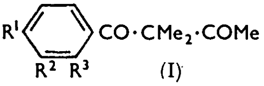
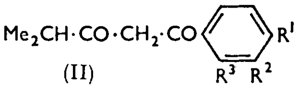
539. *The Rearrangement of Non-enolisable β-Diketones. Part I.**

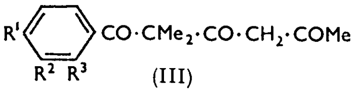
By N. H. Bromham and A. R. Pinder.

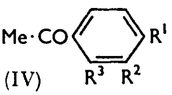
Some further examples of the rearrangement of non-enolisable β-diketones (I) are described. The transformations are promoted by sodium suspended in purified ether, which seems to exclude an intermolecular mechanism of fission and re-synthesis; the diketone (I; $R^2 = NO_2$, $R^1 = R^3 = H$) is stable to sodium in ether, which suggests that the change is not analogous to the intramolecular Baker–Venkataraman rearrangement. Two related cases involving the migration of an acetyl group are described.

During experiments on steroid synthesis [1] it was observed that the non-enolisable β-diketone, α-acetylisobutyrophenone (I; $R^1 = R^2 = R^3 = H$) was transformed by sodium in ether containing a trace of ethanol into α-isobutyrylacetophenone (II; $R^1 = R^2 = R^3 = H$). It was of interest to explore the scope of this rearrangement, and to attempt to elucidate its mechanism.


(I)


(II)


(III)


(IV)

Several diketones of the general formula (I) have therefore been prepared, chiefly by the acetylation of the corresponding isobutyrophenones with acetic anhydride and boron trifluoride.[2] The diketones were always accompanied by small yields of the triketones [3] (III), from which they were easily separated because of the solubility of the latter in alkali. The diketone (I; $R^1 = OMe$, $R^2 = R^3 = H$) was not obtainable by this method of acylation, owing to the deactivating influence of the 4-methoxyl group on the methinyl hydrogen atom in 4-methoxyisobutyrophenone. It was, however, formed when the latter was converted into its sodium enolate, and then treated with acetyl chloride.[4]

The diketones, which gave no colour with ferric chloride and showed two distinct carbonyl bands in their infrared spectra, were mixed in dry ethereal solution with a suspension of powdered sodium in dry ether. Usually, a vigorous reaction set in after a few minutes, and cooling had to be applied. In the original work [1] ethyl acetate was present or a trace of ethanol was added, but it has now been found that the reactions proceed without special addition of these substances; this has been confirmed by other workers [5] for the diketone (I; $R^1 = R^2 = R^3 = H$). The products were isolated by decomposition with ice, alkaline extraction, acidification, and ether-extraction, substituted benzoic acids, which were usually formed simultaneously, being removed by washing with sodium hydrogen carbonate. The products were characterised as their copper complexes. Authentic specimens of the expected rearrangement products were synthesised by Claisen-type condensations between the appropriate acetophenone (IV) and ethyl isobutyrate.[6]

Of the diketones studied, α-acetyl-4-methyl- and -4-chloro-isobutyrophenone (I; $R^1 =$ Me or Cl, $R^2 = R^3 = H$) rearranged to give the corresponding enolic diketones (II), though

---

* For a preliminary report see *Chem. and Ind.*, 1959, 258.

[1] Pinder and Robinson, *J.*, 1955, 3341.

[2] Hauser, Swamer, and Adams, in "Organic Reactions," Wiley, New York, 1954, Vol. VIII, pp. 129 *et seq.*

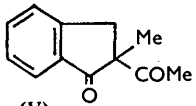
[3] Cf. ref. 1 and Walker, Sanderson, and Hauser, *J. Amer. Chem. Soc.*, 1953, **75**, 4109.

[4] Cf. Hudson and Hauser, *ibid.*, 1941, **63**, 3156, 3163.

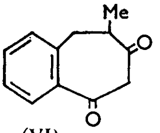
[5] Inamoto, Iwata, and Simamura, *Chem. and Ind.*, 1959, 47.

[6] Ref. 2, Chapter 3.

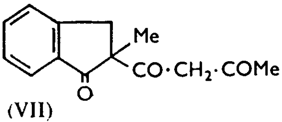
the yield in the latter case was very poor. α-Acetyl-4-methoxyisobutyrophenone (I; $R^1 =$ OMe, $R^2 = R^3 =$ H) reacted vigorously with sodium, to give a product showing enolic properties, but its copper complex could not be obtained crystalline; it was, however, concluded that the product contained some of the expected enolic diketone (II) because on treatment with Brady's reagent in alcoholic sulphuric acid it afforded 4-methoxyacetophenone 2,4-dinitrophenylhydrazone. α-Acetyl-2,4-dimethylisobutyrophenone (I; $R^1 = R^3 =$ Me, $R^2 =$ H) also reacted energetically with sodium, giving a poor yield of an enolic product, from which a crystalline copper complex could not be derived; an infrared comparison between the product and α-isobutyryl-2,4-dimethylacetophenone (II; $R^1 = R^3 =$ Me, $R^2 =$ H) was complicated by the fact that the former contained 2,4-dimethylbenzoic acid, even after repeated washing with sodium hydrogen carbonate.



(V)



(VI)



(VII)

$Me\cdot CO\cdot CMe_2\cdot COMe$

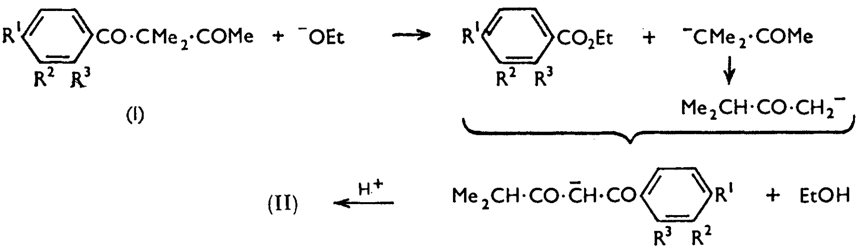
(VIII)

$Me_2CH\cdot CO\cdot CH_2\cdot COMe$

(IX)

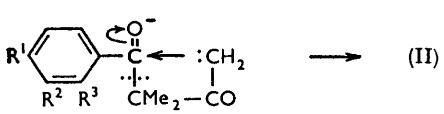
$Ph\cdot CO\cdot \underset{\underset{CHPh}{\|}}{C}\cdot COMe$

(X)



On the other hand α-acetyl-3-nitroisobutyrophenone (I; $R^1 = R^3 =$ H, $R^2 = NO_2$) proved to be stable to sodium under these conditions, and was recovered unchanged.

The reaction of 2-acetyl-2-methylindan-1-one (V) with sodium afforded, not the expected benzocycloheptanedione (VI), but 2-acetoacetyl-2-methylindan-1-one (VII), the formation of which involves the separation of an acetyl group, followed by attack on another molecule of starting material. A case involving the migration of an acetyl group is provided by the isomerisation of 3,3-dimethylacetylacetone (VIII) to isobutyrylacetone (IX). 3-Benzylidenebenzoylacetone (X) did not react with sodium.



Two mechanisms have been suggested briefly for the rearrangements.[1] In the first, an intermolecular change has been postulated in which fission of an acyl group, under the influence of an ethoxide anion, affords an ester. This then condenses with the terminal reactive methyl group, with the formation of the new β-diketone and regeneration of ethanol. Only a catalytic quantity of sodium ethoxide would therefore be required, the transformation of (I) into (II) being as illustrated. This mechanism must be excluded, apparently, because the rearrangement is promoted by sodium alone, in the absence of ethanol, this view being strengthened by recent tracer studies on the rearrangement of the diketone (I; $R^1 = R^2 = R^3 =$ H).[5]

A second possible mechanism is based on an analogy with the Baker–Venkataraman rearrangement of *o*-aroyloxyacetoarones,[7] which has been shown by Wheeler *et al.*[8] to be intramolecular. By analogy, the rearrangement of the diketone (I) would involve a transition state (XI), and would be expected to be facilitated by the presence of strongly electron-attracting groups in the migrating nucleus, as is the case with the Baker–Venkataraman change.[8b] The failure of the nitro-diketone (I; $R^1 = R^3 = H, R^2 = NO_2$) to rearrange, however, suggests that this mechanism is not operative, and further experiments are now being carried out in an effort to elucidate this aspect of the rearrangement.

The behaviour of 2-acetyl-2-methylindan-1-one (V) indicates that, in this case at least, an acetyl group is cleaved from the molecule, and if it can be assumed that the true isomerisations occur by a similar process, the mechanism involved must be intermolecular.

As far as we are aware, these transformations represent the first recorded cases of the migration of an acyl group from one carbon atom to another in the same molecule, apart from a rearrangement involving the migration of an ethoxycarbonyl group in a Michael reaction.[9]

EXPERIMENTAL

α-Acetyl-4-methylisobutyrophenone.—4-Methylisobutyrophenone [10] (88 g.) in acetic anhydride (204 g., 2 mol.) was saturated with boron trifluoride at 0° during 2 hr., with stirring. The syrupy product was poured on ice-cold, concentrated sodium acetate solution, and the oil liberated was isolated with ether, washed several times with cold 4% aqueous sodium hydroxide, then with water, dried (Na_2SO_4), and recovered; fractionation gave *α-acetyl-4-methylisobutyrophenone*, b. p. 109—110°/1·2 mm. (21%) (Found: C, 76·9; H, 8·2. $C_{13}H_{16}O_2$ requires C, 76·5; H, 7·8%), with a fore-run of unchanged monoketone and some residue. Infrared C=O bands (liquid film) were at 1670 (phenyl conjugated) and 1743 cm.$^{-1}$ (unconjugated). Hydrolysis with boiling dilute sulphuric acid afforded acetic acid (*S*-benzylthiuronium salt, m. p. and mixed m. p. 136°) and 4-methylisobutyrophenone (semicarbazone, m. p. and mixed m. p. 101°). A *monosemicarbazone* crystallised from 50% aqueous ethanol in needles, m. p. 196·5° (Found: C, 64·3; H, 7·4; N, 15·9. $C_{14}H_{19}O_2N_3$ requires C, 64·4; H, 7·3; N, 16·1%).

Reaction of α-Acetyl-4-methylisobutyrophenone with Sodium.—The following conditions are typical of those used in these investigations. Ether (Macfarlan's; distilled over sodium) was kept for 7—10 days over fresh sodium wire. In carefully dried apparatus the above diketone (5·0 g.) in dry ether (15 c.c.) was added dropwise to a suspension of powdered sodium (1·1 g.; 2 g.-atoms; weighed under dry light petroleum and powdered in dry xylene), with swirling, precautions being taken to exclude moisture. A reaction developed gradually; after a few minutes it had become quite vigorous and gentle cooling was applied. After 24 hr. most of the sodium had dissolved and the mixture was cooled and decomposed with ice. The ether layer was separated and washed with a little water, and the combined aqueous layers were acidified with 5N-hydrochloric acid, with cooling. The oil liberated was taken up in ether, washed with sodium hydrogen carbonate solution and water, dried, and recovered. The residual *α-isobutyryl-4-methylacetophenone* (*4-methyl-*1-p-*tolylpentane-*1,3-*dione*) (II; $R^1 = Me, R^2 = R^3 = H$) distilled at 130—138° (bath)/0·2 mm. (0·3 g.) (Found: C, 76·6; H, 7·6. $C_{13}H_{16}O_2$ requires C, 76·5; H, 7·8%), was soluble in dilute aqueous sodium hydroxide, and gave a wine-red ferric colour. The *copper complex* crystallised from light petroleum in pale blue rhombic prisms, m. p. 187° (Found: C, 66·4; H, 6·9. $C_{26}H_{30}O_4Cu$ requires C, 66·4; H, 6·4%). With 2,4-dinitrophenylhydrazine the product afforded 1-(2,4-*dinitrophenyl*)-3(or 5)-*isopropyl*-5(or 3)-p-*tolylpyrazole*, orange plates (from ethanol), m. p. 154° (Found: C, 61·9; H, 5·1; N, 15·3. $C_{19}H_{18}O_4N_4$ requires C, 62·3; H, 4·9; N, 15·3%). Acidification of the sodium hydrogen carbonate washings gave *p*-toluic acid, m. p. and mixed m. p. 177°.

α-Isobutyryl-4-methylacetophenone.—4-Methylacetophenone [11] (13·4 g.) in dry ether (100 c.c.) was added dropwise, with swirling, to an ethereal 0·15M-, solution of sodium triphenylmethyl

---

[7] Baker, *J.*, 1933, 1381; 1934, 1953; Mahal and Venkataraman, *Current Sci.*, 1933, **2**, 214; *J.*, 1934, 1767; Bhalla, Mahal, and Venkataraman, *J.*, 1935, 868.

[8] (*a*) Wheeler, *Chem. and Ind.*, 1947, 753, and references there cited; (*b*) Doyle, Gogan, Keane, and Wheeler, *Proc. Roy. Dublin Soc.*, 1948, **24**, 291.

[9] Simamura, Inamoto, and Suehiro, *Bull. Chem. Soc. Japan*, 1954, **27**, 221.

[10] Claus, *J. prakt. Chem.*, 1892, **46**, 480.

[11] Noller and Adams, *J. Amer. Chem. Soc.*, 1924, **46**, 1889.

(733 c.c.; 1·1 mol.), followed by ethyl isobutyrate (11·6 g., 1 mol.) in dry ether (100 c.c.), the whole operation being conducted in dry nitrogen. After 12 hr., with occasional agitation, water was added and the aqueous layer separated, cooled, and acidified. α-Isobutyryl-4-methylacetophenone distilled at 155—156°/10 mm. (4·0 g.) (Found: C, 76·5; H, 8·0%). The copper complex, and the pyrazole formed with 2,4-dinitrophenylhydrazine, had respectively m. p. 187° and 154°, undepressed by admixture with the derivatives described in the previous paragraph. Acid-hydrolysis afforded 4-methylacetophenone 2,4-dinitrophenylhydrazone (m. p. and mixed m. p. 250°).

α-*Acetyl*-2,4-*dimethylisobutyrophenone* (I; $R^1 = R^3 = Me$, $R^2 = H$).—Acetylation of 2,4-dimethylisobutyrophenone [12] (14·9 g.) with acetic anhydride (17·4 g.) and boron trifluoride, as described above, gave, after distillation through a 15 cm. Vigreux column, α-*acetyl*-2,4-*dimethylisobutyrophenone*, b. p. 105—108°/0·3 mm., 96—100°/0·05 mm. (3·1 g.) (Found: C, 76·4; H, 8·3. $C_{14}H_{18}O_2$ requires C, 77·0; H, 8·3%), with unchanged ketone and residual tar. Infrared C=O bands (liquid film) were at 1674 (phenyl conjugated) and 1743 cm.$^{-1}$ (unconjugated).

When an ethereal solution of the diketone was mixed with a suspension of powdered sodium in ether a vigorous reaction occurred within a few minutes. Working up as above gave 2,4-dimethylbenzoic acid (m. p. and mixed m. p. 126—127°) with a trace of a yellow liquid, b. p. about 128° (bath)/0·05 mm., which gave a deep red colour with ferric chloride. It also formed a copper complex (green solution in ether), but this could not be obtained crystalline. A direct infrared comparison with authentic α-isobutyryl-2,4-dimethylacetophenone (see below) indicated that the two were not identical, but the comparison was complicated by the difficulty of removing all the 2,4-dimethylbenzoic acid from the product.

α-*Isobutyryl*-2,4-*dimethylacetophenone* [13] [4-*methyl*-1-(2,4-*xylyl*)*pentane*-1,3-*dione*] (II; $R^1 = R^3 = Me$, $R^2 = H$).—Alcohol-free sodium ethoxide, from sodium (4·6 g.), was suspended in dry ether (50 c.c.), containing ethyl isobutyrate (23·2 g.). 2,4-Dimethylacetophenone [14] (14·8 g.) in dry ether (50 c.c.) was added, with shaking, and the mixture kept at room temperature for 48 hr. After decomposition with ice, the aqueous layer was separated, acidified, and extracted with ether. The extract, after being washed several times with sodium hydrogen carbonate, was dried and concentrated. The *diketone* distilled at 110—115° (bath)/0·05 mm. and had m. p. *ca.* 25° (2·4 g.) (Found: C, 77·4; H, 8·1. $C_{14}H_{18}O_2$ requires C, 77·1; H, 8·3%). The *copper complex* crystallised from ether–light petroleum (b. p. 40—60°) in dark green elongated prisms, m. p. 158—159°.

α-*Acetyl*-4-*chloroisobutyrophenone* (I; $R^1 = Cl$, $R^2 = R^3 = H$).—4-Chloroisobutyrophenone was obtained by Friedel–Crafts acylation of chlorobenzene; [15] it had b. p. 141—142°/17—18 mm., which differs from a recorded value [15] (122—123°/25 mm.), but is in agreement with that given by Bayless and Hauser,[16] who obtained the ketone by a different method. The infrared C=O band (liquid film) was at 1680 cm.$^{-1}$. The 2,4-*dinitrophenylhydrazone* separated from ethanol in orange-yellow plates, m. p. 139·5—140° (Found: C, 53·0; H, 4·5. $C_{16}H_{15}O_4N_4Cl$ requires C, 53·0; H, 4·2%). The ketone (9·8 g.), dissolved in acetic anhydride (13·4 g.), was saturated with boron trifluoride at 0° during 1½ hr. Working up in the usual manner gave, after removal of the alkali-soluble material and fractional distillation *via* a 15 cm. Vigreux column, α-*acetyl*-4-*chloroisobutyrophenone*, b. p. 115—116°/0·3 mm. (4·7 g.) (Found: C, 63·8; H, 6·0. $C_{12}H_{13}O_2Cl$ requires C, 64·2; H, 5·8%), $\nu_{max.}$ (liquid film) 1670 (C=O conjugated with benzene ring) and 1738 cm.$^{-1}$ (unconjugated). A *monosemicarbazone* separated from aqueous methanol in irregular prisms, m. p. 185·5° (Found: C, 55·3; H, 5·2. $C_{13}H_{16}O_2N_3Cl$ requires C, 55·4; H, 5·7%). Acidification of the alkaline washings obtained in the working-up of the diketone afforded 1-p-*chlorophenyl*-2,2-*dimethylhexane*-1,3,5-*trione* (III; $R^1 = Cl$, $R^2 = R^3 = H$), isolated with ether. It distilled at 135° (bath)/0·25 mm. (0·7 g.) (Found: C, 63·3; H, 5·5. $C_{14}H_{15}O_3Cl$ requires C, 63·0; H, 5·6%) and gave a conjugate chelate spectrum (liquid film), with a non-enolisable carbonyl band at 1669 cm.$^{-1}$. The *copper complex* crystallised from benzene–light petroleum (b. p. 60—80°; 1 : 2) in bluish-grey rhombic prisms, m. p. 201° (decomp.) (Found: C, 56·5; H, 4·4. $C_{28}H_{28}O_6Cl_2Cu$ requires C, 56·5; H, 4·7%).

Reaction of α-*Acetyl*-4-*chloroisobutyrophenone with Sodium*.—The diketone (8·1 g.) in dry

---

[12] Ref. 10, p. 482.

[13] Cf. Beyer and Claisen, *Ber.*, 1887, **20**, 2178.

[14] Claus, *ibid.*, 1886, **19**, 230; Verley, *Bull. Soc. chim. France*, 1897, **17**, 910.

[15] Buu-Hoï, Hoan, and Xuong, *Rec. Trav. chim.*, 1952, **71**, 285.

[16] Bayless and Hauser, *J. Amer. Chem. Soc.*, 1954, **76**, 2306.

ether (25 c.c.) reacted vigorously with a suspension of powdered sodium (2·0 g.) in dry ether (25 c.c.). After 48 hr. the product was isolated as described above, yielding 4-chloro-α-isobutyrylacetophenone (1-*p*-chlorophenyl-4-methylpentane-1,3-dione) (II; $R^1 = Cl$, $R^2 = R^3 = H$), b. p. (bath) 130—135°/0·05—0·10 mm. (0·5 g.), identical with an authentic specimen (infrared comparison, see below). The copper complex separated from benzene–light petroleum (b. p. 40—60°) in greyish-blue needles, m. p. 230° (decomp., with some previous softening) alone or mixed with an authentic specimen (see below).

4-*Chloro-α-isobutyrylacetophenone* (cf. preceding paragraph).—4-Chloroacetophenone (15·5 g.) in dry ether (50 c.c.) was added during 10 min. to a vigorously stirred suspension of finely powdered sodamide (10·0 g.) in dry ether (100 c.c.). After 5 min. ethyl isobutyrate (23·2 g.) in dry ether (50 c.c.) was added all at once, and the mixture refluxed on the water-bath for 2 hr., cooled, and poured on ice. The aqueous layer was separated, acidified, and extracted with ether. The extract was washed with sodium hydrogen carbonate solution, dried, and evaporated, yielding 4-*chloro-α-isobutyrylacetophenone* (2·5 g.), b. p. 130° (bath)/0·05 mm. (Found: C, 64·4; H, 5·6. $C_{12}H_{13}O_2Cl$ requires C, 64·2; H, 5·8%). It showed an infrared (liquid film) conjugate chelate spectrum, with wide bands in the 3000 and 1600 cm.$^{-1}$ regions. The product gave a wine-red colour with ferric chloride and formed a *copper complex*, greyish-blue needles [from benzene–light petroleum (b. p. 40—60°)], m. p. 230° (decomp., with some previous shrinking) (Found: C, 56·3; H, 4·2. $C_{24}H_{24}O_4Cl_2Cu$ requires C, 56·4; H, 4·7%). Alkaline hydrolysis of the diketone afforded *p*-chlorobenzoic acid, m. p. and mixed m. p. 235—236°.

3-*Nitroisobutyrophenone*.—Isobutyrophenone (29·4 g.) was added during 30 min. with stirring to a mixture of fuming nitric acid (125 c.c.) and acetic anhydride (165 c.c.)[17] at <5°. The mixture was poured on ice and extracted with ether. The extract was washed with sodium hydrogen carbonate solution and water, dried, and evaporated. The residual 3-*nitroisobutyrophenone* distilled at 115—118°/0·6 mm. (72%) as a pale yellow oil (Found: C, 61·6; H, 5·5. $C_{10}H_{11}O_3N$ requires C, 62·15; H, 5·7%), $\nu_{max.}$ (liquid film) (C=O) 1680 cm.$^{-1}$. Oxidation of the ketone with boiling 2N-nitric acid gave *m*-nitrobenzoic acid, m. p. and mixed m. p. 140°. The 2,4-*dinitrophenylhydrazone* separated from ethanol in orange prismatic needles, m. p. 132° (Found: C, 51·5; H, 4·25. $C_{16}H_{15}O_6N_5$ requires C, 51·5; H, 4·1%). The p-*nitrophenylhydrazone* crystallised from ethanol in brown needles, m. p. 141·5—142° (Found: C, 58·8; H, 4·8. $C_{16}H_{16}O_4N_4$ requires C, 58·5; H, 4·9%).

α-*Acetyl*-3-*nitroisobutyrophenone* (I; $R^1 = R^3 = H$, $R^2 = NO_2$).—The acetylation of 3-nitroisobutyrophenone (20 g.) with acetic anhydride (21·2 c.c.) and boron trifluoride in the usual manner afforded α-*acetyl*-3-*nitroisobutyrophenone* (16·7 g.), b. p. 102—105°/0·06 mm. (after two redistillations) (Found: C, 61·7; H, 6·0; N, 6·3. $C_{12}H_{13}O_4N$ requires C, 61·3; H, 5·6; N, 6·0%). $\nu_{max.}$ (liquid film) (C=O) 1690 (conjugated with benzene ring) and 1746 cm.$^{-1}$ (unconjugated). Hydrolysis with 2N-sulphuric acid gave 3-nitroisobutyrophenone and acetic acid. A *mono*-2,4-*dinitrophenylhydrazone*, prepared in alcoholic sulphuric acid below 15°, separated from ethyl acetate in yellow plates, m. p. 204·5—205° (Found: C, 50·9; H, 4·0. $C_{18}H_{17}O_7N_5$ requires C, 52·1; H, 4·1%). A *mono*-4-*phenylsemicarbazone* crystallised from 75% aqueous ethanol in pale yellow needles, m. p. 149° (Found: C, 62·3; H, 5·5. $C_{19}H_{20}O_4N_4$ requires C, 62·0; H, 5·5%). The diketone showed no reaction towards powdered sodium, sodamide, or sodium hydride, in dry ether, nor was a reaction initiated by the addition of a trace of ethyl acetate or ethanol.

α-*Acetyl*-4-*methoxyisobutyrophenone* (I; $R^1 = OMe$, $R^2 = R^3 = H$).—This diketone was not formed by reaction between acetic anhydride and 4-methoxyisobutyrophenone in the presence of boron trifluoride. 4-Methoxyisobutyrophenone[18] (11·0 g.) in dry ether (10 c.c.) was added dropwise, with swirling, to ethereal 0·25M-sodium triphenylmethyl (250 c.c.) under nitrogen, followed by acetyl chloride (4·9 g.) in ether (10 c.c.). After 1 hour's refluxing, the solution was kept overnight, then water was added and the organic layer separated, dried, and evaporated. The syrupy residue was mixed with an equal volume of methanol, seeded with triphenylmethane, and kept at 0° for several hours. The triphenylmethane was collected and washed with cold methanol. The combined filtrate and washings were freed from solvent by evaporation, and the residue distilled through a short Vigreux column. After a fore-run of unchanged monoketone, α-*acetyl*-4-*methoxyisobutyrophenone* distilled at 99—100°/0·075 mm. (23%) (Found: C, 71·0; H, 8·1. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%) and had $\nu_{max.}$ (liquid film) (C=O) 1670

---

[17] Cf. Morgan and Hickinbottom, *J.*, 1921, **119**, 1879.

[18] Sosa, *Ann. Chim.* (*France*), 1940, **14**, 77.

(phenyl conjugated) and 1743 cm.$^{-1}$ (unconjugated). A *monosemicarbazone* crystallised from ethanol in rectangular plates, m. p. 175·5° (Found: C, 60·3; H, 7·5; N, 15·6. $C_{14}H_{19}O_3N_3$ requires C, 60·6; H, 6·9; N, 15·2%).

*Reaction of α-Acetyl-*4-*methoxyisobutyrophenone with Sodium.*—When the diketone (6·8 g.) in dry ether (15 c.c.) was added to powdered sodium (1·45 g.) in ether (15 c.c.) a slow reaction took place. After 4 days the mixture was worked up in the usual manner, giving *α-isobutyryl*-4-*methoxyacetophenone*, b. p. (bath) 143—148°/0·025 mm. (0·2 g.). The product gave a deep red ferric colour and formed a copper complex, but this could not be obtained crystalline; with 2,4-dinitrophenylhydrazine in alcoholic sulphuric acid it gave 4-methoxyacetophenone 2,4-dinitrophenylhydrazone,[19] m. p. and mixed m. p. 221°. Acidification of the sodium hydrogen carbonate washings gave *p*-anisic acid, m. p. and mixed m. p. 182—183°.

α-Isobutyryl-4-*methoxyacetophenone* (1-p-*Methoxyphenyl*-4-*methylpentane*-1,3-*dione*) (II; $R^1 =$ OMe, $R^2 = R^3 = H$).—4-Methoxyacetophenone [11] (6·0 g.) in dry ether (15 c.c.) was added to ethereal 0·2M-sodium triphenylmethyl (160 c.c.), followed by isobutyryl chloride (4·3 g.) in dry ether. After refluxing for 8 hr. the cooled mixture was extracted twice with cold, dilute sodium hydroxide, and the extracts were acidified with dilute hydrochloric acid. The liberated *α-isobutyryl*-4-*methoxyacetophenone* distilled at 141—150° (bath)/0·01 mm. (0·6 g.) (Found: C, 71·3; H, 7·4. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%). It gave a deep red colour with ferric chloride, and formed a copper complex, which separated from benzene–light petroleum (b. p. 60—80°) in bluish-grey irregular prisms, m. p. 155°. With 2,4-dinitrophenylhydrazine in alcoholic sulphuric acid the product afforded 4-methoxyacetophenone 2,4-dinitrophenylhydrazone,[19] m. p. and mixed m. p. 221°.

Reaction of 2-*Acetyl*-2-*methylindan*-1-*one* (V) *with Sodium.*—2-Acetyl-2-methylindan-1-one [1] (9·8 g.) in dry ether (15 c.c.) was added to a suspension of powdered sodium (2·4 g.) in ether. After the vigorous reaction the mixture was kept for 24 hr., then decomposed with ice and worked up in the manner described. 2-Acetoacetyl-2-methylindan-1-one (VII) distilled at 153—154° (bath)/0·2 mm. (2·35 g.) (Found: C, 72·8; H, 6·4. Calc. for $C_{14}H_{14}O_3$: C, 73·0; H, 6·1%). The copper complex crystallised from benzene in dark green prisms, m. p. 147—148° alone or mixed with a specimen of the copper complex of 2-acetoacetyl-2-methylindan-1-one prepared by the acetylation of 2-acetyl-2-methylindan-1-one.[1] The infrared absorption (liquid film) was of conjugate chelate type, with bands at 1710 (C=O), 2630 (chelated OH), and 1607 cm.$^{-1}$ (chelated C=O). With 2,4-dinitrophenylhydrazine a *pyrazole*, separating from ethanol in orange, rectangular plates, m. p. 171° (Found: C, 61·2; H, 4·1; N, 15·2. $C_{20}H_{16}O_5N_4$ requires C, 61·2; H, 4·1; N, 14·3%), was obtained; it was undepressed in m. p. by admixture with an authentic specimen.

In the acetylation of 2-methylindan-1-one with boron trifluoride and acetic anhydride,[1] there was formed in addition to (V) and (VII) an involatile, neutral *product* in small yield. It crystallised from light petroleum (b. p. 60—80°) in rhombic needles, m. p. 113·5° (Found: C, 72·95; H, 5·7. $C_{14}H_{14}O_3$ requires C, 73·0; H, 6·1%). It is almost certainly a nuclear acetylated product, probably 2,6-diacetyl-2-methylindan-1-one.

Reaction of 3,3-*Dimethylpentane*-2,4-*dione* (VIII) *with Sodium.*—The diketone was obtained by the boron trifluoride acetylation of isopropyl methyl ketone.[20] After separation from alkali-soluble material it distilled at 84—86°/11 mm. and gave no colour with ferric chloride. The diketone (2·2 g.) in dry ether (10 c.c.) was added gradually to powdered sodium (0·8 g.) in ether (10 c.c.). When the vigorous reaction had ended the product was isolated in the usual manner, to give 5-methylhexane-2,4-dione (IX), b. p. 74°/12 mm. (0·2 g.), which formed a copper complex, m. p. 170—171° (lit.,[20] m. p. 170—171°), identical (mixed m. p.) with the copper complex of authentic diketone obtained by acidification of the alkaline extracts in the acetylation above.[20]

We thank Dr. G. Eglinton (University of Glasgow) and Mr. G. Phillips for the infrared measurements, and the Imperial Smelting Corporation and Imperial Chemical Industries Limited (Dyestuffs Division) for gifts of chemicals.

DEPARTMENT OF CHEMISTRY, UNIVERSITY COLLEGE,
CARDIFF.

[*Received, March 2nd*, 1959.]

---

[19] " Organic Reagents for Organic Analysis," Hopkin and Williams, Ltd., 2nd edn., 1950, p. 225.

[20] Hauser and Adams, *J. Amer. Chem. Soc.*, 1944, **66**, 345.