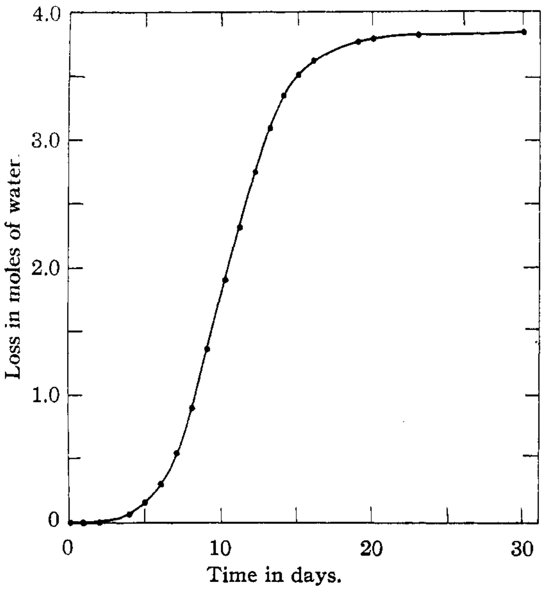

Fig. 1.—Conversion of strontium salt pentahydrate to monohydrate in air at 20°.

saturated by shaking five days at 20° with an excess of the solid strontium salt from levoglucosan, there was contained 40.6 mg. of the strontium salt monohydrate. In 5 cc. of a similar solution from D-altrosan there was 40.2 mg. To a portion of the solution saturated with the salt from levoglucosan then was added solid strontium salt from D-altrosan, and the mixture shaken five days at 20°; the filtered solution contained 40.2 mg. of the monohydrate in 5 cc. A similar value for the solubility, 40.6 mg. in 5 cc., was reached from supersaturation, by shaking the strontium salt from levoglucosan first at 30° (44.8 mg. soluble in 5 cc.), and then at 20°.

One of the authors (N. K. R.) desires to thank the Chemical Foundation of New York for a Research Associateship, and the American Academy of Arts and Sciences for a grant from the Cyrus M. Warren Fund. The authors also express their indebtedness to Dr. W. T. Haskins for carrying out the microanalyses, and to Dr. A. E. Knauf for the sample of levoglucosan which was oxidized.

Summary

The oxidation of D-altrosan with periodic acid, followed by bromine water and strontium carbonate, to the same strontium L′-oxy-D-methylenediglycolate which is obtained from levoglucosan, has shown that D-altrosan possesses the same ring system as levoglucosan, and accordingly is to be designated D-altrosan $\alpha<1,5>\beta<1,6>$.

WASHINGTON, D. C. RECEIVED FEBRUARY 26, 1940

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Ketene Acetals. IV. Polymers of Ketene Diethylacetal[1]

BY PAUL R. JOHNSON,[2] HARRY M. BARNES[3] AND S. M. MCELVAIN

One of the first chemical properties of ketene acetal to be noticed was its readiness to polymerize. The polymer appeared as a thin, white deposit on the interior of the flasks and condensers in which ketene acetal had been distilled and also as a semi-solid gum which settled out of distilled samples of ketene acetal after a few days of standing. It soon was noted that distillation apparatus that had been cleaned with the ordinary chromic acid–sulfuric acid mixture before the distillation of ketene acetal acquired an excessive amount of the polymer on the inner glass surfaces. If, however, the interior of the apparatus were washed with an aqueous alkali solution after the use of the acid cleaning solution, and then rinsed and dried in the usual manner, the amount of polymer formed during the distillation of ketene acetal was scarcely noticeable. Similarly, dusting the interior of the containers in which ketene acetal was kept with sodium or potassium *t*-butoxide practically eliminated the polymerization of the acetal on standing.

Although acidified glass surfaces cause some polymerization of ketene acetal, this catalyst is not efficient enough to allow for the preparation of the polymer in quantity. In the first paper of this series[4] it was reported that heat caused polymerization of the acetal. It is now believed that the polymerization then noted was due to the acidity of the inner surface of the container in which the acetal was heated, since later experiments have shown that ketene acetal may be heated at 190–240° for six hours in *new* Pyrex tubes without any perceptible polymerization. Also, a sample of ketene acetal sealed in a new soft-glass container and kept in diffuse sunlight has remained clear and mobile after three years.

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[1] The third paper of this series is Magnani and McElvain, THIS JOURNAL, **60**, 2210 (1938). This work was supported in part by the Wisconsin Alumni Research Foundation.

[2] du Pont Post-doctorate Research Assistant, 1938–1940.

[3] Wisconsin Alumni Research Foundation Scholar, 1935–1936, Research Assistant, 1937–1938.

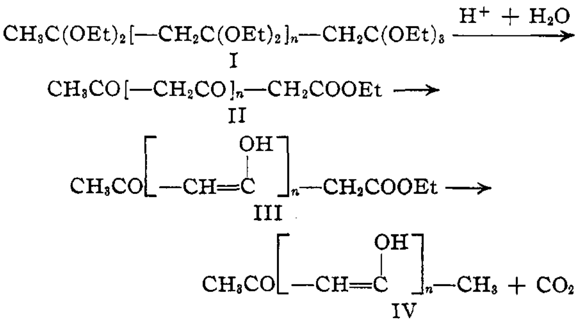
[4] Beyerstedt and McElvain, THIS JOURNAL, **58**, 529 (1936).

A search for other catalysts for this polymerization showed that benzoyl peroxide, which is such an efficient catalyst for the polymerization of many vinyl compounds, has no appreciable effect on ketene acetal, but that a number of metallic chlorides are very powerful catalysts for its polymerization. Barium, mercury and calcium chloride are least effective. In the order of increasing effectiveness as catalysts to transform ketene acetal into an immobile gel are the chlorides of nickel, cobalt, cadmium, zinc, iron, and aluminum. The cobalt and cadmium chlorides cause eventual polymerization to a white solid, but the cobalt polymer becomes discolored after twelve to twenty-four hours. The polymers obtained from nickel, zinc, iron, and aluminum are pasty products which rapidly turn brown or red. The most satisfactory polymer is that obtained with cadmium chloride, and all of the work which is now reported was done with this polymer.

The addition of a trace (6 mg. per 10 g. of acetal) of cadmium chloride to ketene acetal transforms it in a few hours, without any marked thermal effect, into a white, wax-like solid which contains about 45% of unpolymerized ketene acetal. The removal of the monomer by heating (100°) under reduced pressure (0.5 mm.) leaves the polymer as a perfectly dry, white powder. The carbon and hydrogen content of this polymer is practically the same as for ketene acetal; the ethoxyl value is slightly lower than that found for the monomer. The polymer is insoluble in all organic solvents, although ketene acetal and the aromatic hydrocarbons produce a noticeable swelling. The dry polymer is quite stable to heat, showing no evidence of decomposition at temperatures up to 200°. It is completely stable to alkali and is recovered without any apparent change after treatment with boiling 10% sodium hydroxide solution. The polymer is, however, very sensitive to acids. It slowly turns to a brownish-red powder when allowed to stand in the laboratory air for twenty-four hours. Dilute acids at room temperature convert it at once to a red oil which is insoluble in water. Refluxing the polymer with dilute acid converts it to a reddish-black oil which solidifies, on cooling, to a brittle glass. Both of these red polymers are alkali-soluble but are quite insoluble in other solvents. The difference between them appears to be in the extent to which ethoxyl groups have been removed by hydrolysis.

It seemed likely from previous work on unsymmetrically substituted ethylenes[5] that ketene acetal would polymerize in a "head to tail" manner. This supposition was supported by the properties of the red product obtained from the acid hydrolysis of the polymer. The color and alkali solubility of this product indicate a poly-1,3-diketone in an enolic, and hence highly conjugated, form. An unsuccessful attempt to obtain such a poly-1,3-diketone from poly-dichloroethylene has been reported.[6] This type of polyketone was undoubtedly obtained by Marvel and Denoon[5a] as the oxidation product of polyvinyl alcohol with dichromate. Although they did not isolate the polyketone they did obtain acetone from the alkaline hydrolysis of it.

The simplest representations of the white and red polymers from ketene acetal, on the basis of a "head to tail" union, are I and IV. In I and the intermediate compounds, II and III, the ends of the chain are shown completed by the addition of a molecule of alcohol. It is seen that I has a saponifiable end-group, but attempts to estimate n by saponification equivalents were unsatisfactory. The values of the equivalents obtained ranged from 1600 to 3000 and this, together with the fact that the polymer remained insoluble in alcoholic alkali, indicated that adsorption of varying amounts of alkali on the polymer, rather than saponification, had occurred. However, the values obtained from the amount of carbon dioxide evolved during the acid hydrolysis of I to the polyketone (IV) were quite consistent and indicated a molecular weight of 2600–2700 for I. Such molecular weights show n in formula I to be 20–21. Since linear polymers in this range of polymerization are generally soluble in some of the organic solvents, the value of n as determined from the carbon dioxide evolved from the hydrolysis of I



$$CH_3C(OEt)_2[-CH_2C(OEt)_2]_n-CH_2C(OEt)_3 \xrightarrow{H^+ + H_2O}$$

I

$$CH_3CO[-CH_2CO]_n-CH_2COOEt \longrightarrow$$

II

$$CH_3CO\left[-CH{=}\overset{OH}{\overset{|}{C}}\right]_n-CH_2COOEt \longrightarrow$$

III

$$CH_3CO\left[-CH{=}\overset{OH}{\overset{|}{C}}\right]_n-CH_3 + CO_2$$

IV

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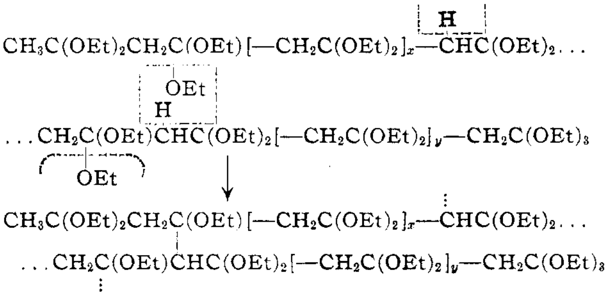
(5) Marvel and co-workers, (a) THIS JOURNAL, **60**, 280, 1045 (1938); (b) *ibid.*, **61**, 1682, 3156, 3234, 3241, 3244 (1939); (c) *ibid.*, **62**, 45 (1940).

(6) Staudinger and Feistt, *Helv. Chim. Acta*, **13**, 832 (1930).

must be considered as a measure of the average length of unit chains that have undergone cross-linking. The nature of this cross-link has not been determined, but it is quite likely that it results from inter-unit loss of alcohol in some such manner as



V

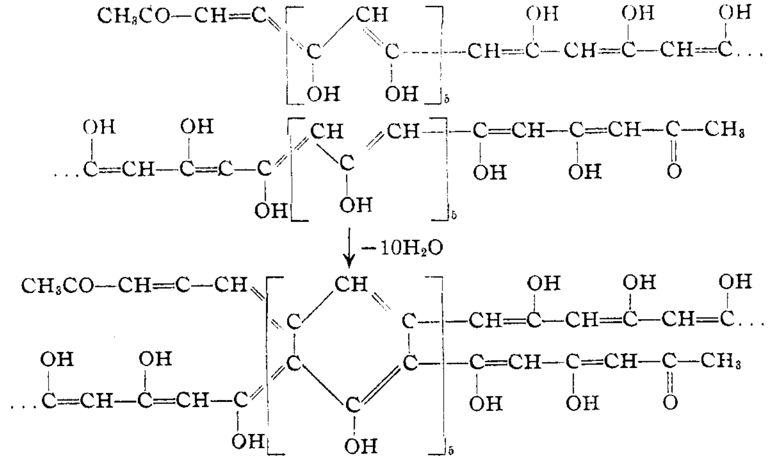
The amount of cross-linking per unit chain is not known but it cannot be very extensive because the ethoxyl content of the polymer (V) is very little lower than that of ketene acetal itself.

Approximate confirmation of the molecular weight of I as calculated from its yield of carbon dioxide was obtained from the other hydrolysis product, the red polymer. The carbon and hydrogen analyses of this polymer suggest an empirical formula of $C_{45}H_{38}O_{17}$, instead of $C_{45}H_{48}O_{22}$ which IV would have if n is 21. This indicates that the red polymer is composed of units of IV cross-linked by bonds resulting from the loss of an average of five molecules of water per unit of IV as in VI. It is unlikely that the end methyl groups in IV are involved in this cross-linkage. If this is the case, the red polymer would yield, on vigorous oxidation, two molecules of acetic acid for each unit of IV and for each molecule of carbon dioxide that had been obtained from the white polymer. On the basis of the empirical formula, $C_{45}H_{38}O_{17}$, 425 g. of the red polymer would be expected to produce 1 mole of acetic acid.

An alkaline solution of the red polymer was attacked rapidly by potassium permanganate and completely oxidized (to a permanent permanganate color) at 100°. On acidification 80% of the carbon of the polymer was evolved as carbon dioxide. Determinations of the acetic acid formed in a number of these oxidations gave values between 558 and 645 as the number of grams of polymer necessary to produce 1 mole of acetic acid. Considering the experimental errors involved in the determination, these results represent maximum values and are sufficiently close to the theoretical value of 425 to lend support to the molecular weight of I as determined by hydrolytic decarboxylation.

Attempts to obtain a neutral equivalent of the red polymer were unsuccessful. The usual colorimetric methods, of course, were not applicable and a potentiometric titration of an alkaline solution of the polymer using an antimony–antimony-oxide electrode gave a titration curve which showed no definite break except at the point of complete precipitation of the polymer.

The red polymer that was obtained by the hydrolysis and decarboxylation of I was very resistant to further hydrolysis. Heating in a bomb at 200° in 10% sulfuric acid for seven hours gave a trace of acetone and some acetic acid. When it was heated with 5% aqueous sodium hydroxide at 240° for twenty-two hours, acetone together with a considerable quantity of acetic acid was obtained. Acidification of the alkaline solution gave a reddish-black precipitate, the analysis of which showed an increase in the ratio of carbon to hydrogen and oxygen over that present in the original red polymer.



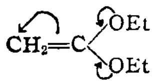
VI

The formation of acetone and acetic acid together with the higher ratio of carbon to hydrogen and oxygen in the polymer remaining after the drastic alkaline hydrolysis of VI suggest that this hydrolysis involves the cleavage of side chains from the cyclic nuclei of VI.

That the color of the red polymer is due to its high conjugation, which is most simply illustrated by the cross-linking of two chains of IV in VI, is shown by the fact that the color can be removed by hydrogenation. This hydrogenation was carried out on an alkaline solution of the polymer, with Raney nickel as the catalyst, at 225° and under 200 atmospheres of pressure. After an initial absorption of hydrogen the reduction stopped due to a coating of a tarry material on the catalyst. The red color of the solution remained but it was finally removed by separating the deactivated catalyst and continuing the reduction with fresh Raney nickel. Acidification of the resulting alkaline solution gave a tan-colored precipitate which amounted to about 12% of the weight of the red polymer taken for hydrogenation. From the filtrate ethyl alcohol and acetic acid could be distilled. Evaporation of the solution left a dark, viscous, alcohol-soluble oil which was not investigated further.

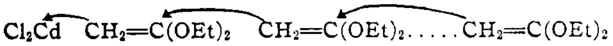
The results described above leave no doubt that, in the main, the ketene acetal polymers are built up by a "head to tail" linking of the monomer. This is further substantiated by the fact that nitric acid completely oxidizes the red polymer without leaving a trace of residue, a fact that shows there is no "head to head, tail to tail" linkage present, since this type of structure would be expected to leave succinic acid on such oxidation.

The mechanism by which ketene acetal undergoes polymerization is suggested by its structure. It is an unusual hetero-enoid system[7] in that two very effective hetero atoms, oxygen, are attached to the same unsaturated carbon atom. The anionoid center which is built up on the methylene carbon by the electromeric shifts from the hetero atoms, thus



$$CH_2{=}C(OEt)_2$$

is very powerful as is shown by the readiness with which ketene acetal adds compounds of the type of water, alcohol, acids, etc., which are capable of furnishing such a cationoid addendum as a proton. If the negative portion of the addendum (*e. g.*, :OH, :OEt, :Br, RCOO:, etc.) is sufficiently mobile it will add to the carbon atom that carries the hetero atoms. If, however, there is no mobile anion (as in the case of the acidified glass surfaces) or if the highly polarized methylene group of the acetal can coördinate with a metal, such as cadmium chloride, a chain reaction may be initiated and propagated in the following manner[8]:



$$Cl_2Cd\ \ CH_2{=}C(OEt)_2\ \ CH_2{=}C(OEt)_2 \ldots\ldots CH_2{=}C(OEt)_2$$

Addition of the proton and the ethoxyl group from a molecule of alcohol to the ends of the polymer chain would release the catalyst from the methylene group and saturate the carbon atom at the other end of the chain.

The Dimer and Trimer of Ketene Diethylacetyl.—When ketene acetal was polymerized with a larger amount of catalyst (36 mg. per 10 g. of acetal) the reaction was very vigorous and the temperature rose sufficiently to cause refluxing of the acetal. The polymer so obtained was a soft gel from which a number of products were removed by distillation under diminished pressure. Up to 100° (0.5 mm.) a mixture of ketene acetal and ethyl orthoacetate, representing 8–15% of the weight of the starting material, distilled. Between 100–130° (0.5 mm.) a product, amounting to about 13% of the starting material and which proved to be a dimer of ketene acetal, came over. At 150–160° (0.5 mm.) another liquid product, amounting to about 20% of the original ketene acetal distilled; also a small amount of ethyl alcohol collected in a cold trap during the distillation of this higher boiling product. The residual polymer is a dry, light tan solid, the properties of which were quite similar to those of the white polymer described above.

The dimer of ketene acetal could not be obtained analytically pure. Although fractionation yielded a product with a constant boiling point and refractive index, the ethoxyl content was generally 2–3% lower than the theoretical value for VII. Work with this dimer was hampered by its tendency to lose alcohol on standing.[9] Freshly prepared samples showed molecular weights of 207–212 as determined by the freezing point of benzene (theoretical for VII, 232) and saponification equivalents of 217–239. Hydrolysis of the dimer by dilute acid yielded acetone and treatment with 95% alcohol containing a trace of hydrochloric acid, converted it, practically quantita-

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(7) Robinson, "Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions," Institute of Chemistry of Great Britain and Ireland, London (1932); Gilman, "Organic Chemistry," Vol. II, John Wiley and Sons, New York, 1938, p. 1679.

(8) Only one chain of ketene acetal molecules is shown coördinated with cadmium chloride; obviously two such chains would be required to give the metal a complete octet of electrons.

(9) For example, one sample showed an ethoxyl content of 74.2% immediately after distillation, but a month later this sample contained only 63.0% ethoxyl.

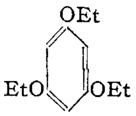
tively, into acetoacetic ester. It absorbed bromine rapidly. All of these properties are readily explained by structure VII.[10]

$$CH_3C(OEt)_2CH{=}C(OEt)_2$$

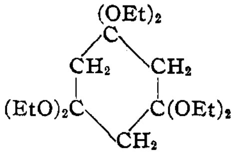
VII

$$CH_3C(OEt)_2CH_2{-}C(OEt)_2CH{=}C(OEt)_2$$

VIII



IX



X

$$CH_3COCH_2COCH_2COOEt$$

XI

The fraction boiling at 150–160° (0.5 mm.) proved to be a mixture of the open chain trimer (VIII) and at least one other product. Fractionation failed to give a product with a constant refractive index although the product boiled over a rather narrow range. Ethoxyl determinations showed that successive fractions had approximately the same composition as ketene acetal. Cryoscopic methods and saponification equivalents gave widely varying values for the molecular weight. When a portion of this fraction was heated with 5% sulfuric acid, a small amount of a solid steam distilled. This product was shown to be 1,3,5-triethoxybenzene (IX). It seems likely that it was formed by the loss of alcohol from the cyclic trimer 1,1,3,3,5,5-hexaethoxycyclohexane (X) during the distillation of the trimer fraction, since alcohol appeared in the cold trap as this fraction was collected. The possibility that IX is formed by cyclization of the open chain trimer (VIII) was shown to be unlikely by the fact that fractions which were known to contain at least 50% of this trimer could not be converted to IX by heating for two hours at 180°.

When the trimer fraction was treated with 95% alcohol containing a trace of acid it was converted into ethyl γ-acetoacetoacetate (XI), which was characterized as the copper derivative and as the lactone of γ-acetoacetoacetic acid. An estimate of the amount of the trimer VIII that was present in the fraction was obtained by distillation under atmospheric pressure of the ethyl acetoacetoacetate formed from the trimer. Acetylacetone was formed by this distillation and the amount collected indicated that the trimer fraction was at least 50% of the open chain trimer VIII.

It should be mentioned that the dimer and trimer of ketene acetal are formed concurrently with the polymer and are not pyrolysis products of it. This is shown by the fact that the polymer prepared from a trace of cadmium chloride may be heated at 155° and under 0.5 mm. pressure for several hours without yielding any distillate. It is believed that the higher temperatures produced by the rapid polymerization of ketene acetal interrupt some of the reaction chains so that considerable amounts of the dimer and trimer are formed along with the polymer.

Substituted Ketene Acetals.—In contrast to the ease with which ketene acetal undergoes polymerization, the halogenated ketene acetals[11] do not polymerize. Samples of these compounds stored in ordinary glass bottles in diffuse daylight are, after eighteen months, clear and mobile. Neither the mono- or dichloro-ketene acetals nor the corresponding bromo compounds showed any tendency to polymerize with cadmium, cobalt or iron chloride. A sample of chloroketene acetal was heated with cadmium chloride at 110° for seventy hours without any apparent change. Another sample of this acetal, after heating for eighteen hours with benzoyl peroxide, still reacted as vigorously with water as did the original material. Boron trifluoride and the boron trifluoride–ether complex react with chloroketene acetal to produce a mobile red oil, but no material of a high polymer nature could be obtained by prolonged heating with this catalyst.

Experimental

Ketene Diethylacetal.—The ketene acetal used in this work was prepared by the action of potassium *t*-butoxide on bromoacetal[12] instead of iodoacetal which was used in the first paper[4] of this series. To 550 g. of *t*-butyl alcohol in a 1-liter round-bottom flask, with a small side tube and reflux condenser fitted with a calcium chloride tube, was added 39 g. (1 atom) of potassium. The alcohol was refluxed until all of the potassium had dissolved (about twelve hours). Then 198 g. (1 mole) of bromoacetal was added to the *t*-butyl alcohol solution and the resulting solution refluxed for about five hours. Without attempting to remove the precipitated potassium bromide, the reaction mixture was fractionated through an 18-in. (46-cm.) Vigreux column, equipped with a total-reflux, partial take-off distilling head and the *t*-butyl alcohol slowly distilled from an oil-bath at a reflux ratio of about 8:1.

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[10] The possibility of this dimer being 1,1,3,3-tetraethoxycyclobutane was considered, but the marked unsaturation of the dimer and the apparent tendency of the cyclic trimer to lose alcohol seemed to support the open chain formula (VII).

[11] Beyerstedt and McElvain, THIS JOURNAL, **59**, 2266 (1937); Magnani and McElvain, *ibid.*, **60**, 2210 (1938).

[12] Filachione, *ibid.*, **61**, 1705 (1939).

When the alcohol ceased distilling at a bath temperature of 125° the pressure was lowered to 200 mm. and the remainder of the alcohol removed at 50–52°. A small amount of intermediate was followed by the distillation of ketene acetal at 83–85° (200 mm.). When an ebullition tube was used during the distillation nitrogen, rather than laboratory air, was drawn through it. The yield of ketene acetal amounted to 70 g. (60% of the theoretical).

Determination of Ethoxyl in Ketene Acetals.—In the past, attempts to apply the Viebock ethoxyl technique to ketene acetals have not been very successful. The results not only have been low, but have varied over a wide range. With ketene acetal and compounds derived from it satisfactory results were never obtained, while with the halogenated ketene acetals it was only by the most careful manipulation that acceptable analyses were made. The difficulty appeared to be due to the rapid hydrolysis of the acetals by the hydriodic acid and loss of ethyl alcohol before it was converted into ethyl iodide. The suggestions of Elek[13] improved the results somewhat but consistently accurate analyses could not be obtained even with these refinements in technique.

It was found necessary to redesign the apparatus so that any alcohol produced by the rapid hydrolysis of the sample could not escape from the reaction chamber without passing through boiling hydriodic acid. The apparatus that was found to give the best results is shown in Fig. 1. Flask A (25 ml.) was charged with 10 ml. of hydriodic acid (sp. g. 1.7), a few crystals of phenol, and about 40 mg. of red phosphorus; flask B (25 ml.) was charged with 2 ml. of hydriodic acid and 20 mg. of red phosphorus; a 5% cadmium sulfate–sodium thiosulfate solution was used in the scrubber C; in the absorption tube D was placed 10 ml. of a 10% solution of sodium acetate in acetic acid, to which 15–30 drops of bromine (approximately 20 drops for every 15 mg. of ethoxyl in the sample) had been added; in the tube E was placed 5 ml. of the acetate–acetic acid solution and about 5 drops of bromine. Before the start of the determination the acid in flask B was heated to gentle refluxing, and a slow stream of carbon dioxide allowed to pass through the system. The sample (15–30 mg.) was weighed into a small glass cup with ground in stopper and dropped into the reaction flask A at room temperature. The flask was reconnected to the apparatus as quickly as possible, and then slowly heated to gentle refluxing. Heating was continued for thirty minutes with a slow stream of carbon dioxide, and for fifteen to thirty minutes with a faster flow of the gas to carry the last traces of the ethyl iodide into the absorbent. The tubes D and E were then removed and their contents washed into an Erlenmeyer flask for the iodometric titration.

This apparatus has been found to give very satisfactory results with compounds related to ketene acetal. However, ketene acetal itself gave consistent values of 76.6% ethoxyl (77.6% is theoretical) regardless of the method of preparation of the compound or wide variations in technique of the determination.

Polyketene Diethyl Acetal.—To 83 g. of freshly distilled ketene acetal was added 50 mg. of powdered cadmium chloride and the polymerization allowed to proceed with occasional shaking. Several hours were required to reach the gel stage, after which the polymer was stirred to distribute the catalyst through the gel. After standing overnight the polymer was a waxy white solid. It was transferred to a distilling flask and heated in an oil-bath at 100° (0.5 mm.) for two hours. During this time 37 g. of ketene acetal collected in a carbon dioxide snow-acetone trap. The remaining polymer was a white powder

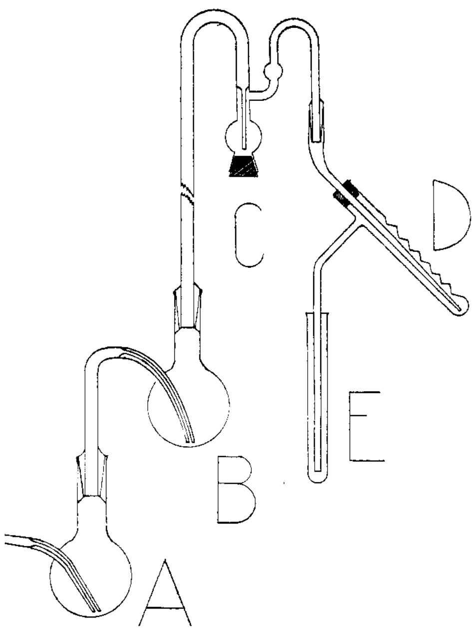

Fig. 1.

Anal. Calcd. for $(C_6H_{12}O_2)_x$: C, 62.02; H, 10.41; OC_2H_5, 77.6. Found: 62.19, 9.85, 76.3.

That the large recovery of ketene acetal is not due to depolymerization is shown by the fact that the monomer could be recovered from the polymer just as well by extraction in a soxhlet extractor with ether as by heating under diminished pressure. Also, heating the remaining polymer for one hour at 155° (0.5 mm.) gave no distillate, while heating at 210° (0.5 mm.) for one and one-half hours gave only a small amount of ethyl alcohol as a distillate.

When the dry polymer was heated at 250° (0.5 mm.) a fairly rapid decomposition took place and ethyl alcohol amounting to 27% of the weight of the original polymer was obtained as a distillate. The material remaining in the flask after this pyrolysis was an acetone-soluble, viscous, red tar.

The white ketene acetal polymer is insoluble in all of the common organic solvents including aniline, anisole, nitrobenzene, acetal and ketene acetal. The latter liquid and the aromatic hydrocarbons caused a noticeable swelling of the polymer. It is remarkably stable to alkali, remaining apparently unchanged after refluxing with a 10% aqueous solution of sodium hydroxide. It is, however, extremely sensitive to acids, being converted into a red oil immediately by aqueous acids. Refluxing with acid gives the red polymer described below.

Hydrolytic Decarboxylation of Polyketene Acetal.—A weighed sample of the polymer was placed in a 50-ml.

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[13] Elek, *Ind. Eng. Chem., Anal. Ed.*, **11**, 174 (1939).

flask having a side arm and attached through a reflux condenser to a carbon dioxide absorption train. To the polymer was then added 25 ml. of a carbon dioxide-free 5% aqueous solution of sulfuric acid and the acid refluxed, with a stream of nitrogen passing through the system, until the ascarite tube in the absorption train attained constant weight. The unit weight of the polymer was calculated on the basis that one polymer unit would produce one molecule of carbon dioxide. Table I shows the data from two representative runs.

TABLE I

Sample, g.	CO_2, g.	Unit wt. of polymer calcd.
3.0464	0.0510	2628
3.1919	0.0515	2727

Hydrolysis of Polyketene Acetal. The Red Polymer.—Polyketene acetal (30 g.) was refluxed for half an hour in 50 ml. of 0.3 *N* sulfuric acid. The mixture was then cooled and the supernatant liquid poured from the viscous red precipitate. The precipitate was treated with 100 ml. of distilled water and the water refluxed for a few minutes, after which it was decanted into the original sulfuric acid solution. After cooling and solidifying the red polymer was ground to a fine powder, washed onto a filter and dried. The yield amounted to 8.9 g.

The aqueous acid solution, obtained by the two decantings, contained some of the red polymer in colloidal suspension. This solution was distilled until 100 ml. of distillate had been collected. The density of this distillate indicated that it contained about 24 g. of ethyl alcohol (theoretical for the amount of polyketene acetal used, 23.3 g.). The distillation of the alcohol caused the suspension of the red polymer to precipitate. By filtration an additional 1.1 g. of this product was obtained, which brought the total yield to 10 g. (theoretical, 11.4 g.).

Anal. Calcd. for $(—CH_2CO—)_x$: C, 57.2; H, 4.76. Found: C, 63.6; H, 4.49. Calcd. for $C_{45}H_{38}O_{17}$: C, 63.5; H, 4.47.

The red polymer is sufficiently soluble in alcohol and acetone to give a light red solution, but it is insoluble in ether, chloroform and benzene. It dissolves readily in dilute alkali to give a deep red, almost black solution from which it is not precipitated by saturation with carbon dioxide. Acidification of the alkaline solution precipitates the polymer as a gelatinous brownish-red precipitate. When heated to 60–70° the red polymer softens and changes to a viscous, dark red oil.

Oxidation of the Red Polymer.—A weighed sample of the solid red polymer was dissolved in 50 ml. of 0.1 *N* sodium hydroxide and carefully washed into a reaction flask which was connected through a reflux condenser to a carbon dioxide absorption train. The solution was heated to boiling and then a 1 *N* solution of potassium permanganate was added in portions from a buret until a permanganate color at 100° persisted for fifteen minutes. The oxidation required about ninety minutes. The mixture then was cooled and 50 ml. of 10% sulfuric acid added. The acidified solution was boiled to expel the carbon dioxide while the system was swept out with nitrogen. The acidified solution was centrifuged and the supernatant liquid decanted from the manganese dioxide which was washed with water and recentrifuged until the washings were neutral to litmus. The washings and original solution were combined and distilled until only 50 ml. remained. The distillate was titrated with standard alkali. Portions of water were added to the residue from the distillation and distilled out until negligible titration was obtained. Acetic acid was shown to be the acid present in the distillate by its Duclaux numbers and the melting point of its *p*-toluidide. Table II shows the results of two such oxidations.

TABLE II

Sample g.	1 *N* $KMnO_4$ used, ml.	CO_2, g.	Millimoles of acetic acid	Polymer per mole acetic acid, g.
0.6836	105	1.2898	1.2238	558
0.4442	68	0.8734	0.6879	645

A 2-g. sample of the white polyketene acetal was hydrolyzed by boiling with 50 ml. of 1% nitric acid. The alcohol formed was removed by distilling out one-half of the solution. The remainder of the solution which contained the red polymer was treated with 5 ml. of concentrated nitric acid and evaporated to dryness on a steam-bath. The black residue was treated with concentrated nitric acid until its color was destroyed. At this point no residue whatsoever remained.

Hydrolysis of the Red Polymer.—After heating the polymer in a sealed tube with 10% sulfuric acid at 200° for seven hours, 85% of it was recovered. The acid solution contained a trace of acetone and some acetic acid. Alkaline hydrolysis was much more satisfactory. A solution of 2 g. of the polymer in 60 ml. of 5% sodium hydroxide was placed in a steel bomb and heated at 240° for twenty-two hours. The hydrolysis solution then was washed into a distilling flask and about one-third of its volume distilled out. Acetone was determined quantitatively in this distillate as the 2,4-dinitrophenylhydrazone, and also by the procedure of Marasco.[14] The two procedures checked and showed the total yield of acetone from the hydrolysis to be 0.08 g.

Acidification of the reddish-black solution, remaining after the removal of the acetone, with dilute sulfuric acid precipitated 1.0 g. of a black substance which contained 73.9% of carbon and 4.6% of hydrogen. The acid solution was distilled, as described above, until all of the acetic acid had been removed. Titration with standard alkali showed that the distillate contained 0.35 g. of acetic acid. It was further identified as the *p*-toluidide.

Hydrogenation of the Red Polymer.—A solution of 11 g. of the red polymer in 100 ml. of 1% sodium hydroxide was refluxed for a short time over Raney nickel, which had been freed from the alcohol under which it was stored by several washings with distilled water. After cooling, the solution was decanted from the nickel and made up to 250 ml. with water that had been used to wash the nickel. This solution, together with 3 g. of washed Raney nickel, was placed in a bomb and shaken with hydrogen under 3500 lb. (233 atm.) pressure at 225° for five and one-half hours. During this time 26 (±2) moles of hydrogen were absorbed on the basis of a molecular weight of 850 (calcd. for $C_{45}H_{38}O_{17}$). The alkaline solution was still red in color

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(14) Marasco, *Ind. Eng. Chem.*, **18**, 701 (1926).

and the catalyst was coated with about 1.2 g. of an acetone-soluble tar. This deactivated catalyst was replaced with fresh catalyst and the hydrogenation continued under the same conditions for another five hours. A small amount of additional hydrogen was absorbed, and the alkaline solution was no longer red, but was yellow with a green fluorescence. From this alkaline solution 0.8 g. of ethyl alcohol was distilled. Acidification of the remaining solution gave a precipitate of 1.4 g. of a tan-colored solid. This product was not investigated further. From the acidified solution 0.54 g. of acetic acid was removed by distillation. After removal of the acetic acid the solution was evaporated at 200 mm. and the residue extracted with alcohol. This alcoholic solution on evaporation left 0.8 g. of a dark, viscous oil.

The Dimer and Trimer of Ketene Acetal.—To 74 g. of freshly distilled ketene acetal was added 300 mg. of cadmium chloride. Polymerization was very rapid and the temperature of the reaction was sufficient to cause refluxing of the ketene acetal. In fifteen minutes after the addition of the catalyst the acetal became a moist solid. After standing overnight, the flask containing the polymer was attached, through a condenser, receiver and cold trap, to a vacuum pump and heated in an oil-bath under 0.5 mm. pressure. The fractions were collected at the bath temperature, in the amounts and in the places as shown in Table III.

TABLE III

Fraction	Bath temp., °C.	Wt., g.	Collected in
1	to 25°	2.4	Trap
2	102–108	3.65	Trap
3	102–108	4.35	Receiver
4	108–130	5.35	Receiver
5	152–159	1.80	Trap
6	152–159	15.00	Receiver

Fractions 1 and 2 were mixed and fractionated and shown to be a mixture of ketene acetal and ethyl orthoacetate. Fraction 3 was fractionated through an 8-in. (21-cm.) Stedman column and yielded 2.45 g. of material boiling at 61–62° (0.5 mm.). By a similar fractionation 2.75 g. of material of the same boiling point was obtained from fraction 4. This material contained the dimer of ketene acetal, the characterization of which is described below. Fraction 5 proved to be ethyl alcohol. Fraction 6, after the removal of a small amount of impure dimer and an intermediate fraction, yielded 12 g. of a product boiling at 91–92° (0.1 mm.) which is discussed below.

The fraction that boiled at 61° (0.5 mm.) showed an ethoxyl content of about 75% (the ethoxyl content of ketene acetal and its dimer (VII) is 77.6%); n^{25}_{D} 1.4258 for the first and last portions of the fractions; d^{25}_{4}, 0.9441; mol. wt. (freezing point of benzene), 207, 212; saponification equivalents varied from 217 to 239 (calcd. value for VII, 232). A sample of this fraction that had been opened from time to time was found, after a month, to have an ethoxyl content of 63%. This lower ethoxyl value may be due to intramolecular loss of alcohol or partial hydrolysis of an acetal group by moisture from the air. No attempt was made to ascertain which of these processes is responsible for the instability of the dimer fraction. Hydrolysis of a portion of this fraction with aqueous 5% sulfuric acid yielded acetone which was characterized as the 2,4-dinitrophenylhydrazone.

A 0.86-g. sample of this fraction was treated with 2 ml. of 95% alcohol containing a trace of hydrochloric acid and the resulting solution heated on a steam-bath under a reflux for ten minutes. The alcohol was removed under diminished pressure and the remaining acetoacetic ester (0.39 g.) was characterized as the semicarbazone, m. p., 129–130°.[15] The dimer does not add absolute alcohol. A 1.0-g. sample of it was allowed to stand with 2 ml. of absolute ethyl alcohol for forty-eight hours. After evaporation of the alcohol under diminished pressure and with a stream of dry nitrogen passing through the liquid, the remaining oil had the same refractive index and ethoxyl content as the starting material. Repetition of the experiment with a trace of hydrogen chloride in the alcohol led to the same results.

The fraction boiling at 91–92° (0.1 mm.), which was obtained from fraction 6 above, had an ethoxyl content of 76% (the ethoxyl content of ketene acetal and its trimer (VIII) is 77.6%). However, the refractive indices of the first and last portions of this fraction varied between 1.4414 and 1.4400. When 2.8 g. of this fraction was refluxed with 3% sulfuric acid for thirty minutes and the resulting mixture distilled, an oily substance, which crystallized on cooling in an ice-bath, came over with the aqueous distillate. After filtration and recrystallization from alcohol, the solid weighed 0.1 g., melted at 43.5°, and contained 64.2% ethoxyl. It was shown to be 1,3,5-triethoxybenzene (% ethoxy, 64.3) by comparison with an authentic specimen prepared by the method of Will and Albrecht.[16]

A 3.2-g. sample of the fraction boiling at 91–92° (0.1 mm.) was treated with 7 ml. of 95% alcohol containing a trace of hydrochloric acid. After standing overnight the excess alcohol was removed under diminished pressure and the remaining oil distilled. It boiled at 87–90° (0.4 mm.) and showed an ethoxyl content of 40.0%. A 0.3-g. portion of this distillate was boiled for a few minutes in 0.3 *N* sulfuric acid and then poured into a saturated solution of copper acetate. The copper derivative which formed immediately was filtered off and dried. It weighed 0.1 g. This blue derivative was suspended in boiling benzene for a few minutes, then filtered and dried. It melted at 183–184°[17] and contained 22.6% ethoxyl (calcd. for the copper derivative of γ-acetoacetoacetic ester, $Cu{\cdot}C_{16}H_{22}O_8$: 22.2%).

Six drops of the trimer fraction were added to 0.5 ml. of 70% sulfuric acid and the mixture warmed to 80° for five minutes. After standing without further heating, for an additional fifteen minutes, an equal volume of water was added. Cooling precipitated the lactone of γ-acetoacetoacetic acid which, after recrystallization from water, melted at 185–187°.[18]

A 1.95-g. portion of the trimer fraction boiling at 91–92° (0.1 mm.) was refluxed with 0.3 *N* sulfuric acid for twenty minutes. After cooling, the mixture was extracted with ether and the ether layer separated and dried. The ether

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[15] Thiele and Stange, *Ann.*, **283**, 29 (1894).

[16] Will and Albrecht, *Ber.*, **17**, 2107 (1884).

[17] Sproxton, *J. Chem. Soc.*, **89**, 1187 (1906).

[18] Collie, *ibid.*, **59**, 609 (1891).

was removed by distillation and the remaining brown liquid heated with a free flame, under atmospheric pressure, until it distilled. Decomposition accompanied the distillation of a yellow oil which came over at 130–140°. The yield of this oil amounted to 0.25 g. and it was shown to be acetylacetone by its conversion to 1-(2,4-dinitrophenyl)-3,5-dimethylpyrazole, m. p. 121–122°, and the comparison of this derivative with an authentic specimen.[19] The 0.25 g. yield of this diketone indicates that the trimer fraction contained at least 50% of the straight chain trimer VIII.

The boiling point of the trimer fraction as well as its content of 1,3,5-triethoxybenzene remained unchanged after a sample of this fraction had been heated at 180° under atmospheric pressure for two hours.

Summary

1. Evidence is presented to show that ketene acetal is converted by cadmium chloride into a white polymer composed of chains having, on an average, 22–23 ketene acetal molecules joined in a head to tail manner. The insolubility of the polymer suggests cross-linking of these chains.

2. The white polymer is converted by acid hydrolysis into an alkali soluble red polymer composed of cross-linked poly-1,3-diketone units which exist in a highly conjugated, enolic form. Molecular weight estimation of this polymer from an end group corresponds fairly well with a similar estimation of the molecular weight of the white polymer.

3. Rapid polymerization of ketene acetal by larger amounts of cadmium chloride produces an open chain dimer and trimer together with 1,3,5-triethoxybenzene. The latter product probably is formed from the cyclic trimer, 1,1,3,3,5,5-hexaethoxycyclohexane.

4. Halogenated ketene acetals cannot be caused to polymerize.

5. An improved method for the preparation of ketene acetal from bromo-acetal is described.

6. The construction and operation of a new apparatus for the determination of the ethoxyl content of the types of acetals encountered in this work are described.

MADISON, WISCONSIN RECEIVED FEBRUARY 23, 1940

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[19] Brady, *J. Chem. Soc.*, 758 (1931).

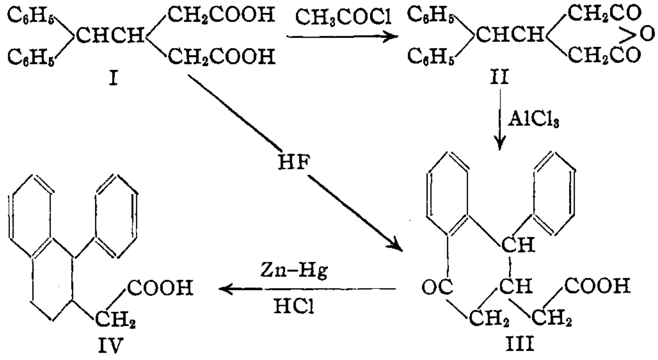
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Synthesis of 2-Methyl-3,4-benzphenanthrene

BY MELVIN S. NEWMAN[1] AND LLOYD M. JOSHEL[2]

Because of the interest in 3,4-benzophenanthrene as a structure possessed of carcinogenic activity, the previously reported synthesis[3] has been modified so that 2-substituted derivatives may be prepared. In this paper is described the synthesis of 2-methyl-3,4-benzphenanthrene[4] and 2-ethyl-3,4-benzphenanthrene.

In the earlier synthesis,[3] β-benzohydrylglutaric acid, I, after conversion to its acid chloride, was cyclized to 1,2,9,10,11,12-hexahydro-2,9-diketo-3,4-benzphenanthrene from which 2,9-disubstituted derivatives were prepared. The present modification consists in treating the anhydride, II, of β-benzohydrylglutaric acid with aluminum chloride whereby 1,2,3,4-tetrahydro-4-keto-1-phenyl-2-naphthaleneacetic acid, III, was isolated in 63% yield. The same keto-acid was obtained more easily in 89% yield by treatment of the acid, I, with anhydrous hydrogen fluoride.[5] By reduction III was converted into 1,2,3,4-tetrahydro-1-phenyl-2-naphthaleneacetic acid, IV.[4]



The remaining steps required for the synthesis of 2-methyl-3,4-benzphenanthrene and 2-ethyl-

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[1] The Elizabeth Clay Howald Scholar at The Ohio State University, 1939–1040.

[2] This material was largely contained in a Dissertation presented by L. M. J. to The Ohio State University in partial fulfillment of the requirements for the Ph.D. degree, June, 1938. Completing experiments were conducted by L. M. J. at Harvard University under tenure of a Finney-Howell Research Fellowship.

[3] Newman and Joshel, THIS JOURNAL, **60**, 485 (1938).

[4] Hewett, *J. Chem. Soc.*, 596 (1936).

[5] Fieser and Hershberg, THIS JOURNAL, **61**, 1272 (1939).