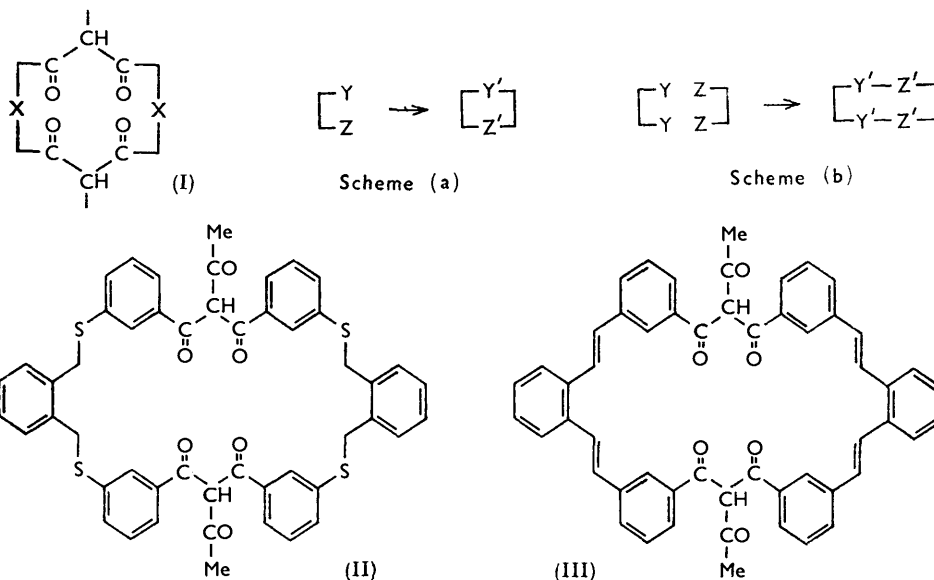


987. *Macrocyclic Bis-(1,3-diketones).*

By M. M. COOMBS and R. P. HOUGHTON.

The two macrocyclic bis-(2-acetyl-1,3-diketones) (II) and (III) have been synthesised from the magnesium chelates of the $\alpha\omega$ -bis-(1,3-diketones) (IVe) and (XIe) respectively by condensation with the corresponding $\alpha\omega$ -bis(acid chlorides) in dilute solution. Other methods for the preparation of macrocyclic bis-(1,3-diketones) have been investigated, and several acyclic $\alpha\omega$ -bis-(1,3-diketones) have been obtained as intermediates or model compounds.

1,3-DIKETONES form stable chelate compounds having a 1 : 2 metal-ligand composition with a wide range of metals. The stability constants of many of these chelates have been measured¹ and, in general, the stability of the chelates formed by a given ligand with metals within the same group of the Periodic Table decreases with increasing atomic radius. In order to obtain a reagent which would form chelate compounds selectively with metals of a given ionic radius, it was envisaged that a compound in which two 1,3-diketone units were held rigidly apart with respect to each other would exhibit favourable properties. In other fields precedents for this concept are provided by the porphyrin pigments² which show a high degree of selectivity for certain metal ions, and by phthalocyanine,³ the metal chelates of which show the maximum stability when the metal atom has an atomic radius between 1.24 and 1.43 Å. It was considered that, in the 1,3-diketone series, selectivity would be demonstrated by a macrocyclic structure of the type (I), in which X represents a suitable rigid framework. This paper describes the synthesis of two such compounds, the macrocycles (II) and (III).



Macrocyclic compounds are usually synthesised according to the scheme (a), in which the ring is formed by joining the ends of a suitably substituted chain.⁴ In the present work the alternative scheme (b) was used, and two chains bearing different reactive groups

¹ "Stability Constants," Chemical Society Spec. Publ. No. 6, London, 1957.

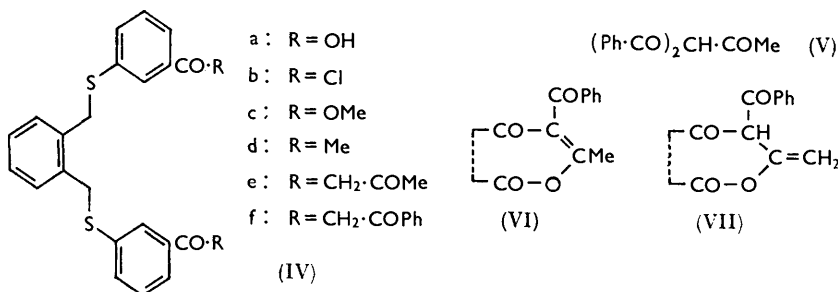
² Barnes and Dorough, *J. Amer. Chem. Soc.*, 1950, **72**, 4045.

³ Barrett, Dent, and Linstead, *J.*, 1936, 1719.

⁴ Rodd, "Chemistry of Carbon Compounds," Vol. IIA, Elsevier, London, 1953, p. 266.

were condensed to give the macrocycle. The cyclisation, which involved building the ring about a central metal atom, was carried out under the conditions normally employed for the synthesis of large ring compounds, *i.e.*, in dilute solution.⁵ Aromatic 1,3-diketones of the dibenzoylmethane type were prepared because they are stronger chelating agents than the aliphatic or partly aliphatic diketones, and also because the use of aromatic nuclei presents a simple means of constructing rigid molecules.⁶

Addition of one mol. of *o*-xylylene dibromide to two mol. of the dipotassium salt of *m*-mercaptobenzoic acid⁷ gave the bis(acid) (IVa), which with thionyl chloride was converted into the bis(acid chloride) (IVb). The acid chloride was treated with methanol to give the bis(methyl ester) (IVc), and with the ethoxymagnesium derivative of diethyl malonate⁸ to give a tetraester, which on hydrolysis and decarboxylation afforded the bis(methyl ketone) (IVd). Base-catalysed condensation of ethyl acetate with the bis(methyl ketone), as outlined below, gave the bis(methyl 1,3-diketone) (IVe).



As condensation of the bis(acid chloride) (IVb) with the bis(carbanion) derived from (IVe) appeared to be a feasible method of constructing the macrocycle (II), the following preliminary experiments were carried out. Addition of one mol. of benzoyl chloride to one of the sodium derivative of benzoylacetone, which was formed *in situ* by treatment of the diketone with triphenylmethylsodium in ether, gave an 80% yield of 1,1-dibenzoylacetone (V). However, when one mol. of the bis(acid chloride) (IVb) was added to two mol. of the sodium derivative, the reaction was complicated. Besides unchanged benzoylacetone (45% recovery), the product consisted of approximately equal parts of a neutral and an acidic gum. The former had infrared absorption bands at 1800 and 1760 (vinyl ester),⁹ 1690 and 1655 cm.⁻¹, and probably consisted of a mixture of enol esters, *e.g.*, (VI). The alkali-soluble material showed absorption at 1790 (vinyl ester), 1715, 1695, and 1655 cm.⁻¹ and a broad band centred at 1600 cm.⁻¹ (enolised 1,3-diketone),¹⁰ and probably contained the enol ester (VII) in addition to other 1,3-diketones.

As use of the sodium derivative of benzoylacetone was unpromising, attention was turned to the magnesium chelate (VIII), which was prepared by heating a mixture of benzoylacetone and magnesium in dry benzene. The chelate was also prepared by refluxing the diketone with magnesium and ethanol in ether, but the infrared absorption spectrum indicated that the material obtained by this method was solvated with ethanol (band at 3450 cm.⁻¹), and this was confirmed by the microanalytical data. The magnesium chelate of benzoylacetone had previously been prepared by Weygand and Forkel,¹¹ who concluded (from an analysis for magnesium only) that the chelate, when prepared in ethanol, was unsolvated in contrast to the chelates formed by this diketone with the other

⁵ Lüttringhaus, *Annalen*, 1937, **528**, 181; Bennett, *Trans. Faraday Soc.*, 1941, **37**, 794.

⁶ Baker, McOmie, and Ollis, *J.*, 1951, 200.

⁷ Stewart and Smiles, *J.*, 1921, 1792.

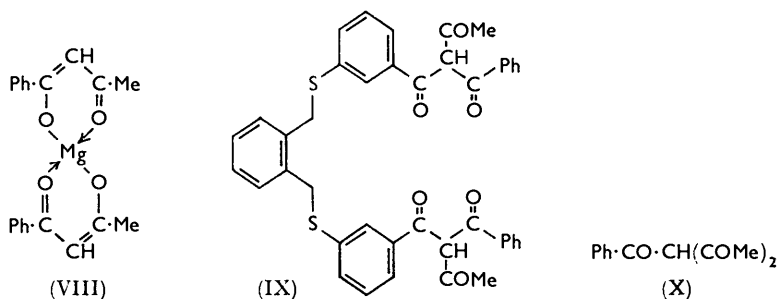
⁸ Walker and Hauser, *J. Amer. Chem. Soc.*, 1946, **68**, 1386.

⁹ Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Co., London, 2nd edn., 1958, p. 182.

¹⁰ Bellamy and Beecher, *J.*, 1954, 4487.

¹¹ Weygand and Forkel, *J. prakt. Chem.*, 1927, **116**, 293.

alkaline-earth metals. It now appears that their conclusion was incorrect, and was in fact based on erroneous data, for in our hands analysis of the magnesium chelates of 1,3-diketones usually gave magnesium values * which were 1—2% high. It was also found that the magnesium chelate of a 1,3-diketone could be conveniently prepared by addition of the diketone to the ethoxymagnesium derivative of diethyl malonate.



Addition of the bis(acid chloride) (IVb) to a solution of the chelate (VIII) in a mixture of benzene and diethylene glycol dimethyl ether gave the bis-(2-acetyl-1,3-diketone) (IX), which was isolated as the copper chelate (40% yield). The structure of the chelate was established by analytical and molecular-weight determinations, and by the infrared absorption spectrum which showed, in addition to the carbonyl band due to six-membered chelate systems,¹⁰ a strong band at 1645 cm⁻¹. This band was found to be characteristic of the enol form of 2-acetyl-1,3-diketones and also their metal chelates (see Table 1) and

TABLE I.

Infrared spectra of 1,3-diketones and their metal chelates.

Benzoylacetone	(1613, 1580)	1,1-Dibenzoylacetone:	
Magnesium chelate	1607, 1573, 1522	Enol form	1650 (1592, 1575, 1563)
Bis(methyl 1,3-diketone) (IVe)	(1603, 1563, 1548)	Triketone form	1705, 1671
Magnesium chelate	1592, 1562, 1508	Magnesium chelate	1646, 1592, 1572
Copper chelate	1560, 1512	Copper chelate	1640, 1580—1560vb
Bis(methyl 1,3-diketone) (XIe)	(1626, 1587), 972	1-Acetyl-1-benzoylacetone (X)	1650, 1590b
Magnesium chelate	1585, 1515, 961	Copper chelate	1640, 1560—1540vb
Copper chelate	1560, 1513, 956	Macrocycle (II)	1642, 1563b
Bis(diketone) (XIVa)	(1597, 1563)	Copper chelate	1642, 1538
Copper chelate	1587, 1546, 1515	Macrocycle (III)	1647 (1585, 1550), 960
Bis(diketone) (XIVb)	(1600, 1567)	Copper chelate	1642, 1540, 960
Copper chelate	1585, 1550, 1522	Copper chelate of (IX)	1645, 1560
Bis(diketone) (XIVc)	(1600, 1570)	Copper chelate of (XIII)	1640, 1543, 952
Copper chelate	1587, 1550, 1511b		

The maxima given are those of bands in the 1800—1500 cm⁻¹ region, and those of bands due to *trans*-CH:CH groups. Figures in parentheses are the positions of the maxima of a broad composite band. All the bands are strong or very strong.

is undoubtedly due to the unchelated carbonyl group. Benzoyl chloride reacted with the chelate (VIII) to give an almost quantitative yield of 1,1-dibenzoylacetone (V); and the triketone (X) was similarly prepared from benzoyl chloride and the magnesium chelate of acetylacetone.

For the synthesis of the macrocycle (II) a 0.003M-solution in benzene and diethylene glycol dimethyl ether of equimolecular quantities of the bis(acid chloride) (IVb) and the magnesium chelate of the bis(methyl 1,3-diketone) (IVe) was kept for fourteen days at room temperature. The 1,3-diketonic material was isolated as a mixture of copper

* Magnesium was determined as the oxide by weighing the residue after the microanalysis for carbon and hydrogen.

chelates which was chromatographed on silica gel to give the copper chelate of the macrocycle contaminated with material which had infrared absorption bands at 1790 and 1730 cm^{-1} . Removal of the latter material by chlorobenzene, and decomposition of the insoluble copper chelate with hydrochloric acid, gave the macrocycle (II) in 24% yield based on the magnesium chelate of the bis(methyl 1,3-diketone). The structure of the macrocycle was indicated by analytical and molecular-weight determinations, and by the infrared absorption spectrum, which in the 1500—1800 cm^{-1} region showed only the characteristic bands of the 2-acetyl-1,3-diketone systems.

It is evident that in these condensations the magnesium fulfils two functions. It induces sufficient negative charge at the 2-positions to enable these carbon atoms to act as nucleophilic centres, and also, by firmly binding the enolic oxygen atoms, it inhibits attack upon these by the second acid chloride group before this in turn suffers condensation. After the work described above had been completed, a paper by Barry¹² appeared, in which it was shown that the action of acid chlorides on the copper chelate of a 1,3-diketone also resulted in high yields of triketones. The use of magnesium chelates for this type of reaction appears to have been confined to the acylation and aroylation of ethyl acetoacetate.¹³

Before the macrocycle was successfully synthesised as described above, attempts were made to effect the cyclisation by a double Claisen condensation between the bis(methyl ester) (IVc) and the bis(methyl ketone) (IVd). It was found that in the presence of sodium ethoxide the latter condensed smoothly with ethyl acetate, used as solvent, to give the bis(methyl 1,3-diketone) (IVe) in 60% yield. When methyl benzoate was used in place of ethyl acetate the bis(phenyl 1,3-diketone) (IVf) was obtained, as the copper chelate, in only 7% yield. In an attempt to improve the yield of the last reaction the use of sodamide in liquid ammonia, and of triphenylmethylsodium in ether as condensing agents was investigated, for it is known that the Claisen reaction between methyl ketones and aromatic esters proceeds more readily with reagents which are more nucleophilic than sodium ethoxide.¹⁴ When these condensing agents were used, however, no pure compounds were isolated, and the 1,3-diketonic materials obtained showed strong infrared absorption bands at 1715 and 1680 cm^{-1} . Condensation of the bis(methyl ketone) (IVd) with the bis(methyl ester) (IVc) under a variety of conditions failed to give 1,3-diketonic material in significant amount, and this method of effecting the cyclisation was therefore abandoned. While this work was in progress, Martin, Shamma, and Fernelius¹⁵ described the preparation of bis-(1,3-diketones) of the type $(\text{R}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO})_2\text{R}'$, where R is aryl or alkyl and R' arylene or alkylene, by Claisen condensation between one mol. of a diester and two mol. of a methyl ketone. Their yields were low (5—33%), thus confirming our conclusion that the double Claisen condensation is unsatisfactory for the preparation of bis-(1,3-diketones). It is interesting that Hauser and Cain¹⁶ obtained a good yield of bis-(1,3-diketone) by condensation between 1,1'-diacetylferrocene and methyl benzoate in the presence of sodium amide in liquid ammonia, and a similar preparation of 1,4-di(acetoacetyl)benzene in 79% yield from 1,4-diacetylbenzene and ethyl acetate with powdered sodium has been described in a patent.¹⁷

The presence of the $\text{CH}_2\text{-S}$ linkages in the macrocycle (II) allows some flexibility, and as an example of a more rigid analogue the structure (III) was chosen because it has dimensions similar to those of the sulphur-containing macrocycle. The intermediates (XI) required for the synthesis of (III) were prepared from phthalaldehyde by an extension of the reaction recently described by Campbell and McDonald,¹⁸ in which condensation

¹² Barry, J., 1960, 670.

¹³ Viscontini and Merckling, *Helv. Chim. Acta*, 1952, **35**, 2280.

¹⁴ "Organic Reactions," Vol. VIII, John Wiley and Sons Inc., New York, 1954, p. 59.

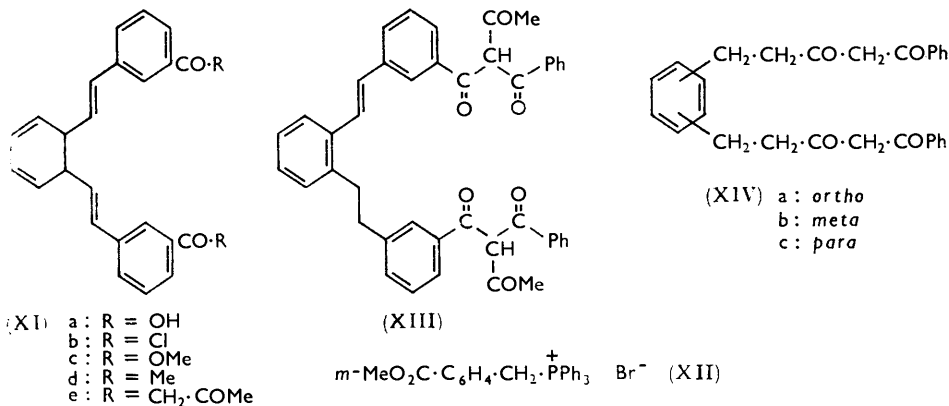
¹⁵ Martin, Shamma, and Fernelius, *J. Amer. Chem. Soc.*, 1958, **80**, 4891.

¹⁶ Hauser and Cain, *J. Org. Chem.*, 1958, **23**, 1142.

¹⁷ Wilkins and Wittbeaker, U.S.P. 2,659,711/1953.

¹⁸ Campbell and McDonald, *J. Org. Chem.*, 1959, **24**, 1246.

of terephthalaldehyde with the triphenylphosphonium salt of substituted benzyl bromides gave the expected *trans-trans*-distyrylbenzenes in high yield. Methyl *m*-bromomethylbenzoate¹⁹ readily gave the triphenylphosphonium salt (XII). This (2 mol.) and phthalaldehyde (1 mol.) were treated with lithium ethoxide in ethanol. The resultant mixture of esters, upon alkaline hydrolysis, afforded a mixture of acids which was dissolved in



benzene containing a trace of iodine. The solution, on exposure to diffuse daylight, slowly deposited the bis(acid) (XIa) which had ultraviolet absorption maxima at 2830 and 3070 Å (ϵ 32,900 and 25,000 respectively). The infrared spectrum showed a strong band at 953 cm^{-1} indicative of at least one *trans*-CH:CH group, while the nuclear magnetic resonance spectrum* of the bis(methyl ester), which was obtained from the acid by treatment with diazomethane, confirmed the *trans-trans*-structure (XIc). A comparison of the infrared spectrum of the pure *trans-trans*-bis(ester) (XIc) with that of the mixture of esters obtained directly from the Wittig reaction showed that the latter material contained very little of the *trans-trans*-bis(ester), and it therefore appears that this reaction is an exception to the general rule that double bonds formed in the Wittig reaction have predominantly the *trans*-configuration.²⁰

The bis(acid) (XIa) was converted into the bis(acid chloride) (XIb), the bis(methyl ketone) (XId), and the bis(methyl 1,3-diketone) (XIe) by the methods used in the other series. The bis(acid chloride) (XIb) reacted with the magnesium chelate of benzoylacetone to give the bis-(2-acetyl-1,3-diketone) (XIII), and with methanol to give the bis(methyl ester) (XIc) which was identical with that prepared from the acid (XIa) by treatment with diazomethane. Condensation of the magnesium chelate of the bis(methyl 1,3-diketone) (XIe) with the bis(acid chloride) (XIb) in a dilute solution of benzene and dioxan gave a mixture from which the macrocycle (III) was isolated, by means of the copper chelate, in 21% yield.

In an attempt to prepare other types of bis-(1,3-diketones) condensation of the dianion of benzoylacetone with dihalogen compounds was studied, the conditions described by Harris and Hauser²¹ for the alkylation of 1,3-diketones with benzyl chloride being used. Addition of one mol. of *o*-, *m*-, or *p*-xylylene dibromide to two mol. of benzoyl acetone and four equivalents of potassium amide in liquid ammonia gave the corresponding bis-(1,3-diketones) (XIV) in 15–25% yield. These bis(diketones) formed monomeric 1:1 chelates with copper, indicating that the side chains are sufficiently flexible to allow the

* Bands due to olefinic protons at 3.70 and 2.89 ($J = 16.2$ cycles/sec.), expressed as τ values, as defined by Tiers (*J. Phys. Chem.*, 1958, **62**, 1151). We are indebted to Dr. D. T. Thompson of this Department for recording and interpreting the spectrum.

¹⁹ Fuson and Cook, *J. Amer. Chem. Soc.*, 1940, **62**, 1180.

²⁰ Trippett, *Adv. Org. Chem.*, 1960, **1**, 83.

²¹ Harris and Hauser, *J. Amer. Chem. Soc.*, 1958, **80**, 6360.

two 1,3-diketone groups to chelate with the same copper atom. Similar condensations between the dianion of acetylacetone and the three isomeric xylylene dibromides gave 1,3-diketonic oils from which no pure compounds could be isolated.

All the bis-(1,3-diketones) described in this paper are very largely enolised, as indicated by their infrared absorption spectra which show the broad band between 1500 and 1600 cm^{-1} characteristic of the hydrogen-bonded chelate system.¹⁰ Models of these compounds, except those of the bis(diketones) (XIV), show that the four oxygen atoms of the enolised 1,3-diketone systems lie at the corners of a square of side approximately 3 Å, and as expected the compounds form 1:1 chelates with copper. In the infrared absorption spectra of the copper chelates, including those of (XIV), the broad absorption band between 1500 and 1600 cm^{-1} present in the spectra of the parent 1,3-diketones is usually split into several strong bands, but the absence of additional carbonyl absorption bands indicates that the four oxygen atoms of the enolised 1,3-diketone systems are firmly bound to the metal.

The stability constants of the chelates formed by the macrocycles (II) and (III), and by the bis-(1,3-diketones) (IVe) and (XIV) with magnesium, calcium, and strontium were kindly measured by Professor G. Schwarzenbach and Dr. G. Anderegg of the Eidg. Technische Hochschule, Zürich, and we are most grateful to them for the figures given in Table 2 and for the following interpretation of their results. The data confirm that the compounds examined were bis-(1,3-diketones), the values of $\text{p}K_2$ being only slightly lower than those of $\text{p}K_1$. In the compounds (IVe) and (XIV) the first proton leaves the molecule at approximately the same pH as in acetylacetone, but the macrocycles (II) and (III) are more acidic than acetylacetone, possibly owing to electron withdrawal by the acetyl groups. (A similar comparison may be made between acetylacetone and 1,1-diacetylacetone, for which the $\text{p}K$ values in aqueous solution are 8.9 and 5.9 respectively.²²) Presumably for the same reason, the chelates of the macrocycles are less

TABLE 2.

Stability constants of the chelates of bis-(1,3-diketones).

All values were obtained by Dr. G. Anderegg from titrations with a glass electrode in 1:3 (v/v) water-dioxan at 20°, and an ionic strength ($I = 0.1$) kept constant by sodium perchlorate. L^{2-} denotes the ligand anion obtained by removing two protons from one molecule of the bis(diketones) or from two molecules of acetylacetone.

$$K_{\text{HL}^-} = [\text{HL}^-]/[\text{H}^+][\text{L}^{2-}]; \quad K_{\text{H}_2\text{L}} = [\text{H}_2\text{L}]/[\text{H}^+][\text{HL}^-]; \quad K_{\text{ML}} = [\text{ML}]/[\text{M}^{2+}][\text{L}^{2-}]; \\ K_{\text{MHL}^+} = [\text{MHL}^+]/[\text{M}^{2+}][\text{HL}^-].$$

Square brackets denote concentrations in mole l^{-1} .

Compound	$\log K_{\text{HL}^-} = \text{p}K_1$	$\log K_{\text{H}_2\text{L}} = \text{p}K_2$	$\log K_{\text{ML}}$			$\log K_{\text{MHL}^+}$		
			Mg	Ca	Sr	Mg	Ca	Sr
(II)	8.44	7.64	6.65	5.35	4.19	4.07	3.27	2.58
(III)	8.88	8.36	8.00	6.61	5.14	4.20	3.24	2.77
(IVe)	10.31	10.52	9.27	6.75	5.31	5.73	4.46	3.43
(XVa)	10.76	10.68	8.12	5.98	4.68	5.46	4.16	3.27
(XVb)	10.91	10.43	9.08	6.86	5.41	5.15	3.90	3.11
(XVc)	11.09	10.45	—	—	—	5.12	4.14	3.32
Acetylacetone ...	10.67	—	5.23	4.11	3.32	—	—	—

stable than those of the acyclic bis-(1,3-diketones). The stability of the chelates of all the compounds examined shows the usual order $\text{Mg} > \text{Ca} > \text{Sr}$. The difference between the stability constants of the magnesium chelates of the macrocycles and of the acyclic bis-(1,3-diketones) is greater than the corresponding differences for the calcium and strontium chelates, which suggests that the steric requirements of the larger cations (Ca^{2+} , ionic radius 0.99 Å; Sr^{2+} , 1.13 Å)²³ are met slightly better than those of the smaller magnesium ion (ionic radius, 0.65 Å)²³ by both macrocycles; however, the initial object of constructing a specific chelating agent has not been realised.

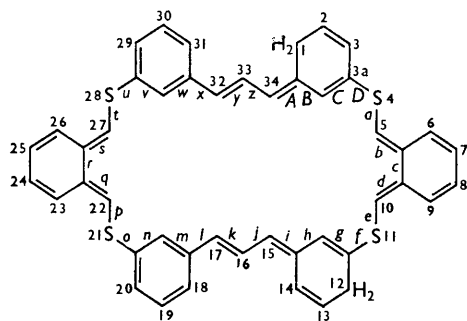
²² Schwarzenbach and his co-workers, unpublished work.

²³ Pauling, *J. Amer. Chem. Soc.*, 1927, **49**, 765.

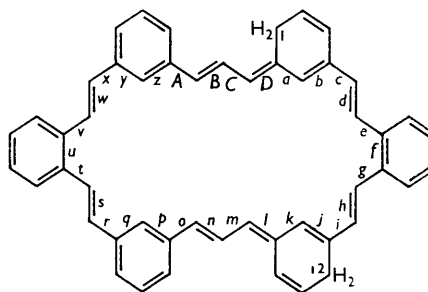
The chelates of both the acyclic and the macrocyclic bis-(1,3-diketones) are more stable than those of acetylacetone, indicating that the presence of a second 1,3-diketone group in these compounds helps to stabilise their chelates. Of the three isomeric bis-(1,3-diketones) (XIVa, b, and c) the *meta*- appears to be more favourable than the *ortho*-structure for the formation of chelates; the results for the *para*-compound were inconsistent, probably because of the formation of chelates which did not have a 1 : 1 metal-ligand composition. In this connection it was observed that only a very poor yield of the 1 : 1 copper chelate of the *para*-compound was obtained under conditions which readily gave good yields of the copper chelates of the *ortho*- and the *meta*-isomer.

All the bis-(1,3-diketones) examined also formed chelates of the type (MHL⁺), in which only one of the 1,3-diketone groups is bound to the metal, the other group retaining its proton. As expected, the chelates of this type formed by the macrocycles were less stable than the corresponding chelates of the acyclic bis-(1,3-diketones), while the latter were about as stable as those of the type (ML) formed by acetylacetone. From titrations which were run in the presence of an excess of metal it appeared that chelates of the type (M₂L²⁺), in which the two 1,3-diketone groups are bound to different metal atoms, were not formed to an appreciable extent, except possibly with compound (XIVc).

Note on Nomenclature.—Systematic names for the macrocycles (II) and (III) are formed from cyclotriacontane with benzo-ring fusion, in accordance with the principles of the Ring Index,²⁴ the "ane" ending being replaced by "in" to denote the "least hydrogenated" forms (IIa) and (IIIa); the "extra" (indicated) hydrogen atom is allotted to the position carrying the lowest number in the finally numbered molecule. When the ring-fusions are denoted, the Ring Index principle is extended beyond *a*—*z* by using capital letters; the lettering begins at a sulphur atom in (IIa) and at a fused benzene ring in (IIIa). We thank the Editors for assistance in naming these compounds.



(IIa)



(IIIa)

EXPERIMENTAL

Microanalyses were by Miss J. Cuckney and the staff of the Organic Microanalytical Laboratory. Molecular weights were determined by the ebullioscopic method (in chlorobenzene). Infrared spectra were obtained with samples prepared as Nujol mulls. Unless stated to the contrary, light petroleum refers to the fraction of b. p. 40—60°.

m-Mercaptobenzoic Acid.—Benzoic acid was converted successively into *m*-chlorosulphonylbenzoic acid, di-(*m*-carboxyphenyl) disulphide, and *m*-mercaptobenzoic acid by Stewart and Smiles's procedure.⁷ The acid, which was obtained in an overall yield of 22%, had m. p. 140—143° (lit.,⁷ m. p. 146—147°), and was used without further purification.

o-Phenylenedi-[*m*-methylenethio]benzoic Acid (IVa).—Potassium hydroxide (40.1 g.) in water (30 ml.) was added to *m*-mercaptobenzoic acid (111 g.) in ethanol (450 ml.) under nitrogen. *o*-Xylylene dibromide (96 g.) in chloroform (450 ml.) was added with stirring during 2 hr. The mixture was stirred and heated under reflux for a further 2 hr. and the solvent was then removed

²⁴ "The Ring Index," American Chemical Society, Washington, 1959, 2nd edn., p. xxii.

under reduced pressure. The residue was dissolved in 1.25N-sodium hydroxide (700 ml.), and this solution was extracted with chloroform. The aqueous layer was filtered then acidified with concentrated hydrochloric acid, to give the *bis(acid)* (113 g.) as a granular solid, m. p. 217—224°. A sample crystallised from ethanol as needles, m. p. 227—228° (Found: C, 63.8; H, 4.25; S, 15.2. $C_{22}H_{18}O_4S_2$ requires C, 64.0; H, 4.5; S, 15.3%).

The *bis(acid)* (1.0 g.) was boiled under reflux with acetic acid (50 ml.) containing 30% hydrogen peroxide (10 ml.) for 3 hr. and cooled. *o-Phenylenedi-[(m-methylenesulphonyl)benzoic acid] monohydrate* separated as needles (0.96 g.), m. p. 297—300°; the analytical sample was dried at 100° *in vacuo* (Found: C, 53.7; H, 4.3; S, 13.05. $C_{22}H_{18}O_8S_2 \cdot H_2O$ requires C, 53.65; H, 4.1; S, 13.05%).

o-Phenylenedi-[(m-methylenethio)benzoyl Chloride] (IVb).—The *bis(acid)* (104 g.) was boiled with thionyl chloride (500 ml.) for 2 hr. The excess of reagent was removed under reduced pressure and the residual oil was extracted with hot light petroleum (b. p. 60—80°; 8 × 250 ml.). The extracts were cooled to give the *bis(acid chloride)* (80.5 g.) as needles, m. p. 72—74° (Found: C, 58.8; H, 4.3; Cl, 16.05; S, 4.2. $C_{22}H_{16}Cl_2O_2S_2$ requires C, 59.05; H, 3.6; Cl, 15.85; S, 4.3%).

The *bis(acid chloride)* (1.0 g.) was refluxed with dry methanol (25 ml.) for 2 hr. On cooling, the solution gave *dimethyl o-phenylenedi-[(m-methylenethio)benzoate]* (IVc) (0.9 g.), m. p. 76—77° (Found: C, 65.55; H, 5.4; S, 14.5. $C_{24}H_{22}O_4S_2$ requires C, 65.7; H, 5.05; S, 14.6%).

o-Phenylenedi-[(m-methylenethio)acetophenone] (IVd).—Magnesium turnings (2.7 g.) were allowed to react with absolute ethanol (2.5 ml.) containing carbon tetrachloride (0.25 ml.). After the initial reaction had subsided the mixture was diluted with dry ether (75 ml.), and diethyl malonate (17 ml.) in absolute ethanol (10 ml.) and dry ether (15 ml.) was added dropwise during 30 min. The mixture was stirred and refluxed for a further 3½ hr. by which time only a trace of magnesium remained. To 25 ml. of this solution was added with stirring the *bis(acid chloride)* (IVb) (4.47 g.) in ether (25 ml.) and carbon tetrachloride (10 ml.). The mixture was heated under reflux for 3½ hr., cooled, and decomposed with cold 5N-sulphuric acid. The organic layer was washed with water and evaporated, to yield an amber-coloured syrup which was heated under reflux for 6 hr. with water (10 ml.), acetic acid (15 ml.), and concentrated sulphuric acid (2 ml.). The product, which solidified on cooling, was collected, washed with water, and crystallised from butan-1-ol, to give the *bis(methyl ketone)* (3.22 g.), m. p. 141—141.5°, ν_{max} . 1670 cm^{-1} (Found: C, 70.6; H, 5.3; S, 15.5. $C_{24}H_{22}O_2S_2$ requires C, 70.9; H, 5.45; S, 15.8%); this gave a *bis-(2,4-dinitrophenylhydrazone)*, m. p. 224° (decomp.) (Found: C, 56.25; H, 4.2; N, 14.95. $C_{36}H_{28}N_8O_8S_2$ requires C, 56.55; H, 3.7; N, 14.65%).

o-Phenylenedi-[(m-methylenethio)acetoacetylbenzene] (IVe).—The *bis(methyl ketone)* (IVd) (7.45 g.), suspended in dry ethyl acetate (300 ml.), was added to sodium ethoxide (from sodium, 1.75 g.), and the mixture was stirred and heated under reflux for 4 hr. After being cooled, the mixture was added to water (50 ml.) at 0°, the organic layer was extracted with 0.2N-sodium hydroxide (50 ml.), and the extract was added to the aqueous layer. The combined aqueous solution was kept at 0° for 5 min., and the solid which separated was collected, washed with dry ether (20 ml.), and suspended in water (50 ml.). The suspension was acidified with concentrated hydrochloric acid, and the organic material was extracted with ether to yield material (5.43 g.) of m. p. 65—67°. Crystallisation from methanol gave pale yellow prisms of the *bis(methyl 1,3-diketone)*, m. p. 72—73° (Found: C, 68.25; H, 5.45; S, 13.3. $C_{28}H_{26}O_4S_2$ requires C, 68.55; H, 5.35; S, 13.1%).

This compound, in ether, was shaken with aqueous cupric acetate to give the *copper chelate*, which crystallised from chloroform–light petroleum as bright green needles, m. p. 202—204° (Found: C, 60.8; H, 4.75%; M, 570. $C_{28}H_{24}CuO_4S_2$ requires C, 60.65; H, 4.3%; M, 554).

o-Phenylenedi-[(m-methylenethio)benzoylacetylbenzene] (IVf).—Sodium ethoxide (from sodium, 0.45 g.) was heated at 160°/0.5 mm. for 2 hr. The flask was filled with dry nitrogen, and methyl benzoate (20 ml.) and the *bis(methyl ketone)* (IVd) (2.0 g.) were introduced, and a condenser was arranged so that methanol formed during the reaction would distil off. The mixture was stirred and heated at 120° for 1½ hr. under dry nitrogen, cooled, diluted with ether, and extracted with aqueous sodium hydroxide. The aqueous solution was acidified with dilute sulphuric acid, and the liberated oil was extracted with ether. The extract was washed with sodium hydrogen carbonate solution and shaken with aqueous cupric acetate to give a dark green, sticky solid (1.0 g.), which was collected and dissolved in chloroform (100 ml.). Gradual addition of light petroleum caused the separation, in three crops (0.19 g., 0.18 g., and

0.05 g.), of a pale green microcrystalline solid which recrystallised from chloroform-light petroleum to give the *copper chelate* of the bis(phenyl-1,3-diketone) (IVf) as green prisms, decomp. 245° (Found: C, 65.3; H, 4.5; S, 9.3. $C_{38}H_{28}CuO_4S_2 \cdot H_2O$ requires C, 65.7; H, 4.35; S, 9.2%).

When the above condensation was carried out in liquid ammonia (30 ml.) containing sodamide (from sodium, 0.6 g.) according to Hauser and Cain's method,¹⁶ the alkali-soluble product was an orange oil (0.4 g.) which showed strong infrared absorption bands at 1715, 1681, and 1563 (broad) cm^{-1} . With aqueous cupric acetate the oil gave a yellowish-green solid which darkened but did not melt below 320°.

A similar result was obtained with triphenylmethylsodium in ether-benzene, and no crystalline material was obtained.

Reactions with the Sodium Derivative of Benzoylacetone.—(a) *1,1-Dibenzoylacetone*. Etheral 0.10N-triphenylmethylsodium solution²⁵ (45.3 ml., 5 millimoles) was quickly added with stirring to benzoylacetone (0.811 g., 5 millimoles) in dry ether (50 ml.) under dry nitrogen, followed by a mixture of benzoyl chloride (0.703 g., 5 millimoles) and ether (20 ml.) during 15 min. at 20°. After 2 hr. water was added and the material soluble in aqueous sodium hydroxide but insoluble in sodium hydrogen carbonate solution was isolated (1.06 g.; m. p. 79–85°). Recrystallisation from light petroleum (b. p. 80–100°) gave prisms of 1,1-dibenzoylacetone (0.68 g.), m. p. 81–83° (lit.,²⁶ m. p. 80–85°).

(b) *Reaction with the bis(acid chloride) (IVb)*. Benzoylacetone (0.972 g., 6 millimoles) in ether (60 ml.) was treated with etheral triphenylmethylsodium (6 millimoles) as before. A solution of the bis(acid chloride) (IVb) (1.331 g., 3 millimoles) in benzene (50 ml.) was added dropwise during 15 min., and stirring was continued at room temperature for 4 hr. Water was added and the product was separated into a neutral fraction (2.32 g.) and a fraction (1.04 g.) which was soluble in aqueous sodium hydroxide. The former was extracted with hot light petroleum to remove triphenylmethane and evaporated to yield a resin (0.46 g.) which had strong infrared absorption bands at 1800, 1760, 1690, and 1655 cm^{-1} . The fraction soluble in alkali was also extracted repeatedly with light petroleum, and from the extracts was recovered benzoylacetone (0.44 g.), m. p. 52–54°, raised to 54–56° when mixed with an authentic sample, m. p. 60–61°. The residue, an amber-coloured gum (0.55 g.), had infrared absorption bands at 1790, 1715, 1695, 1655, and 1570 (broad) cm^{-1} . No crystalline materials were obtained from the petroleum-insoluble fractions.

Magnesium Chelate of Benzoylacetone (VIII).—(a) A mixture of benzoylacetone (3.24 g.), magnesium (0.27 g.), and dry benzene (15 ml.) was refluxed for 65 hr. The suspension was decanted from the unchanged magnesium, and filtered to give the *chelate* (2.02 g., 58%), m. p. 282–283° (Found: C, 69.55; H, 5.55. $C_{20}H_{18}MgO_4$ requires C, 69.3; H, 5.2%).

(b) Benzoylacetone (6.21 g.) in dry ethanol (25 ml.) and dry benzene (25 ml.) was added dropwise during 15 min. to a boiling suspension of magnesium (0.46 g.) in dry ethanol (50 ml.). The mixture was refluxed for a further 1 hr., then filtered and concentrated under reduced pressure to about 25 ml. The solid which separated was washed with cold benzene (10 ml.) to leave the solvated *chelate* (6.33 g., 91%), m. p. 278–279° raised to 281–282° by one recrystallisation from ethanol-benzene (Weygand and Forkel¹¹ give m. p. "about 267°") [Found: C, 66.9; H, 6.1%; *M*, 736. ($C_{20}H_{18}MgO_4$)₂·2EtOH requires C, 67.3; H, 6.2%; *M*, 784]. The infrared absorption spectrum was almost identical with that of the sample described above, but showed an additional band at 3450 cm^{-1} (OH stretching).

1,1-Dibenzoylacetone (V) from the Magnesium Chelate.—A cooled solution of the magnesium chelate (471 mg.) of benzoylacetone in diethylene glycol dimethyl ether (5 ml.) was diluted with dry benzene (50 ml.), treated with benzoyl chloride (0.80 ml.), kept at room temperature for 21 hr., and shaken with *n*-hydrochloric acid (10 ml.). The organic layer was extracted with 0.2N-sodium hydroxide (2 × 25 ml.), and the extracts were acidified with 2N-hydrochloric acid. Extraction with ether afforded a product (619 mg.), m. p. 70–75°, which was recrystallised from light petroleum (b. p. 80–100°) to give the enol form of 1,1-dibenzoylacetone (516 mg., 81%), m. p. 79–82°, partly solidifying at 90–95°, then remelting at 101–105°. The triketo-form, m. p. 109–110°, was obtained as needles by slowly recrystallising a sample of the enol form from ethanol (Claisen²⁶ gives m. p.s 80–85° and 107–110° for the enol and the triketo-form respectively).

²⁵ *Org. Synth.*, Collective Vol. II, John Wiley and Sons, Inc., New York, 1943, p. 607.

²⁶ Claisen, *Annalen*, 1896, **291**, 75.

Addition of the triketone (enol form, 2.66 g.) in benzene (15 ml.) to a boiling suspension of magnesium (0.12 g.) in dry ethanol (10 ml.) gave the *magnesium chelate* (2.66 g., 96%) which crystallised from 2-ethoxyethanol as a yellow powder, m. p. 275° (Found: C, 73.5; H, 5.2. $C_{34}H_{28}MgO_6$ requires C, 73.6; H, 4.7%).

Copper Chelate of o-Phenylenedi-[(m-methylenethio)- α -benzoylacylbenzene] (IX).—The bis(acid chloride) (IVb) (1.72 g.) in dry benzene (100 ml.) was added to the magnesium chelate (1.33 g.) of benzoylacetone in diethylene glycol dimethyl ether (25 ml.), and the mixture was kept at room temperature for 36 hr. Isolation of the 1,3-diketonic material in the usual way afforded an orange gum (1.89 g.) which was shaken in ether (25 ml.) with saturated aqueous cupric acetate (20 ml.). The solid which separated was collected and recrystallised from chloroform–light petroleum to give the *copper chelate* (1.03 g., 40%), m. p. 190–192° raised to 198–199° when chromatographed on silica gel in chloroform (Found: C, 66.4; H, 4.7; S, 8.8%; *M*, 724. $C_{49}H_{32}CuO_6S_2$ requires C, 66.3; H, 4.25; S, 8.45%; *M*, 760).

3-Benzoylpentane-2,4-dione (X) from the *Magnesium Chelate of Acetylacetone*.—Acetylacetone (14.8 g.) in dry ethanol (100 ml.) was added dropwise during 30 min. to a boiling suspension of magnesium (2.0 g.) in dry ethanol (20 ml.). The mixture was refluxed for a further 2 hr. and then filtered and cooled to give the chelate (10.0 g., 61%) as needles, m. p. 269–270° (decomp.) (Found: C, 53.9; H, 6.3. Calc. for $C_{10}H_{14}MgO_4$: C, 53.9; H, 6.35%) (Hatch and Sutherland²⁷ give m. p. 265–267°). A solution of the chelate (1.75 g.) in hot diethylene glycol dimethyl ether (25 ml.), was cooled and diluted with dry benzene (100 ml.). Benzoyl chloride (1.82 g.) was added and the mixture was kept at room temperature for 20 hr. Isolation of the 1,3-diketonic material gave an oil (2.34 g.) which was dissolved in light petroleum (10 ml.). The solution was kept at 0° for 24 hr. to give the enol form of the triketone (1.84 g., 70%) as prisms, m. p. 31–31.5° (lit.,²⁸ m. p. 35°). The copper chelate crystallised from dioxan as light blue plates, m. p. 230–231° (decomp.) (lit.,²⁸ m. p. 224–225°).

Magnesium Chelate of o-Phenylenedi-[(m-methylenethio)acetoacetylbenzene].—(a) Treatment of the bis(methyl 1,3-diketone) (IVe) (3.50 g.) in dry benzene (25 ml.) with magnesium (0.73 g.) in dry ethanol (20 ml.) according to the usual method gave the *chelate* (2.37 g., 59%), m. p. 190–193° raised to 195–196° by one recrystallisation from ethanol–chlorobenzene (Found: C, 64.2; H, 5.2%; *M*, 555. $C_{28}H_{24}MgO_4S_2 \cdot EtOH$ requires C, 64.5; H, 5.4%; *M*, 559).

(b) Diethyl malonate (6.1 g.) in dry dioxan (30 ml.) was added dropwise to a boiling suspension of magnesium (0.93 g.) in dry ethanol (5 ml.). The mixture was refluxed for a further 30 min., then cooled and diluted with dry ether (100 ml.). The bis(methyl 1,3-diketone) (IVe) (18.7 g.) in dry benzene (50 ml.) was added, and after 30 min. the mixture was filtered and concentrated under reduced pressure to give the chelate (15.0 g., 70%), m. p. 188–190°, which had an infrared absorption spectrum identical with that of the sample described above.

16,33-Diacetyl-5,10,16,17,22,27,33,34-octahydro-15,32H-hexabenzo[c, gh, mn, r, vw, BC] [1,6,16,21]tetraethiacyclotriacontin-15,17,32,34-tetraone (II).—The magnesium chelate (6.38 g.) of the bis(methyl 1,3-diketone) (IVe) was dissolved in diethylene glycol dimethyl ether (150 ml.), and the solution was diluted with dry benzene (4 l.). The bis(acid chloride) (IVb) (5.15 g.) in dry benzene (100 ml.) was added and the mixture was kept at room temperature for 14 days. The benzene was removed under reduced pressure and the residual solution was shaken vigorously for 5 min. with a mixture of chloroform (250 ml.), ice (200 g.), and concentrated hydrochloric acid (40 ml.). The chloroform layer was separated, washed with water (2 \times 250 ml.), and evaporated under reduced pressure, to give a solid. This was shaken in chloroform (500 ml.) with aqueous cupric acetate (5 g. in 200 ml.), and the chloroform layer was separated, concentrated under reduced pressure to about 350 ml., and added to a column of acid-washed silica gel (500 g.). The column was developed with chloroform, and the main band was eluted and evaporated to give a solid which was extracted with hot benzene (4 \times 50 ml.) and boiling chlorobenzene (25 ml.); this left the crude copper chelate (3.44 g., 32%) of the macrocycle (II) as a green solid, m. p. >340°, which could not be satisfactorily purified (Found: C, 63.7; H, 4.3; S, 14.55. Calc. for $C_{50}H_{38}CuO_6S_4$: C, 64.8; H, 4.15; S, 13.85%). A suspension of the chelate (3.44 g.) in chloroform (50 ml.) was shaken with concentrated hydrochloric acid (50 ml.) at 0°. The organic layer was washed with water, and chlorobenzene (50 ml.) was added. The chloroform was removed under reduced pressure, the residual chlorobenzene solution was heated to the b. p., and hot ethanol (100 ml.) was added. The *macrocycle* (2.44 g., 76%) which

²⁷ Hatch and Sutherland, *J. Org. Chem.*, 1948, **13**, 249.

²⁸ Claisen, *Annalen*, 1893, **277**, 200.

slowly crystallised from the solution had m. p. 198—200°, raised to 208—209° by two recrystallisations from chlorobenzene-ethanol (Found: C, 69.5; H, 4.9; S, 14.8%; *M*, 813. $C_{50}H_{40}O_6S_4$ requires C, 69.4; H, 4.7; S, 14.8%; *M*, 865).

m-Methoxycarbonyltriphenylphosphonium Bromide (XII).—A solution of methyl *m*-bromomethylbenzoate¹⁹ (55 g.) and triphenylphosphine (100 g.) in xylene (500 ml.) was stirred and refluxed for 5 hr. The solid which separated was washed with ether and dried at 60°, to give the *salt* (109 g., 92%), m. p. 221—223°, raised to 225—226° by one recrystallisation from ethanol (Found: C, 64.65; H, 5.8; Br, 14.9. $C_{27}H_{24}BrO_2P, EtOH$ requires C, 64.8; H, 5.6; Br, 14.7%).

trans-trans-o-Phenylenedi-(m-vinylidenebenzoic acid) (XIa).—Lithium ethoxide (from lithium, 70 mg.) in ethanol (100 ml.) was added to a solution of phthalaldehyde²⁹ (0.50 g.) and the phosphonium salt (XII) (5.0 g.) in ethanol (50 ml.). The mixture was kept at room temperature for 6 hr., then diluted with water (200 ml.). Extraction with chloroform (30 ml., 10 ml.) yielded a viscous oil which was refluxed for 4 hr. with sodium hydroxide (0.70 g.) in methanol (50 ml.) and water (15 ml.). The bulk of the methanol was removed under reduced pressure and the aqueous residue was extracted with ether and acidified. Extraction with chloroform afforded a gum (1.74 g.) which was dissolved in benzene (30 ml.) and ether (30 ml.) containing iodine (20 mg.) and illuminated with diffuse daylight. The *acid* (1.05 g., 75%) which slowly separated had m. p. 272—274° raised to 277—278° by one recrystallisation from aqueous dimethylformamide (Found: C, 77.6; H, 4.9. $C_{24}H_{18}O_4$ requires C, 77.8; H, 4.9%), λ_{max} 2830 and 3070 Å (ϵ 32,900 and 25,000 respectively) in dioxan.

trans-trans-o-Phenylenedi-(m-vinylidenebenzoyl Chloride) (XIb).—A mixture of the bis(acid) (XIa) (4.61 g.) and thionyl chloride (15 ml.) was refluxed for 3 hr. The excess of the reagent was removed under reduced pressure and the residue was recrystallised from carbon tetrachloride-light petroleum (b. p. 60—80°), to give the *bis(acid chloride)* (3.70 g., 73%) as a pale yellow solid, m. p. 114—115°. A sample of m. p. 118—119° was obtained by recrystallisation from benzene-light petroleum (b. p. 80—100°) (Found: C, 70.3; H, 4.3. $C_{24}H_{16}Cl_2O_2$ requires C, 70.8; H, 4.0%).

trans-trans-o-Phenylenedi-(m-vinylidene- α -benzoylacetoacetylbenzene) (XIII).—The bis(acid chloride) (XIb) (548 mg.) in dry benzene (30 ml.) was added to the magnesium chelate (511 mg.) of benzoylacetone in diethylene glycol dimethyl ether (10 ml.) and dry benzene (60 ml.). After 40 hr. the 1,3-diketonic material was isolated as a viscous oil (740 mg.) which was treated with aqueous cupric acetate in the usual way. The product was chromatographed on silica gel in chloroform, and recrystallised from dioxan to give the *copper chelate* (140 mg., 14%) as a light green solid, m. p. 298—299° (Found: C, 73.4; H, 4.6; Cu, 8.6%; *M*, 729. $C_{44}H_{32}CuO_8$ requires C, 73.35; H, 4.5; Cu, 8.6%; *M*, 720). Treatment of the chelate (140 mg.) in chloroform (10 ml.) with *n*-hydrochloric acid (10 ml.) gave the *bis-(1,3-diketone)* (115 mg., 90%) as a glass (Found: C, 80.0; H, 5.6. $C_{44}H_{34}O_8$ requires C, 89.2; H, 5.2%).

Dimethyl trans-trans-o-Phenylenedi-(m-vinylidenebenzoate) (XIc).—(a) A suspension of the bis(acid chloride) (XIb) (215 mg.) in methanol (20 ml.) was refluxed for 2 hr. The methanol was removed under reduced pressure and the residue was washed with carbon tetrachloride (25 ml.) to leave the *bis(methyl ester)* (175 mg., 83%) as plates, m. p. 161—162° (Found: C, 78.0; H, 5.8. $C_{26}H_{22}O_4$ requires C, 78.4; H, 5.6%), λ_{max} 2460, 2830, and 3160 Å (ϵ 22,900, 39,700, and 28,300 respectively) in dioxan.

(b) A suspension of the bis(acid) (XIa) (208 mg.) in tetrahydrofuran (10 ml.) was treated with an excess of ethereal diazomethane. After 2 hr. the mixture was washed with 0.5*N*-sodium hydroxide and evaporated under reduced pressure to leave a solid (163 mg., 73%), m. p. 159—160°, which had an infrared absorption spectrum identical with that of the sample described above.

trans-trans-o-Phenylenedi-(m-vinylideneacetophenone) (XIId).—Diethyl malonate (6.0 g.) in dry dioxan (45 ml.) was added dropwise during 20 min. to a boiling suspension of magnesium (0.92 g.) in dry ethanol (10 ml.). The mixture was refluxed for a further 1 hr., cooled and diluted with ether (50 ml.). The bis(acid chloride) (XIb) (6.28 g.) in dioxan (45 ml.) was added during 15 min. and the mixture was stirred and refluxed for 4 hr., then shaken with 2*N*-sulphuric acid (50 ml.) at 0°. The organic layer was separated, and the oil obtained by removal of the solvent was refluxed for 6 hr. in water (20 ml.), acetic acid (40 ml.), and sulphuric acid (6 ml.). The product was filtered off, washed with water (200 ml.), and recrystallised once from butan-1-ol

²⁹ Bill and Tarbell, *Org. Synth.*, 1954, **34**, 82.

to give the *bis(methyl ketone)* (3.14 g., 50%), m. p. 130—133° raised to 135—136° by a further recrystallisation from butan-1-ol (Found: C, 83.5; H, 6.7. $C_{26}H_{22}O_2 \cdot \frac{1}{2}C_4H_9 \cdot OH$ requires C, 83.35; H, 6.75%), λ_{max} , 2550, 2810, and 3110 Å (ϵ 25,700, 39,200, and 28,400 respectively) in ethanol.

trans-trans-o-Phenylenedi-(m-vinylideneacetoacetylbenzene) (XIe).—A mixture of the *bis(methyl ketone)* (XIId) (4.18 g.), sodium ethoxide (from sodium, 1.05 g.), dry ethyl acetate (250 ml.), and dry benzene (150 ml.) was stirred and refluxed for 18 hr. The solid was filtered off and shaken with chloroform (50 ml.) and 0.2N-hydrochloric acid (50 ml.). The organic layer was washed with water (3 × 50 ml.), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was recrystallised once from butan-1-ol, to give the *bis(methyl 1,3-diketone)* (1.90 g., 38%), m. p. 126—128°, raised to 129—130° by a further recrystallisation from butanol (Found: C, 78.5; H, 6.0. $C_{30}H_{26}O_4 \cdot \frac{1}{2}BuOH$ requires C, 78.8; H, 6.4%). The compound formed a green *copper chelate* which crystallised from chlorobenzene as plates, m. p. >340° (Found: C, 70.2; H, 4.8; Cu, 12.2%; *M*, 494. $C_{30}H_{24}CuO_4$ requires C, 70.4; H, 4.7; Cu, 12.4%; *M*, 512).

Addition of the *bis(methyl 1,3-diketone)* (560 mg.) in benzene (10 ml.) and dioxan (10 ml.) to a boiling suspension of magnesium (150 mg.) in dry ethanol (5 ml.) gave the *magnesium chelate* (566 mg., 97%) which, crystallised from butan-1-ol, had m. p. 255—258° (decomp.) (Found: C, 70.5; H, 5.7%; *M*, 513. $C_{30}H_{24}MgO_4 \cdot 2H_2O$ requires C, 70.8; H, 5.5%; *M*, 508).

16,33-Diacetyl-16,17,33,34-tetrahydro-15,32H-hexabenz[ab, f, jk, pq, v, yz]cyclotriacontin-15,17,32,34-tetraone (III).—The *bis(acid chloride)* (XIb) (2.31 g.) in dry benzene (100 ml.) was added to the *magnesium chelate* (2.81 g.) of the *bis(methyl 1,3-diketone)* (XIe) in dry dioxan (100 ml.) and dry benzene (4 l.). The mixture was kept at room temperature for 13 days and then the 1,3-diketonic material was isolated and converted into a mixture of copper chelates as described under the preparation of the macrocycle (II). The mixture of chelates in chloroform (400 ml.) was chromatographed on acid-washed silica gel (500 g.), and the main band was eluted with chloroform to give a solid. The latter was washed with hot benzene (100 ml.) and boiling chlorobenzene (10 ml.) to leave the *copper chelate* (1.18 g., 25%) of the macrocycle (III) as a grey powder, m. p. >340° (Found: C, 76.2; H, 4.7; Cu, 7.5%. $C_{54}H_{38}CuO_8$ requires C, 76.6; H, 4.5; Cu, 7.5%). Treatment of the chelate (1.04 g.) in chloroform (50 ml.) with 5N-hydrochloric acid (50 ml.) at 0° afforded the *macrocycle* (0.83 g., 86%) which darkened at 190—195° but did not melt (Found: C, 82.8; H, 5.2%; *M*, 803. $C_{54}H_{40}O_8$ requires C, 82.6; H, 5.1%; *M*, 785).

o-Di-(5-phenyl-3,5-dioxopentyl)benzene (XIVa).—Finely powdered benzoylacetone (8.1 g., 0.05 mole) was added with stirring to a solution of potassamide (from potassium, 3.9 g., 0.1 mole) in liquid ammonia (150 ml.). After $\frac{1}{2}$ hr., *o*-xylylene dibromide (6.7 g., 0.025 mole) in benzene (50 ml.) was rapidly added. The mixture was stirred for 1½ hr., and then ammonium chloride (5 g.) was added. The ammonia was allowed to evaporate while ether was added periodically to maintain a volume of 150 ml. Water (150 ml.) was added, the mixture was acidified with dilute sulphuric acid, and the organic layer was separated and extracted with 2N-sodium hydroxide (3 × 50 ml.). The yellow aqueous solution and the brown syrup which was deposited were separated, and each was acidified with dilute sulphuric acid and then extracted with ether. The yellow solution thus yielded benzoylacetone (2.5 g.), m. p. 55—57°; the syrup yielded sticky brown crystals which were dissolved in methanol (100 ml.). This methanol solution was heated with charcoal, filtered, and cooled, to give the *bis-(1,3-diketone)* (1.54 g.) as straw-coloured needles, m. p. 95—96° unchanged by a further recrystallisation from methanol (Found: C, 78.65; H, 6.3. $C_{28}H_{28}O_4$ requires C, 78.85; H, 6.15%).

Cupric acetate (0.1 g.) in ethanol (15 ml.) was added to the *bis(diketone)* (0.2 g.) in ethanol (50 ml.). The precipitate which separated was collected and dissolved in dioxan. Addition of light petroleum gave the greyish-green *copper chelate* (0.15 g.), m. p. 254° (Found: C, 68.75; H, 4.9; Cu, 12.8%; *M*, 490. $C_{28}H_{24}CuO_4$ requires C, 68.9; H, 4.95; Cu, 13.05%; *M*, 488).

m-Di-(5-phenyl-3,5-dioxopentyl)benzene.—A similar preparation with *m*-xylylene dibromide (6.7 g.) afforded benzoylacetone (3.56 g.), m. p. 52—56°, and the *bis-(1,3-diketone)* (XIVb) (1.65 g.), m. p. 85—86° (Found: C, 78.9; H, 5.9%). When treated with cupric acetate as described above, the *bis(diketone)* (0.2 g.) formed a *copper chelate* (0.1 g.), m. p. 287° (Found: C, 69.1; H, 4.85; Cu, 12.9%; *M*, 492).

p-Di-(5-phenyl-3,5-dioxopentyl)benzene.—Under the same conditions, *p*-xylylene dibromide

(6.7 g.) yielded the *bis*-(1,3-diketone) (XIVc) (2.3 g.), m. p. 123—127°, raised to 128—129° by two recrystallisations from methanol (Found: C, 78.7; H, 6.1%). Benzoylacetone (2.4 g.), m. p. 55—57°, was recovered. The precipitate obtained by treatment of the bis(diketone) (0.2 g.) with cupric acetate, as described above, was only partly soluble in dioxan. Addition of light petroleum to the solution afforded the greyish-green *copper chelate* (15 mg.), m. p. 305°, of the diketone (XIVc) (Found: C, 68.7; H, 5.3; Cu, 13.2%).

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