967. 3-*Formyl*cyclo*hexane*spirocyclo*pentane*-2 : 4-*dione and* 2-*Formyl*-5 : 5-*dimethyl*cyclo*hexane*-1 : 3-*dione.*

By B. D. Akehurst and J. R. Bartels-Keith.

3-Formyl*cyclo*hexane*spirocyclo*pentane-2 : 4-dione and 2-formyl-5 : 5-dimethyl*cyclo*hexane-1 : 3-dione have been synthesised, and their ultraviolet and infrared absorption spectra studied and compared with those of 3-formylpentane-2 : 4-dione. Derivatives and degradative experiments are reported for the two new compounds, and 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-9-(2-hydroxy-4 : 4-dimethyl-6-oxo*cyclo*hex-1-enyl)-3 : 3 : 6 : 6-tetramethyl-1 : 8-dioxoxanthen has been obtained by the action of dimedone on 2-formyl-5 : 5-dimethyl*cyclo*hexane-1 : 3-dione.

2-Acyl-1 : 3-diketones have interest particularly since several have biological activity. Two acyclic examples, 3-formylpentane-2 : 4-dione [1] and triacetylmethane,[2] have long been known, and many cyclic 2-acyl-1 : 3-diketones have been isolated from natural sources (for references see Chan and Hassall [3]).

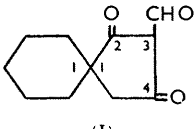
---

[1] Claisen, *Ber.*, 1893, **26**, 2731.

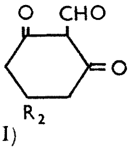
[2] Nef, *Annalen*, 1893, **277**, 71.

[3] Chan and Hassall, *J.*, 1956, 3495.

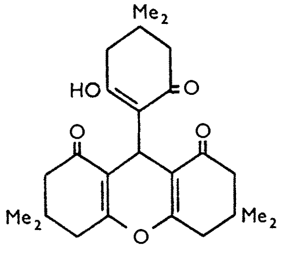
Although several 2-acyl-1 : 3-diketones have been described, 2-formyl-1 : 3-diketones have not been studied systematically. The present paper records the synthesis of 3-formyl*cyclo*hexane*spirocyclo*pentane-2 : 4-dione (I) and 2-formyl-5 : 5-dimethyl*cyclo*hexane-1 : 3-dione (II; R = Me). Condensation of 5 : 5-dimethyl*cyclo*hexane-1 : 3-dione with ethyl orthoformate in the presence of acetic anhydride, followed by alkaline hydrolysis, gave the formyl-diketone (II; R = Me), with comparable amounts of 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-9-(2-hydroxy-4 : 4-dimethyl-6-oxo*cyclo*hex-1-enyl)-3 : 3 : 6 : 6-tetramethyl-1 : 8-dioxoxanthen[4] (III). Formation of the xanthen (III) by the action of ethyl orthoformate on 5 : 5-dimethyl*cyclo*hexane-1 : 3-dione has been noted previously.[5]



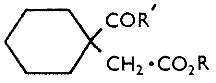
(I)



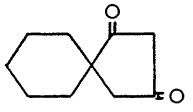
(II)



(III)



(IV)



(V)

Unlike 2-formyl*cyclo*hexane-1 : 3-dione (II; R = H) which Rogers and Smith[6] obtained only as an unstable oil, 2-formyl-5 : 5-dimethyl*cyclo*hexane-1 : 3-dione (II; R = Me) is crystalline (m. p. 77°) and readily dissolves in common solvents. It behaved as a monobasic acid (p*K* 3·65) and gave an intense orange colour with ferric chloride, a crimson colour with titanous chloride[7] in methanol (transient green in the presence of pyridine), and a blue crystalline copper complex. Like 2-formyl*cyclo*hexane-1 : 3-dione[6] (II; R = H), it readily gave a crystalline anil. On oxidation with alkaline hydrogen peroxide it gave formic acid and ββ-dimethylglutaric acid, and on acid hydrolysis it gave the condensation product (III). The latter was also obtained, in good yield, on condensation of the formyl-diketone (II; R = Me) with 2 mols. of dimedone, which confirms the structure (III)[4, 5] for this compound.

*cyclo*Hexane*spirocyclo*pentane-2 : 4-dione (V) on treatment with ethyl orthoformate and acetic anhydride in boiling ethyl acetate, followed by hydrolysis, gave 3-formyl*cyclo*hexane*spirocyclo*pentane-2 : 4-dione (I). This compound gave colours with ferric chloride and with titanous chloride similar to those given by the keto-aldehyde (II; R = Me) with these reagents, and formed a crystalline copper complex and an anil. It is a monobasic acid with p*K* 2·9 in 50% aqueous ethanol.

3-Formyl*cyclo*hexane*spirocyclo*pentane-2 : 4-dione (I) on oxidation with alkaline hydrogen peroxide gave formic acid and 1-carboxy*cyclo*hexylacetic acid (isolated as its anhydride), but on acid hydrolysis gave a high-melting substance of unknown constitution. Similar high-melting products were obtained when solutions of the formyl-diketone were kept for long periods.

*cyclo*Hexane*spirocyclo*pentane-2 : 4-dione (V) was prepared by a modification of Rothstein and Thorpe's synthesis.[8] Ethyl 1-chlorocarbonyl*cyclo*hexylacetate (IV; R = Et, R′ = Cl), on treatment with dimethylcadmium, gave ethyl 1-acetyl*cyclo*hexylacetate (IV; R = Et, R′ = Me) which on hydrolysis to the acid and re-esterification with diazomethane furnished pure methyl 1-acetyl*cyclo*hexylacetate (IV; R = R′ = Me). Cyclisation of this ester by de Rosanbo's method[9] gave the diketone (V).

[4] Vorländer and Guthke, *Ber.*, 1929, **62**, 549.
[5] Meek, Turnbull, and Wilson, *J.*, 1953, 811.
[6] Rogers and Smith, *J.*, 1955, 341.
[7] Weygand and Csendes, *Chem. Ber.*, 1952, **85**, 45.
[8] Rothstein and Thorpe, *J.*, 1926, 2015.
[9] de Rosanbo, *Ann. Chim.* (*France*), 1923, **19**, 327.

The ultraviolet absorption spectra of 3-formyl*cyclo*pentane*spirocyclo*pentane-2 : 4-dione (I), 2-formyl-5 : 5-dimethyl*cyclo*hexane-1 : 3-dione (II; R = Me), and 3-formylpentane-2 : 4-dione have been determined in several solvents (Table 1). Comparison of these results with previous studies of the ultraviolet absorption spectra of 2-acyl-1 : 3-diketones [3, 10] shows that, in solvents in which ionisation is suppressed, all these compounds show two bands, in the regions of 240 and 275 mμ respectively, due to the undissociated enols. In the presence of alkali, ionisation is essentially complete and, while the band near 275 mμ suffers little change, the band near 240 mμ is shifted to longer wavelengths. For 2-acyl*cyclo*hexane-1 : 3-diones other than the formyl compounds, and for 3-formylpentane-2 : 4-dione, the two bands due to the anion overlap completely, whereas the anion of compound (II; R = Me) shows a strong band at 260 mμ with an inflexion due to the second band near 275 mμ. Compound (I) provides an extreme case, where the band at 245 mμ is unchanged on passage from the enol to the anion, so that two bands are observed in all solvents. The ultraviolet absorption spectra of compounds (I) and (II; R = Me) were determined in aqueous rubidium hydroxide as well as in sodium hydroxide. Each compound showed virtually identical absorption in the two media, indicating that differential cation effects such as alkali-metal chelation cannot account for the observed differences between the ultraviolet absorption spectra of the anions of these two compounds.

TABLE 1. *Ultraviolet absorption spectra.*

Solvent	$\lambda_{\text{max.}}$ (mμ)	ε
	3-Formylpentane-2 : 4-dione	
EtOH + 5% of HCl	236, 275	22,190, 19,250
0·1N-NaOH	272	37,140
	*2-Formyl-5 : 5-dimethyl*cyclo*hexane-1 : 3-dione* (II; R = Me)	
Acetonitrile	232, 277	10,390, 9,690
0·1N-HCl	235, 272	13,460, 12,930
EtOH	234, 265 i,* 275·5	7,290, 9,930, 10,390
0·1N-NaOH	260, 272 i	17,180, 16,080
0·1N-RbOH	260, 272 i	16,790, 15,690
	*3-Formyl*cyclo*hexane*spirocyclo*pentane-2 : 4-dione* (I)	
Acetonitrile	243, 277·5	13,360, 11,330
0·1N-HCl in 20% EtOH	245, 269	15,540, 12,350
EtOH	245, 277·5	16,700, 12,580
0·1N-NaOH	245, 274·5	19,820, 15,440
0·1N-RbOH	245, 274·5	18,930, 14,780

* i denotes an inflexion.

The ultraviolet absorption spectra of compound (II; R = Me) in acetonitrile and in 0·1N-hydrochloric acid are closely similar, indicating that this compound is not appreciably ionised in acetonitrile. In ethanol, however, it must be considerably ionised, since in this solvent there is an inflexion in the region of 265 mμ due to the anion, in addition to the bands due to the enol. These considerations must apply also to the ultraviolet absorption spectrum of 2-formyl*cyclo*hexane-1 : 3-dione (II; R = H), for which Rogers and Smith [6] report maxima at 240 and at 255 mμ (in methanol).

The infrared absorption spectra of these compounds have also been determined (Table 2). No absorption occurs in the region 3500—3100 cm.$^{-1}$ normally associated with the hydroxyl group, but the spiran (I) in the solid state shows weak general absorption in the region 2500—1850 cm.$^{-1}$. Neither 3-formylpentane-2 : 4-dione nor the compound (II; R = Me) has detectable hydroxyl bands in the solid state, but the latter in carbon tetrachloride solution does show general absorption, too broad and weak to measure, on either side of the C–H stretching bands near 2900 cm.$^{-1}$. 3-Formylpentane-2 : 4-dione shows a band at 2840 cm.$^{-1}$ assigned to the formyl group, and may therefore exist partly

---

[10] Smith, *J.*, 1953, 803.

in the aldehyde form. This band is not observed in the case of compounds (I) or (II; R = Me).

The absence of absorption characteristic of isolated carbonyl groups indicates that all three compounds are completely enolised. In each case, however, the solids show strong bands in the region 1687—1668 cm.$^{-1}$. For compounds (I) and (II; R = Me) in solution, these bands occur at significantly higher frequencies, and are then close to the characteristic frequencies (1715 and 1680 cm.$^{-1}$) of αβ-unsaturated carbonyl groups in five- and in six-membered rings respectively.[11] In addition, compounds (I) and (II; R = Me) show a band in the region 1647—1633 cm.$^{-1}$, attributed to the hydrogen-bonded αβ-unsaturated carbonyl group. This assignment implies the presence of intramolecular hydrogen-bonding in both compounds, since in each case the band is observed in essentially the same position in the solid as in solution. All three compounds show intense bands in the region 1598—1540 cm.$^{-1}$, attributed to conjugate chelation.[3,12] In the case of 3-formylpentane-2 : 4-dione, the broadness and intensity of this absorption probably accounts for the failure to observe a band near 1630 cm.$^{-1}$; likewise compound (II; R = Me) in solution shows a band due to conjugate chelation near 1590 cm.$^{-1}$ while the solid shows intense absorption extending from the maximum at 1633 cm.$^{-1}$ as far as 1550 cm.$^{-1}$.

TABLE 2. *Infrared absorption frequencies* (*cm.*$^{-1}$).

3-Formylpentane-2 : 4-dione	Dione (II; R = Me)		Spiran (I)		
In Nujol	In Nujol	In CCl$_4$	In Nujol	In CHCl$_3$ + 1% of EtOH	Assignment
2840	—	—	—	—	Formyl CH
—	—	—	2500—1850	—	OH (H-bonded)
1674	1668	1684	1687	1706	C=O (conjugated)
	1633 *	1637	1647	1647	Conjugated chelated system
1540 *		1594 †	1569	1598	

* Very broad, intense bands. † Partly overlapped by solvent absorption.

These findings are consistent with the physical properties of 3-formylpentane-2 : 4-dione and the dione (II; R = Me), which in each case suggest strong intramolecular hydrogen-bonding, but are more difficult to reconcile with the physical properties of the spiran (I). The behaviour of this compound suggests that intramolecular hydrogen-bonding is weaker in this case than in that of the analogue (II; R = Me) or of 3-formylpentane-2 : 4-dione. This effect is probably due to strain in the *cyclo*pentane ring of the spiran, which would result in a larger separation between the formyl and ring-carbonyl groups. A similar effect of ring-strain has been noted for 7-hydroxyphthalide.[13]

2-Formyl-5 : 5-dimethyl*cyclo*hexane-1 : 3-dione (II; R = Me) showed antifungal activity, causing stunting of the germ-tubes of *Botrytis allii* at 6·3 p.p.m., while in this test 3-formyl*cyclo*hexane*spirocyclo*pentane-2 : 4-dione (I) was inactive. Both compounds showed slight antibacterial activity.

EXPERIMENTAL

M. p.s are corrected. Microanalyses are by Messrs. W. Brown and A. G. Olney. Infrared measurements were made with a Grubb-Parsons S 3A single-beam spectrometer through which dry air was continuously circulated. Ultraviolet absorption was determined with a Unicam S.P. 500 Spectrophotometer. p*K* values were determined in water unless otherwise stated.

3-Formylpentane-2 : 4-dione was prepared by Claisen's method,[1] and after recrystallisation from light petroleum (b. p. 40—60°) followed by sublimation at 40—48°/1 mm. had m. p. 40—42° (sealed capillary) (Found: p*K* 4·6). The compound gave a deep orange colour with aqueous ferric chloride, a wine-red colour with titanous chloride [7] in methanol (blue in the

---

[11] Grove and Willis, *J.*, 1951, 877.

[12] Cf. Rasmussen, Tunnicliff, and Brattain, *J. Amer. Chem. Soc.*, 1949, **71**, 1068; Bellamy and Beecher, *J.*, 1954, 4487.

[13] Duncanson, Grove, and Zealley, *J.*, 1953, 1331.

presence of pyridine), and a violet lower phase when shaken with chloroform and aqueous cupric acetate. The copper complex was obtained as purple crusts, m. p. 215—216° from ethanol, or as deep blue prisms, m. p. 213—214° from chloroform–carbon tetrachloride.

*2-Formyl-5 : 5-dimethyl*cyclo*hexane-1 : 3-dione.*—5 : 5-Dimethyl*cyclo*hexane-1 : 3-dione (dimedone) (2·50 g.), ethyl orthoformate (7·5 g.), and acetic anhydride (10·8 g.) were heated under reflux for 45 min. Evaporation of the product under reduced pressure gave a dark residue which was treated with 3N-sodium hydroxide (15 ml.). The alkaline mixture was washed with ether (50 ml.), and the ether washings were shaken with 3N-sodium hydroxide (8 × 10 ml.). The combined alkaline extracts on acidification with concentrated hydrochloric acid, extraction with ether (4 × 50 ml.), and evaporation of the dried ethereal extracts, gave a crystalline residue which was sublimed twice at 100°/20 mm., to give *2-formyl-5 : 5-dimethyl*cyclo*hexane-1 : 3-dione* as prisms, m. p. 74—76·5° (0·52 g.). Recrystallisation from light petroleum (b. p. 60—80°) followed by sublimation at 75°/16 mm. raised the m. p. to 76—77° [Found: C, 64·0; H, 7·5%; equiv., 167; *M* (Rast), 233. $C_9H_{12}O_3$ requires C, 64·3; H, 7·2%; *M*, 168]. The compound liberated carbon dioxide from sodium carbonate solution.

The *copper complex*, prepared by the addition of 2-formyl-5 : 5-dimethyl*cyclo*hexane-1 : 3-dione to a solution of cupric acetate monohydrate in methanol and evaporation of the mixture under reduced pressure, formed blue leaflets, m. p. 310—310·5° (decomp.), from chloroform–ethanol (Found: C, 54·3; H, 5·7; Cu, 15·2. $C_{18}H_{22}O_6Cu$ requires C, 54·3; H, 5·6; Cu, 16·0%). The *anil* prepared in the usual manner formed leaflets, m. p. 136·5—137·5°, from light petroleum (b. p. 60—80°) (Found: C, 74·0; H, 7·3; N, 6·2. $C_{15}H_{17}O_2N$ requires C, 74·1; H, 7·0; N, 5·8%), $\lambda_{max.}$ 234, 255, 349 mμ (ε 9600, 10,350, 27,070) in EtOH. Infrared absorption bands were: (i) in Nujol, 1675 and 1595 (broad) cm.$^{-1}$; (ii) in CCl_4, 1675, 1610, 1598, and 1574 cm.$^{-1}$.

The ethereal solution remaining after the extraction with aqueous sodium hydroxide was washed with 25% sodium chloride solution, dried, and evaporated. A solution of the residue in ethanol (20 ml.) was treated with 3N-sodium hydroxide (10 ml.), and the ethanol removed at 25° under reduced pressure. The sodium salt which separated was collected, washed with ether, and an aqueous solution acidified, giving 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-9-(2-hydroxy-4 : 4-dimethyl-6-oxo*cyclo*hex-1-enyl)-3 : 3 : 6 : 6-tetramethyl-1 : 8-dioxoxanthen (III), m. p. 223—226° (0·45 g.). Recrystallisation from methanol furnished needles, m. p. 227—228° (decomp.) alone or mixed with a specimen prepared according to Vorländer and Guthke's method [4] [Found: C, 73·0, 72·6; H, 8·0, 7·9%; *M* (Rast), 471; equiv., 353; p*K* 8·0 (in 50% aqueous ethanol). Calc. for $C_{25}H_{32}O_5$: C, 72·8; H, 7·8%; *M*, 412·5], $\lambda_{max.}$ 236 mμ (ε 22,210) in EtOH. The two samples had identical infrared absorption spectra in Nujol (bands at 3240, 1654, 1619, and 1587 cm.$^{-1}$). The compound gave no colour with ferric chloride in aqueous methanol.

*Oxidation of 2-Formyl-5 : 5-dimethyl*cyclo*hexane-1 : 3-dione.*—A solution of the formyl-diketone (78 mg.) in 0·2N-sodium hydroxide (25 ml.) and 6% hydrogen peroxide (6 ml.) was set aside at room temperature. After 3 days further 6% hydrogen peroxide (4 ml.) was added, and after 6 days the solution was acidified with 3N-sulphuric acid (3 ml.) and distilled to small bulk (10 ml.). The distillate was neutralised with 0·1N-barium hydroxide (5 ml.), saturated with carbon dioxide, boiled for 5 min., and filtered hot. Evaporation of the filtrate gave a white residue (26 mg.), giving a strong positive reaction for formate in the chromotropic acid test.[14] The residue from the distillation, on continuous extraction with ether (20 hr.) and evaporation of the dried ethereal extract, gave crystals, m. p. 95—97·5° (72 mg.), which on recrystallisation from benzene gave colourless plates (63 mg.), m. p. 98—99·5° alone or mixed with ββ-dimethylglutaric acid.

*Acid Hydrolysis of 2-Formyl-5 : 5-dimethyl*cyclo*hexane-1 : 3-dione.*—The formyl-diketone (11·5 mg.) in N-sulphuric acid (2 ml.) was heated for 4 hr. at 120° under reflux in a current of nitrogen. The mixture was then cooled and the crystalline product collected (4·8 mg.); it had m. p. 225—226·5° alone or mixed with the xanthen (III).

*Condensation of 2-Formyl-5 : 5-dimethyl*cyclo*hexane-1 : 3-dione with Dimedone.*—The formyl-diketone (30 mg.) and dimedone (50 mg., 2 mols.) in ethanol (5 ml.) were heated under reflux for 1·5 hr., and the mixture concentrated and cooled. The pinkish needles which appeared were collected and washed with ethanol. Evaporation of the filtrate and treatment of the residue with ether gave further material which was washed with ether and combined with the remainder of the product, giving in all 67 mg. (91%) of the condensation product, m. p. 224—227°, alone or mixed with the xanthen (III).

---

[14] Feigl, " Spot Tests," 4th edn., Vol. II, p. 245, Elsevier, Amsterdam.

*1-Acetyl*cyclo*hexylacetic acid.* Ethyl 1-carboxy*cyclo*hexylacetate[8, 15] (41·4 g.) was heated with thionyl chloride (33 g.) until evolution of hydrogen chloride ceased. Removal of the excess of thionyl chloride under reduced pressure yielded crude ethyl 1-chlorocarbonyl*cyclo*hexylacetate.

A solution of methylmagnesium bromide (from 9·4 g. of magnesium and an excess of methyl bromide in 200 ml. of dry ether) at 0° was treated with anhydrous cadmium chloride (37·6 g.), then stirred until it gave a negative Gilman reaction[16] for Grignard reagent (15 min.). After removal of most of the ether, dry benzene (130 ml.) was added, and further solvent (50 ml.) distilled off. Further benzene (240 ml.) was then added and the mixture heated to the b. p. A solution of the foregoing acid chloride in benzene (60 ml.) was next added as rapidly as possible to the hot dimethylcadmium solution. After the vigorous reaction had subsided, the mixture was heated under reflux for 10 min., and, after a further 10 min., cooled and treated cautiously with ice and 3N-sulphuric acid. The benzene layer was separated, washed with 5% sodium carbonate solution and with saturated sodium chloride solution, dried, and evaporated. The oily product (35·9 g.) was heated under reflux with 50% (w/v) potassium hydroxide (36 ml.) and ethanol (72 ml.) for 2 hr. After removal of the ethanol under reduced pressure the solution was acidified and extracted with ether. Evaporation of the ethereal extract gave an orange oil (30·6 g.) which was distilled under reduced pressure. The distillate (27·2 g.; b. p. 155—175°/13 mm.) was dissolved in ether (150 ml.) and extracted with saturated sodium hydrogen carbonate solution (6 × 40 ml.), and the combined aqueous extracts were washed with ether (50 ml.) and acidified. Extraction of the product with ether (4 × 75 ml.) and evaporation of the extracts gave an oil (23·0 g., 65%) which crystallised. Recrystallisation from benzene–light petroleum (b. p. 60—80°) gave the pure keto-acid, m. p. 78—80° (18 g., 50%).

cyclo*Hexane*spirocyclo*pentane-2 : 4-dione.*—Sodium methoxide (from 2·43 g. of sodium) was powdered and suspended in dry ether (30 ml.). Methyl 1-acetyl*cyclo*hexylacetate (20·9 g.; b. p. 131—132°/11 mm.; n_D^{20} 1·4695; prepared in 99% yield from the above acid) was added and the mixture shaken for 48 hr. at room temperature. Ice and an excess of 3N-sulphuric acid were then added, and the solid which separated was collected (5·0 g.; m. p. 179—180°). Evaporation of the ether layer gave further material (1·1 g.). Recrystallisation of the combined products from aqueous ethanol gave transparent prisms, m. p. 180° (5·4 g., 30%) (Found: C, 71·9; H, 8·5. Calc. for $C_{10}H_{14}O_2$: C, 72·3; H, 8·5%). Ultraviolet absorption spectrum: (i) in EtOH containing 5% of 10N-HCl, $\lambda_{max.}$ 243 mμ (ε 15,190); (ii) in 0·1N-NaOH, $\lambda_{max.}$ 260 mμ (ε 27,700). Infrared absorption bands (in $CHCl_3$) at 1728 and 1668 cm.$^{-1}$.

*3-Formyl*cyclo*hexane*spirocyclo*pentane-2 : 4-dione.*—*cyclo*Hexane*spirocyclo*pentane-2 : 4-dione (1·066 g.), ethyl orthoformate (4·7 g.), acetic anhydride (7·0 g.), and dry ethyl acetate (40 ml.) were heated under reflux for 6 hr. and the mixture evaporated under reduced pressure. The partly crystalline residue on sublimation at 100—130°/0·5 mm. gave a yellow solid (0·725 g.) which was dissolved in 0·5N-sodium hydroxide at 0°. The cold solution when filtered and made just acid with 3N-hydrochloric acid at 0° gave the *formyl-diketone* which separated as cream-coloured leaflets, m. p. 151—155·5° (0·492 g., 40%). Recrystallisation from methanol–ether at <0° raised the m. p. to 159—160·5° [Found: C, 68·2; H, 7·4%; equiv., 196. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·3%; equiv. (monobasic), 194].

The compound gave an intense orange colour with ferric chloride, a violet colour with titanous chloride in methanol, and a transient deep green colour with the latter reagent in the presence of pyridine. It was readily soluble in most organic solvents, except ether and light petroleum. It was sparingly soluble in water but dissolved readily in dilute aqueous sodium hydroxide, and decomposed slowly in the presence of water or of mineral acids, giving a brown crystalline solid, m. p. 185—195°, of unknown constitution.

The *copper complex* prepared as above formed turquoise-blue prisms, m. p. 300—304° (decomp.), from chloroform–methanol (Found: C, 58·0; H, 6·0; Cu, 13·8. $C_{22}H_{26}O_6Cu$ requires C, 58·7; H, 5·8; Cu, 14·1%). The *anil* formed needles, m. p. 133·5°, from chloroform–light petroleum (b. p. 60—80°) (Found: C, 76·0; H, 7·1; N, 5·5. $C_{17}H_{19}O_2N$ requires C, 75·8; H, 7·1; N, 5·2%), $\lambda_{max.}$ 237, 350 (sh), 353 mμ (ε 15,600, 26,060, 26,260), in EtOH. Infrared absorption bands: (i) in Nujol, 3200, 1700, 1634, and 1589 cm.$^{-1}$; (ii) in CCl_4, 1703, 1630, and 1585 cm.$^{-1}$.

*Oxidation of 3-Formyl*cyclo*hexane*spirocyclo*pentane-2 : 4-dione.*—The formyl-diketone (76

---

[15] Cf. Harding, Haworth, and Perkin, *J.*, 1908, **93**, 1958; Lapworth and McRae, *J.*, 1922, **121**, 2754.

[16] Gilman and Schulze, *J. Amer. Chem. Soc.*, 1925, **47**, 2002.

mg.) on oxidation with alkaline hydrogen peroxide by the method described above gave a volatile acid fraction of which the barium salt (10 mg.) gave a positive reaction for formate.[14] The non-volatile oxidation products on continuous extraction with ether and evaporation of the extracts yielded a solid, m. p. 95—115° (69 mg.), which sublimed at 160—200°/20 mm. The oily sublimate was dried over potassium hydroxide and extracted with light petroleum (b. p. 40—60°). The concentrated extracts when cooled to −60° deposited colourless leaflets m. p. 49—53° (22 mg.). Further recrystallisation from the same solvent raised the m. p. to 53—54°, raised to 53·5—55° on admixture with the anhydride of 1-carboxy*cyclo*hexylacetic acid.

Acid Hydrolysis of 3-*Formyl*cyclo*hexane*spirocyclo*pentane*-2 : 4-*dione*.—The formyl-diketone (8·2 mg.) was heated with N-sulphuric acid (2 ml.) at 120° under reflux in a current of nitrogen for 4 hr. The mixture when cooled deposited a yellow substance, m. p. 193—196·5° (4·6 mg.), which could not be further characterised.

We are indebted to Dr. L. A. Duncanson for determining the infrared absorption spectra, to Mr. H. G. Hemming for the biological assays, and to several colleagues for suggestions and criticisms.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, AKERS RESEARCH LABORATORIES,
THE FRYTHE, WELWYN, HERTS.
[*Received, June* 18*th*, 1957.]