tinued elution then showed increasing amounts of acetylenic material.

The *cis* fraction was concentrated and freed of volatiles at 0.001 mm.; yield 2.1 g., $n^{20}\text{D}$ 1.5830; $\lambda\lambda_{\text{max.}}$ 254 mμ (ε 27,000), 260 mμ (21,200), 312.5 mμ (ε 21,200).*

Anal. Calcd. for $C_{21}H_{32}O$: C, 83.94; H, 10.74. Found: C, 83.80; H, 10.74.

Stereoisomerization of 4,5-*cis*-XIX to 4,5-*trans*-XIX.—A 2.0-g. sample of the chromatographed *cis* isomer was stereoisomerized by contact with iodine for 10 minutes, worked up and chromatographed on a 3 × 35 cm. column of alumina deactivated with 10% of water. Collection of the main fraction was begun when $E_{358\ \text{m}\mu}/E_{325\ \text{m}\mu} = 1$. By this time a contaminant ($\lambda_{\text{max.}}$ 295 mμ) observed in the foregoing eluates had been removed. Progressive elution (3% ether–petroleum ether) was accompanied by an increase in $E_{358\ \text{m}\mu}/E_{325\ \text{m}\mu}$, and was continued until the Carr–Price test showed negligible solute.

Concentration under vacuum and final removal of solvent at 0.001 mm. gave 0.8 g. of product, $n^{20}\text{D}$ 1.634; $\lambda\lambda_{\text{max.}}$ 325 mμ (ε 46,000), 340 mμ (ε 62,500), 358 mμ (ε 54,400).*

Anal. Calcd. for $C_{21}H_{32}O$: C, 83.94; H, 10.74. Found: C, 84.02; H, 10.70.

Acknowledgment.—The authors are indebted to Mr. Joseph Grodsky for the microanalyses and to Mr. Walter Gall for technical assistance.

Raritan, New Jersey

[Contribution from the Department of Chemistry of the University of Wisconsin]

Ketene Acetals. XXXII. The Condensation of Ketene Dimethylacetal with Various Aldehydes and Ketones

By S. M. McElvain, Edward R. Degginger and John D. Behun

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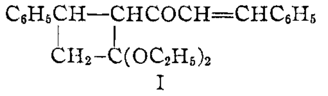
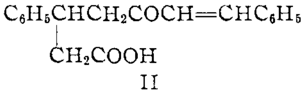
Ketene dimethylacetal reacts with acrolein, cinnamaldehyde and benzalacetone to yield the dihydropyrans III, IV and V. These unsaturated cyclic *ortho* esters are hydrolyzed to the corresponding aldehydo and keto esters. Caproaldehyde condenses with the ketene acetal to give methyl 2-octenoate; acetaldehyde similarly gives methyl crotonate. Benzaldehyde and acetone do not react; formaldehyde causes some reduction of the ketene acetal to dimethylacetal with the concurrent oxidation of the formaldehyde to glyoxal.

The reactions of ketene diethylacetal with a variety of α,β-unsaturated carbonyl compounds were reported in the eighth[1a] and fourteenth[1b] papers of this series. Dibenzalacetone was found to react with one equivalent of the ketene acetal at 125° to yield a product, to which the structure I was assigned because of its hydrolysis in dilute acid solution to β-phenyl-γ-cinnamoylbutyric acid (II).[1a] Benzalacetone gave only a non-distillable product, which was thought to be a mixture of the ketene acetal polymer and self-condensed benzalacetone; benzalacetophenone yielded a product analogous to I that could be hydrolyzed to β-phenyl-γ-benzoylbutyric acid; phorone did not react with the ketene acetal.[1a]



$$\begin{array}{l} C_6H_5CH{-}CHCOCH{=}CHC_6H_5 \\ \quad | \qquad\ \ | \\ \quad CH_2{-}C(OC_2H_5)_2 \end{array}$$

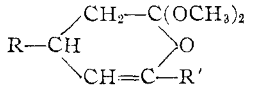
I



$$\begin{array}{l} C_6H_5CHCH_2COCH{=}CHC_6H_5 \\ \quad\ | \\ \quad CH_2COOH \end{array}$$

II

The present paper describes the reaction of ketene dimethylacetal, used in preference to the diethylacetal because of its greater stability at higher temperatures, with certain α,β-unsaturated aldehydes and ketones as well as with simple aldehydes. Acrolein reacted with this ketene acetal at 100° in a period of 24–40 hours to give 2,2-dimethoxy-2,3-dihydropyran (III) in 65–70% yields; the reaction time could be reduced to 8 hours if a temperature of 150° were used. Also the condensation could be effected in 0.5 hour at the reflux temperature of the reactants in the presence of 5 mole per cent. of aluminum *t*-butoxide; however, in this case the yield of III dropped to about 40%. The structure of III was shown by (a) the presence of an enol ether band and the absence of the carbonyl band in its infrared spectrum and (b) its hydrolysis to methyl γ-formylbutyrate.



III, R = R′ = H
IV, R = C_6H_5; R′ = H
V, R = C_6H_5; R′ = CH_3

Cinnamaldehyde reacted with the ketene acetal in 24 hours at 150° to give 59% of the dihydropyran IV; after this time 30–35% of the aldehyde and 20–35% of the ketene acetal were recovered from the reaction mixture. When the reaction time at 150° was reduced to four hours the yield of IV dropped to 28%; a reaction temperature of 200° did not improve the yield and at 100° the yield of IV was only 23%. Hydrolysis of IV yielded methyl β-phenyl-γ-formylbutyrate, which was converted by oxidation and saponification to β-phenylglutaric acid.

Although benzalacetone and ketene diethylacetal at 125° gave mainly polymeric material,[1a] it was found in the present work that this ketone and ketene dimethylacetal react at 150–200° to give low yields (27–30%) of the dihydropyran V, which may be hydrolyzed to methyl β-phenyl-γ-acetylbutyrate. A considerable amount of a non-volatile, polymeric material was formed simultaneously with V. It appears that the reaction temperature used in the earlier work[1a] was not sufficiently high to permit the simple condensation of these reactants to compete successfully with their polymerization reactions.

The conclusive evidence supporting the structure III strongly indicates that the cyclobutane structure I should be discarded in favor of a dihydropyran structure corresponding to III, IV and V. All of the reactions reported for these original ad-

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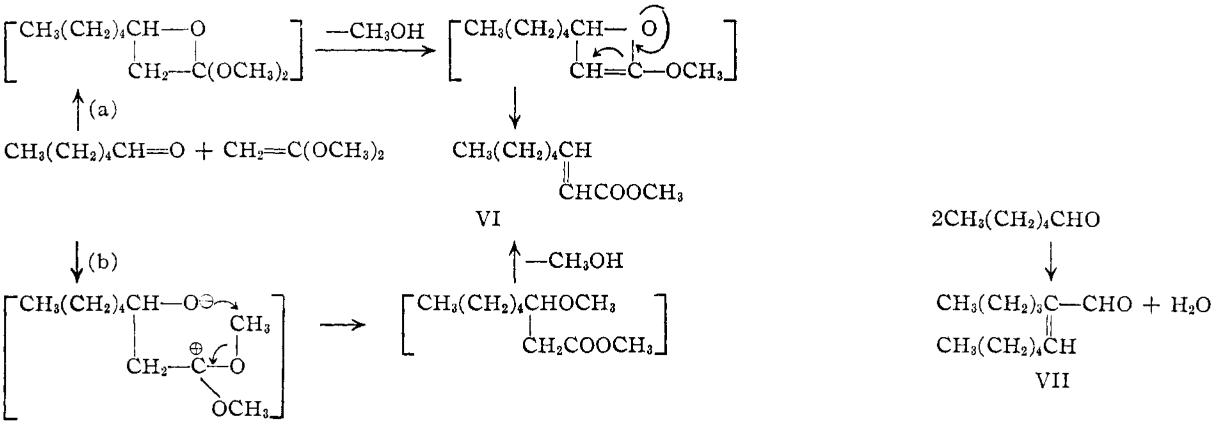
[1] (a) S. M. McElvain and H. Cohen, This Journal, **64**, 260 (1942); (b) S. M. McElvain and E. Engelhardt, *ibid.*, **66**, 1077 (1944).

ducts may be accommodated by the new structure as well as by I. An analogous revision of the structure of the adduct of ketene acetal to benzoquinone has been made.[1b]

Turning to simple aldehydes and ketones it was found that neither benzaldehyde nor acetone gave any detectable condensation product with ketene dimethylacetal at temperatures of 180–200°. However, caproaldehyde and the ketene acetal in a 1:1 ratio reacted at 150° to give low yields (16–18%) of methyl 2-octenoate (VI). Associated with this product was an approximately equivalent amount of the unsaturated aldehyde VII, resulting from the self-condensation of the caproaldehyde. The other reaction products were methyl acetate and methyl orthoacetate formed from the reaction of the ketene acetal with the water and methanol eliminated in the formation of VII and VI. When a 3:1 ratio of the ketene acetal to the aldehyde was used in this reaction the yield of VI was raised to 28% and approximately one-third of the ketene acetal was recovered. The structure of VI was shown by its hydrogenation to methyl caprylate and its ozonolysis to caproic acid. The manner in which VI is produced is not certain as either path a or b seems reasonable. A distinction between these possible reaction courses obviously could be made if the reaction were run with an aldehyde containing a labeled oxygen.



The ketene acetal reacted similarly with acetaldehyde to yield methyl crotonate (14%) and some crotonaldehyde (5%). The latter compound appeared to condense with the ketene acetal to yield a dihydropyran analogous to IV. Methyl acetate (24%) and methyl orthoacetate (17%) were the main low-boiling constituents.

The addition of dry gaseous formaldehyde to the ketene acetal caused the polymerization of the reaction mixture, but when polyoxymethylene and the ketene acetal were heated at 200° for 6 hours, approximately one-half of the reaction mixture was a low-boiling fraction consisting of dimethyl acetal, methyl acetate and methanol. There was a higher-boiling fraction, which doubtless contained glyoxal dimethylacetal since derivatives of glyoxal were obtained from it. These products indicate that with formaldehyde there occurred a somewhat more complex reaction in which a portion of the ketene acetal was reduced to dimethyl acetal with the concurrent oxidation of formaldehyde to glyoxal.

Experimental

2,2-Dimethoxy-2,3-dihydropyran (III).—A mixture of 22 g. (0.25 mole) of ketene dimethylacetal[2] (b.p. 89–91°) and 15 g. (0.275 mole) of acrolein was placed in a combustion tube with an inside diameter of 2.5 cm. The mixture was chilled in a Dry Ice–acetone-bath and sealed in such a fashion that about 3 inches of air space remained over the surface of the solution. The sealed tube was placed in a hydrogenation bomb of appropriate size containing about 10 ml. of absolute alcohol (to balance the pressure in the glass tube) and heated at 150° for 8 hours. The tube, containing the pale yellow reaction product, was again chilled prior to opening.

The reaction mixture was distilled through a 25-cm. Vigreux column and 24.8 g. (70%) of 2,2-dimethoxy-2,3-dihydropyran (III) was collected; b.p. 47–48° (7 mm.), 60–62° (16 mm.), $n^{25}D$ 1.4427, d^{25}_4 1.055.

Anal. Calcd. for $C_7H_{12}O_3$: C, 58.31; H, 8.39; CH_3O, 43.1. Found: C, 58.10; H, 8.33; CH_3O, 41.8.

The infrared spectrum of III showed no carbonyl absorption below 6 μ but had a strong absorption band in the 6.1 μ region, which is characteristic of enol ethers[3a] and ketene acetals.[3b]

When 11.6 g. (0.176 mole) of acrolein was added rapidly to a mixture of 16.5 g. (0.16 mole) of ketene acetal, 25 ml. of thiophene-free benzene and 2.46 g. of aluminum *t*-butoxide, refluxing commenced immediately and continued for 2 minutes. Heating was continued by means of an oil-bath for 1 hour, during which time the color of the mixture changed from a pale to a deep yellow. After excess acrolein and the benzene solvent were removed, 11.8 g. (43%) of III was obtained by distillation.

Methyl γ-Formylbutyrate.—To an immiscible mixture of 14.4 g. (0.1 mole) of III and 1.8 g. (0.1 mole) of water, a drop of concentrated hydrochloric acid was added. The mixture immediately became homogeneous and sufficient heat was liberated to cause refluxing for several minutes. When this reaction had subsided, 8 ml. of benzene was added and distilled off in order to remove any excess water azeotropically. The remaining solution was distilled through a 25-ml. modified Claisen flask to yield 9.7 g. (74%) of the aldehyde-ester, b.p. 85–90° (15 mm.). Redistillation of this material gave a product, b.p. 79–80° (6 mm.), $n^{25}D$ 1.4246, d^{25}_4 1.069; this product contained 23.1% methoxyl (calcd. 23.8) and had a sapn. equiv. of 128 (calcd. 130).

The aldehyde-ester converted readily to a yellow crystalline 2,4-dinitrophenylhydrazone when warmed with a solution of 2,4-dinitrophenylhydrazine in methanol. The derivative, which separated immediately, was washed twice with 50% aqueous methanol and dried in air; m.p. 110–111.5°. The melting point of methyl γ-formylbutyrate-

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(2) S. M. McElvain and H. F. McShane, THIS JOURNAL, **74**, 2662 (1952).

(3) (a) W. H. T. Davison and G. R. Gates, *J. Chem. Soc.*, 2607 (1953); (b) R. E. Starn, Jr., Ph.D. Thesis, University of Wisconsin, 1953.

2,4-dinitrophenylhydrazone has been reported as 105–106°[4]; it was prepared with xylene as a solvent. Following this procedure, orange-yellow needles melting at 107–108° were obtained.

2,2-Dimethoxy-4-phenyl-2,3-dihydropyran (IV).—A mixture of 20 g. (0.15 mole) of freshly distilled cinnamaldehyde and 13.2 g. of ketene dimethylacetal (0.15 mole) was heated at 150° for 24 hours in a sealed tube. The amber reaction mixture was distilled from a 50-ml. flask at reduced pressure. The fraction (21.1 g.) boiling at 138–150° (18 mm.) was collected and redistilled through a 30-cm. Vigreux column to yield 19.5 g. (59%) of IV, b.p. 150–154° (11 mm.). An analytical sample of this product boiled at 154–155° (13 mm.), n^{25}_{D} 1.5277, d^{25}_{4} 1.083.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.91; H, 7.27; CH_3O, 58.7. Found: C, 70.87; H, 7.34; CH_3O, 59.1.

Methyl γ-Formyl-β-phenylbutyrate.—To a mixture of 16.3 g. of the dihydropyran IV and 1.33 g. of water, four drops of concentrated hydrochloric acid was added. The mixture was warmed on the steam-bath for 2 hours. The resulting deep yellow, homogeneous solution was dissolved in 25 ml. of ether and washed once with water. The ether layer was dried over Drierite and the solvent removed by distillation. Distillation of the hydrolysis product at reduced pressure yielded 13 g. of crude distillate, b.p. 162–173° (11 mm.). Redistillation gave 10 g. (66%) of aldehyde-ester which boiled at 112° (0.3 mm.), n^{25}_{D} 1.5124, d^{20}_{4} 1.082. This ester showed a saponification equivalent of 200 (calcd. 206).

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.90; H, 6.80. Found: C, 70.10; H, 6.99.

The aldehyde-ester formed a 2,4-dinitrophenylhydrazone readily in a neutral solution of 2,4-dinitrophenylhydrazine in 95% ethanol; m.p. 116–120°. Two recrystallizations from a mixture of one part ethyl acetate and four parts 95% ethanol gave yellow-orange needles, which after drying at 100° (0.1 mm.) for 4 hours melted at 121–124°.

Anal. Calcd. for $C_{18}H_{18}N_4O_6$: C, 55.95; H, 4.66. Found: C, 56.24; H, 4.66.

Methyl γ-formyl-β-phenylbutyrate (4 g.) in 50 ml. of acetone was chilled to 0° and a solution of 2.04 g. of potassium permanganate in 200 ml. of water added slowly over a period of 20 minutes with stirring. The resulting reaction mixture was filtered free of manganese dioxide and the precipitate washed with small portions of hot water and acetone; the washings and the filtrate were combined. Most of the acetone was removed by evaporation at reduced pressure and dilute hydrochloric acid was then added until the mixture was acidic. The organic acid was extracted from the aqueous solution with three 25-ml. portions of ether. After removal of the ether, the remaining acid-ester was dissolved in 20 ml. of 1.3 *N* alcoholic sodium hydroxide and heated for several hours on the steam-bath. A considerable quantity of white precipitate formed during this time. After cooling, the supernatant liquid was decanted and the white salt washed with several portions of absolute ethanol. The dried salt (3 g.) was dissolved in 20 ml. of water and the solution heated with 0.5 g. of Darco and filtered. The filtrate was poured onto 30 g. of cracked ice containing 2 ml. of concentrated hydrochloric acid. A pale, yellow solid, which became gummy on standing, precipitated. The acid was dissolved in ether to separate it from the water which adhered to the walls of the flask. The ether was dried over Drierite and, after evaporation of the ether, a yellow, glass-like residue resulted. On standing for two days with intermittent scratching of the sides of the flask, crystalline rods began to form. The addition of small quantities of benzene facilitated the crystallization. The resulting powder (1.5 g.) was filtered and dried in air; it melted, after a recrystallization from benzene, at 123–133°. Two additional recrystallizations from benzene gave white β-phenylglutaric acid which melted at 141–141.5°; reported[5] 140°; neut. equiv. 104 (calcd. 104).

2,2-Dimethoxy-4-phenyl-6-methyl-2,3-dihydropyran (V).—A mixture of 21.9 g. (0.15 mole) of benzalacetone and 13.2 g. (0.15 mole) of ketene dimethylacetal was heated at 200° for 24 hours in a sealed tube, after which time the mixture was distilled. A small forerun of methyl acetate, methyl orthoacetate and ketene acetal comprised the first fraction and was followed by a 20.7-g. fraction of a mixture of benzalacetone and V; b.p. 104–126° (1 mm.). Redistillation gave 10.5 g. (30%) of pure V; b.p. 106–108° (0.4 mm.), n^{25}_{D} 1.5167, d^{25}_{4} 1.062.

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.81; H, 7.64. Found: C, 71.81; H, 7.77.

Methyl γ-Acetyl-β-phenylbutyrate.—To a mixture of 7.5 g. (0.032 mole) of V and 0.58 g. (0.032 mole) of water, a drop of concentrated hydrochloric acid was added and the mixture heated on the steam-bath for 3 hours. During this time, the mixture became homogeneous. The keto-ester was dissolved in 30 ml. of ether and the solution dried over Drierite. After removal of the ether, 5.5 g. (79%) of the keto-ester was distilled; b.p. 121–122° (0.1 mm.), n^{25}_{D} 1.5070, sapn. equiv. 230 (calcd. 220).

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.91; H, 7.03. Found: C, 71.04; H, 7.53.

The semicarbazone of this keto-ester was readily prepared by standard procedures and crystallized from a mixture of three parts of ether and one part of petroleum ether (b.p. 40–60°). The impure derivative was recrystallized from a mixture of equal parts of ether, petroleum ether and absolute ethanol yielding a white, crystalline semicarbazone, which after drying at 100° (0.5 mm.) for 3 hours melted at 121–124°.

Anal. Calcd. for $C_{14}H_{19}O_3N_3$: C, 60.65; H, 6.86. Found: C, 61.02; H, 6.70.

Attempted Reaction of Ketene Dimethylacetal with Benzaldehyde and Acetone.—A mixture of 15.9 g. (0.15 mole) of freshly distilled benzaldehyde and 13.2 g. (0.15 mole) of ketene dimethylacetal was heated for 6 hours at 150° in a sealed tube. The pale yellow reaction mixture was distilled through a 30-cm. Vigreux to yield 11.2 g. of ketene acetal and 14.9 g. of benzaldehyde, b.p. 58–61° (8 mm.).

When the reaction was conducted at 200°, the ketene acetal was converted to methyl acetate (15%), methyl orthoacetate (25%) and polymeric residue (50%). Some unidentified gaseous material also was formed.

A mixture of 8.7 g. (0.15 mole) of dry acetone and 13.2 g. (0.15 mole) of ketene dimethylacetal was placed in a 42-ml. capacity hydrogenation bomb and heated at 200° for 20 hours. Some unidentified gases were formed. The reaction mixture, on distillation, gave 6.5 g. of acetone (b.p. 56–60°) and 10.5 g. of ketene acetal (b.p. 75–91°).

Methyl 2-Octenoate (VI).—A mixture of 40 g. (0.4 mole) of freshly distilled caproaldehyde (b.p. 128–129°) and 35.2 g. (0.4 mole) of ketene acetal was heated at 200° for 24 hours in a 270-ml. capacity hydrogenation bomb. Some gaseous products were formed during the reaction and 74.1 g. of reaction mixture was recovered. The mixture was distilled into eight fractions through a 30-mm. Stedman column: (1) b.p. 25–55°, 0.6 g.; (2) b.p. 55–60°, 5.9 g.; (3) b.p. 60–100°, 3.4 g.; (4) b.p. 100–108°, 13.9 g.; (5) b.p. 108–115°, 10.2 g.; (6) b.p. 40–62° (7 mm.), 3.8 g.; (7) b.p. 60–80° (1.4 mm.), 16.8 g.; (8) b.p. 82–105° (0.3 mm.), 6.8 g.; residue, 10.6 g.

Fractions 7 and 8 were redistilled into 19 separate fractions which were divided into three groups on the basis of refractive indexes: (a) 12 g. (19%) of methyl 2-octenoate (VI), b.p. 53–56° (0.9 mm.); (b) 4.5 g. of intermediate material, b.p. 57–103° (0.9 mm.); and (c) 6.1 g. of 5-formylundecene-5 (VII), b.p. 121–150° (0.9 mm.). The wide boiling range of fraction c was caused by superheating the distillate. An analytical sample of VI boiled at 89–91° (9 mm.), n^{25}_{D} 1.4370, d^{25}_{4} 0.894, sapn. equiv. 160 (calcd. 156).

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.23; H, 10.26; CH_3O, 19.9. Found: C, 69.59; H, 10.71; CH_3O, 19.2.

By using the same reaction conditions and employing a 3:1 ratio of ketene acetal to caproaldehyde, the yield of VI was increased to 28% and one-third of the ketene acetal was recovered.

The *p*-bromophenacyl ester of 2-octenoic acid was prepared from VI after saponification by standard procedures and melted at 91–92.5°, reported[6] 92°.

The hydrogenation of 7.25 g. (0.464 mole) of unsaturated ester VI dissolved in 50 cc. of absolute methanol was carried out over 0.73 g. of palladium (10%) on carbon catalyst. The theoretical amount of hydrogen was taken up in 4

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[4] S. Harris, *et al.*, This Journal, **67**, 2096 (1945).

[5] v. Braun and Weissbach, *Ber.*, **64**, 1787 (1931).

[6] G. B. Bachman, This Journal, **55**, 4279 (1933).

minutes. The catalyst was filtered off and, after removal of the methanol, 5.2 g. (71%) of methyl caprylate was distilled, b.p. 131–135° (10 mm.), n^{25}_{D} 1.4161, d^{25}_{4} 0.872, M_D 45.46 (calcd. 45.31).

This ester was converted *via* the acid to the *p*-phenylphenacyl ester, m.p. 66.5–67.5°, reported[7] 67°. The same derivative, prepared from an authentic sample of caprylic acid, gave no depression in a mixed melting point determination.

Ozone was bubbled into a solution of 6.28 g. (0.04 mole) of VI in 5 cc. of methyl acetate at a rate of 20 liters per minute for 4 hours. The mixture was chilled in a Dry Ice–acetone-bath during the ozonization to prevent the evaporation of the solvent. The ozonide was decomposed by warming the solution with 7 ml. of 30% hydrogen peroxide for 10 minutes and then permitting the mixture to stand overnight. The acids were extracted with three 10-ml. portions of ether, the ether layer dried over Drierite and the methyl acetate and ether removed by evaporation. The acid was neutralized with 30% sodium hydroxide and an insoluble white solid filtered off. After acidification of the filtrate, the acid was extracted with ether. After removal of the ether, the remaining fatty acid was converted to its *p*-phenylphenacyl ester (reported[7] 63.5°), m.p. 61–62.5°, which gave no depression of melting point when mixed with the *p*-phenylphenacyl ester of an authentic sample of caproic acid.

Self-condensation of *n*-Caproaldehyde.—In a 270-ml. capacity hydrogenation bomb, 150 g. (1.48 moles) of freshly distilled caproaldehyde was heated at 200° for 24 hours. About 5 g. of black residue was filtered off and the unreacted caproaldehyde removed by distillation. Further distillation yielded 60 g. of a pale yellow product, b.p. 101–114° (8 mm.). Careful fractionation of this material gave 29 g. of **5-formylundecene-5 (VII)**, b.p. 110° (7 mm.), n^{25}_{D} 1.4540, d^{25}_{4} 0.837.

Anal. Calcd. for $C_{12}H_{22}O$: C, 79.12; H, 12.09. Found: C, 78.21; H, 11.78.

This unsaturated aldehyde readily forms a red-orange 2,4-dinitrophenylhydrazone, which after recrystallization from 95% ethanol and drying at 90° (0.05 mm.) for 5 hours melted at 131–132.5°.

Anal. Calcd. for $C_{18}H_{26}N_4O_4$: C, 59.66; H, 7.18. Found: C, 59.66; H, 7.08.

When fraction c, from the caproaldehyde–ketene acetal reaction distillate, was treated with alcoholic 2,4-dinitrophenylhydrazine, the identical red-orange derivative was formed, m.p. 131–132.5°. No depression was observed in the mixed melting of these two derivatives.

Reaction of Acetaldehyde with Ketene Dimethylacetal.—A mixture of 30 g. (0.68 mole) of freshly distilled acetaldehyde and 60 g. (0.68 mole) of ketene dimethylacetal was heated at 150° for 24 hours in a 270-ml. capacity hydrogenation bomb. About 9% of the reaction mixture was lost as unidentified gaseous products leaving 81.7 g. of liquid material for distillation. Distillation gave the following fractions: (1) b.p. 52–55°, 9 g.; (2) b.p. 55–58°, 7 g.; (3) b.p. 58–68°, 5.5 g.; (4) b.p. 68–100°, 4 g.; (5) b.p. 100–109.5°, 9 g.; (6) b.p. 109–115°, 10 g.; (7) b.p. 115–118°, 5 g.; (8) b.p. 118–132°, 3 g.; (9) b.p. 46–72° (7 mm.), 8.6 g.; (10) b.p. 72–90° (7 mm.), 2 g.; (11) b.p. 52–69° (0.05 mm.), 4.2 g. pale yellow; (12) b.p. 125–175° (2 mm.), 6.8 g. yellow; residue, 7.6 g.

Fractions 1 and 2 were combined and redistilled. On the basis of refractive indices, the material was shown to be relatively pure methyl acetate; however, the addition of 2,4-dinitrophenylhydrazine gave a small yield of yellow crystals of acetaldehyde 2,4-dinitrophenylhydrazone, m.p. 165–167°. Fractions 5, 6 and 7 were combined and 95% of this material distilled from 102–117°; this distillate appeared to be a mixture of crotonaldehyde (b.p. 104–105°), methyl orthoacetate (b.p. 107–109°) and methyl crotonate (b.p. 119–120°). The lower boiling (102–106°) fraction produced a red 2,4-dinitrophenylhydrazone, m.p. 185–187°; reported[8] for crotonaldehyde 2,4-dinitrophenylhydrazone, 190°. This fraction as well as the next fraction boiling up to 112° gave a noticeable exothermic reaction with dilute hydrochloric acid indicating the presence of the orthoester. The fraction boiling at 110–117° was treated with dilute hydrochloric acid and the resulting ester, after washing with water to remove methyl acetate and methanol, was dried and distilled to yield 5 g. of methyl crotonate, b.p. 28–30° (0.18 mm.), n^{25}_{D} 1.4190, d^{25}_{4} 0.936. About 7 g. of methyl crotonate was present in fractions 8 and 9 as estimated by the refractive indices of these fractions.

The *p*-bromophenacyl ester was prepared from the 28–30° (0.18 mm.) boiling material after saponification, m.p. 94.5–96°; reported[9] for *p*-bromophenacyl crotonate, 95–96°.

The amount of crotonaldehyde, methyl orthoacetate and methyl crotonate formed was estimated at 4.5 g. (5%), 15.5 g. (17%) and 12.5 g. (14%), respectively. The higher boiling reaction products contained no other products that could be isolated.

Reaction of α-Polyoxymethylene with Ketene Dimethylacetal.—A mixture of 88 g. (1 mole) of ketene acetal and 30 g. (1 mole) of α-polyoxymethylene[10] was heated at 200° for 6 hours in a 270-ml. capacity hydrogenation bomb. The recovered reaction mixture (114.8 g.) was distilled through a 25-cm. Stedman column into the following fractions: (1) b.p. 43–67°, 52.8 g.; (2) b.p. 67–135°, 10.6 g.; (3) b.p. 135–141° and 50–72° (11 mm.), 16.7 g.; (4) 72–130° (11 mm.), 14.4 g.; residue, 21.7 g.

A 1-g. sample of fraction 3 gave 0.15 g. of glyoxal bis-2,4-dinitrophenylhydrazone, m.p. 309–312° after recrystallization of a 1:1 mixture of absolute ethanol and pyridine, reported[11] 311–312°. This derivative gave the correct carbon, hydrogen and nitrogen analyses. A 1-g. sample of fraction 3, when heated with 10% sulfuric acid and the reaction mixture distilled, gave a distillate that yielded 0.1 g. of glyoxal bis-semicarbazone, m.p. 265–267°, reported[12] 270°. From fraction 1 sufficient of acetaldehyde 2,4-dinitrophenylhydrazone was isolated from a 1-g. sample to indicate the presence of a minimum of 3.5% of acetaldehyde dimethylacetal in this fraction. Saponification of a sample of fraction 1 showed the presence of a minimum of 37.5% of methyl acetate in this fraction; the acetic acid produced in this saponification was characterized as the *p*-phenylphenacyl ester, m.p. 108–109°. Treatment of a sample of fraction 1 with α-naphthyl isocyanate gave sufficient methyl α-naphthylcarbamate, m.p. 121–123°, to show the presence of 30.6% of methanol in this fraction.

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(7) N. Drake, *et al.*, This Journal, **52**, 3715 (1930).

(8) O. L. Brady, *J. Chem. Soc.*, 756 (1931).

(9) v. Auwers, *et al.*, *Ann.*, **432**, 46 (1923).

(10) J. F. Walker, "Formaldehyde," Reinhold Publishing Corp., New York, N. Y., 1944, pp. 79–80.

(11) T. L. Jacobs and W. J. Whitcher, This Journal, **64**, 2635 (1942).

(12) C. Harries and P. Temme, *Ber.*, **40**, 171 (1907).