

A STUDY OF THE POLYMERIZATION PRODUCTS OF DIKETENE^{1,2}

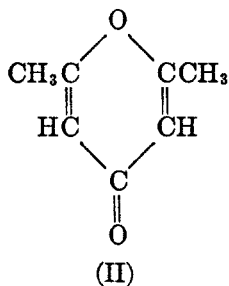
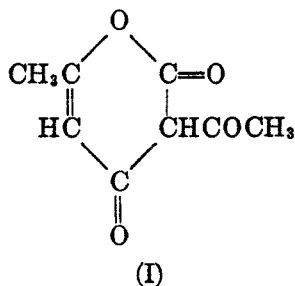
ARTHUR B. STEELE, ALBERT B. BOESE, AND MALCOLM F. DULL

Received December 27, 1948

INTRODUCTION

Although a considerable amount of literature on the polymerization of diketene has developed in recent years (1-5), there appears to have been no study of the mechanism of the polymerization nor of the chemical nature of the products other than the ketene tetramer, dehydracetic acid. This study was undertaken with the object of discovering the course of the reaction, and more particularly of characterizing any additional polymerization products which might be isolated.

Although pure diketene is relatively stable, and not subject to polymerization alone or in neutral solvents at temperatures below 0°, it does undergo ready polymerization at elevated temperatures and in the presence of other materials such as acids, alkalis, and certain salts. With complete transformation of the monomer there is obtained a viscous to semi-solid mass of deep red color. We have now resolved this mixture into three pure components, the expected dehydracetic acid (I) and two others that have not been reported by other investigators.



Diketene of 99.5% purity was polymerized in boiling benzene solution in the presence of sodium phenoxide, according to the procedure of Boese (5). Carbon dioxide was evolved. Processing the reaction products led to the isolation of (I) in 54% yield, 2,6-dimethylpyrone (II) in 4% yield, and a white solid (III), $C_{19}H_{16}O_6$, in 8% yield.

The same products were obtained on polymerization of diketene in benzene, toluene, and xylene solution in the presence of either sodium phenoxide, sodium acetate, tributyl-, or triethyl-amine. Treatment of pure dehydracetic acid under the same conditions caused no reaction.

The chemical nature of (III) is indicated by a variety of means, including infrared and ultraviolet absorption studies and chemical tests. It is a neutral

¹ Presented before the Division of Organic Chemistry, 113th Meeting, American Chemical Society, Chicago, Illinois, April 19-23, 1948.

² Abstracted from a thesis submitted by Arthur B. Steele in partial fulfillment of the requirements for the degree of doctor of philosophy.

substance containing no reactive functional groups, characterized by pronounced susceptibility to oxidation, hydrogenolysis, and absorption of bromine from the liquid state.

Examination of the ultraviolet absorption curve (Fig. 1) in the light of the findings of other investigators (6-10) leads to a number of conclusions regarding the substance.

1. No benzenoid system is present.
2. The maximum at $\lambda = 3020 \text{ \AA}$ indicates the presence of at least one pair of closely associated double bonds, one of which may be a carbonyl bond, although the ketone band at 2800 \AA is absent. An enolic structure is not indicated.

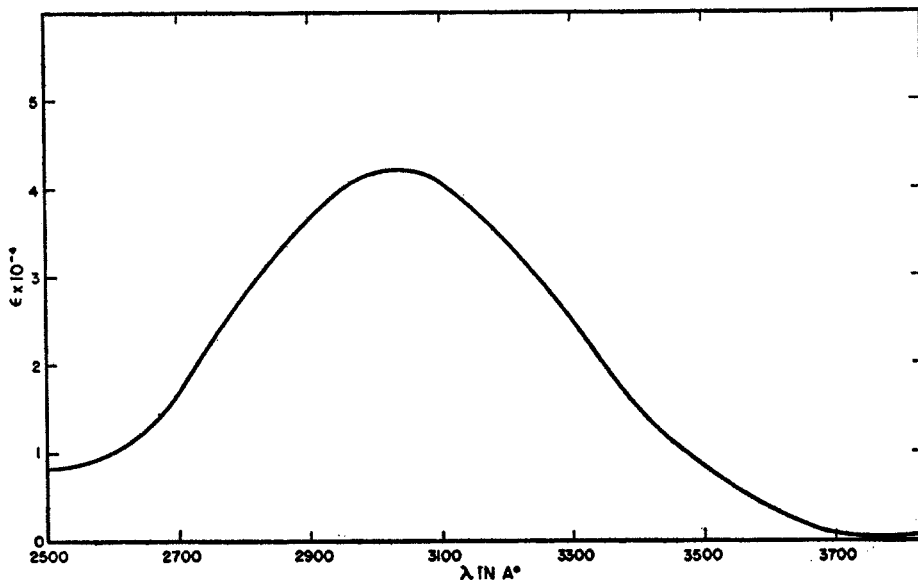


FIG. 1. SPECTROSCOPIC STUDY. ULTRAVIOLET ABSORPTION SPECTRA
Unknown, $2.94 \times 10^{-5} \text{ M.}$ in acetic acid in 1 cm. cell.

3. The breadth of this parabolic band suggests the presence of several groups contributing as vectors to the maximum at 3020 \AA .
4. There is marked similarity between this curve and those of diketene and dehydracetic acid.
5. The ϵ values of the substance and those of dehydracetic acid are of the same magnitude.

The infrared absorption data (Fig. 2) support the following conclusions (11):

1. Because absorption bands at wave lengths in excess of 10 microns are attributable to the vibrations of the molecule as a unit, these bands serve to "finger print" the molecule rather than to indicate presence or absence of functional linkages within the molecule.
2. The absence of "free" hydroxyl groups (in which the hydrogen atom is not affected by any atom except the oxygen to which it is bonded) is indicated, since no absorption is found between 3700 and 3500 cm.^{-1} .

3. Hydroxyl groups subject to intermolecular association and/or internal chelation might provide the band at 3330 cm^{-1} .

4. The triple-bond structure appears to be absent, for no band is observed in the range of $2000\text{--}2300\text{ cm}^{-1}$.

5. The non-appearance of a double band at $1800\text{--}1850\text{ cm}^{-1}$ and $1750\text{--}1800\text{ cm}^{-1}$ indicates the absence of an anhydride group.

6. The absence of an ester carbonyl group is indicated by the lack of a band at $1725\text{--}1750\text{ cm}^{-1}$.

7. The very strong absorption at 1710 cm^{-1} suggests the presence of the keto carbonyl group.

8. The carboxyl structure appears to be absent, for no double band at $1660\text{--}1685\text{ cm}^{-1}$ and $3500\text{--}3700\text{ cm}^{-1}$ is evident.

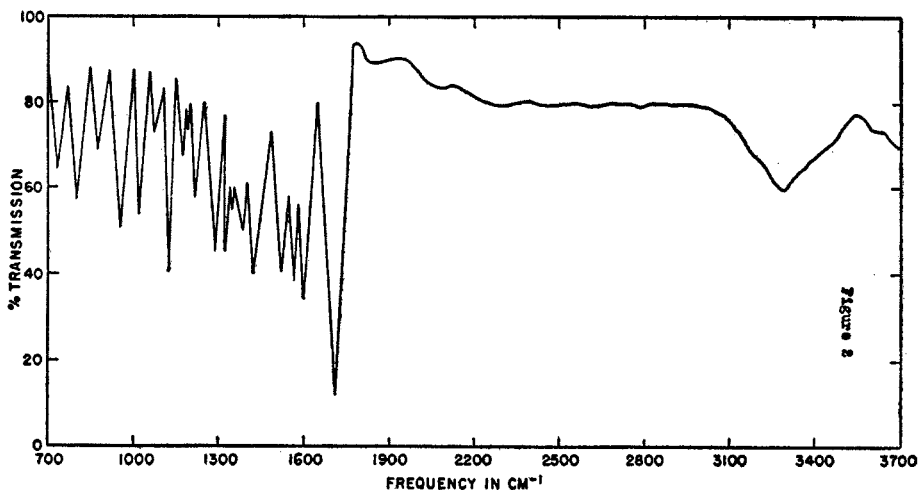


FIG. 2. SPECTROSCOPIC STUDY. INFRARED ABSORPTION

36% by weight of unknown in mineral oil paste. Rock salt disks, 11 microns apart.

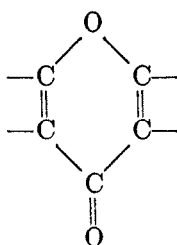
9. The absence of random aliphatic $\text{C}=\text{C}$ linkages is indicated by the absence of a band at $1640\text{--}1660\text{ cm}^{-1}$. However, the presence of a conjugated aliphatic linkage is suggested by a band at 1600 cm^{-1} . The carbon-carbon unsaturation of a benzenoid structure, giving rise to two bands at 1600 cm^{-1} and at 1500 cm^{-1} , is not evidenced.

10. The bands at 1350 , 1392 , and 1410 cm^{-1} suggest the presence of methyl groups.

11. The triplet absorption band at 1350 , 1392 , and 1410 cm^{-1} indicates the presence of the γ -pyrone structure (12).

12. The ketene structure appears to be absent, for no band at 2150 cm^{-1} is evident.

The general conclusion to be drawn from ultraviolet and infrared absorption measurements is that (III) probably contains one or more γ -pyrone rings (IV) with methyl or substituted methyl side chains. This inference is supported by

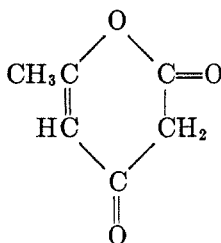


(IV)

an examination of the chemical properties of the substance. Chemical characterization, however, was complicated by the extreme insolubility of the substance in the usual solvents.

The absence of reactive functional groups is indicated by the negative results of all the usual qualitative tests except oxidation, hydrogenolysis, and bromination. Simple hydrogenation does not occur. An acetic acid solution of (III) was not affected by hydrogen at 1800 p.s.i. and 70° in the presence of platinum catalyst.

Clemmensen reduction gives triacetic lactone (V) and (II). It is believed



(V)

that (II) results from spontaneous dehydration of a precursor which is *sym*-diacetylacetone. Hydrogenolysis in the presence of various catalysts gives (I), (II), and (V), while reduction with hydrogen iodide yields (II).

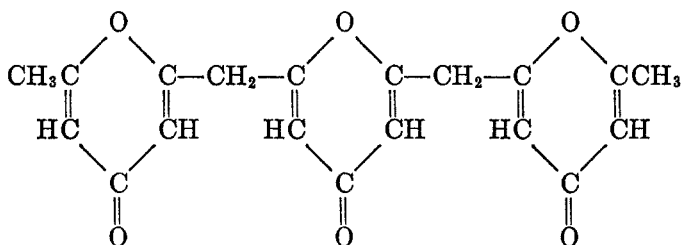
Oxidation with peracetic acid gives (V). Treatment with nitric acid at 40–45° gives four moles of oxalic acid per mole reacted. Oxidation with aqueous periodic acid gives oxalic and acetic acids and carbon dioxide, while treatment with lead tetraacetate in glacial acetic acid causes an evolution of carbon dioxide and the formation of tars. Kühn-Roth oxidation gives unreproducible results, but indicates that the molecule contains two or four carbons oxidizable to acetic acid.

Prolonged digestion with hydrochloric acid gives (V), while treatment with alkali results in complete disruption of the molecule.

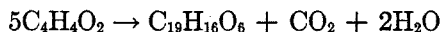
Reaction with liquid bromine gives an unstable addition product which rapidly loses hydrogen bromide, giving $C_{19}H_{10}Br_6O_6$. This demonstrates the presence of six equivalent carbon-carbon double bonds with at least six hydrogen atoms in probably equivalent positions.

These observations accord with the view that the parent ring system is that of γ -pyrone (13).

Hydrogenolysis to (I), (II), and (V) under a variety of conditions, catalytic and otherwise, and resistance to simple hydrogenation are also indicative of pyrone rings, while the evidence of oxidation and of bromination is consistent with this view. Quantitatively, the presence of three pyrone rings is indicated by bromination. On the basis of the foregoing evidence, it is believed that (III) is 2,6-bis-(6-methyl-4-oxo-2-pyranylmethyl)pyrone.

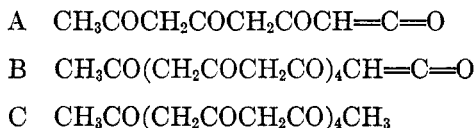


This structure is believed to accord with the experimental facts which have been established, and it remains to consider the mechanism by which such a compound could be produced from diketene. The following molecular equation represents the over-all process.



Carbon dioxide is evolved during the polymerization, while the formation of small amounts of acetone can be accounted for by the reaction of some diketene with water, giving acetoacetic acid which decomposes to acetone and carbon dioxide.

The basic catalyst may be considered to promote reaction of diketene as acetylketene, $\text{CH}_3\text{COCH}=\text{C}=\text{O}$. Condensation starts with two molecules giving (A), and continues until a C_{20} chain is reached (B).



At this stage water adds at the ketene position and decarboxylation occurs to form (C). Enolization of (C) and dehydration gives rise to (III). If water adds at (A) instead of (B), the product of decarboxylation would be *sym*-diacetylacetone. The latter is subject to spontaneous loss of water, yielding (II), which was found.

No compound possessing two γ -pyrone structures within the molecule is anticipated by this mechanism, for such a compound would require a fractional number of diketene units in the linear polymer.

Probably the polymerization of diketene occurs through the carbonyl group and may be followed by rearrangement of the resultant enolic structures to those shown in the equations. This mode of addition would be analogous to the aldol type reaction proposed by Boese (14) for the formation of α,β -unsaturated methyl ketones by reaction of diketene with aldehydes. While this reaction

occurs readily under uncatalyzed conditions, the related reaction with methyl ketones was found in this work to occur very slowly at elevated temperatures, and not at all with other ketones. This result is in line with the known inertness of ketone carbonyl groups relative to those of aldehydes.

EXPERIMENTAL

Diketene. The diketene used in these studies was the commercial product of the Carbide and Carbon Chemicals Corporation. Before each experiment it was redistilled to give a material boiling at 64–65° at 80 mm., and freezing at –6.9°. By analysis a purity in excess of 99 per cent by weight was indicated.

Polymerization of diketene. To 1000 ml. of refluxing benzene containing 1 g. of sodium phenoxide, 900 g. of diketene was added during two hours with constant stirring. The polymerization being exothermic, the diketene was added at such a rate as to maintain refluxing without the application of external heat. During the polymerization it was noted that carbon dioxide was evolved concurrently with the addition of diketene. Quantitatively, approximately 12 mole per cent, based on diketene, was found in the vent gas. After all the diketene had been introduced, refluxing was continued for one hour after which the resulting red solution was allowed to stand at room temperature for sixteen hours. At the end of this time, the odor of diketene had entirely disappeared.

The crude crystalline material which separated was filtered and washed with methanol, the washings being combined with the filtrate. A first crop of 489 g. of crude dehydracetic acid was thus obtained. By concentrating the filtrate to half its original volume on the steam-bath a second crop of 110 g. was recovered from the cooled mother liquor. Small quantities of acetone were detected in the distillate.

The crude acid was dissolved in 1500 ml. of hot methanol and filtered while hot. While most of the crude product was soluble there did remain 58 g. (8%) of a methanol-insoluble material which on recrystallization from glacial acetic acid appeared as a colorless crystalline substance melting at 235–236°.

From the cooled methanol filtrate there was obtained 491 g. (54%) of pure dehydracetic acid, identified by a mixed melting point determination with known material.

The benzene solution remaining from the separation of dehydracetic acid was freed of benzene by low-pressure stripping and the residue distilled under vacuum. A fraction of 41 g., boiling at 140–145° at 10 mm., was recovered. The residue, a dark tarry material, could not be further distilled.

The distillate was redistilled, giving 27 g. (4%) of product boiling at 136–138° at 14 mm. Recrystallization of this material from acetone gave pure 2,6-dimethylpyrone, melting at 131–132°, and identified by analysis, mixed melting point, and conversion to γ -lutidone (15). The still residue was recrystallized from methanol and found to be mainly dehydracetic acid.

IDENTIFICATION OF THE UNKNOWN SUBSTANCE

Solubility. The unknown substance (III) from the above separation is virtually insoluble in all common solvents except boiling 1,4-dioxane and glacial acetic acid, in which it dissolves to the extent of 7.2 grams and 5.2 grams, respectively, per 100 grams of solvent at the boiling point.

Analysis. Qualitative analysis showed the presence of only carbon and hydrogen. Combustion gave C, 67.10%; H, 4.75%; and O (by difference), 28.15%.

Molecular weight. The molecular weight was determined by the method of comparative ebulliometric measurement developed by Swietoslawski (16). Acetic acid was chosen as the best solvent for this purpose. Glacial acetic acid, the boiling temperature of which was 0.064° higher than the condensation temperature, was used in an improved simple

ebulliometer in series with a differential ebulliometer³. The data indicate a molecular weight of 339.

Ultraviolet absorption measurements. All determinations were made in glacial acetic acid, distilled until the distillate passed the ebulliometric specifications stated above.

The ultraviolet data were obtained photographically with a standard Beckman spectrophotometer, the light source being a hydrogen discharge tube between 2200 and 3200 Å and a tungsten filament above 3200 Å. A built-in Brown recorder registered per cent transmission of light directly. The spectrum was examined from 2500 Å to 3800 Å at 10 Å intervals. The result is shown in Fig. 1.

*Infrared absorption measurements*⁴. A sample of (III) was finely ground and mixed with mineral oil to form a paste containing 36% by weight of the unknown. This paste was pressed between two rock-salt discs so that the optical path between the discs was about 11 microns long. The infrared absorption of this assembly was then compared to that of another similar assembly in which the material between the discs was mineral oil alone.

The comparison was made on a Perkin-Elmer infrared spectrometer provided with wavelength drive, automatic signal attenuator, a General Motors amplifier, and a Brown recorder. The resulting spectra were recorded on a photostatic reproduction. The percentage transmission, I/I_0 , over the entire wave length from 1.2 to 16.2 microns was calculated. To provide a graphic representation of the data, a plot of percentage transmission and wave number as abscissa and ordinates, respectively, is shown in Fig. 2.

Bromination. A solution of 11 g. of (III) in 150 g. of liquid bromine was sealed in glass and stored at 2° to 4° for ten days. Excess bromine was removed by distillation, leaving a viscous red oil which, even at ordinary temperatures, spontaneously lost hydrogen bromide with the production of a yellow solid. On recrystallization from acetone there was recovered 2.4 g. of yellow needles, melting at 92–93°.

Anal. Calc'd for $C_{19}H_{10}Br_6O_6$: Br, 59.0. Found: Br, 58.9.

Hydrogenolysis. By the Clemmensen procedure. Into a suitable apparatus was charged 45 g. of (III) in 1500 g. of glacial acetic acid. At 110° to 115°, zinc dust containing a trace of mercury was added slowly to provide continuous ebullition by the evolved hydrogen. These conditions were maintained for 52 hours, after which time the crude mixture was filtered hot to remove salts and unreacted zinc. On cooling, 35 g. of unchanged (III) was recovered by filtration. The filtrate was concentrated by stripping at 38–40° at 40 mm. The residue from this operation was a viscous liquid which slowly crystallized to a low-melting semi-solid mass. On storage at room temperature for five days, the crude product spontaneously changed to a high-melting solid. Fractional distillation produced 2.4 g. of substance identified as 2,6-dimethylpyrone, boiling at 130–132° at 14 mm., and melting at 131–132°.

The still residues from this distillation were recrystallized from water, giving 0.35 g. of a white crystalline product melting at 189–190°. This product was found by analysis and mixed melting point determinations with known material to be triacetic lactone.

By the Adkins procedure. In a series of experiments a three-liter pressure autoclave, equipped with an Aminco shaker mechanism and a heating jacket, was charged with acetic acid, Raney nickel, and (III). In each run the temperature of hydrogenation at a hydrogen pressure of 1000 p.s.i. was progressively increased to provide conditions of greater severity. The details are shown in Table I.

In each experiment the reaction mixture was discharged and filtered hot to remove the catalyst. Unchanged (III) was recovered by filtration on cooling and the filtrate fractionally distilled under low pressures, the distillate and the residues being examined for organic material other than solvent.

³ The authors are indebted to Dr. W. Swietoslawski and Dr. J. R. Anderson of Mellon Institute, Pittsburgh, Pa., for making available ebulliometric apparatus and for helpful advice.

⁴ The authors are indebted to Wayne G. White, Carbide and Carbon Chemicals Corporation, South Charleston, West Virginia, for the experimental infrared absorption data.

In Runs 1 and 2, the starting material was recovered quantitatively.

In Run 3, there was obtained 0.85 gram of solid residue which, after recrystallization from acetone, yielded 0.35 g. of 2,6-dimethylpyrone.

Run 4 provided only slightly higher conversion with approximately 99 per cent of the starting material being recovered.

Under the more drastic conditions of Run 5 approximately 4 g. of the starting material was converted to other products. The residue from the distillation was taken up in hot methanol and cooled, giving a white solid. Recrystallization from methanol yielded 0.90 g. of dehydracetic acid, melting at 110–111°.

After the removal of the catalyst from the reaction mixture in Run 6 there was precipitated on cooling only 32 g. of the starting material. Low-pressure stripping of the solvent produced a residue of viscous tar which gradually solidified to a soft mush, badly discolored to a dark red. Distillation of this residue yielded only a trace of 2,6-dimethylpyrone. Decomposition prevented further exploration by this method. Fractional crystallization failed to yield an identifiable product.

Reduction with hydrogen iodide. A mixture of 10 g. of (III) and 200 g. of a 32% glacial acetic acid solution of hydrogen iodide containing a trace of red phosphorus was placed in a sealed tube of about 500 ml. capacity and heated for 48 hours at 150–155°. When cool, the tube was opened and excess hydrogen iodide and acetic acid removed by low-pressure strip-

TABLE I
CONDITIONS OF HYDROGENOLYSIS: ADKINS PROCEDURE

RUN NO.	WEIGHT (IV) (g.)	WEIGHT ACETIC ACID (g.)	WEIGHT RANEY Ni (g.)	TEMPERATURE °C.	TIME HRS.
1	30	1000	5	25	18
2	30	1000	5	75	10
3	30	1000	5	105	6
4	45	1500	8	120	10
5	30	1000	5	145	6
6	45	1500	8	200	12

ping through a fractionating column. The tar-like residue, weighing 9.3 g., was incapable of resolution by solvent crystallization. Distillation produced 2 g. of 2,6-dimethylpyrone.

This reduction was repeated at 175°, resulting in the formation of heavier tars and only a trace of the pyrone.

Oxidation. With nitric acid. Twenty grams of (III) was dissolved in 200 g. of concentrated nitric acid (70% by weight) at 20°. The solution was maintained at this temperature for 10 hours and then carefully diluted with ice water to ten times the initial volume, the temperature being maintained below 20° throughout the dilution. The starting material was recovered unchanged.

In a second experiment at 40–50° oxalic acid was obtained. This was determined quantitatively by the precipitation of its calcium salt. It was found that 10.30 g. of (III), equivalent to 6.71 g. of carbon, yielded 15.02 g. of calcium oxalate, equivalent to 2.818 g. of carbon. Thus 42% of the carbon in (III) is oxidizable to oxalic acid.

With peracetic acid. Oxidation of (III) was accomplished by treating 15 g. of the substance in 100 g. of glacial acetic acid with peracetic acid, prepared from 714 g. (7.0 moles) of acetic anhydride and 300 g. of 30% hydrogen peroxide (available peracetic acid 16.8% by weight). The reaction mixture was maintained at 100° for ten hours. No crystalline product precipitated on cooling. After removal of water and acetic acid by low-pressure stripping through a fractionating column there remained 2.6 g. of triacetic lactone, melting at 187–189°. A mixed melting point with known material was unchanged.

Hydrolysis with hydrochloric acid. A solution of 25 g. of (III) and 500 g. of glacial acetic

acid was heated to 95° and concentrated hydrochloric acid (36% in water) slowly added until the system was saturated with hydrogen chloride as judged by continuous ebullition by evolved excess hydrogen chloride. The reaction system was maintained for 35 hours at 98–100°. No solid phase separated on cooling. Excess hydrogen chloride, water, and acetic acid were removed by low-pressure stripping, yielding a balsam-like residue from which only the starting material could be isolated by selective solvent extraction. Low-pressure distillation produced a crystallizable distillate, boiling over a wide range. The distillate was recrystallized from water and 3.2 g. of triacetic lactone recovered.

General chemical characterization. Detecting the presence of functional groups was complicated by the extreme insolubility of the compound in common organic solvents. On testing the unknown substance (III) with the appropriate reagents the following facts were established.

- a. It contains no carboxyl group, either as free acid or ester.
- b. Iodoform test was negative.
- c. Tollens Reagent and Fehling's Solution were not reduced.
- d. Ferric chloride solution showed no significant coloration.
- e. Phenylhydrazine failed to produce a phenylhydrazone under the usual conditions.
- f. Chlorination by the action of phosphorus pentachloride or thionyl chloride only charred the compound to carbon.
- g. It showed relatively high solubility in cold concentrated mineral acids; 70 per cent nitric acid, 98 per cent sulfuric acid, 85 per cent phosphoric acid, and 36 per cent hydrochloric acid. On dilution of these acid solutions with cold water the product was precipitated unchanged.
- h. Aqueous alkali, aqueous ammonia, and organic amines dissolved the unknown substance while converting it to resinous tars.
- i. It showed no susceptibility to nitration or sulfonation.
- j. No unsaturation toward bromine at 20°C. in dilute solution was observed.

The reaction of diketene with 2-butanone. A mixture of 420 g. (5.0 moles) of diketene and 360 g. (5.0 moles) of methyl ethyl ketone, boiling at 79–80° (n_D^{20} 1.3786), was heated on a steam-bath at 95–100° for 250 hours.

Fractional distillation through a column of 20 theoretical plates at 5 to 1 reflux ratio yielded 11 g. of an unsaturated material distilling at 147–148° at 751 mm., d_4^{25} 0.8692. It gave a liquid oxime boiling at 96–97° at 10 mm., and on hydrogenation over Raney nickel at room temperature yielded 4-methyl-2-hexanone, *semicarbazone*, m.p. 105–106°.

The original unsaturated substance was thus identified as 4-methyl-3-hexene-2-one (17).

SUMMARY

The polymerization of diketene has been studied under alkali-catalyzed conditions.

Four previously unreported products have been isolated. They are carbon dioxide, acetone, 2,6-dimethylpyrone, and a heretofore unknown substance characterized as 2,6-bis-(6-methyl-4-oxo-2-pyranilylmethyl)pyrone.

A mechanism is proposed by which these compounds may be formed from diketene and evidence in its support is discussed.

PITTSBURGH, PA.

REFERENCES

- (1) CHICK AND WILSMORE, *Proc. Chem. Soc.*, **26**, 217 (1911); *J. Chem. Soc.*, **97**, 1970 (1911).
- (2) PEYTRAL, French Patent 722,477 (1931).
- (3) HURD, SWEET, AND THOMAS, *J. Am. Chem. Soc.*, **55**, 335 (1933).
- (4) LAW, U. S. Patent 2,019,983 (1936).

- (5) BOESE, U. S. Patent 2,229,204 (1941).
- (6) BURY, *J. Am. Chem. Soc.*, **57**, 2115 (1935).
- (7) SKLAR, *J. Chem. Phys.*, **5**, 669 (1937).
- (8) LEWIS AND CALVIN, *Chem. Rev.*, **25**, 273 (1939).
- (9) BRANCH AND CALVIN, *The Theory of Organic Chemistry*, Prentice-Hall, Inc., New York, 1941, p. 155.
- (10) CALVIN, MAGEL, AND HURD, *J. Am. Chem. Soc.*, **63**, 2174 (1941).
- (11) BARNES, GORE, LIDDEL, AND WILLIAMS, *Infrared Spectroscopy*, Reinhold Publishing Corp., New York, 1944.
- (12) ROSS, *Proc. Roy. Soc. (London)*, **113A**, 208 (1926).
- (13) MORTON, *The Chemistry of Heterocyclic Compounds*, McGraw-Hill Book Company, New York and London, 1946, pp. 148-183.
- (14) BOESE, *Ind. Eng. Chem.*, **32**, 16 (1940).
- (15) RASSWEILER AND ADAMS, *J. Am. Chem. Soc.*, **46**, 2763 (1924).
- (16) SWIETOSLAWSKI, *Ebulliometric Measurements*, Reinhold Publishing Corp., New York, 1945.
- (17) SUIDA AND POLL, *Monatsh.*, **48**, 188 (1927).