789. *Heterocyclic Syntheses with Malonyl Chloride. Part I. Pyrano-1 : 3-dioxins from Ketones.*

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The vigorous reaction between malonyl chloride and acetone has been reinvestigated and found not to yield phloroglucinol as hitherto claimed. The reaction is general for ketones and yields 2 : 2-disubstituted derivatives of 6'-chloro-2' : 4-diketopyrano(3' : 4'-5 : 6)-1 : 3-dioxin, a new unsaturated hetero-dicyclic system. Structural evidence for the products is presented and their formation discussed.

According to Komninos (*Compt. rend.*, 1918, **167**, 781; *Bull. Soc. chim.*, 1918, **23**, 449) malonyl chloride and acetone react vigorously in the presence of marble, to give phloroglucinol and a red product (decomp. 160°), claimed to be 3 : 5-diketohexanoyl chloride,* $Cl{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}COMe$, convertible into phloroglucinol by carbonate and hot water. Reinvestigation has shown that neither compound is formed;† the product is a chloropyrono-1 : 3-dioxin (III; R = R' = Me).

We found that the reaction affords a colourless compound (I) (decomp. 183°), $C_9H_7O_5Cl$, which could not be converted into phloroglucinol. The compound was neutral but reacted slowly with cold water and alcohol to give acid solutions which gave red colours with ferric chloride. Ketones other than acetone yielded similar chloro-products, listed in Table 1.

Table 1. *Products from malonyl chloride and ketones.*

Ketone	Product	M. p.	Light absorption in dioxan $\lambda_{max.}$ (Å)	ϵ
$COMe_2$	$C_9H_7O_5Cl$ (I)	183° †	3020 *	9,700
			3140	10,900
			3180 *	9,700
$COPh_2$	$C_{19}H_{11}O_5Cl$ (II)	179 †	2450 *	14,200
			2510	16,700
			2580	15,300
			2900 *	7,100
			3040	8,200
			3120 *	7,100
COPhMe	$C_{14}H_9O_5Cl$	147	2800	4,700
			3140	10,000
$COMePr^n$	$C_{11}H_{11}O_5Cl$	89°	3140	8000
$COEt_2$	$C_{11}H_{11}O_5Cl$	104	—	—
*cyclo*Hexanone	$C_{12}H_{11}O_5Cl$	129	—	—
$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$	$C_{12}H_{11}O_7Cl$	118 †	—	—
$CH_3{\cdot}CO{\cdot}CO_2Et$	$C_{11}H_9O_7Cl$	87·5	—	—

* Inflection.
† With decomp.

These have a characteristic absorption band at *ca.* 3140 Å. Their formation may be represented: $RR'CO + 2CH_2(COCl)_2 = RR'C_7HO_5Cl + 3HCl$. The reaction with benzophenone shows that only the CO group of the ketone is involved.

Treatment of the benzophenone compound (II) with boiling ethanol and then with ammonia in the cold gave benzophenone and malonamide. With boiling water, carbon dioxide (83% of 3 mols.), hydrogen chloride (1 mol.), benzophenone (1 mol.), and acetone (as the 2 : 4-dinitrophenylhydrazone) were obtained, as shown by the equation

$$C_{19}H_{11}O_5Cl + 3H_2O = Ph_2CO + HCl + 3CO_2 + Me_2CO$$

The formation of acetone and carbon dioxide suggested that the molecule of the chloro-compound contained a bismalonyl residue, *i.e.*, a potential acetonetricarboxylic grouping.

The benzophenone compound (II) was then heated for a short time with three mols. of ethanol. Hydrogen chloride was evolved and, from the residue, which contained benzophenone and gave a red colour with ferric chloride, a crystalline copper derivative was

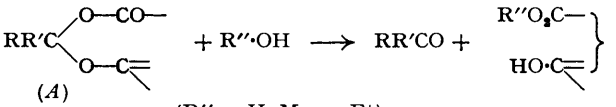
* Geneva nomenclature, $CO_2H = 1$.

† References to the reaction as a synthesis of phloroglucinol (*e.g.*, Beilstein's "Handbuch, etc.," 4th Edn., 1st Ergänzungsband, Vol. VI, p. 545; Richter, "The Chemistry of the Carbon Compounds," Elsevier, New York, 1946, Vol. III, p. 230; Bernthsen, "A Textbook of Organic Chemistry," Blackie and Son, Glasgow, 1942, p. 403) consequently need revision.

prepared. This was identical with the copper enolate of triethyl acetone-1 : 1 : 3-tricarboxylate, synthesised unambiguously *via* the reaction of malonic monoethyl ester chloride with ethyl magnesiomalonate. Similar degradation of the acetone-derived chloro-compound (I) with boiling ethanol led to the same copper derivative.

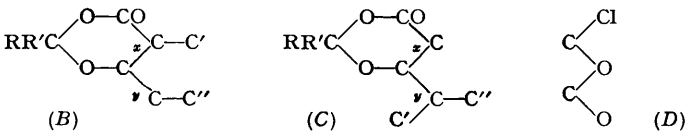
The benzophenone compound (II) in dioxan reacted with cold water, yielding benzophenone and a crystalline water-soluble acid, in accordance with the equation $C_{19}H_{11}O_5Cl + H_2O = Ph_2CO + C_6H_3O_5Cl$. The acid, which gave a deep red colour with ferric chloride, was evidently the source of the smaller fragments obtained in the reaction of (II) with hot water. With methanol and ethanol in dioxan in the cold, (II) underwent fissions to benzophenone and crystalline enolic products, $C_7H_5O_5Cl$ and $C_8H_7O_5Cl$, respectively, which were probably the methyl and ethyl esters of the acid. On attempted hydrolysis of the ethyl compound with one equivalent of sodium hydroxide, carbon dioxide was evolved, and from the solution ethyl acetoacetate was isolated as the 2 : 4-dinitrophenylhydrazone. Reaction of the acid with diazomethane, in an attempt to obtain its methyl ester, yielded a chlorine-free enolic product, $C_8H_8O_6$. However, an identical compound was formed from the methyl compound $C_8H_7O_5Cl$ and diazomethane, and so the suspected connection between the water and the methanol product was established.

The fission of the benzophenone compound (II) to these products could be explained thus:



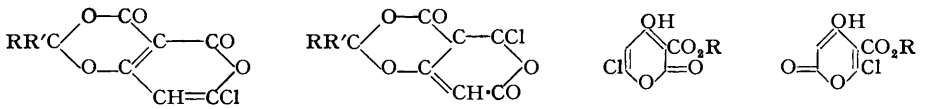
(*A*) (R'' = H, Me, or Et)

and there were two ways, (*B*) and (*C*), in which the C_6-acetone-1 : 1 : 3-tricarboxylic residue could be linked to the ketone moiety as in (*A*). One of the linkings *x* and *y* was necessarily



(*B*) (*C*) (*D*)

a double bond. Atoms Cl, H, and 2O had still to be accommodated so as to indicate that the chlorine atom was less reactive than in a COCl group and that positions C' and C'' were potential carboxyl groups. The arrangement (*D*) satisfactorily met these requirements and could be accommodated best on skeleton (*B*); (*C*) leads to a four-membered ring structure. Hence the possible formulæ for the malonyl chloride–ketone products were reduced to (III) and (IV).

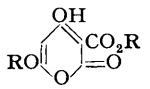


(III) (IV) (V*a*) (V*b*)

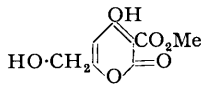
It followed that the acid degradation product and its methyl and ethyl esters were (V*a* or *b*; R = H, Me, and Et).

The related pyrones (VI) of established constitution (Staudinger and Becker, *Ber.*, 1917, **50**, 1016) were found to have light-absorption spectra similar to those of the acid and its esters (see Table 2), which confirmed the pyrone structures. Reaction of the methyl chloro-ester with sodium methoxide gave a crystalline methoxy-derivative, $C_7H_5O_5$·OMe, identical with the pyrone (VI; R = Me). Hence the degradation products were 6-chloro-4-hydroxy-2-pyrone-3-carboxylic acid derivatives (V*a*; R = H, Me, and Et). [The compound $C_8H_8O_6$ obtained by diazomethane, and isomeric with (VI; R = Me) was most probably the 6-hydroxymethyl derivative (VII).] It followed that the malonyl chloride–

ketone products (Table 1) had the structure (III). The compounds were 2 : 2-disubstituted derivatives of 6′-chloro-2′ : 4-diketopyrano(3′ : 4′-5 : 6)-1 : 3-dioxin.



(VI)



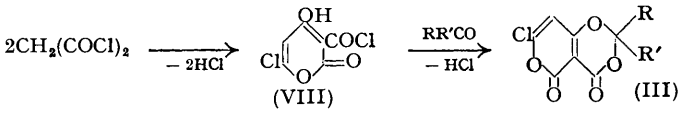
(VII)

TABLE 2. *Light absorption of pyrone derivatives in dioxan.*

	Compound		$\lambda_{max.}$ (Å)	ϵ
(VI)	(synthesised by Staudinger's method)	R = Me	3050	18,400
		R = Et	3040	15,500
	[from degradation of (II)]	R = H	2950 *	8,600
			3040	10,100
(V*a*)		R = Me	3040	12,300
		R = Et	3040	11,500
			3190 *	10,500
(VI)	[from degradation of (II)]	R = Me	3040	17,600

* Inflection.

The following scheme is proposed, to account for the production of the pyrono-1 : 3-dioxins :



The first stage is a self-condensation of malonyl chloride (not hitherto demonstrated), induced by the ketone as a very weak base [cf. the formation of the pyrones (VI)]. Evidence for this was obtained by treating malonyl chloride with a non-reactive base of comparable strength (see Braude, *J.*, 1948, 1971). The effect of dioxan is shown in Table 3. The appearance of the characteristic absorption band at 3040 Å indicates that a pyrone, presumably (VIII), is formed quite rapidly at room temperature. (Stronger bases, *e.g.*, tertiary amines, react vigorously with malonyl chloride, producing dark tars.)

TABLE 3. *Light absorption of solutions of malonyl chloride.*

Solvent (dry)	*c* (% w/v)	Time (hrs.)	$\lambda_{max.}$ (Å)	$E^{1\%}_{1\ cm.}$
Dioxan	0·618	1	2800	40
			2930	31
			3040	26
		25	3040 (only)	135
*cyclo*Hexane	0·496	—	End absorption only (no change with time)	

Alternative schemes can be formulated in which the first step is an addition of malonyl chloride to the ketone to yield a monoester chloride, $COCl{\cdot}CH_2{\cdot}CO_2{\cdot}CClRR'$ (cf. the action of carbonyl chloride or oxalyl chloride on keto-compounds; Staudinger, *Ber.*, 1909, **42**, 3966). The next stages, to yield (III), would involve condensation of this ester either with itself, followed by elimination of one ketone residue, or with malonyl chloride. These schemes seem unlikely because the first step would consume the ketone—*i.e.*, the proton acceptor—required to induce formation of the pyrone ring at a succeeding stage. Experiment shows that (III; R = R′ = Me) is formed in high yield from acetone with an excess of malonyl chloride. Spontaneous condensation of malonyl chloride or malonic monoester chloride has not been observed. These compounds appear to be stable for long periods.

No representatives of the unsaturated pyrano(3′ : 4′-5 : 6)-1 : 3-dioxin ring system have hitherto been described, although a few derivatives of the fully reduced system are known (Späth, Lorenz, and Freund, *Ber.*, 1943, **76**, 722; 1944, **77**, 354). The new system is highly reactive and is being further investigated, together with implications deriving from the proposed mode of formation.

EXPERIMENTAL

Reaction of Malonyl Chloride with Acetone.—(a) *Repetition of Komninos's experiments.* Malonyl chloride (8·6 g., 6 c.c.) and acetone ("AnalaR"; 3·5 g., 4·3 c.c.) were mixed and small marble chips (6 g.) added. When the evolution of heat and gas slackened, acetone (2 c.c.)

was added and the mixture kept overnight protected from atmospheric moisture. Extraction (3 times) with hot acetone afforded a product (pale yellow prisms; 3·2 g.), m. p. *ca.* 180° (decomp., with darkening from 135°), identical with that given by method (*b*), below.

The filtrate was made alkaline with 2N-sodium hydroxide and evaporated to dryness, and the residue extracted with boiling ethanol. Evaporation of the extract afforded a semi-solid residue, which yielded no phloroglucinol by treatment with water and ether.

The yellowish crystalline product (above) (3 g.), water (10 c.c.), and marble chips (5 g.) were warmed together on the steam-bath for 2 hours. The filtrate contained chloride ion, but gave no characteristic colours with ferric chloride or Brady's reagent. Evaporation of the filtrate to dryness left calcium salts, and no phloroglucinol was obtained by ether-extraction.

(b) *Modified procedure.* A mixture of acetone (" AnalaR "; 10 c.c.) and malonyl chloride (3·5 c.c.) was heated under reflux until solid appeared, then cooled and treated with dry ether. Recrystallisation of the golden tablets (2·6 g., 63%, based on malonyl chloride) from dry benzene afforded colourless prisms, m. p. 183° (decomp.), of 6′-*chloro*-2′ : 4-*diketo*-2 : 2-*dimethylpyrano*-(3′ : 4′-5 : 6)-1 : 3-*dioxin* (I) [Found : C, 46·9; H, 3·4; Cl, 15·25%; *M* (cryoscopic in bromoform), 234. $C_9H_7O_5Cl$ requires C, 46·9; H, 3·1; Cl, 15·4%; *M*, 230·6]. The yield was increased by using equivalent amounts of the reactants, but the product was more highly coloured. The compound did not react with aqueous sodium hydrogen carbonate during 5 minutes and gave no colour with ferric chloride in aqueous ethanol. When kept at room temperature in ethanol, and in aqueous dioxan, the solutions developed acidity and then gave red ferric colours.

Reaction of Benzophenone with Malonyl Chloride.—Benzophenone (15·2 g.) and malonyl chloride (16·2 c.c., 2 mols.) were heated at 100° until hydrogen chloride evolution ceased. Trituration of the product with dry ether gave 6′-*chloro*-2′ : 4-*diketo*-2 : 2-*diphenylpyrano*(3′ : 4′-5 : 6)-1 : 3-*dioxin* (II) (24·45 g., 82%), which crystallised from benzene as very pale buff needles, m. p. 179° (decomp.) [Found : C, 63·9; H, 3·3; Cl, 9·8%; *M* (cryoscopic in bromoform), 299. $C_{19}H_{11}O_5Cl$ requires C, 64·3; H, 3·1; Cl, 10·0%; *M*, 354·7]. A solution in aqueous ethanol gradually became acid and then gave a reddish-purple colour with ferric chloride.

Reaction of Other Ketones with Malonyl Chloride.—The products listed in the annexed Table were prepared as above.

No.	CO compound	Malonyl chloride (c.c.)	Product triturated with *	Pyrano(3′ : 4′-5 : 6)-1 : 3-dioxin	Yield (%)	Form and solvent *
1	$CH_3{\cdot}CO{\cdot}CO_2Et$ (2·2 c.c.)	4	Et_2O	2-*Carbethoxy*-6′-*chloro*-2′ : 4-*diketo*-2-*methyl*-	48	CCl_4
2	$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$ (2·5 c.c.)	4	,,	2-*Carbethoxymethyl*-6′-*chloro*-2′ : 4-*diketo*-2-*methyl*-	60	Needles, CCl_4
3	$COMePr^n$ (2·24 c.c.)	4	Pet (b)	6′-*Chloro*-2′ : 4-*diketo*-2-*methyl*-2-n-*propyl*-	92	Leaflets, Pet (b)
4	$COEt_2$ (10 c.c.)	3·5 (+5 g. $CaCO_3$)	†	6′-*Chloro*-2 : 2-*diethyl*-2′ : 4-*diketo*-	32	Needles, Pet (a)
5	$COPh_2Me$ (2·4 c.c.)	4	—	6′-*Chloro*-2′ : 4-*diketo*-2-*methyl*-2-*phenyl*-	62	Needles, CCl_4
6	*cyclo*Hexanone (2·1 c.c.)	3·9	Et_2O	6′-*Chloro*-2′ : 4-*diketo*-2-spirocyclo*hexyl*-	53	Plates, CCl_4

* Pet = light petroleum, b. p. (a) 60—80°, (b) 80—100°.
† Product isolated by extraction with chloroform.

No.	M. p.	Formula	Found (%) C	H	Cl	Required (%) C	H	Cl
1	87·5°	$C_{11}H_9O_7Cl$	45·45	3·25	11·9	45·75	3·15	12·3
2	118	$C_{12}H_{11}O_7Cl$	47·55	3·8	11·85	47·6	3·65	11·7
3	89	$C_{11}H_{11}O_5Cl$	51·4	4·6	14·05	51·1	4·3	13·7
4	104	,,	50·7	4·3	13·8, 13·6	,,	,,	,,
5	147	$C_{14}H_9O_5Cl$	57·0	3·1	12·15	57·1	3·1	12·1
6	129	$C_{12}H_{11}O_5Cl$	53·2	4·5	13·6	53·2	4·1	13·1

Degradation of the Benzophenone Product.—(a) *With boiling ethanol.* (i) The compound (II) (1 g.) and ethanol (0·45 c.c.) were heated on the steam-bath till evolution of hydrogen chloride ceased. Ether and ammonia (*d* 0·88) were added, and the mixture was shaken and kept for 24 hours. On evaporation, the ethereal layer gave benzophenone, m. p. 43—44°, and the aqueous layer gave malonamide, which after recrystallisation from ethanol had m. p. 164° (Found : N, 27·15. Calc. for $C_3H_6O_2N_2$: N, 27·4%), undepressed by authentic material.

(ii) *Formation of triethyl acetonetricarboxylate.* The compound (II) (0·71 g.), dry dioxan (1 c.c.), and ethanol (0·345 c.c.) were heated together on the steam-bath for 10 minutes. The

solution was shaken with cupric acetate (0·2 g.) in water (10 c.c.), and then with light petroleum (b. p. 40—120°) to remove benzophenone. The aqueous layer was filtered and cooled; the pale green crystalline precipitate had m. p. 85° alone and in admixture with an authentic specimen of the hydrated copper enolate of triethyl acetone-1 : 1 : 3-tricarboxylate (m. p. 85°) (see below).

(b) *With cold ethanol.* The compound (II) (1 g.) was dissolved in chloroform, and ethanol (0·45 c.c.) added with stirring. Next day, the solution was clarified and evaporated under reduced pressure. The residue was stirred with light petroleum (b. p. 80—100°), and the mixture filtered (filtrate *P*). Crystallisation of the solid from light petroleum (b. p. 80—100°) afforded *ethyl 6-chloro-4-hydroxy-2-ketopyran-3-carboxylate* (V*a*; R = Et) (0·3 g.) as needles, m. p. 121° (Found: C, 43·2; H, 3·3; Cl, 15·9. $C_8H_7O_5Cl$ requires C, 43·95; H, 3·25; Cl, 16·2%). In aqueous dioxan a deep reddish-purple colour was given with ferric chloride. Evaporation of filtrate *P* yielded benzophenone, m. p. *ca.* 40°, which was characterised as the 2 : 4-dinitrophenylhydrazone, m. p. 234°, undepressed by an authentic specimen.

On addition of the pyran (V*a*; R = Et) (0·68 g.) in dioxan (4 c.c.) to sodium hydroxide (0·25 g., 1 equiv.) in water (8 c.c.), there was a rapid evolution of carbon dioxide. After acidification with 2N-hydrochloric acid (3·1 c.c.) and addition of Brady's reagent, the 2 : 4-dinitrophenylhydrazone of ethyl acetoacetate was precipitated. This crystallised from ethanol and had m. p. 89°, undepressed by authentic material.

(c) *With boiling water.* The benzophenone compound (II) (340 mg.) and water (0·1 c.c.) were heated under reflux for 15 minutes. Gaseous acidic products were aspirated in a stream of dry, carbon dioxide-free nitrogen and absorbed in an excess of standard aqueous barium hydroxide. The evolved carbon dioxide (83·15% of 3 mols.) and hydrogen chloride (1·01 mol.) were estimated as barium carbonate and by back-titration of the barium hydroxide filtrate, respectively. The condenser was removed from the reaction vessel, which was then warmed in a current of nitrogen, and the gases were passed into Brady's reagent. Acetone 2 : 4-dinitrophenylhydrazone was precipitated, having m. p. 119·5°, undepressed by authentic material. The residue consisted of benzophenone (17·5 mg., 1·00 mol.), m. p. 35—40°; the 2 : 4-dinitrophenylhydrazone had m. p. 232°, undepressed by authentic material.

(d) *Reaction with cold water.* Compound (II) (1·42 g.) was dissolved in dry dioxan (25 c.c.) by heat, the solution cooled, and water (0·14 c.c.) added. Next day, the solution was concentrated to small bulk under reduced pressure and ether was added. The *6-chloro-4-hydroxy-2-ketopyran-3-carboxylic acid* (V*a*; R = H) (0·5 g.) crystallised as needles, m. p. 134·5°, from light petroleum (b. p. 80—100°) (Found: C, 38·2; H, 1·95; Cl, 18·75. $C_6H_3O_5Cl$ requires C, 37·85; H, 1·6; Cl, 18·6%). It gave a deep red colour with ferric chloride, and dissolved with effervescence in aqueous ammonium hydrogen carbonate.

(e) *Reaction with methanol.* The compound (II) (7·6 g.), dissolved in dioxan by heat, was treated in the cold with methanol (1·6 c.c.). Next day, the solution was evaporated to small bulk, and light petroleum (b. p. 60—80°) and ether were added. From benzene, the *methyl* ester (V*a*; R = Me) (3·7 g., 90%) separated as needles, m. p. 149° (Found: C, 41·45; H, 2·8; Cl, 17·05. $C_7H_5O_5Cl$ requires C, 41·1; H, 2·4; Cl, 17·35%). In aqueous dioxan a deep red colour was given with ferric chloride.

Methyl 4-Hydroxy-6-hydroxymethyl-2-ketopyran-3-carboxylate.—(i) To 6-chloro-4-hydroxy-2-ketopyran-3-carboxylic acid (320 mg.) in dioxan, a solution of diazomethane in ether (undried) was added in portions until gas evolution ceased. Evaporation, and trituration of the residue with light petroleum (b. p. 40—60°), gave a chlorine- and nitrogen-free product (Lassaigne's test), which gave a deep red colour with ferric chloride. The *methyl 4-hydroxy-6-hydroxymethyl-2-ketopyran-3-carboxylate* (50 mg.) had m. p. 147° after recrystallisation from benzene (Found: C, 48·1; H, 4·4. $C_8H_8O_6$ requires C, 48·0; H, 4·05%). A mixture with methyl 4-hydroxy-2-keto-6-methoxypyran-3-carboxylate (m. p. 149°) (below) had m. p. 120—122°.

(ii) Similarly, methyl 6-chloro-4-hydroxy-2-ketopyran-3-carboxylate (300 mg.) in dioxan with ethereal diazomethane (undried) afforded the 6-hydroxymethyl product (50 mg.), m. p. and mixed m. p. 147°.

Conversion of Methyl 6-Chloro-4-hydroxy-2-ketopyran-3-carboxylate into the 6-Methoxy-derivative with Sodium Methoxide.—Sodium (0·15 g.), dissolved in methanol (several c.c.), was added, during 5 minutes, to the pure chloro-pyran (0·65 g.) in dioxan (50 c.c.), with cooling. A precipitate formed at once. After 30 minutes, the mixture was just acidified with dilute sulphuric acid (*ca.* 50 c.c.), and the solution extracted with ether (50 + 25 c.c.). The combined extracts were dried (Na_2SO_4) and then evaporated under reduced pressure. From benzene–light petroleum (b. p. 60—80°), colourless halogen-free needles separated (90 mg.), which had m. p. 148·5° depressed to 120° by the starting material (Found: C, 47·8; H, 4·1. Calc. for

$C_8H_8O_6$: C, 48·0; H, 4·05%). The m. p. was not depressed by authentic methyl 4-hydroxy-2-keto-6-methoxypyran-3-carboxylate prepared by Staudinger and Becker's method (*loc. cit.*). The 6-methoxy-pyran gave an orange colour with ferric chloride in ethanol.

Degradation of the Acetone Compound with Ethanol.—The compound (I) (1 g.) was heated with ethanol (0·75 c.c.) on the steam-bath for 15 minutes. Hydrogen chloride was evolved. The resulting oil was kept under reduced pressure for several minutes, and then shaken with cupric acetate (0·4 g.) in water (10 c.c.). The pale green precipitate (1·3 g.; 98%) had m. p. 85° undepressed by an authentic specimen (see below) of the hydrated copper enolate of triethyl acetone-1 : 1 : 3-tricarboxylate.

*Triethyl Acetone-*1 : 1 : 3-*tricarboxylate.*—Malonic monoethyl ester chloride (42 g.) in dry ether (15 c.c.) and ethyl ethoxymagnesiomalonate [prepared from ethyl malonate (44·6 g.), according to Breslow, Baumgarten, and Hauser, *J. Amer. Chem. Soc.*, 1944, **66**, 1286] were heated under reflux for 30 minutes, then chilled and treated with an excess of dilute sulphuric acid. The *magnesium* derivative of triethyl acetone-1 : 1 : 3-tricarboxylate (18 g.), which separated, formed prismatic needles, m. p. 119°, from ethyl acetate (Found: Mg, 4·65. $C_{24}H_{34}O_{14}Mg$ requires Mg, 4·25%). The ethereal layer was combined with ethereal extracts (2 × 250 c.c.) of the aqueous phase, dried (Na_2SO_4), and evaporated. Ethyl malonate was removed under reduced pressure and the residue extracted with 5% sodium hydroxide solution. The extract was washed with ether and neutralised with dilute sulphuric acid, and the oily triethyl acetone-1 : 1 : 3-tricarboxylate (11·2 g.) isolated with chloroform. The pale green hydrated copper enolate, prepared from the ester according to Willstätter (*Ber.*, 1899, **32**, 1272), had m. p. 85°.

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