. Methyl o-anisate distilled at 128°/10 mm. (lit.,[23] b. p. 140—144°/15 mm.). The ester (96 g.) was boiled under reflux for 15 min. with 10% aqueous sodium hydroxide (400 c.c.), and the clear solution cooled and acidified with concentrated hydrochloric acid. o-Anisic acid was collected and crystallised from aqueous methanol. The pure acid (81 g.) had m. p. 99—100° (lit.,[23] m. p. 99—101°) and gave no colour with alcoholic ferric chloride. The S-*benzylthiuronium salt* separated from ethanol in prisms, m. p. 159° (decomp.) (Found: C, 60·3; H, 5·7. $C_{16}H_{18}O_3N_2S$ requires C, 60·4; H, 5·7%).

Reduction of o-*Anisic Acid with Sodium in Liquid Ammonia.*—The pure acid (10 g.) in methanol (4 c.c.) was added gradually with stirring to liquid ammonia (300 c.c.), followed by sodium (9·1 g.), in small pieces, during 1 hr. When all the sodium had dissolved ammonium chloride (50 g.) in water (120 c.c.) was added, with stirring, and the mixture left for several hours for complete evaporation of the ammonia. The clear solution was freed from neutral matter with ether, acidified with concentrated hydrochloric acid, and extracted thoroughly with ether. Evaporation of the combined, dried extracts gave a syrup (8·0 g.), which effervesced slowly, with evolution of carbon dioxide. Purification of this product proved extremely difficult, owing to the ease of decarboxylation, but its subsequent reactions indicated that it was mainly 1 : 4-dihydro-o-anisic acid (III) (Found: equiv., 152, 159. $C_8H_{10}O_3$ requires equiv., 154), $\lambda_{max.}$ 240 mμ (ε 2900). The S-*benzylthiuronium salt* separated from ethyl acetate–ethanol (1 : 1) in prisms, m. p. 146—147° (Found: C, 59·7; H, 6·2. $C_{16}H_{20}O_3N_2S$ requires C, 60·0; H, 6·25%), showing a large depression in m. p. when mixed with S-benzylthiuronium o-anisate. The p-*bromophenacyl ester* separated from methanol in rhombic plates, m. p. 78° (Found: C, 54·7; H, 4·6. $C_{16}H_{15}O_4Br$ requires C, 54·7; H, 4·3%).

The syrupy acid (2·0 g.) was hydrolysed by boiling N-hydrochloric acid (25 c.c.) for 30 min. The solution was neutralised with sodium carbonate and extracted with ether. Evaporation of the dried extract gave *cyclo*hex-2-enone, b. p. 53—54°/9 mm. (0·7 g.) (2 : 4-dinitrophenyl-hydrazone, m. p. and mixed m. p. 166—167°).

When the acid (4 g.) in glacial acetic acid (15 c.c.) was mixed with chromic acid (1·9 g.) in water (3 c.c.) an exothermic reaction occurred. After several hours the solution was diluted with water and extracted with ether. The dried extract was evaporated, the last traces of acetic acid being removed *in vacuo*. The residue (3·4 g.) of o-anisic acid crystallised from aqueous methanol in prisms, m. p. and mixed m. p. 99°.

From the syrupy acid crystals separated during several days. These recrystallised from acetic acid in prisms, m. p. 166—167° (decomp.) (Found: C, 60·7, 61·1; H, 6·0, 6·2; Me, 8·9%; M, 283. $C_{15}H_{18}O_6$ requires C, 61·2; H, 6·1; OMe, 10·5%; M, 294). The *compound* was

[22] Graebe, *Annalen*, 1905, **340**, 204.
[23] Cohen and Dudley, *J.*, 1910, **97**, 1732.

soluble in sodium hydrogen carbonate solution, with evolution of carbon dioxide; it gave a deep red colour with alcoholic ferric chloride.

Reaction of the Syrupy Acid with Diazomethane.—The acid (5 g.) in dry ether (50 c.c.) was kept with excess of an ethereal solution of diazomethane at 0° overnight; the solution was washed with sodium hydrogen carbonate solution and water, dried, and evaporated. The residual *methyl* 1-*methoxy*tricyclo[5 : 1 : 0 : 0$^{3 : 5}$]*octane-2-carboxylate* (VI) distilled at 79—80°/18 mm. and had n_D^{20} 1·4600 (4·5 g.) (Found: C, 67·0, 67·5; H, 7·9, 8·25; OMe, 24·5. $C_{11}H_{16}O_3$ requires C, 67·3; H, 8·2; 2OMe, 31·6%) and no ultraviolet absorption above 215 mμ. Infrared absorption bands were at 1724 (ester C=O group), 1163 (ester group), 1075 (aliphatic ether), 1010 (*cyclo*propane ring), and 2915 cm.$^{-1}$ (methylene groups). The product had a pleasant, terpene-like odour; it was stable for several minutes to cold, aqueous potassium permanganate solution, gave no colour with ferric chloride, and did not react with 2 : 4-dinitrophenylhydrazine in the presence of sulphuric acid.

Reaction of the Syrupy Acid with Methyl-lithium.—A solution of methyl-lithium in ether [prepared from lithium metal (4·6 g.), methyl iodide (55 g.), and ether (400 c.c.); cf. van Dorp and Arens[7]] (180 c.c.; 2 mols.) was treated under nitrogen with the acid (8·5 g.) in ether (150 c.c.) during 1 hr., with stirring. After an additional hour's stirring the mixture was poured on ice, and the organic layer separated, washed with sodium hydrogen carbonate solution and water, dried, and evaporated through a short Vigreux column. The oily residue (6·2 g.) was boiled with N-hydrochloric acid (25 c.c.) under nitrogen for 1 hr. Ether-extraction of the cooled solution gave an oil (3·5 g.), which was distilled fractionally *in vacuo* through a vacuum-jacketed Vigreux column. The main fraction distilled at 57°/10 mm. (2·8 g.), having n_D^{20} 1·4799 (Found: C, 74·75; H, 8·2. Calc. for C_6H_8O: C, 74·9; H, 8·4%). The 2 : 4-dinitrophenylhydrazone separated from ethanol in deep orange needles, m. p. 164° alone or mixed with *cyclo*hex-2-enone 2 : 4-dinitrophenylhydrazone (m. p. 164—165°). The higher-boiling fraction (0·5 g.) had b. p. 92°/18 mm., n_D^{20} 1·4880 (Found: C, 77·5; H, 9·8. Calc. for $C_8H_{12}O$: C, 77·4; H, 9·7%). The 2 : 4-dinitrophenylhydrazone crystallised from ethyl acetate in bright red needles, m. p. 202—203°, undepressed by admixture with 1-acetyl*cyclo*hexene 2 : 4-dinitrophenylhydrazone (m. p. 203°).

2-Acetyl-2-chlorocyclohexan-1-one.—Sulphuryl chloride (29·7 g., 0·22 mole) in carbon tetrachloride (50 c.c.) was added during 1 hr. to a stirred solution of 2-acetyl*cyclo*hexanone[24] (28 g., 0·2 mole) in carbon tetrachloride (100 c.c.), the temperature being kept below 20°. Stirring was continued for a further 2 hr.; the clear solution was then washed with water and saturated sodium hydrogen carbonate solution (2 × 25 c.c. each), and dried (Na$_2$SO$_4$). Evaporation of the solvent *in vacuo* through a short Vigreux column gave a reddish oil which redistilled (Vigreux column) at 50—51°/0·1 mm. (21 g.) and had n_D^{25} 1·4790 (Found: C, 54·7, 54·8; H, 6·5, 6·5; Cl, 20·5, 20·3. $C_8H_{11}O_2Cl$ requires C, 55·0; H, 6·3; Cl, 20·3%), strong carbonyl band at 1713 cm.$^{-1}$ and a C–Cl (?) band at 803 cm.$^{-1}$ (spectrum not of conjugate chelate type). 2-*Acetyl*-2-*chlorocyclohexanone* had a sharp, lachrymatory odour, and solidified to elongated prisms, m. p. ~8°, insoluble in dilute, aqueous sodium hydroxide, giving no colour with ferric chloride, and not reacting with cupric acetate. With 2 : 4-dinitrophenylhydrazine in ethanol containing a few drops of concentrated sulphuric acid it gave an amorphous, orange precipitate, which did not contain chlorine. Attempts to purify this compound were unsuccessful.

Dehydrochlorination of 2-Acetyl-2-chlorocyclohexanone.—(a) When the above chloro-ketone (5 g.) and freshly distilled dry collidine (15 c.c.) were heated, sudden reaction occurred at 180° (bath temperature) with separation of collidine hydrochloride. Heating was continued at 180° for 30 min., then the mixture was cooled, diluted with ether, and filtered. The hydrochloride was washed with ether (yield, 4·45 g.; theor., 4·51 g.), and the combined filtrate and washings were shaken in turn with dilute hydrochloric acid (3 × 30 c.c.), water, ice-cold, dilute sodium hydroxide solution (2 × 25 c.c.), and water, dried and evaporated. A dark brown oil (0·15 g.) remained which mainly decomposed when an attempt was made to distil it at 11 mm.

The alkaline extracts were acidified with 5N-hydrochloric acid, and the oil liberated was isolated with ether (yield, 3·5 g.), recovered, redissolved in ether (10 c.c.), and kept at 0° overnight. The crystals (1·0 g.) so obtained (A; see below) were collected and washed with a little ether. The filtrate was evaporated; the residue of (?) 2-*acetylcyclo*hex-3-*enone* (XII), distilled *in vacuo*, had b. p. 98—99°/9·5 mm., 101—102°/10·5 mm., n_D^{25} 1·5377 (0·6 g.) (Found: C, 69·6, 69·4; H, 7·4, 7·3. $C_8H_{10}O_2$ requires C, 69·5; H, 7·3%), ultraviolet absorption max. at 240

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[24] "Organic Reactions," Vol. VIII, p. 130.

(ε 6640) and 325 mμ (ε 2600) (in MeOH), 238 (ε 6500) and 322 mμ (ε 3300) (in *cyclo*hexane), and infrared absorption (conjugate chelate spectrum) bands at 3030 (shoulder), 1636, 1603, 1444, 1410, 1172, and 1146 cm.$^{-1}$. Much involatile material remained. The product formed a *copper complex* when shaken in ether with aqueous cupric acetate; this separated from benzene–light petroleum (b. p. 60—80°) (1 : 1) in greyish-green matted needles, m. p. 192° (Found: C, 57·2; H, 5·45. $C_{16}H_{18}O_4Cu$ requires C, 56·9; H, 5·3%). When shaken in ethereal suspension with dilute sulphuric acid the complex was smoothly reconverted into the product $C_8H_{10}O_2$, which was soluble in dilute sodium hydroxide solution, being precipitated on acidification. With alcoholic ferric chloride it gave a deep purple colour. Attempts to make the semicarbazone, oxime, and phenylhydrazone resulted in oils; with 2 : 4-dinitrophenylhydrazine there was obtained an amorphous orange-red compound, which when purified by chromatography on bentonite–kieselguhr gave a microcrystalline product, m. p. 248—252° (decomp.) (Found: C, 47·1; H, 3·6; N, 21·5. Calc. for bis-2 : 4-dinitrophenylhydrazone, $C_{20}H_{18}O_8N_8$: C, 49·6; H, 3·6; N, 22·5%).

(*b*) A stirred solution of lithium chloride (3·6 g.) and the chloro-ketone (5 g.) in dimethylformamide (50 c.c.) was heated at 100—110° under nitrogen for 4 hr.,[12] then cooled, poured into water (100 c.c.), and extracted with benzene (3 × 50 c.c.). The extracts were washed with cold, dilute hydrochloric acid, sodium hydrogen carbonate solution, and water, dried, and evaporated. The residue was partly crystalline and afforded the same two products as in (*a*), in similar yield.

Dimeric Product, $C_{16}H_{20}O_4$.—The deposit (A; see above) crystallised from methanol in very pale yellow rhombic prisms, m. p. 136° (0·9 g.) (Found: C, 69·4; H, 7·3; *C*-Me, 10·2%; *M*, 274. $C_{16}H_{20}O_4$ requires C, 69·6; H, 7·2; 2*C*-Me, 10·8%; *M*, 276). Ultraviolet absorption: max. at 250 (ε 14,400), 288 mμ (ε 9870). Infrared absorption (Nujol mull): typical conjugate chelate spectrum, almost complete enolisation. The *substance* was soluble in dilute sodium hydroxide solution, gave a deep blue colour with alcoholic ferric chloride, and formed a crystalline copper complex, m. p. >250°, with aqueous cupric acetate, but this did not recrystallise satisfactorily.

Dehydrogenation of $C_8H_{10}O_2$.—Palladium–charcoal (30%; 0·2 g.)[25] was added to the product $C_8H_{10}O_2$ (0·5 g.). A vigorous reaction occurred and the mixture was heated under nitrogen at 220—230° for 1 hr. After cooling, ether was added and the solution filtered. Evaporation yielded an oil which distilled at 93—94°/8 mm. (0·3 g.), had n_D^{25} 1·5520, and afforded an oxime,[26] m. p. 116—117°, and a phenylhydrazone,[27] m. p. 110—111°, both alone or admixed with the corresponding derivatives of *o*-hydroxyacetophenone. A similar product was obtained when the compound $C_8H_{10}O_2$ was boiled under reflux for several hours with dilute sodium hydroxide; no carboxylic acid was isolated.

Hydrogenation of $C_8H_{10}O_2$.—The compound (0·29 g.) in ethanol (10 c.c.) was shaken in hydrogen at room temperature and pressure with 10% palladised charcoal for 2 hr. (absorption 39 c.c.; 1 mol. = 47 c.c.). The catalyst was removed and the solvent evaporated *in vacuo*. The residual oil distilled at 97°/10 mm. (0·25 g.) (Found: C, 68·7; H, 8·6. Calc. for $C_8H_{12}O_2$: C, 68·5; H, 8·6%). Shaking it in ether with aqueous cupric acetate gave a copper complex which crystallised from ethanol in green leaflets, m. p. 162—163°, alone or mixed with an authentic specimen of the copper complex of 2-acetyl*cyclo*hexanone.[28]

Oxidation of $C_8H_{10}O_2$.—A solution of the compound (1·0 g.) in dry, permanganate-stable acetone (50 c.c.) was stirred and cooled to 0°. Finely powdered potassium permanganate was added in small quantities at a time, at 0—5°, until a permanent pink colour was obtained. After 30 minutes' further stirring, the solution was filtered and the residue washed with a little acetone and dried at room temperature. The dry solid was mixed with water (100 c.c.), and the manganese dioxide removed by filtration. The filtrate was acidified with hydrochloric acid and subjected to continuous ether-extraction for 12 hr. Evaporation of the dried extract gave succinic acid (0·3 g.), m. p. 185° (bis-*p*-bromophenacyl ester, m. p. 211°), both alone or mixed with authentic specimens.

Ozonolysis of the product $C_8H_{10}O_2$ by the method of Linstead, Elvidge, and Whalley[29]

[25] Linstead and Thomas, *J.*, 1940, 1127.
[26] Lindemann and Thiele, *Annalen*, 1926, **449**, 63.
[27] Torrey and Brewster, *J. Amer. Chem. Soc.*, 1913, **35**, 426; Bogert and Marcus, *ibid.*, 1919, **41**, 83.
[28] Borsche, *Annalen*, 1910, **377**, 88; Meerwein and Vossen, *J. prakt. Chem.*, 1934, **141**, 149.
[29] Linstead, Elvidge, and Whalley, " A Course in Modern Techniques of Organic Chemistry," Butterworths, London, 1955, pp. 116—121.

gave, after several hours, only *o*-hydroxyacetophenone [2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 211—212° (Found: C, 53·2; H, 3·7; N, 18·2. Calc. for $C_{14}H_{12}O_5N_4$: C, 53·2; H, 3·8; N, 17·7%). Nummy and Tarbell [30] give m. p. 212—213°].

3-*Benzylideneacetylacetone.*—The preparation of this compound has been described only very briefly.[17] Benzaldehyde (10·6 g.) and acetylacetone (10·0 g.) were mixed and cooled to −10°, and piperidine (1 c.c.) was added dropwise during a few minutes. The reaction was allowed to proceed at 0° for 3 days. The turbid mixture was diluted with ether and washed in turn with dilute hydrochloric acid, dilute sodium hydroxide, and water. The dried ethereal solution was evaporated. The residual 3-benzylideneacetylacetone had b. p. 168—170°/13 mm. (12·5 g.) (lit.,[17] b. p. 179—181°/12 mm.). Ultraviolet absorption: max. at 282 mμ (ε 19,700). Infrared absorption (liquid film): strong carbonyl bands at 1650 and 1703 cm.$^{-1}$; C꞊C band (?) at 1610 cm.$^{-1}$; no evidence of enolisation. The product was insoluble in dilute aqueous alkali, did not give a colour with ferric chloride, and did not react with aqueous cupric acetate.

3-*Ethylideneacetylacetone.*—Acetaldehyde (11·0 g.) and acetylacetone (25·0 g.) were condensed in chloroform in the presence of dry hydrogen chloride.[17] The product was fractionated twice through a 25 cm. Vigreux column. The fraction, b. p. up to 80°/10 mm. (8·5 g.), was mainly unchanged acetylacetone; the fraction, b. p. 80—81°/10 mm. (14·0 g.) (Found: C, 66·5; H, 7·8. Calc. for $C_7H_{10}O_2$: C, 66·7; H, 7·9%), was a colourless liquid with a pungent odour, ultraviolet absorption max. at 220 mμ (ε 10,600) and 285 mμ (ε 665); 218 mμ (ε 12,600) (in *cyclo*hexane), and an infrared absorption (liquid film) curve very similar to that of 3-benzylideneacetylacetone (see above) [strong carbonyl bands at 1660 and 1733 cm.$^{-1}$; C꞊C band (?) at 1630 cm.$^{-1}$; no evidence of enolisation].

Condensation of Propionaldehyde and Acetylacetone.—Similarly propionaldehyde (16·0 g.) and acetylacetone (25·0 g.) in chloroform (200 c.c.) gave a fraction, b. p. up to 86°/17 mm. (8·0 g.), chiefly acetylacetone, and a fraction, b. p. 88—93°/17 mm. (mainly 89—90°) (13·0 g.) which, refractionated several times, had b. p. 82°/14 mm. (11·5 g.) (Found: C, 68·5; H, 8·8. $C_8H_{12}O_2$ requires C, 68·6; H, 8·6%) and ultraviolet absorption max. at 222 (ε 15,200) and 290 mμ (ε 11,200) (in MeOH), 220 (ε 15,000) and 290 mμ (ε 11,500) (in *cyclo*hexane), and its infrared absorption (liquid film) was a typical conjugate chelate spectrum of a highly enolised compound. The product 3-*acetylhex-3-en-2-one*, was immediately soluble in dilute aqueous alkali and gave a deep purple colour with ferric chloride and a *copper complex*, dark green needles (from benzene), m. p. 188° (decomp.) (Found: C, 56·0; H, 6·5. $C_{16}H_{22}O_4Cu$ requires C, 56·2; H, 6·4%).

Queen's University, Belfast.
University College, Cardiff.

[30] Nummy and Tarbell, *J. Amer. Chem. Soc.*, 1951, **73**, 1500.