# ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF THE MORTON CHEMICAL CO.[1]]

## Polymers Containing Chelated Aluminum

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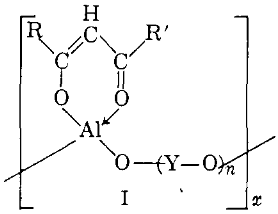
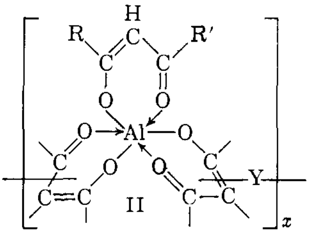
RECEIVED FEBRUARY 11, 1959

The formation and properties of two types of chelated aluminum polymers have been studied. Monochelated polymers prepared from diisopropoxy or dichloro aluminum monochelates generally have been found to be hydrolytically unstable solids of limited thermal stability. There was evidence of disproportionation occurring which led to the more stable trichelated compound and aluminum oxide. Polymers of trichelated aluminum have been prepared both by reaction of trichelate diesters with organic diols and by reaction of a diisopropoxy monochelate with various dichelating agents. These polymers are more resistant to hydrolysis than are the monochelated polymers. They range in molecular weight from 450 to 2620 and vary from low-melting, soluble, thermally unstable glassy materials to intractable powders stable at 360°. Explanations based on steric factors and on interchange of chelate ligands are advanced for this wide range of properties.

The stability of metal chelates[3] has led us to investigate the preparation and properties of condensation polymers containing aluminum in the polymer chain in which the aluminum is stabilized by chelation. It was hoped that such polymers would be hydrolytically and thermally stable. We have studied the formation of polymers of two types, represented by structures I and II, in which Y is a bivalent organic radical.

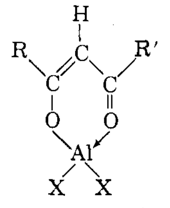


I



II

**Materials of Structure I.**—As starting materials for polymers of structure I we prepared stable monochelates of aluminum, examples of which have not been reported previously. Treatment of aluminum isopropoxide or aluminum chloride with limited amounts of chelating agents has given high yields of compounds III-VI. Attempts to prepare compound VII failed. Distillation to purify the product yielded only 1,2-dimethoxyethane and tarry residues.



III, R, R' = $CH_3$, X = $OCH(CH_3)_2$
IV, R = $CH_3$, R' = $OC_2H_5$, X = $OCH(CH_3)_2$
V, R, R' = $OC_2H_5$, X = $OCH(CH_3)_2$
VI, R, R' = $CH_3$, X = Cl
VII, R, R' = $CH_3$, X = $OCH_2CH_2OCH_3$

In attempts to prepare polymers of structure I in which *n* equals 0 the monochelates III-V were dissolved in toluene and treated with water–isopropyl alcohol mixtures. With compounds IV and V glassy solids were obtained, analyses and molecular weights of which indicated formation of low polymers. These decomposed in the presence of moisture to form hydrated alumina. Treatment of compound III with water gave a 64% yield of tris-(2,4-pentanediono)-aluminum, formed by disproportionation, and an insoluble solid containing 39.8% aluminum.

Reaction of compounds III and VI with various diols, as summarized in Table I, yielded materials shown by analysis not to be polymers, but to be reaction products of one mole each of chelate and diol (as in structure I, *n* = 1, *x* = 1, with –OH and –H as end groups). The analyses did not always indicate pure materials, but consistently showed the proper ratios for this interpretation. These were hydrolyzed readily, some in cold water, others on boiling. A consistent hydrolytic product of the materials prepared from compound III was the trichelate, tris-(2,4-pentanediono)-aluminum. This disproportionation indicates an intrinsic instability of materials of structure I.

**Trichelated Aluminum Polymers.**—Polymers of structure II were prepared in an effort to achieve greater hydrolytic stability than was found with structure I. These were made by two means: (A) the formation of mixed trichelates such that two of the chelate rings had functional groups capable of forming linear polymers by further reaction, and (B) reaction of monochelate III with dichelating agents with elimination of isopropyl alcohol.

Method A assumes the possibility of synthesis and the stable existence of mixed aluminum trichelates, since these have not been reported previously. It was found that reaction of one part of the monochelate III with two equivalents of ethyl acetoacetate and ethyl diacetylacetate gave good yields of 2,4-pentanediono-bis-(ethyl acetoacetato)-aluminum (VIII) and 2,4-pentanediono-bis-(3-carbethoxy-2,4-pentanediono)-aluminum (IX), respectively. It also was found possible to prepare compound VIII by the direct reaction of 2,4-pentanedione and ethyl acetoacetate with aluminum isopropoxide, and even by merely heating a 1:2 molar mixture of tris-(2,4-pentanediono)-aluminum and tris-(ethyl acetoacetato)-

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(1) This research was carried out by the Ringwood Chemical Corp., a predecessor of the Morton Chemical Co., and was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF 18(600)-1599. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) Deceased.

(3) P. Schmidt, *Angew. Chem.*, **64**, 536 (1952); Chemische Werke Albert, British Patents 718,283, 718,284, 718,340 (1954); 721,938 (1955).

Table I

Reactions of Monochelates III and VI with Diols

| | | Analyses of products, % | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Calculated[a] | | | | Found | | | |
| Compd. | Diol | C | H | Cl | Al | C | H | Cl | Al |
| III | Ethylene glycol | 41.2 | 6.42 | | 13.2 | 41.7 | 5.72 | | 13.0 |
| III | Diethylene glycol | 43.5 | 6.90 | | 10.9 | 42.2 | 6.58 | | 11.2 |
| III | Butanediol-1,4 | 46.6 | 7.38 | | 11.6 | 47.6 | 6.83 | | 12.4 |
| III | Resorcinol | 52.4 | 5.20 | | 10.7 | 52.4 | 5.37 | | 10.8 |
| III | 2,2-Bis-(4-hydroxyphenyl)-propane | 64.8 | 6.26 | | 7.3 | 64.2 | 6.18 | | 7.3 |
| VI | Ethylene glycol | | | 15.9 | 12.1 | | | 15.5 | 13.0 |
| VI | Diethylene glycol | | | 13.3 | 10.1 | | | 13.3 | 10.9 |
| VI | 2,2-Bis-(4-hydroxyphenyl)-propane | | | 9.1 | 6.9 | | | 9.0 | 6.8 |

[a] Calculated for structure I, $n = 1$, $x = 1$, with –OH and –H as end groups.

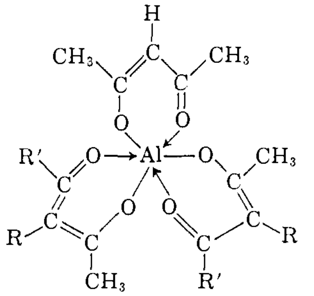
Table II

Polymerization of Trichelate VIII with Diols

| | | | Analyses, % | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Calculated[a] | | | Found | | |
| Dio | Softening point of polymer, °C. | Mol. wt. | C | H | Al | C | H | Al |
| Ethylene glycol | 105–120 | 1370[b] 2020[c] | 50.85 | 5.40 | 7.62 | 49.49 | 5.30 | 8.18 |
| Diethylene glycol | 105–110 | 980[c] | 51.26 | 5.82 | 6.77 | 49.64 | 6.00 | 6.84 |
| Triethylene glycol | 75–130 | 1100[c] | 51.58 | 6.15 | 6.10 | 49.88 | 6.24 | 6.24 |
| Butanediol-1,3 | 100–110 | 2620[b] | 53.40 | 6.06 | 7.06 | 52.90 | 6.01 | 7.49 |
| Butanediol-1,4 | 95–150 | 940[c] | 53.40 | 6.06 | 7.06 | 53.32 | 6.26 | 7.40 |
| Pentanediol-1,5 | 80–110 | 1570[c] | 54.54 | 6.36 | 6.81 | 54.00 | 6.59 | 6.35 |

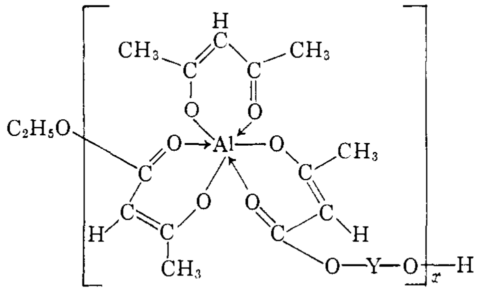
[a] Calculated for structure X, $x = \infty$. [b] Determined by acetylation of hydroxyl end groups. [c] Determined cryoscopically in benzene.

aluminum. This last finding was rather unexpected since it implies the facile migration of chelate ligands hitherto regarded as quite stable.



VIII, R = H, R' = OEt
IX, R = $CO_2Et$, R' = $CH_3$

Trichelate VIII was heated in 1:1 ratio with a number of diols in order to form polymers of structure X, with the results summarized in Table II.



X

Y = radical derived from diol, HO-Y-OH

Attempts to increase the molecular weights of these polymers by heating *in vacuo* at 200–250° resulted in volatilization of tris-(2,4-pentanediono)-aluminum, along with oils which showed positive color tests with ferric chloride. Heating of compound VIII above 220° also resulted in decomposition. The evidence thus points to extensive disruption of the chelate rings of these polymers under moderate heating.

Similar results were obtained with the formation of polyesters by reaction of compound IX with diols. The polymers formed were of very low molecular weight.

In method B trivalent aluminum with a coördination number of six to which one monochelated group is strongly attached should form linear polymers (structure II) when treated with molecules having two chelating groups. Similar polymers have been formed by reaction of bis-(1,3-diketones) with bivalent metals having a coordination number of four.[4] A number of such dichelating agents were prepared and treated with the monochelate III in equimolar ratios. Results are summarized in Table III.

Examples 1–4 of Table III afford a direct comparison with method A, since the polymers should be identical to those prepared from compound VIII and the corresponding diols (see Table II). Except for lower molecular weights of the polymers prepared by method B, the polymers from the two methods did prove to be identical as judged by elemental analyses and infrared spectra. In addition, the polymers of method B were similar to those of method A in that they were not chelated strongly enough to have great thermal stability. Slow decomposition set in above 200° with volatilization of tris-(2,4-pentanediono)-aluminum in each case.

The insolubility and infusibility of the products of examples 5–7 of Table III may be explained by rigidity of the polymer chain backbone. Any rotation or bending in the chain is structurally

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[4] J. P. Wilkins and R. L. Wittbecker, U. S. Patent 2,649,711 (1953).

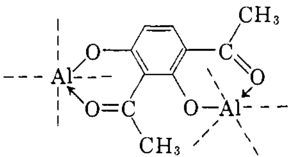
TABLE III

POLYMERIZATION OF COMPOUND III WITH DICHELATING AGENTS

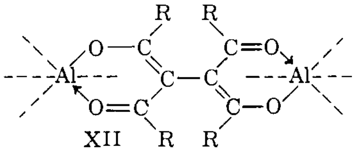
| | | | | | Analyses of products, % | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Calculated for structure II | | | Found | | |
| | Dichelating agent | Appearance of product | Melting range, °C. | Mol.[a] wt. | C | H | Al | C | H | Al |
| 1 | Ethylene bis-(acetoacetate) | Hard, yell. clear[b] | 130–150 | 770 | 50.85 | 5.40 | 7.62 | 52.23 | 5.60 | 7.58 |
| 2 | Diethylene glycol bis-(acetoacetate) | Hard, yell. clear[b] | 80–150 | 930 | 51.26 | 5.82 | 6.77 | 50.98 | 5.95 | 7.32 |
| 3 | Tetramethylene bis-(acetoacetate) | Pale yell. clear[b] | 75–95 | 1160 | 53.40 | 6.06 | 7.06 | 53.69 | 5.92 | 6.92 |
| 4 | Pentamethylene bis-(acetoacetate) | Pale yell. clear[b] | 40–55 | 450 | 54.54 | 6.36 | 6.81 | 56.74 | 6.93 | 6.07 |
| 5 | 2,4-Diacetylresorcinol | Granular, tan[c] | >360 | .. | 56.61 | 4.75 | 8.48 | 58.17 | 4.98 | 7.70 |
| 6 | $\alpha,\alpha'$-Bis-(ethylacetoacetate) | Granular, tan[b] | >360 | 1860 | | | 7.06 | | | 7.35 |
| 7 | 1,1,2,2-Tetraacetylethane | Granular, white | >360 | | 55.90 | 5.94 | 8.37 | 57.06 | 6.06 | 8.23 |
| 8 | 1,1,2,2-Tetrabenzoylethane | Recovd. most of starting mater. | ..... | .. | ... | .. | .. | ... | .. | ... |
| 9 | $\alpha,\alpha$-Methylene bis-(ethyl acetoacetate) | Brittle, brown[b] | 110–130 | 1275 | 54.54 | 6.36 | 6.81 | 53.85 | 6.43 | 7.11 |
| 10 | 1,1,3,3-Tetraacetylpropane | Deep red, clear[b] | 90–150 | 1070 | 57.14 | 6.29 | 8.02 | 56.97 | 5.79 | 11.80 |
| 11 | 1,1,3,3-Tetrabenzoylpropane | Brittle, amber[b] | 130–145 | 920 | | | | | | |

[a] By freezing point in benzene. [b] Soluble in benzene. [c] Insoluble in all organic media.

impossible in example 5 (structure XI). In examples 6 and 7 (structure XII) steric repulsion of the side chains may hinder rotation.[5] In example 8, where the starting material was recovered, the bulkiness of the phenyl groups (structure XII, R = $C_6H_5$) may have prevented formation of the trichelate structure. A methylene group separates the chelate rings of the chain in examples 9–11, and the greater flexibility should account for the solubility and fusibility of these polymers.



XI



XII

Two factors appear to have contributed chiefly to the low molecular weights of all these polymers: steric hindrance and low thermal stability. The latter prevented achievement of high molecular weight by the usual technique of heating *in vacuo*, since such conditions promoted interchange of chelate ligands with cross-linking and volatilization of the trichelate monomer formed as by-product. The intractable residues and trichelate sublimates commonly encountered bear this out, and limit the practical use of these polymers.

## Experimental[6]

**Monochelated Aluminum Diisopropoxides. General Procedure.**—To a solution of 204 g. (1.0 mole) of aluminum isopropoxide in 300 ml. of Skellysolve C was added with stirring 1.0 mole of the chelating agent over a period of 15 minutes. Isopropyl alcohol and solvent were removed by distillation, and the clear viscous oil was distilled *in vacuo*.

**2,4-Pentanedionoaluminum diisopropoxide** (III) now was obtained from 2,4-pentanedione as a clear, viscous, yellow oil, b.p. 142° (0.5 mm.), in 86% yield. It crystallized to a cream-colored solid, m.p. 115–120°, after standing for several days. The cryoscopic molecular weight in benzene was 494, about twice the calculated value of 244.3.

*Anal.* Calcd. for $C_{11}H_{21}O_4Al$: C, 54.09; H, 8.67; Al, 11.05. Found: C, 53.34; H, 9.26; Al, 11.15.

**(Ethyl acetoacetato)-aluminum diisopropoxide** (IV), obtained from ethyl acetoacetate in 92% yield, was a viscous, colorless oil, b.p. 150° (0.2 mm.). Attempts to induce crystallization failed.

*Anal.* Calcd. for $C_{12}H_{23}O_5Al$: C, 52.55; H, 8.45; Al, 9.84. Found: C, 51.79; H, 8.36; Al, 9.87.

**(Ethyl malonato)-aluminum diisopropoxide** (V), from ethyl malonate in 85% yield, was an extremely viscous, colorless oil, b.p. 183° (0.25 mm). Crystallization attempts failed.

*Anal.* Calcd. for $C_{13}H_{25}O_6Al$: C, 51.31; H, 8.28; Al, 8.87. Found: C, 50.90; H, 8.25; Al, 8.88.

All three compounds were soluble in common organic solvents, and hydrolyzed slowly in the atmosphere.

**2,4-Pentanedionoaluminum Dichloride** (VI).—To a stirred suspension of 200 g. (1.5 moles) of anhydrous aluminum chloride in 1500 ml. of benzene was added slowly 150 g. (1.5 moles) of 2,4-pentanedione. The mixture was refluxed until evolution of hydrogen chloride had nearly ceased. The solvent was distilled and the viscous, brown residue distilled *in vacuo*. The product was a yellow, viscous oil, b.p. 92–93° (0.5 mm.), yield 218 g. (75%). It crystallized to a pale yellow solid, m.p. 55–58°, over a period of several days. It was readily soluble in alcohols, ketones and aromatic hydrocarbons. It hydrolyzed slowly upon exposure to the atmosphere.

*Anal.* Calcd. for $C_5H_7O_2Cl_2Al$: C, 30.48; H, 3.58; Cl, 36.00; Al, 13.70. Found: C, 30.72; H, 3.87; Cl, 35.90; Al, 13.65.

**Hydrolysis of Compound III.**—To a stirred solution of 54.2 g. (0.222 mole) of compound III in 100 ml. of anhydrous toluene maintained at 25° was added a solution of 4.0 ml. (0.222 mole) of distilled water in 25 ml. of anhydrous isopropyl alcohol over a period of 30 minutes. The resulting clear solution was distilled until isopropyl alcohol and most of the toluene had been removed. The turbid residue was heated *in vacuo* over a steam-bath, leaving a white solid containing needle-like crystals. Continuous extraction with chloroform left an infusible, insoluble white powder containing 39.8% aluminum. From the extract was obtained 21.6 g. of white crystals, m.p. 192–193°, undepressed on admixture with authentic tris-(2,4-pentanediono)-aluminum.[7] The infrared spectrum in carbon tetrachloride was identical with that of the latter: 2950, 1600, 1530, 1468, 1428, 1395, 1290, 1192, 1030 and 935 cm.$^{-1}$.

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[5] 3-Isopropyl-2,4-pentanedione does not form stable chelates because of interference with the planar configuration; A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, p. 175.

[6] Analyses were performed by the Clark Microanalytical Laboratory, Urbana, Ill., and by Mr. V. R. Bassi of this Laboratory. Melting points are uncorrected.

[7] R. C. Young, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 25.

*Anal.* Calcd. for $C_{15}H_{21}O_6Al$: C, 55.55; H, 6.53; Al, 8.32. Found: C, 54.82; H, 6.43; Al, 8.43.

**Hydrolysis of Compound IV.**—The foregoing procedure was followed. After distillation of isopropyl alcohol and toluene, a clear, viscous oil remained. It was heated at 260° and 0.5 mm. for one hour. When cooled it was a clear amber, brittle solid. Analyses indicated a polymer of structure I, $n = 0$, $x = 5$, with HO– and –H as end groups. The calculated molecular weight is 878, while the value found by acetylation with acetic anhydride in pyridine was 850.

*Anal.* Calcd. for $C_{30}H_{47}O_{21}Al_5$: C, 41.01; H, 5.39; Al, 15.36. Found: C, 40.40; H, 6.03; Al, 15.41.

The polymer decomposed above 280°. It was soluble in organic media, but films cast from benzene turned to insoluble powders in the atmosphere.

**Hydrolysis of Compound V.**—The foregoing procedure again was followed. The colorless, viscous oil obtained was heated to 260° at 0.5 mm. A colorless distillate, 12 g., was collected. The density, refractive index and odor indicated ethyl malonate. The cooled residue was an insoluble, infusible white solid, analysis of which did not suggest any simple polymer of the structure I, $n = 0$, type, but rather a material having the formula $HO(Al(C_7H_{11}O_4)\text{-}O)_2AlO$, in which one-third the aluminum atoms had lost their chelate ligands. The calculated molecular weight is 464; the value determined by acetylation was 395.

*Anal.* Calcd. for $C_{14}H_{23}O_{12}Al_3$: C, 36.22; H, 4.99; Al, 17.43. Found: C, 36.07; H, 5.97; Al, 17.19.

**2,4-Pentanedionoaluminum Bis-(2-methoxyethoxide) (VII).**—To 500 ml. of purified 2-methoxyethanol heated on a steam-bath was added in small portions 27.0 g. (1.0 mole) of granular aluminum (20 × 30 mesh). No catalyst was required. Evolution of hydrogen commenced at once, and the reaction was complete after two hours. Excess 2-methoxyethanol was removed by distillation *in vacuo*. Attempts to distil the viscous residue at 150–200° (0.5 mm.) caused decomposition to a brown tar. The Dry Ice trap contained 40 g. of colorless liquid miscible with water and inert toward sodium. The physical constants, b.p. 84–86°, $d^{20}_{20}$ 0.870, $n^{25}_D$ 1.3780, indicated it to be 1,2-dimethoxyethane.

Therefore, to 1.0 mole of crude aluminum 2-methoxyethoxide was added slowly 100 ml. (1.0 mole) of 2,4-pentanedione. An exothermic reaction ensued and 2-methoxyethanol was distilled. Attempts to distil the yellow sirupy residue yielded only 1,2-dimethoxyethane. The brown tarry residue crumbled to an insoluble powder in the atmosphere.

**Polymerization of Compound III with Diols. General Procedure.**—To a stirred solution of 36.6 g. (0.15 mole) of compound III in 50 ml. of toluene was gradually added with stirring at 25° a solution of 0.15 mole of the diol in 50 ml. of anhydrous isopropyl alcohol. The reaction mixture was slowly distilled until isopropyl alcohol had been removed and the head temperature had reached 110°. At this point the products from reactions with aliphatic diols were in solution. They were precipitated as white solids by pouring the toluene solutions into petroleum ether. The solids were washed with petroleum ether and dried *in vacuo* at 100°. The products from reactions with aromatic diols precipitated as white solids during distillation of isopropyl alcohol and were filtered, washed with petroleum ether and dried *in vacuo* at 100°. Results are summarized in Table I.

The three products from aliphatic diols were suspended in water at 25° and shaken for several minutes. They were filtered and extracted continuously with ether. Evaporation of the ether extracts yielded white crystals of tris-(2,4-pentanediono)-aluminum, while the ether-insoluble material did not dissolve in any organic solvents. The two products from aromatic diols appeared stable in cold water, but when boiled in water for several minutes yielded tris-(2,4-pentanediono)-aluminum upon ether extraction. In the last case 2,2-bis-(4-hydroxyphenyl)-propane, m.p. 150–152°, was also recovered in small amount.

All five products darkened when heated above 250° and yielded sublimed crystals of tris-(2,4-pentanediono)-aluminum. The polymer from 2,2-bis-(4-hydroxyphenyl)-propane was readily soluble in methanol, and films cast from such solutions were clear, hard and colorless, and appeared stable indefinitely in the atmosphere.

**Polymerization of Compound VI with Diols. General Procedure.**—To a stirred solution of 59.1 g. (0.30 mole) of compound VI in 100 ml. of benzene at 25° was gradually added a solution of 0.30 mole of the diol in 100 ml. of anhydrous methyl ethyl ketone. The clear solution was refluxed until evolution of hydrogen chloride had nearly ceased. The evolved gas was collected in a water trap and titrated with standard sodium hydroxide solution. In each case less than 0.3 mole was found, whereas complete polymerization requires evolution of 0.6 mole. After refluxing, the solvent was removed by heating on a steam-bath at 10 mm. pressure. The residue was pulverized, washed with petroleum ether and dried. Results are summarized in Table I.

Analyses of products agree closely for compounds in which one chlorine atom of compound VI is replaced by the diol. The products decomposed to black tars when heated at 250–300°. When allowed to stand in the atmosphere they slowly gave off hydrogen chloride and became insoluble in all solvents.

**2,4-Pentanediono Bis-(ethyl acetoacetato)-aluminum (VIII). Procedure A.**—To 102.5 g. (0.42 mole) of compound III was added 109 g. (0.84 mole) of ethyl acetoacetate. The viscous solution was heated and isopropyl alcohol distilled. The residue was distilled *in vacuo*, the product coming over as a very viscous, clear, colorless oil, b.p. 138–139° (0.15 mm.), $d^{20}_{20}$ 1.160, $n^{20}_D$ 1.5239, in 94.5% yield. It did not crystallize after standing several months, was stable in the air and in cold water, but hydrolyzed slowly in boiling water. When heated above 220° it decomposed slowly to a black tar. The compound was soluble in organic solvents and insoluble in water. The cryoscopic molecular weight in benzene was 369, indicating no association.

*Anal.* Calcd. for $C_{17}H_{25}O_8Al$: C, 53.12; H, 6.56; Al, 7.02. Found: C, 53.01; H, 6.42; Al, 6.99.

**Procedure B.**—To a solution of 408.5 g. (2.0 moles) of aluminum isopropoxide in 500 ml. of Skellysolve C was added with stirring 200 g. (2.0 moles) of 2,4-pentanedione and 460 g. (4.0 moles) of ethyl acetoacetate. Solvent and isopropyl alcohol were distilled, and the residue distilled *in vacuo*. The yield was 622 g. (81%).

**Procedure C.**—A mixture of 32.4 g. (0.1 mole) of tris-(2,4-pentanediono)-aluminum and 82.4 g. (0.2 mole) of tris-(ethyl acetoacetato)-aluminum were heated until solution was obtained, then distilled *in vacuo*. The yield was 105 g. (91%).

The infrared spectra in carbon tetrachloride of the products of procedures A, B and C along with that of a 1:2 molar mixture of tris-(2,4-pentanediono)-aluminum and tris-(ethyl acetoacetato)-aluminum were identical: 1615, 1530, 1430, 1400, 1380, 1300, 1180, 1100, 1065, 1022 and 982 cm.$^{-1}$.

**2,4-Pentanediono Bis-(3-carbethoxy-2,4-pentanediono)-aluminum (IX).**—To a stirred solution of 24.4 g. (0.1 mole) of compound III in 100 ml. of Skellysolve C was added a solution of 34.4 g. (0.2 mole) of ethyl diacetylacetate[8] in 20 ml. of Skellysolve C. The solution was refluxed two hours and isopropyl alcohol and some Skellysolve C distilled. It was then allowed to stand overnight at room temperature. The white crystalline precipitate was filtered and recrystallized from a benzene–Skellysolve C mixture, m.p. 137–140°, yield 29.5 g. (68%); infrared spectrum in carbon tetrachloride: 3000, 1725, 1600, 1540, 1450, 1410, 1385, 1315, 1295, 1260, 1085, 1032 and 932 cm.$^{-1}$.

*Anal.* Calcd. for $C_{21}H_{29}O_{10}Al$: C, 53.80; H, 6.23; Al, 5.77. Found: C, 53.88; H, 6.01; Al, 5.73.

**Ethylene Bis-(acetoacetate).**—No information was found in the literature concerning glycol diesters of acetoacetic acid. Ethyl acetoacetate (78 g., 0.60 mole) and ethylene glycol (15.5 g., 0.25 mole) were heated together and ethanol was distilled slowly until the temperature reached 200°. The remaining oil was then distilled *in vacuo*. After a forerun of ethyl acetoacetate, the diester came over as a pale yellow oil, b.p. 150–152° (0.5 mm.), $d^{20}_{20}$ 1.1832, $n^{20}_D$ 1.4609, yield 63%. The infrared spectrum, as expected, was nearly identical with that of ethyl acetoacetate: 3000, 1765, 1735, 1670, 1643, 1450, 1415, 1363, 1315, 1225, 1150 and 1045 cm.$^{-1}$.

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[8] A. Spassow, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 390.

*Anal.* Calcd. for $C_{10}H_{14}O_6$: C, 52.17; H, 6.13; mol. wt., 230. Found: C, 52.04; H, 6.00; mol. wt. (cryoscopic in benzene), 231.

**Diethylene Glycol Bis-(acetoacetate).**—Ethyl acetoacetate was transesterified with diethylene glycol in the manner described above. The product was a pale yellow oil, b.p. 178–180° (0.9 mm.), $d^{20}_{20}$ 1.1579, $n^{20}_{D}$ 1.4612, yield 74.5%.

*Anal.* Calcd. for $C_{12}H_{18}O_7$: C, 52.55; H, 6.62. Found: C, 51.73; H, 6.42.

**Tetramethylene Acetoacetate.**—Ethyl acetoacetate was transesterified with butanediol-1,4 in the manner described. The product was a pale yellow oil, b.p. 163–164° (0.3 mm.), $d^{20}_{20}$ 1.1140, $n^{20}_{D}$ 1.4598, yield 84%.

*Anal.* Calcd. for $C_{12}H_{18}O_6$: C, 55.81; H, 7.02. Found: C, 55.80; H, 6.87.

**Pentamethylene Acetoacetate.**—Ethyl acetoacetate was transesterified with pentanediol-1,5 in the manner described above. The product was a viscous, pale yellow oil, b.p. 165–166° (0.2 mm.), $d^{20}_{20}$ 1.1235, $n^{20}_{D}$ 1.4601, yield 86%.

*Anal.* Calcd. for $C_{13}H_{20}O_6$: C, 57.34; H, 7.40. Found: C, 57.33; H, 7.51.

**2,4-Diacetylresorcinol** is reported as being prepared by the Fries rearrangement of resorcinol diacetate, the product being an isomeric mixture with the 2,4-isomer predominating. The procedure of Phillips and co-workers[9] was, therefore, followed. The yield of 2,4-isomer, m.p. 84–85°, was 62%.

**1,1,2,2-Tetraacylethanes. General Procedure.**—These compounds were prepared by treating an ether suspension of the sodium salt of the proper diketo compound with iodine, following the method of Menzies and Wiltshire.[10] 1,1,2,2-Tetraacetylethane, from 2,4-pentanedione, was obtained as sparingly soluble, white cubic crystals, m.p. 190–192°, in 20% yield. **1,1,2,2-Tetrabenzoylethane**, from dibenzoylmethane was obtained as pale orange crystals, m.p. 226–228°, in 38% yield.

*Anal.* Calcd. for $C_{30}H_{22}O_4$: C, 80.80; H, 4.94. Found: C, 81.03; H, 4.87.

**α,α'-Bis-(ethyl acetoacetate).**—The foregoing procedure for the tetraacylethanes was followed, employing here the sodium salt of ethyl acetoacetate. The product was a white solid, m.p. 60–65°, yield 21%.

**1,1,3,3-Tetraacetylpropane.**—A modification of the method of Menzies and Wiltshire[10] for this compound was followed. A mixture of 200 g. (2.0 moles) of 2,4-pentanedione, 75 g. (1.0 mole) of 40% aqueous formaldehyde and 1 ml. of piperidine was stirred at 0–5° for 16 hours. It was then distilled *in vacuo*, unreacted materials being collected in a Dry Ice trap. The product was a pale yellow oil, b.p. 124–126° (0.3 mm.), $d^{20}_{4}$ 1.087, $n^{20}_{D}$ 1.4767, yield 83%. It did not crystallize after standing several months. The cryoscopic molecular weight in benzene was 220; the calculated value is 212.

**1,1,3,3-Tetrabenzoylpropane.**—The foregoing procedure was followed, dibenzoylmethane being substituted for 2,4-pentanedione. The product precipitated from the reaction mixture as a white solid, which, after recrystallization from a benzene–alcohol mixture, melted at 179–181°. The yield was 55%.

*Anal.* Calcd. for $C_{31}H_{24}O_4$: C, 80.90; H, 5.25. Found: C, 80.95; H, 5.18.

**α,α'-Methylene Bis-(ethyl acetoacetate).**—The same procedure was followed, substituting ethyl acetoacetate for 2,4-pentanedione. The product was a colorless oil, b.p. 142–143° (0.5 mm.), $d^{20}_{20}$ 1.092, $n^{20}_{D}$ 1.4543, yield 66%.

**Polymerization of Compound VIII with Diols. General Procedure.**—The chelate VIII (0.1 mole) and the diol (0.1 mole) were dissolved in 100 ml. of xylene and refluxed with stirring. Ethanol and xylene were distilled slowly until the reaction temperature reached 160°. The mixture then was heated at 190–200° (1 mm.) for 20–30 minutes and the resulting viscous amber oil poured out and allowed to cool to a hard, brittle, glassy solid. All the polymers obtained were soluble in most organic solvents except the paraffins. The results are summarized in Table II.

The polymers from diethylene glycol and triethylene glycol were rubbery near their softening points. Extremely long, but brittle fibers could be drawn from the melts of the other four polymers. All the polymers when heated *in vacuo* at 200–250° decomposed with sublimation of tris-(2,4-pentanediono)-aluminum and volatilization of oils that gave deep color tests with ferric chloride. The residues were dark tars.

**Polymerization of Compound IX with Ethylene Glycol.**—A solution of 4.68 g. (0.01 mole) of compound IX and 0.6 g. (0.01 mole) of ethylene glycol in 5 ml. of dioxane was heated slowly and the dioxane distilled. After a final heating period at 170° (1 mm.) for one hour, the resulting viscous amber mass could be drawn into brittle fibers. It cooled to a hard glass, was soluble in benzene, and softened at 150–200°. Its cryoscopic molecular weight was 1120. When heated above 170° it decomposed.

**Polymerization of Compound IX with Diethylene Glycol.**—A solution of 4.68 g. (0.01 mole) of compound IX and 1.06 g. (0.01 mole) of diethylene glycol in 50 ml. of benzene was refluxed 6 hours. Since there was no sign of polymerization at this point, the run was repeated with the addition of 0.75 g. of *p*-toluenesulfonic acid. After 12 hours of refluxing, followed by removal of solvent at 130–140° (1 mm.), and cooling to 25°, a hard, yellowish, transparent solid remained. It was soluble in benzene and the cryoscopic molecular weight was 830.

**Polymerization of Compound III with Dichelating Agents. General Procedure.**—Equimolar quantities of compound III and a dichelating agent were dissolved in xylene and refluxed with stirring. Isopropyl alcohol and solvent were slowly distilled. Results are summarized in Table III.

In examples 5, 6 and 7 of Table III where the products precipitated during the distillation period, they were filtered, washed successively with benzene and petroleum ether, and dried *in vacuo*. In the other examples, the concentrated reaction mixture, usually a viscous sirup, was heated at reduced pressure until all volatile matter appeared to be removed. Molecular weights, where possible, were determined cryoscopically in benzene.

In example 8, the reaction could not be driven to completion. Even after continued refluxing in xylene, followed by heating at 160° (15 mm.), nearly half the tetrabenzoylethane was recovered.

The infrared spectra of the products of examples 1, 2, 3 and 4 were practically identical with those of examples 1, 2, 5 and 6 of Table II, respectively: 3350, 2850–2900, 1600, 1510, 1380–1390, 1270–1280, and 1160–1165 cm.$^{-1}$. Moreover, these materials, when heated at 200–250°, decomposed to brown tars and sublimed as crystals of tris-(2,4-pentanediono)-aluminum.

The polymerization with 1,1,3,3-tetraacetylpropane (example 10) appeared to be complicated by a side-reaction characteristic of such tetraketones, *viz.*, dehydration to a substituted cyclohexenone. Unlike all the other polymers observed, the product possessed a pungent odor and was deep red, suggesting extended conjugation. When heated *in vacuo* above 170°, it decomposed, yielding sublimed tris-(2,4-pentanediono)-aluminum and a yellow distillate, the infrared spectrum of which contained an unsaturated carbonyl compound.

All the polymers of Table III were unchanged by prolonged suspension in water at 25°. In boiling water, gelatinous white precipitates slowly formed, except for the polymer of example 10 which was unchanged after 30 minutes.

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[9] G. H. Phillips, A. Robertson and W. B. Whalley, *J. Chem. Soc.*, 4951 (1952).

[10] R. C. Menzies and E. R. Wiltshire, *ibid.*, 2242 (1931).