From the Research Laboratories, CIBA (A.R.L.) Ltd., Duxford, Cambridge, England

Metal-containing Polymers

III. Chelated Polyphenols and the Derived Epoxy Resins[1]

By M. E. B. JONES, M. F. LYNCH, D. A. THORNTON, and R. F. WEBB

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SUMMARY:

The synthesis of *p*-hydroxybenzoylacetone, 4-hydroxy-3-methylbenzoylacetone and 1-*p*-hydroxyphenyl-1,3-pentandione is reported, together with the production of certain chelated polyphenols and the derived glycidyl ethers. The hardening of these resins and the thermal stability of the cured products and certain intermediates has been studied. Analogously constituted chelated aromatic diamines have also been prepared and their use as hardeners for epoxy resin systems examined.

ZUSAMMENFASSUNG:

Es wird über die Synthese von *p*-Hydroxybenzoylaceton, 4-Hydroxy-3-methylbenzoylaceton und 1-*p*-Hydroxyphenylpentandion-1,3 und über die Herstellung von gewissen Chelatpolyphenolen und den davon abgeleiteten Glycidyläthern berichtet. Die Härtung dieser Harze und die thermische Stabilität der ausgehärteten Produkte wurde untersucht. Analog aufgebaute chelierte aromatische Diamine wurden auch hergestellt und ihre Anwendung für das Aushärten von Epoxydharzen untersucht.

Introduction and Discussion

Many co-ordination polymer systems containing β-diketone ligands are known but in general such polymers exhibit low solubility in organic solvents and are difficult to process. The well-known ease of curing of epoxy resins and the wide range of curing agents which may be employed has encouraged us to examine the production of a range of bis- and polyepoxides containing a central β-diketone chelate system and the present paper is concerned with the preparation of chelate-containing polyphenols and the derived glycidyl ethers which are similar to the commercially available epoxy resins derived from epichlorohydrin and 2,2-bis(*p*-hydroxyphenyl)propane ("bisphenol A").

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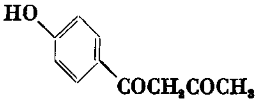
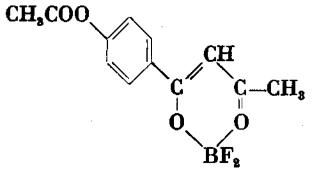
[1] Part II, M. E. B. JONES, D. A. THORNTON, and R. F. WEBB, Makromolekulare Chem. 49 (1961) 69.

The key intermediate in the present series was *p*-hydroxybenzoylacetone (I), which was obtained in high yield by addition of *p*-acetoxyacetophenone in acetic anhydride to the boron trifluoride-acetic acid complex in a mixture of acetic acid and ethylene dichloride. In preparative runs, the difluoroboron complex (II) first formed was not isolated but converted directly to *p*-hydroxybenzoylacetone by treatment with aqueous sodium acetate, sodium hydrogen carbonate and sodium hydroxide.



(I)

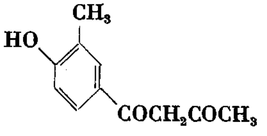


(II)

In separate experiments, the difluoroboron complex (II) and *p*-acetoxybenzoylacetone were isolated and characterized. Although toluene, anisole, mesitylene and even benzene may be directly acetoacetylated by boron trifluoride-acetic anhydride, similar treatment of phenyl acetate gave a difficultly separable mixture of *p*-hydroxyacetophenone and the required *p*-hydroxybenzoylacetone. It was shown that *p*-hydroxyacetophenone cannot be directly converted to the β-diketone under the conditions employed and it is therefore concluded that the reaction with phenyl acetate proceeds by two routes: (i) acetylation at the para position to *p*-acetoxyacetophenone which may then be further acetylated to the β-diketone, or (ii) a Fries rearrangement to *p*-hydroxyacetophenone which does not undergo further reaction.

Attempts to prepare the phenolic β-diketone (I) by the condensation of ethyl acetoacetate with *p*-hydroxybenzoyl chloride and ketonic hydrolysis of the product, or by the Claisen condensation of *p*-hydroxyacetophenone with ethyl acetate, gave poor yields of the desired product. In a similar Claisen condensation of ethyl *p*-hydroxybenzoate with acetone, no diketone was isolated.

Other phenolic ligands (III) and (IV) were prepared by the direct acylation procedure and together with the compound (I) were converted into bis- and tris-phenols by chelation with copper, beryllium, magnesium, zinc and aluminum salts. It is worthy of note that the copper(II) chelate of the ligand (IV) was very much more soluble in organic solvents than the copper(II) chelates derived from ligands (I) and (III).



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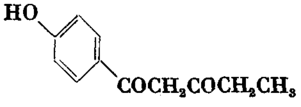


(IV)

The thermal stability of the chelates of *p*-hydroxybenzoylacetone with various metals was examined in air at 248 °C. and the order of stability (see Table 1) Al > Be > Zn > Mg > Cu confirmed the changes observed in the infrared spectra (in Nujol) of the chelates before and after the period of exposure to heat. The infrared spectra of the aluminum and beryllium chelates were unchanged over the period of the test whilst a slight broadening of the absorption peaks occurred with the zinc and magnesium compounds; the final spectrum of the copper compound exhibited only the Nujol peaks and the black material remaining after the test probably consisted of cupric oxide.

The beryllium chelate of *p*-hydroxybenzoylacetone could be converted into epoxy resins by treatment with epichlorohydrin using either solid sodium hydroxide or by the azeotropic method employing solid potassium carbonate. These resins were obtained either as viscous liquids or as solids with a softening point below 100 °C. depending on the conditions employed and the ratio of bisphenol to epichlorohydrin employed. A similar range of products may be obtained from 2,2-bis(*p*-hydroxyphenyl)propane.

The chelated beryllium-containing epoxy resins (which exhibited greater thermal stability than the parent bisphenol) underwent reaction with a wide variety of conventional curing agents to form insoluble, infusible thermoset products, although careful control of the initial curing temperature was necessary to avoid the formation of an excessively exothermic reaction. As an example, when the resins were cured with 4,4′-diaminodiphenylmethane, highly cross-linked products were obtained which possessed a high degree of thermal stability compared with that possessed by similarly-cured commercial epoxy resins.

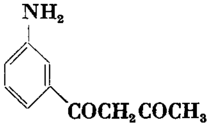
The zinc, magnesium and aluminum chelates of the ligand (I) were decomposed by strong alkali and, like the copper(II) chelate, were too insoluble in organic solvents for the milder azeotropic process to be used for conversion into their glycidyl ethers. The copper chelate was converted into the glycidyl ether by use of epichlorohydrin and sodium hydroxide. The dark green solid product softened at 220 °C. and proved difficult to cure since, on fusion, gross decomposition of the product occurred. When an attempt was made to use liquid hardeners, the amount of hardener was too small to wet the chelate; furthermore, on warming the mixture, an exothermic reaction occurred, yielding an inhomogeneous product.

Mixtures of the copper-containing epoxy resin and conventional epoxy resins based on 2,2-bis(*p*-hydroxyphenyl)propane could however be satisfactorily cured with both amine and anhydride curing agents. Thus a mixture of a commercial liquid epoxy resin and the copper chelate resin was cured with 4,4'-diaminodiphenylmethane to yield castings possessing a satisfactory degree of thermal stability. The heat distortion temperatures of the cured products were practically identical with those of the epoxy resin derived from 2,2-bis(*p*-hydroxyphenyl)propane cured with the same hardening agents.

As an alternative route to chelate-containing thermosetting epoxy resin compositions, the production of chelated diamine curing agents was also investigated. The simple ligands, *m*- and *p*-aminobenzoylacetone,(V) and (VI), proved difficult to obtain. We were unable to repeat the reduction by stannous chloride of the corresponding nitrobenzoylacetones reported by Gabriel and Gerhard[2] since in all cases removal of the complexed metal by treatment with acid and hydrogen sulphide was accompanied by hydrolysis to the monoketones. A variety of other reduction methods was investigated (see experimental section); those employing metals or metal ions were eliminated on account of complex formation with the β-diketone grouping, whilst the use of non-aqueous, non-neutral reducing agents gave resinous products. Formation of the β-diketone grouping after the introduction of the amino group was similarly unseccessful.

Ultimately, the chelated diamines derived from the ligands (V) and (VI) were produced directly by ketalisation of the nitro β-diketones, reduction in methanol with Raney nickel and hydrogen, removal of the ketal groups with dilute acid and precipitation of the desired chelates with the appropriate metal salts.

However, the metal chelates of *m*- and *p*-aminobenzoylacetone were not useful hardeners for epoxy resin systems since they required too high a fusion temperature and in all cases fusion of the diamino chelate curing agent with an epoxy resin caused an exothermic reaction resulting in severe decomposition of the product. Work on these curing agents was therefore discontinued.



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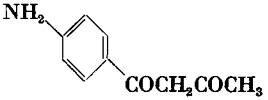

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[2] S. Gabriel and W. Gerhard, Ber. dtsch. chem. Ges. 54 (1921) 1617.

Experimental

p-Hydroxybenzoylacetone (I)

Method a

p-Hydroxyacetophenone (500 g., 1 mole) and ethyl acetate (1380 g., 4.3 moles) were slowly added with cooling to sodium wire (206 g., 2.3 atoms). When the reaction had subsided, the mixture was boiled under reflux for 4 hrs., cooled, poured cautiously into water and extracted with ethyl acetate. The aqueous layer was run into excess of an aqueous solution of cupric acetate, the resulting olive green precipitate of bis[1-(*p*-hydroxyphenyl)-1,3-butandiono]copper(II) was collected, washed (acetone) and dried. A small portion, on recrystallisation from ethanol, yielded the analytically pure chelate, m.p. 278—280 °C.

Anal.,	Calcd. for $C_{20}H_{18}O_6Cu$	C 57.49	H 4.34	Cu 15.21
	Found	C 57.52	H 4.38	Cu 15.87

The remainder of the chelate was boiled with 2 *N* sulphuric acid. After cooling, the precipitate was collected, dried and recrystallized from benzene. The *p*-hydroxybenzoylacetone, m.p. 112—112.5 °C. thus obtained, weighed 79.5 g. (12 %).

Anal.,	Calcd. for $C_{10}H_{10}O_3$	C 67.39	H 5.65
	Found	C 67.70	H 5.69

Method b

A solution of ethyl acetate (36 g., 2.2 moles) in sodium-dried toluene (50 ml.) was added to a suspension of sodium ethoxide (25 g., 2 moles) in toluene (600 ml.). The mixture was boiled under reflux for 7 hrs., cooled, poured into water, and the toluene layer separated. The aqueous layer was partially neutralized and added to excess of an aqueous solution of cupric acetate. The resulting olive green precipitate of bis[1-(*p*-hydroxyphenyl)-1,3-butandiono]copper(II) was decomposed by shaking with 3 *N* sulphuric acid. After extraction of the acid solution with chloroform and removal of the solvent, the dried product was recrystallized from benzene, yielding 4.8 g. (15 %) of *p*-hydroxybenzoylacetone.

Method c

One half of a solution of sodium (36 g., 2 atoms) in absolute ethanol (600 ml.) was added to ethyl acetoacetate (100 g., 2.3 moles). To this mixture one half of a solution of *p*-hydroxybenzoyl chloride (121 g., 1 mole) in sodium-dried ether (2.5 *l.*) was slowly added, the temperature being maintained between 0 and 10 °C. After allowing to stand for 1 hr., the remaining sodium ethoxide solution and the remaining chloride solution were slowly added in successive portions over 5 hrs. After allowing to stand 3 days, the product was filtered off and dried. A suspension of the solid product in ice-cold water (1 *l.*), was acidified with cold, dilute sulphuric acid. The resulting 1-*p*-hydroxyphenyl-2-carbethoxy-1,3-butandione was collected by filtration and hydrolyzed by boiling with dilute sulphuric acid (1 vol. acid: 4 vols. water) for 3 hrs. The precipitated oil was separated and cooled, when it solidified. The product was recrystallized from benzene, yielding 27.5 g. (20 %) of *p*-hydroxybenzoylacetone.

Method d

Boron trifluoride was passed rapidly into acetic acid (120 g.) with ice cooling until the complex solidified. Ethylene dichloride (80 ml.) was added to facilitate stirring. A mixture of p-acetoxyacetophenone (71.5 g., 1 mole) and acetic anhydride (81.5 g., 2 moles) was added over 4 min. After stirring for 2.5 hrs., the mixture was added to a solution of sodium acetate (131 g., 4 moles) in water (2 *l.*). Ethylene dichloride and some water were removed by distillation and the resulting solution boiled under reflux for 40 min. After cooling, the solid material was collected. The aqueous layer was partially neutralized with aqueous sodium bicarbonate and extracted with ether. The solid and the ether extracts were combined and extracted with 5% (w/v) aqueous sodium hydroxide. Acidification with dilute hydrochloric acid yielded the product which was collected and dried, m.p. 109—112°C., 55.8 g. (78%).

Method e

A mixture of p-acetoxyacetophenone (23.4 g., 1 mole), acetic anhydride (27.2 g., 2 moles) and ethylene dichloride (30 ml.) was saturated with boron trifluoride. After stirring for $^1/_2$ hr., the complex was hydrolyzed by boiling with a solution of sodium acetate (66 g., 6.2 moles) in water (300 ml.). Ethylene dichloride and some water were removed by distillation. The residue was cooled, extracted with chloroform, and the solution washed (water, aqueous sodium bicarbonate, water) and extracted with 5% (w/v) aqueous sodium hydroxide. After acidification of the alkaline extract with dilute sulphuric acid, the precipitated solid was collected, washed (water) and dried, 13.2 g. The product (in methanol), mixed with excess of aqueous cupric acetate, yielded 10.3 g. (37.5%) of bis[1-(p-hydroxyphenyl)-1,3-butandiono]copper(II) (infrared spectrum identical with that of the material obtained by method a).

The above reaction was repeated but hydrolysis of the boron difluoride complex was attempted by allowing to stand in aqueous sodium acetate at room temperature overnight. The ethylene dichloride was removed and the residual solution (p_H 4) was cooled, the precipitated solid being collected and dried. Extraction with methanol caused some material to dissolve. The solution, on reaction with aqueous cupric acetate, yielded bis[1-(p-acetoxyphenyl)-1,3-butandiono]copper(II), m.p. 248°C. after recrystallisation from benzene.

Anal.,	Calcd. for $C_{24}H_{22}O_8Cu$	C 57.41	H 4.42
	Found	C 57.76	H 4.35

The methanol-insoluble material, recrystallized from benzene, yielded the difluoroboron complex (II).

Anal.,	Calcd. for $C_{12}H_{11}O_4BF_2$	B 4.04	F 14.18
	Found	B 3.23	F 13.57

The reaction was repeated. After hydrolysis of the difluoroboron complex by boiling with aqueous sodium acetate, the solution was extracted with chloroform. Removal of the solvent from the chloroform extract yielded a solid residue, which, after recrystallisation from n-hexane, gave p-acetoxybenzoylacetone, m.p. 68—70°C., identical with the sample whose preparation is described below.

p-Acetoxybenzoylacetone

p-Hydroxybenzoylacetone (5 g., 1 mole) was dissolved in a solution of sodium hydroxide (1.7 g., 1.6 moles) in water (20 ml.). Acetic anhydride (4.3 g., 1.6 moles) and ice (30 g.) were added and the mixture shaken. The precipitated product was collected, washed (water), dried and recrystallized from aqueous methanol and finally from *n*-hexane, m.p. 70—70.5 °C.

Anal.,	Calcd. for $C_{12}H_{12}O_4$	C 65.45	H 5.50	O 29.07
	Found	C 66.05	H 5.63	O 28.32

p-Acetoxybenzoylacetone (2.0 g.), a normal solution of sodium hydroxide (11.2 ml., 1 mole), water (12 ml.) and methanol (5 ml.) were boiled together under reflux for 35 min. The solution was cooled and acidified. The precipitate was collected, washed and dried, m.p. 110—111 °C. This material was *p*-hydroxybenzoylacetone identical with that prepared as above.

Reaction of p-hydroxyacetophenone with acetic anhydride in the presence of boron trifluoride

When a mixture of *p*-hydroxyacetophenone and acetic anhydride was saturated with boron trifluoride and the product worked up in the usual way, 87 % of the original monoketone was recovered unchanged from the reaction mixture.

Bis[1-(p-hydroxyphenyl)-1,3-butandiono]copper(II)

p-Hydroxybenzoylacetone (29.5 g., 2 moles) in methanol (150 ml.) was added dropwise to a solution of cupric nitrate (20 g., 1 mole) in water (200 ml.) and concentrated ammonia (d. 0.88, 30 ml.). The precipitate was collected, washed with water and dried, affording the green bis[1-(*p*-hydroxyphenyl)-1,3-butandiono]copper(II) (36 g., 99 %), m.p. 280—282 °C. after recrystallisation from 2-ethoxyethanol and identical with the material prepared as described above.

Bis[1-(p-hydroxyphenyl)-1,3-butandiono]beryllium(II)

p-Hydroxybenzoylacetone (101 g., 2 moles) in hot methanol (300 ml.) was added to beryllium sulphate tetrahydrate (50 g., 1 mole) in hot water (1 *l.*). Urea (50 g.) was added, the solution heated and stirred for 4 hrs. After filtration, the collected solid was washed with water, dried and recrystallized from nitrobenzene, affording the colourless bis [1-(*p*-hydroxyphenyl)-1,3-butandiono]beryllium(II) (86.2 g., 84 %), m.p. 255 °C.

Anal.,	Calcd. for $C_{20}H_{18}O_6Be$	C 66.12	H 4.99
	Found	C 65.86	H 4.87

Bis[1-(p-hydroxyphenyl)-1,3-butandiono]magnesium(II)

p-Hydroxybenzoylacetone (8.9 g., 2 moles) in hot methanol (50 ml.) was added to anhydrous magnesium sulphate (3.0 g.) and urea (15 g.) in hot water (120 ml.). The mixture was heated 3 hrs. and maintained at room temperature for 60 hrs. The filtered product was washed with water, dried and recrystallized from methanol, affording the colourless bis[1-(*p*-hydroxyphenyl)-1,3-butandiono]magnesium(II), m.p. above 300 °C.

Anal.,	Calcd. for $C_{20}H_{18}O_6Mg$	C 63.43	H 4.79	Mg 6.42
	Found	C 63.58	H 5.09	Mg 5.87

Bis[1-(p-hydroxyphenyl)-1,3-butandiono]zinc(II)

p-Hydroxybenzoylacetone (82 g., 2 moles) in hot methanol (200 ml.) was added to zinc acetate dihydrate (50 g., 1 mole) in hot water (1 *l*.). The mixture was stirred and heated $^1/_2$ hr., filtered whilst hot, the precipitate washed with water, dried and recrystallized from dioxan, affording the colourless bis[1-(*p*-hydroxyphenyl)-1,3-butandiono]zinc(II) (32 g.), m.p. above 300 °C.

Anal., Calcd. for $C_{20}H_{18}O_6Zn$	C 57.24	H 4.32	O 22.88	Zn 15.58
Found	C 56.90	H 4.23	O 22.94	Zn 14.97

A sample dried at 50 °C. had the following analysis:

Anal., Calcd. for $C_{20}H_{18}O_6Zn, H_2O$	C 54.88	H 4.61
Found	C 55.20	H 4.97

The filtrate on cooling, deposited *p*-hydroxybenzoylacetone (48.0 g.). Allowing for recovered β-diketone, the yield of the zinc chelate was 91.6%.

Tris[1-(p-hydroxyphenyl)-1,3-butandiono]aluminum(III)

Method a

p-Hydroxybenzoylacetone (7.2 g., 3 moles) in hot methanol (40 ml.) was added to aluminum nitrate nonahydrate (5.0 g., 1 mole) in normal sodium hydroxide solution (100 ml.). The p_H of the solution was slowly lowered to 10 by addition of dilute nitric acid. The precipitated product was collected, washed with water, dried and recrystallized from methyl isobutyl ketone, affording the colourless tris[1-(*p*-hydroxyphenyl)-1,3-butandiono]aluminum(III), m.p. above 320 °C.

Anal., Calcd. for $C_{30}H_{27}O_9Al$	C 64.6	H 4.9
Found	C 64.1	H 4.7

Method b

p-Hydroxybenzoylacetone (5.0 g.) and aluminum acetylacetonate (3.0 g.) were ground together to a fine powder. The temperature of the mixture was gradually raised with simultaneous reduction of pressure until fusion occurred. Acetylacetone distilled, leaving a residue of tris[1-(*p*-hydroxyphenyl)-1,3-butandiono]aluminum(III) identical with the above specimen.

Table 1. Thermal stability of chelates of *p*-hydroxybenzoylacetone

Metal	Weight of sample (g.)	Percentage loss in weight after various times (hrs.) in air at 248 °C.			
		5	12	36	44
Be	0.1522	15	18	22	23
Al	0.1693	7	10	19	23
Zn	0.1744	22	25	32	34
Mg	0.1438	21	26	37	39
Cu	0.1415	31	55	82	83

Thermal stability tests on metal chelates of p-hydroxybenzoylacetone

Samples of the beryllium, aluminum, zinc, magnesium, and copper chelates of *p*-hydroxybenzoylacetone weighing approximately 0.15 g. were heated in air at 248 °C. for 44 hrs. These samples were withdrawn at various times, allowed to cool to room temperature and weighed. The weight loss undergone by these materials, expressed as a percentage of the original weight, is given in Table 1.

Reaction of bis[1-(p-hydroxyphenyl)-1,3-butandiono]beryllium(II) with epichlorohydrin and hardening of the resin obtained

Method a

Bis[1-(*p*-hydroxyphenyl)-1,3-butandiono]beryllium(II) (8.0 g.) was dissolved in a mixture of epichlorohydrin (70 ml.) and methyl isobutyl ketone (100 ml.). Anhydrous potassium carbonate (3.04 g.) was added and the mixture boiled under reflux with stirring. Water was continuously removed in a Dean and Stark trap until no further quantity azeotroped. The residual mixture was boiled with charcoal and filtered, the filtrate being distilled under reduced pressure to remove the solvents. The residual gum (5.44 g.) solidified on cooling, softening point 70—80 °C. The infrared spectrum exhibited an absorption peak at 10.95 μ, indicative of the presence of a glycidyl group which was absent in the spectrum of the original bisphenol.

Method b

Sodium hydroxide (6.9 g.) in a solution of 2-methoxyethanol (10 ml.) in water (10 ml.) was added to a solution of bis[1-(*p*-hydroxyphenyl)-1,3-butandiono]beryllium(II) (250 g., 1 mole) in a solution of epichlorohydrin (380 g., 6 moles) in ethylene glycol monomethyl ether (500 ml.) heated to 60 °C. Seven further portions of solid sodium hydroxide (total 55.5 g., 2 moles) were added over 4 hrs., the mixture being stirred and the temperature maintained at 60 °C. After stirring for one further hour, the mixture was cooled, filtered, diluted with chloroform (1 *l*.), washed once with hot water, five times with cold water, and dried over sodium sulphate. The solvents were removed under reduced pressure (25 mm.) until the bath temperature reached 160 °C., the product remaining as a viscous liquid.

The molten beryllium-containing epoxy resin (10 g.) was poured with stirring into molten 4,4′-diaminodiphenylmethane (at 110 °C.). (2.2 g.). The temperature was maintained at 60 °C. for 1 hr. and at 120 °C. for 2 hrs. Castings of the cured resin having the dimensions 3.8 · 3.8 · 0.3 cm. were exposed to 200 °C. for 235 hrs. and to 254 °C. for 75 hrs. The percentage loss of weight was 4.3%. The castings retained a considerable degree of mechanical strength after the period of exposure. Similar castings derived from a conventional epoxy resin based on 2,2-bis(*p*-hydroxyphenyl)propane and similarly cured with 4,4′-diaminodiphenylmethane underwent 15.3% loss of weight under identical exposure conditions. The final product was exceedingly brittle.

Reaction of bis[1-(p-hydroxyphenyl)-1,3-butandiono]copper(II) with epichlorohydrin and hardening of the resin obtained

A normal solution of sodium hydroxide (1.38 litres) was added to bis[1-(*p*-hydroxyphenyl)-1,3-butandiono]copper(II) (310 g., 1 mole) suspended in water (2.5 *l*.) at 50 °C.

Epichlorohydrin (136 g., 2 moles) was added and the mixture stirred vigorously for $^1/_2$ hr. A further portion of sodium hydroxide solution (1 N, 70 ml., total: 2 moles) was added and the mixture stirred for 3 hrs. The suspension was filtered, the solid product washed with water until the washings were neutral, and dried, yielding 1430 g. of the dark green solid product. The infrared spectrum exhibited an absorption peak at 10.95 μ indicative of the presence of a glycidyl group.

Since fusion of the epoxy resin caused gross decomposition to occur, it was found necessary to incorporate with the resin prior to cure, a substantial quantity of a conventional epoxy resin based on 2,2-bis(*p*-hydroxyphenyl)propane. The copper-containing epoxy resin (30 g.) was added with stirring to a mixture of a liquid commercial epoxy resin (essentially the diglycidyl ether of 2,2-bis(*p*-hydroxyphenyl)propane) (100 g.) and 4,4′-diaminodiphenylmethane (27 g.) previously heated to 110°C. The temperature was maintained at 60°C. for 2 hrs. and at 140°C. for 4 hrs. Castings of the cured resin having the dimensions 3.8·3.8·0.3 cm. were exposed to 200°C. for 235 hrs. and to 254°C. for 75 hrs. The percentage loss of weight was 10.4%. Similar castings derived from the commercial liquid epoxy resin and 4,4′-diaminodiphenylmethane without the inclusion of the copper-containing epoxy resin underwent 15.3% loss of weight under identical exposure conditions. Similar mixtures of copper-containing epoxy resin and commercial epoxy resin could be cured successfully with phthalic anhydride but the castings obtained possessed a lower degree of thermal stability than those cured with 4,4′-diaminodiphenylmethane.

1-p-Hydroxyphenyl-1,3-pentandione

This compound was prepared from *p*-acetoxyacetophenone (178 g.) exactly as described in method d for the preparation of *p*-hydroxybenzoylacetone using propionic anhydride in place of acetic anhydride. After two recrystallisations from benzene, the product weighed 113 g. (59%), m.p. 43—44°C.

Anal., Calcd. for $C_{11}H_{12}O_3$	C 68.74	H 6.30	O 24.98
Found	C 68.73	H 6.01	O 25.24

Bis[1-(p-hydroxyphenyl)-1,3-pentandiono]copper(II)

On mixing a methanolic solution of 1-*p*-hydroxyphenyl-1,3-pentandione (2 moles) with an aqueous solution of cupric acetate (1 mole), the product was immediately precipitated. The chelate was collected, dried and recrystallized from methyl isobutyl ketone, m.p. 239—240°C.

Anal., Calcd. for $C_{22}H_{22}O_6Cu$	C 59.24	H 4.97	O 21.53	Cu 14.25
Found	C 58.24	H 4.95	O 22.61	Cu 14.03

Bis[1-(p-hydroxyphenyl)-1,3-pentandiono]copper(II) diglycidyl ether

When prepared exactly as described for the beryllium chelate in method a above, the product was obtained as a dark green solid, m.p. 186—190°C. after recrystallisation from benzene.

Anal., Calcd. for $C_{28}H_{30}O_8Cu$	C 60.26	H 5.42	O 22.94	Cu 11.39
Found	C 59.49	H 5.40	O 23.52	Cu 11.62

Another sample prepared as described above for the beryllium chelate by method b had m.p. 176—178°C. after recrystallisation from benzene.

Anal., Calcd. for $C_{28}H_{30}O_8Cu$	C 60.26	H 5.42
Found	C 59.80	H 5.19

The product was cured with 4,4′-diaminodiphenylmethane to a tough, infusible thermoset polymer.

4-Hydroxy-3-methylbenzoylacetone

This compound was prepared from 4-acetoxy-3-methylacetophenone as described in method d for the preparation of *p*-hydroxybenzoylacetone. The viscous liquid reaction product could not be obtained crystalline, hence, for purification, it was converted into the copper chelate which was then warmed with dilute hydrochloric acid and filtered. The filtrate was cooled, the precipitated solid collected, dried and recrystallized from benzene, m.p. 95—96 °C.

Anal., Calcd. for $C_{11}H_{12}O_3$	C 68.74	H 6.30	O 24.98
Found	C 68.77	H 6.32	O 24.74

Bis[1-(3′-methyl-4′-hydroxyphenyl)-1,3-butandiono]copper(II)

4-Hydroxy-3-methylbenzoylacetone was treated with cupric nitrate in methanol solution as described for the preparation of bis[1-(*p*-hydroxyphenyl)-1,3-butandiono]copper-(II). The product, green crystals, m.p. 280—282 °C. was too insoluble for conversion to the glycidyl ether by conventional techniques.

Anal., Calcd. for $C_{22}H_{22}O_6Cu$ Cu 14.2 Found Cu 15.5

p-Nitrobenzoylacetone bis(ethylene ketal)

p-Nitrobenzoylacetone (311 g., 1 mole) in benzene (500 ml.) was heated with stirring with ethylene glycol (340 g., 3.7 moles) and *p*-toluenesulfonic acid (5 g.), water being collected in a DEAN and STARK trap. When water ceased to be evolved, the acid was neutralized with excess of sodium ethoxide and the benzene solution washed and dried. After removal of the benzene, distillation of the product gave *p*-nitroacetophenone ethylene ketal (145 g.), b.p. 125 °C./0.1 mm., m.p. 106.5—107.5 °C. (from light petroleum),

Anal., Calcd. for $C_{10}H_{11}NO_4$	C 57.41	H 5.30	N 6.70
Found	C 57.93	H 5.55	N 6.58

and *p*-nitrobenzoylacetone bis(ethylene ketal) (195 g., 44%), b.p. 185 °C./0.1 mm., m.p. 76—77 °C. (from methanol),

Anal., Calcd. for $C_{14}H_{17}NO_6$	C 56.94	H 5.80	N 4.74
Found	C 56.78	H 5.92	N 4.59

p-Aminobenzoylacetone bis(ethylene ketal)

p-Nitrobenzoylacetone bis(ethylene ketal) (40 g.) was hydrogenated in methanol at room temperature and atmospheric pressure over RANEY nickel. Absorption of hydrogen was complete after 20 hrs. Nickel and methanol were removed and the residue recrystallized from methanol, m.p. 103—104 °C., 34 g. (91%).

Anal., Calcd. for $C_{14}H_{19}NO_4$	C 63.38	H 7.22	N 5.28
Found	C 63.60	H 7.25	N 5.20

Bis[1-(p-aminophenyl)-1,3-butandiono]copper(II)

p-Aminobenzoylacetone bis(ethylene ketal) (10 g.) was dissolved in aqueous hydrochloric acid (2.5 N, 40 ml.). A fine precipitate began to form but was dissolved by dilution. The solution was filtered into an excess of ammoniacal cupric sulphate. The fine, brown precipitate was collected, washed (water) and dried. Recrystallization from 2-ethoxyethanol yielded the light green product, m.p. 267 °C. (decomp.), 2.5 g. (34 %).

Anal., Calcd. for $C_{20}H_{20}N_2O_4Cu$	C 57.75	H 4.85	N 6.74	Cu 15.28
Found	C 57.70	H 5.00	N 6.48	Cu 15.53

m-Nitrobenzoylacetone bis(ethylene ketal)

m-Nitrobenzoylacetone (175 g.) was treated as described above for the isomeric *p*-nitrobenzoylacetone. Distillation of the product yielded *m*-nitroacetophenone ethylene ketal (45 g.), b.p. 143—158 °C./0.8 mm., m.p. 70—71 °C. (from light petroleum),

Anal., Calcd. for $C_{10}H_{11}NO_4$ N 6.70 Found N 6.71

and *m*-nitrobenzoylacetone bis(ethylene ketal) (105 g., 41 %), b.p. 175—180 °C./0.8 mm., m.p. 50—51 °C. (from light petroleum),

Anal., Calcd. for $C_{14}H_{17}NO_6$ N 4.74 Found N 4.49

m-Aminobenzoylacetone bis(ethylene ketal)

m-Nitrobenzoylacetone bis(ethylene ketal) (28.6 g.) was reduced in methanol at room temperature and atmospheric pressure with hydrogen over Raney nickel. Absorption of hydrogen was complete after 5 hrs. Nickel was removed by filtration and the filtrate concentrated under reduced pressure. The product crystallized on standing, m.p. 112—112.5 °C., 24 g. (90 %).

Anal., Calcd. for $C_{14}H_{19}NO_4$	C 63.38	H 7.22	N 5.28
Found	C 63.64	H 7.26	N 5.37

Bis[1-(m-aminophenyl)-1,3-butandiono]copper(II)

A solution of *m*-aminobenzoylacetone bis(ethylene ketal) (10 g.) in dilute hydrochloric acid (2.5 N, 20 ml.), which had been allowed to stand 20 min., was added slowly with stirring to a solution of cupric sulphate pentahydrate (5 g.) in excess of aqueous ammonia. The bright green product was collected, washed, dried and recrystallized from methyl isobutyl ketone, m.p. 239 °C., 2.4 g. (32 %).

Anal., Calcd. for $C_{20}H_{20}N_2O_4Cu$	C 57.75	H 4.85	N 6.74	Cu 15.28
Found	C 57.39	H 5.00	N 6.72	Cu 14.69

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