

814. Some Experiments with cyclopentanones.

By R. M. ACHESON.

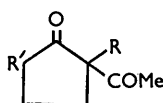
A number of unsuccessful attempts to prepare 2-acetylcyclopent-2-enone from 2-acetylcyclopentanone, 2-furylacetone, and 3-methylcyclohex-3-enone, and the preparation of these compounds, are described.

ALTHOUGH 2-acetylcyclo-hexene and -pentene react with the sodium derivative of 6-methoxy-tetralone to yield tetracyclic compounds¹ these products have not proved valuable in the synthesis of steroids because methods of introducing substituents at position 17 are not yet available. The use of 5-monosubstituted 1-acetylcyclopentenenes in this synthesis appears unpromising as the double bond is almost certain to migrate under the influence of the alkali, but this argument does not inevitably apply when the cyclopentene has two substituents or a carbonyl group at position 5.

The unknown 2-acetylcyclopent-2-enone (I) was therefore the objective, and the first attempt was *via* 2-acetylcyclopentanone. This cyclopentanone has been obtained from cyclopentanone and ethyl acetate in the presence of sodium,² but the low yield (12%) and the necessity of purification through the copper salt was not encouraging. Replacement of the sodium by its hydride gave even less 2-acetylcyclopentanone with some dicyclopentylidenecyclopentanone, earlier obtained³ from cyclopentanone and sodium ethoxide. However cyclisation of ethyl 6-oxoheptanoate with sodium hydride gave the ketone (II) in satisfactory yield. 6-Oxoheptanoic acid, with a little glutaric acid, was more conveniently obtained from 2-methylcyclohexanone with aqueous potassium permanganate than by the use of other oxidants.⁴



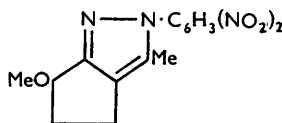
(I)



(II) R, R' = H

(III) R = Br, R' = H

(IV) R = H, R' = Br



(V)

2-Acetylcyclopentanone reacted very readily with the theoretical quantity of bromine in aqueous potassium chlorate⁵ but the resulting solution was very strongly acid and monobromination was incomplete. Better results were obtained in aqueous sodium acetate, the product after distillation being a colourless lachrymatory oil of the expected composition. The bromine probably initially attacks position 2, giving the derivative (III), but as the compound gave a sticky copper derivative and a deep red ferric chloride colour, rearrangement to the isomer (IV) or to 2-bromoacetylcyclopentanone had taken place.⁶ Although the bromo-compound may be a mixture of all three isomers Kuhn-Röth determinations showed the presence of one C-Me group and therefore exclude the presence of

¹ Peak and Robinson, *J.*, 1937, 1581.

² Kuhn, Köhler, and Köhler, *Z. physiol. Chem.*, 1936, **242**, 171.

³ Wallach, *Ber.*, 1896, **29**, 2955.

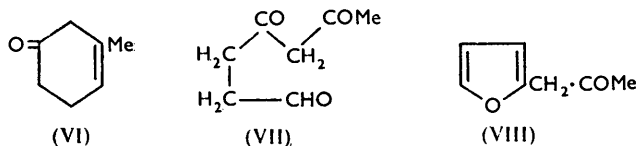
⁴ Ruzicka, Seidel, Schinz, and Pfeiffer, *Helv. Chim. Acta*, 1948, **31**, 422; G.P. 812,073 (*Chem. Abs.*, 1953, **47**, 2769).

⁵ Catch, Elliott, Hey, and Jones, *J.*, 1948, 272.

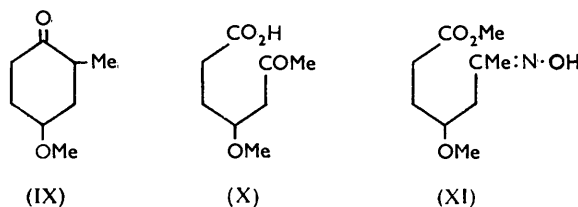
⁶ Cf. Conrad, *Ber.*, 1896, **29**, 1042; Epprecht, *Annalen*, 1894, **278**, 69.

much 2-bromoacetyl cyclopentanone unless a rearrangement took place under the conditions of oxidation. The compound is therefore probably largely the ketone (IV), but neither dehydrobromination with collidine or silver nitrate in pyridine, nor acid hydrolysis, gave identifiable products; 2-acetyl cyclopentanone gave 6-oxoheptanoic acid with either dilute acid or alkali and no cyclopentanone could be detected. The bromo-ketone (IV) with 2:4-dinitrophenylhydrazine in methanolic sulphuric acid gave a yellow crystalline derivative containing one C-Me and one methoxyl group, and it did not lose methanol when heated alone. 2-Chloro-2-methyl cyclohexanone similarly gives 2-methoxy-2-methyl cyclohexanone 2:4-dinitrophenylhydrazone.⁷ The cyclopentanone derivative may be compound (V) or an isomer.

Alternative schemes based on the formation and cyclisation of the aldehyde (VII) were then examined. 3-Methyl cyclohex-3-ene (VI), prepared in a comparatively high state of purity by a modification of Birch's method,⁸ was ozonised at -80° in ethyl acetate and hydrogenated over palladised charcoal at -10° . Although the theoretical quantities of ozone and hydrogen were absorbed attempts to isolate the aldehyde (VII), or to cyclise it *in situ* to the ketone (I) by acid catalysis, gave only products of high molecular weight.



2-Acetylfuran (VIII) was treated with acid, in the hope that it would yield the aldehyde (VII) which might simultaneously cyclise to the ketone (I): however it was either unaffected by aqueous or alcoholic sulphuric acid, or converted into black tars when the acid concentration was raised above $\sim 30\%$ or when heated. Tars were also obtained in attempts to prepare 2-acetyl-2:5-dihydro-2:5-dimethoxyfuran from the ketone (VIII) with bromine in methanol.⁹ 2-Acetylfuran oxime formed an oily toluene-*p* sulphonate which also gave black tars when shaken with ethanol,¹⁰ instead of the desired 1:1-diethoxyhept-2-ene-4:6-dione which it was proposed to reduce to the saturated acetal. Several attempts to prepare the last compound from acetone and ethyl $\gamma\gamma$ -diethoxybutyrate, obtained from the β -formylpropionate and ethyl orthoformate, also failed.



As 2-methyl cyclohexanone was so easily oxidised to 6-oxoheptanoic acid it was hoped that the 4-methoxy-derivative (IX) would similarly yield 4-methoxy-6-oxoheptanoic acid (X) which after esterification might undergo Dieckmann condensation followed by loss of methanol, leading to 2-acetyl cyclopent-2-ene (I). 4-Methoxy-2-methylphenol was obtained from *p*-methoxyphenol by treatment with formaldehyde and dimethylamine, followed by hydrogenation over Raney nickel, a much more convenient catalyst than the copper chromite previously used.¹¹ Further hydrogenation, after removal of all traces of amine which prevented reaction, yielded the cyclohexanol , which was oxidised to the cyclohexanone (IX) with chromic acid. Unfortunately attempts to oxidise this ketone to the acid (X) with potassium permanganate failed and the ether linkage appeared to be

⁷ Warnhoff and Johnson, *J. Amer. Chem. Soc.*, 1953, **75**, 494.

⁸ Birch, *J.*, 1946, 593.

⁹ Cf. Clauson-Kaas, Limborg, and Fakstorp, *Acta Chem. Scand.*, 1948, **2**, 109.

¹⁰ Cf. Vargha, Ramonczai, and Bite, *J. Amer. Chem. Soc.*, 1948, **70**, 371.

¹¹ Reeve and Sadle, *ibid.*, 1950, **72**, 3252.

attacked. An alternative method¹² of ring opening with ethyl nitrite and sodium ethoxide gave ethyl 6-hydroxyimino-4-methoxyheptanoate (XI) in poor yield; hydrolysis with oxalic acid gave no ketonic product, while boiling with dilute alkali followed by treatment with 2 : 4-dinitrophenylhydrazone gave the derivative from β -formylpropionic acid.

cyclopentane-1 : 2-dione has been obtained from *cyclopentanone* by bromination, hydrolysis to 2-hydroxycyclopentanone, and oxidation with ferric chloride without isolation of the intermediates. With 2 : 4-dinitrophenylhydrazine in methanolic sulphuric acid it gave the hydrazones of 2-methoxycyclopent-2-enone, while with excess of aqueous or alcoholic reagent the normal bis-derivative was formed. 2-Methoxycyclopent-2-enone was obtained from the diketone with diazomethane.

EXPERIMENTAL

6-Oxoheptanoic Acid.—After 2-methylcyclohexanone (45 g.) had been stirred with potassium permanganate (108 g.) and water (3.6 l.) for about 12 hr. at room temperature almost no permanganate remained. The mixture was clarified with sulphur dioxide, acidified with concentrated sulphuric acid (22 ml.), and continuously extracted with ether (24 hr.). Distillation of the dried extract gave 6-oxoheptanoic acid (39 g.), b. p. 158—162°/9 mm., as plates, m. p. 33—34°, and glutaric acid (2.4 g.), b. p. 185—190°/9 mm., m. p. or mixed m. p. 97°. 6-Oxoheptanoic acid 2 : 4-dinitrophenylhydrazone separated from ethanol in orange-yellow prisms, m. p. 144° (Found : C, 48.1; H, 4.8; N, 17.7. $C_{13}H_{16}O_6N_4$ requires C, 48.1; H, 4.9; N, 17.3%). Methyl 6-oxoheptanoate, b. p. 108—112°/13 mm. (35.9 g.), prepared from the acid (41.2 g.) by 4 hours' refluxing with methanol (50 ml.) and concentrated sulphuric acid (3 ml.), gave a 2 : 4-dinitrophenylhydrazone, yellow needles (from methanol), m. p. 123—124° (Found : C, 49.7; H, 5.6. $C_{14}H_{18}O_6N_4$ requires C, 49.7; H, 5.3%).

2-Acetylcyclopentanone (II).—(i) Sodium hydride (9.6 g.) was added to a mixture of ethyl 6-oxoheptanoate (7.2 g.) in ether (50 ml.) under nitrogen and reaction started by the addition of a drop of ethanol and warming; more ester (10 g.) in ether was then added and the reaction completed according to Swamer and Hauser's procedure.¹³ Sodium ethoxide has also¹⁴ been used for the cyclisation. 2-Acetylcyclopentanone (10 g.), isolated by ether, had b. p. 82—86°/12 mm., n_D^{17} 1.4920, and gave a deep violet ferric chloride colour in ethanol.

(ii) Sodium hydride (9.6 g.) reacted with ethyl acetate (35.2 g.) and *cyclopentanone* (24.8 g.) under Swamer and Hauser's conditions.¹³ Distillation of the product, purified by its copper salt, gave 2-acetylcyclopentanone (2.3 g.), n_D^{18} 1.4917, b. p. 75—80°/11 mm., and a pale yellow unidentified oil (4.9 g.), b. p. 162—164°/12 mm. Distillation of the product which did not form a copper salt gave dicyclopentylidene*cyclopentanone*, b. p. 194—198°/11 mm., as yellow needles, m. p. 84—85° (Found : C, 83.0; H, 9.3%; C-Me, 0.0; M, 243. Calc. for $C_{15}H_{20}O$: C, 83.2; H, 9.3%; M, 216). Wallach³ gives b. p. 190°/12 mm. and m. p. 76—77°. It did not form a semicarbazone or a crystalline 2 : 4-dinitrophenylhydrazone, and Wallach was unable to prepare an oxime. It had an ultraviolet absorption max. in EtOH at 3000 Å (ϵ 15,300), and infrared absorption bands in paraffin paste at 5.91 (CO), 6.17, and 6.22 μ with an inflexion at 6.08 μ .

2-Acetylcyclopentanone was very slowly hydrolysed by cold 10% aqueous potassium hydroxide, but boiling 20% aqueous potash (2½ hr.)¹⁵ or aqueous 4N-sulphuric acid gave 6-oxoheptanoic acid (80%), m. p. or mixed m. p. 35°. No *cyclopentanone* could be detected.

The mixture of red and yellow crystals obtained when 2-acetylcyclopentanone (0.3 g.), 2 : 4-dinitrophenylhydrazine (0.5 g.), methanol (25 ml.), and sulphuric acid (0.5 ml., d 1.84) were left at room temperature for 16 hr. was separated as the red material (0.05 g.) did not dissolve in boiling methanol (15 ml.). The red material, probably 2-acetylcyclopentanone bis-2 : 4-dinitrophenylhydrazone was obtained as red-brown prisms, m. p. 219° (decomp.), by dissolution in a large volume of boiling ethyl acetate followed by almost complete evaporation (Found : C, 47.6; H, 4.1; N, 23.4. $C_{19}H_{18}O_8N_8$ requires C, 46.9; H, 3.7; N, 23.0%). The methanol-soluble 2-(2 : 4-dinitrophenyl)-3-methylcyclopenta[c]pyrazole or an isomer, formed from one of the two monodinitrophenylhydrazones possible on cyclodehydration, separated from this solvent in yellow prisms, m. p. 165° (Found : C, 54.1; H, 4.2; N, 19.2. $C_{13}H_{12}O_4N_4$ requires C, 54.2; H, 4.2; N, 19.4%).

¹² Woodward and Doering, *J. Amer. Chem. Soc.*, 1945, **67**, 860.

¹³ Swamer and Hauser, *ibid.*, 1950, **72**, 1352.

¹⁴ Blaise and Köhler, *Bull. Soc. chim. France*, 1910, **7**, 710.

¹⁵ Cf. Hauser, Swamer, and Ringler, *J. Amer. Chem. Soc.*, 1948, **70**, 4023.

Bromination of 2-Acetylcyclopentanone.—Bromine (0.64 g.) was added with shaking to a mixture of the ketone (1.5 g.), water (10.0 ml.), and sodium acetate (5.0 g.) at room temperature; the colour disappeared very quickly. The oily product was collected with ether, washed with (2–3%) aqueous sodium hydrogen carbonate and water, dried, and immediately distilled, to give bromo-2-acetylcyclopentanone as a colourless lachrymatory oil, b. p. 75–77°/0.2 mm. (1.8 g.), n_D^{27} 1.553 (Found: C, 40.9; H, 4.4; Br, 39.2; C-Me, 5.5. Calc. for $C_7H_9O_2Br$: C, 41.0; H, 4.4; Br, 39.0; 1C-Me, 7.3%). It decomposed if distillation was attempted at 10 mm., gave a deep red ferric chloride colour in ethanol and a sticky green copper salt, and decomposed to a black tar in a few hours at room temperature.

The deep red solution obtained on mixing the bromo-ketone (1.0 g.), 2:4-dinitrophenylhydrazine (3.0 g.), methanol (50 ml.), and concentrated sulphuric acid (5 ml.) deposited a dark red solid (1.0 g.) at room temperature in 18 hr. After crystallisation from ethyl acetate this solid gave 2-(2:4-dinitrophenyl)-6-methoxy-3-methylcyclopenta[c]pyrazole (V, or an isomer), separating from ethanol in yellow needles, m. p. 147° (Found: C, 52.8, 52.9; H, 4.2, 4.5; N, 17.8; Br, 0.0; OMe, 10.0, 10.7; C-Me, 6.0. $C_{14}H_{14}O_5N_4$ requires C, 52.8; H, 4.4; N, 17.6; 1OMe, 9.7; 1C-Me, 4.7%). No other crystalline material could be obtained from the mother-liquors.

3-Methylcyclohex-3-enone (VI).—2:5-Dihydro-3-methylanisole⁸ (20.5 g.) was shaken with saturated aqueous sodium hydrogen sulphite, saturated with sulphur dioxide, at 0°. After 12 hr. the precipitate (41 g.) was collected, washed with methanol and ether, and decomposed with potassium carbonate (40 g.) in water (120 ml.). Evaporation of the dried ether extracts gave largely 3-methylcyclohex-3-enone (7.8 g.), b. p. 61–62°/14 mm., λ_{max} , 2310 (ϵ 1800 in methanol) (cf. Birch⁸). The ultraviolet absorption was unchanged after the material had remained at room temperature for 3 weeks in a Pyrex flask. The *semicarbazone*, prepared in the cold, was washed with aqueous potassium carbonate and dried before crystallisation, and separated from ethyl acetate in long thin plates, m. p. 157–158° (Found: C, 57.3; H, 7.5; N, 24.8. $C_8H_{13}ON_3$ requires C, 57.5; H, 7.8; N, 25.2%). Birch⁸ gives m. p. 159–161° but no analysis or ultraviolet data. The ultraviolet absorption spectrum in methanol showed λ_{max} , 2280 (ϵ 13,000).

Methyl $\alpha\beta$ -Epoxy- β -2-furyl- α -methylpropionate.—A dry methanol (75 ml.) solution of sodium (6.9 ml.) was added during 3 hr. to a vigorously stirred mixture of methyl α -chloropropionate (37.6 g.), furfuraldehyde (20.0 g.), and methanol (25 ml.) at 0°. After 12 hours' stirring at 20° the methanol was removed *in vacuo* at this temperature and the residue treated successively with ether (150 ml.) and aqueous *N*-hydrochloric acid (110 ml.) at 0°. The ether extracts were dried, washed with aqueous sodium hydrogen carbonate, and evaporated, giving the required ester (23.9 g.), b. p. 116–221°/11 mm. Wolff¹⁶ gives b. p. 112–116°/9 mm.

2-Acetylonylfuran (VIII).—The above ester (13.3 g.) dissolved in 2 min. when shaken with a cold solution of sodium hydroxide (3.5 g.) in water (20 ml.) and methanol (5 ml.), and after 5 min. aqueous 7*N*-sulphuric acid (26 ml.) was added. Much carbon dioxide was evolved. Ether extracts were washed with aqueous sodium hydrogen carbonate, dried, and evaporated, giving 2-acetylonylfuran (4.0 g.), smelling of horse-radish, b. p. 70–72°/13 mm. (Found: C, 68.0; H, 6.6. $C_7H_8O_2$ requires C, 67.7; H, 6.5%). Darzens¹⁷ gives b. p. 179–180° but no analysis. The *semicarbazone* separated from ethanol in prisms, m. p. 173–174° (Found: C, 53.0; H, 6.2; N, 23.5. $C_8H_{11}O_3N_3$ requires C, 53.0; H, 6.1; N, 23.2%). Darzens¹⁷ gives m. p. 173–174° but no analysis. The *oxime* was a liquid, b. p. 110°/8 mm. (Found: C, 60.4; H, 6.5; N, 10.2. $C_7H_9O_2N$ requires C, 60.4; H, 6.5; N, 10.1%). A crystalline 2:4-dinitrophenylhydrazone was not formed in methanolic sulphuric acid.

*2-Hydroxy-5-methoxy-*NN*-dimethylbenzylamine.*—40% Aqueous formaldehyde (23 g.) was added during 80 min. to *p*-methoxyphenol (30 g.) in 35% aqueous dimethylamine (110 g.) with stirring below 25°. After 1 hr. at room temperature the mixture was heated on a steam-bath for 4 hr. Two layers were formed. The lower layer, and a benzene extract of the aqueous layer, were washed with water, dried, and distilled, giving the phenol (33 g.), b. p. 114–122°/1 mm., as yellow prisms, m. p. 47° (lit.,¹¹ m. p. 50–51°).

4-Methoxy-2-methylphenol.—The foregoing amine (58 g.) in ethanol (45 ml.) was hydrogenated over Raney nickel at 180–200°/100 atm. Reduction was complete in 2 hr. and the crude product obtained on evaporation of the filtered ethanol solution was washed in ether with 2*N*-sulphuric acid, dried, and distilled as an almost colourless oil (38 g.), b. p. 132–138°/15 mm., m. p. 70° (lit.,¹¹ 70.5°).

¹⁶ Wolff, G.P. 702,007 (*Chem. Abs.*, 1942, **36**, 95).

¹⁷ Darzens, *Compt. rend.*, 1906, **142**, 215.

4-Methoxy-2-methylcyclohexanol.—4-Methoxy-2-methylphenol (25 g.) was hydrogenated at 160—170°/120 atm. over Raney nickel in the presence of a trace of ethanol. Reduction was complete in 1 hr., and the *cyclohexanol* (22.1 g.), collected with ether, distilled as a peppermint-smelling oil, b. p. 102—106°/13 mm., n_D^{17} 1.4692 (Found: C, 66.6; H, 11.3; OMe, 21.9. $C_8H_{16}O_2$ requires C, 66.7; H, 11.1; OMe, 21.5%). Its *p-nitrobenzoate*, prepared in pyridine, separated from ethanol in prisms, m. p. 127° (Found: C, 61.3; H, 6.7. $C_{15}H_{18}O_5N$ requires C, 61.4; H, 6.5%). On one occasion when the temperature reached 190° during the reduction about one-third of the product was hexahydro-*o*-cresol, b. p. 70—74°/11 mm., n_D^{18} 1.4649 (Found: C, 73.5; H, 12.2. Calc. for $C_7H_{14}O$: C, 73.7; H, 12.3%), whose infrared absorption spectrum was identical with that of an authentic specimen.

4-Methoxy-2-methylcyclohexanone (IX).—Sodium dichromate dihydrate (20.2 g.) in water (30 ml.) and sulphuric acid (8 ml.) was added, with vigorous stirring, in 10—15 min. to a mixture of 4-methoxy-2-methylcyclohexanol (24 g.), water (130 ml.), and concentrated sulphuric acid (18 ml.). An exothermic reaction took place and the mixture was kept at 45° for a total of 30 min. The *cyclohexanone* separated as the upper layer, and after the addition of methanol (3 ml.) to destroy excess of dichromate, it was collected in ether, washed with aqueous potassium hydrogen carbonate, and dried. Distillation gave an oil (16.7 g.), b. p. 92—97°/15 mm. (Found: C, 67.8; H, 10.2. $C_8H_{14}O_2$ requires C, 67.6; H, 9.9%). The 2:4-dinitrophenylhydrazone separated from ethanol in yellow needles, m. p. 138° (Found: C, 52.2; H, 5.9; N, 17.4. $C_{14}H_{18}O_5N_4$ requires C, 52.2; H, 5.6; N, 17.4%).

Ethyl 6-Hydroxyimino-4-methoxyheptanoate.—4-Methoxy-2-methylcyclohexanone (6.16 g.), followed by freshly dried and distilled ethyl nitrite (4.0 ml.), was added to a solution of sodium (1.0 g.) in dry ethanol (150 ml.) at 0°. After 18 hr. at this temperature, carbon dioxide was passed through the solution at room temperature to neutrality. The dark solution was treated with charcoal, filtered, and evaporated, and the dark residue distilled. The *oxime* (2.2 g.) was obtained as a pale yellow oil, n_D^{20} 1.4646, b. p. 164—170°/7 mm., 115°/0.07 mm. (Found: C, 55.0; H, 8.8; N, 6.4; OMe + OEt, 31.8. $C_{10}H_{18}O_4N$ requires C, 55.3; H, 8.8; N, 6.5; 1OMe + 1OEt, 35.0%). Unless great care is taken at the beginning of the distillation the dark residue undergoes a vigorous decomposition to a black froth, from which it is possible to isolate very little of the desired product.

The hydroxyimino-ester (0.7 g.) was refluxed for 30 min. with aqueous 2N-sodium hydroxide (20 ml.), and the solution acidified and extracted with ether. Evaporation of the extract gave an oil which with 2:4-dinitrophenylhydrazine in 2N-hydrochloric acid gave a yellow precipitate, identical with that obtained on treating the extracted aqueous solution with this reagent. Recrystallisation of the precipitate from aqueous acetic acid gave γ -(2:4-dinitrophenylhydrazono)butyric acid as yellow prisms (Found: C, 42.6; H, 3.6; N, 19.4. Calc. for $C_{10}H_{10}O_6N_4$: C, 42.6; H, 3.5; N, 19.9%), m. p. and mixed m. p. 199—200°; the infrared absorption spectra of this and an authentic specimen were also identical.

Ethyl γ -Diethoxybutyrate.—Ethyl β -formylpropionate (35.3 g.), ethanol (47 ml.), ethyl orthoformate (45 g.), and ammonium chloride (0.75 g.) were refluxed for 70 min., ethanol and ethyl formate were removed, and the residue was cooled, diluted with ether (100 ml.), and treated with ice-water (20 ml.). Evaporation of the dried ether extracts gave the acetal (49.1 g.), b. p. 111—116°/16 mm., n_D^{20} 1.4180 (Found: C, 58.5; H, 9.8. Calc. for $C_{10}H_{20}O_4$: C, 58.8; H, 9.8%) (lit.,¹⁸ b. p. 101—102°/12 mm.).

Ethyl β -formylpropionate with 2:4-dinitrophenylhydrazine in aqueous 2N-hydrochloric acid gave the *hydrazone*, which separated from ethanol as yellow needles, m. p. 200° (Found: C, 42.6; H, 3.6; N, 19.4. $C_{10}H_{10}O_6N_4$ requires C, 42.6; H, 3.5; N, 19.9%).

cyclopentane-1:2-dione.—A mixture of *cyclopentanone* (60 ml.), acetic acid (31 ml.), and water (135 ml.) was vigorously stirred and a few drops of bromine were added. The whole was then heated at ca. 70° until the colour disappeared, to start the reaction. The remaining bromine (total 38.5 ml.) was then added during 15 min. with stirring, the temperature being kept at 55—60° by external cooling. If the temperature is allowed to exceed 60° for an appreciable time an inferior yield of a less pure product is obtained.¹⁹ The stirred mixture was then neutralised (Congo-red) with solid sodium carbonate, and the pale yellow bromocyclopentanone (93 g.), which separated below the aqueous layer, was washed twice with water.

This crude bromo-ketone (127.5 g.) was stirred vigorously (important) with water (830 ml.) at 95—98° until dissolution was complete (10 min.).²⁰ Then ferric chloride (200 g.; anhydrous)

¹⁸ Carrière, *Ann. Chim.*, 1922, 17, 70.

¹⁹ Cf. Kötze, Blendermann, Kárpáti, and Rosenbusch, *Annalen*, 1913, 400, 51.

²⁰ Cf. Inhoffen, *Chem. Ber.*, 1954, 491.

in hot water (250 ml.) was added during 5 min. with vigorous stirring. After a few more minutes at 95—98° the mixture was cooled to *ca.* 40°, saturated with ammonium sulphate, and continuously extracted with ether. Distillation of the dried extract gave *cyclopentane-1:2-dione* (30.7—33.0 g.), b. p. 78—86°/8 mm., yellow prisms, m. p. 55—56° (lit.,²⁰ m. p. 55—56° for a product from 2-chlorocyclopentanone). The diketone with 2:4-dinitrophenylhydrazine in methanolic sulphuric acid gave *2-methoxycyclopent-2-enone 2:4-dinitrophenylhydrazone*, which separated from ethyl acetate in orange-red prisms, m. p. 207—208° (slight decomp.) (Found: C, 48.8; H, 4.2; N, 20.0; OMe, 8.1. $C_{12}H_{12}O_5N_4$ requires C, 49.3; H, 4.1; N, 19.2; OMe, 10.6%). Use of an excess of the reagent, or of water as solvent, leads to the *bis-2:4-dinitrophenylhydrazone*, orange-red prisms (from acetic acid), m. p. 250—252° (decomp.) (Found: C, 44.6; H, 3.1; N, 24.2. $C_{17}H_{14}O_8N_8$ requires C, 44.5; H, 3.1; N, 24.5%).

2-Methoxycyclopent-2-enone.—When diazomethane (9.7 g.) in ether (570 ml.) was added to *cyclopentane-1:2-dione* (21.5 g.) in ether (83 ml.) a vigorous reaction took place. After about 1 hr. the mixture was distilled, giving *2-methoxycyclopent-2-enone* (17.2 g.), n_D^{20} 1.4980 b. p. 112—114°/16 mm. (Found: C, 64.5; H, 7.1. $C_6H_8O_2$ requires C, 64.3; H, 7.1%).

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