The presence of the CH_3CO– group was indicated by the good iodoform test obtained from a drop of this material. Preparation of the semicarbazone (m. p. 103°) and the 2,4-dinitrophenylhydrazone[17] (m. p. 108–108.5°) further confirmed its identity.

α-Phenylvinyl Allyl Ether.—When 1.31 g. of this ether was refluxed gently under atmospheric pressure for fifteen minutes, a red-brown color developed. After cooling, the system was distilled at 12–13 mm. The entire volatile portion (0.93 g.) came over between 105–116°. A small amount of a deep red-brown, viscous material remained as residue. The refractive index $n^{20}D$ of the distillate was 1.5417.

The semicarbazone was prepared in the usual manner and found to melt, after two recrystallizations, at 156–157°. The oxime was also recrystallized twice and had the melting point of 53°.[18] A mixed m. p. with a sample of authentic acetophenone oxime (m. p. 57–58°) showed definitely that these two materials were different. Simple mixing gave a sticky mass, which was completely melted at 45.5°. This distillate is, therefore, identified as γ-butenyl phenyl ketone.

Ozonolysis of Allylacetaldehyde.—One gram of allylacetaldehyde was dissolved in 100 cc. of dry carbon tetrachloride and an excess of a 5% ozone-in-oxygen stream passed into the solution at 0°. The resulting ozonide was hydrolyzed in the presence of the solvent with 70 cc. of water and the reaction completed by refluxing for one and one-half hours. At this point, the freshly-prepared and well-washed silver oxide from 15 g. of silver nitrate was added and the mixture was further refluxed for one hour. After the evaporation of the carbon tetrachloride by gentle heating on the steam-bath, the mixture was filtered.

Most of this filtrate was distilled, the distillate made up to 110 cc., and a determination of the Duclaux values made.

	Cc. alkali required
Original 10 cc.	2.90
First 10 cc. distilled	1.20
Second 10 cc. distilled	1.30
Third 10 cc. distilled	1.40

Duclaux values found: 4.14, 4.48, 4.83. The theoretical values for formic acid are: 3.95, 4.40 4.55. This distillate slowly decolorized potassium permanganate solution.

After the formic acid had been distilled off, the residue was treated with excess of hydrochloric acid to precipitate the remaining silver. After filtering, the filtrate was evaporated to dryness.

A small amount of this residue was dissolved in water and neutralized with dilute sodium hydroxide. The *p*-bromophenacyl ester of the acid was prepared in the usual manner and was recrystallized from an alcohol–acetone mixture; m. p. 209–210°. A mixed melting point with authentic *p*-bromophenacyl succinate (m. p. 213.5–214°) showed the identity of the two materials. The value was 212–212.5°.

Summary

A number of methods of preparing vinyl allyl ethers have been investigated.

These ethers were found to rearrange smoothly upon heating at temperatures of 175–255°. Only one product was found to any appreciable extent in each case, indicating a clean-cut reaction. It was shown that allylacetaldehyde, allylacetone, and ω-allylacetophenone were formed in this way, respectively, from vinyl allyl ether, α-methyl vinyl allyl ether, and α-phenylvinyl allyl ether. These three ethers are listed in the order of decreasing thermal stability.

The rearrangement of vinyl allyl ether to allylacetaldehyde is analogous to the rearrangement of phenyl allyl ether to *o*-allylphenol.

EVANSTON, ILLINOIS RECEIVED MAY 31, 1938

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[17] Allen, THIS JOURNAL, **52**, 2958 (1930), reports m. p. of 104°

[18] Helferich and Lecher, *Ber.*, **54**, 930 (1921), report the m. p. of the semicarbazone of γ-butenyl phenyl ketone as being 156–157°, and that of the oxime as 53–54°.

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

The Polycondensation of Acrolein

BY EVERETT E. GILBERT[1] AND JOHN J. DONLEAVY

It has been shown[2] that in the presence of dilute aqueous alkalies, α-methylacrolein polycondenses by a Michael mechanism to yield hydroxy polyaldehydes. The purpose of this communication is to report a similar reaction for acrolein.

Several investigators have recorded the precipitation of a white solid upon the addition of alkalies to an aqueous solution of acrolein. McLeod[3] obtained a product softening at 83° and decomposing with evolution of gas at 94–95°. The substance was soluble in alcohol, but insoluble in water and in hydrocarbon type solvents. Upon heating, thermal depolymerization occurred with the formation of acrolein. Another observer[4] obtained a white powder softening at

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[1] This communication describes work done by Everett E. Gilbert in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Gilbert and Donleavy, THIS JOURNAL, **60**, 1737 (1938).

[3] McLeod, *Am. Chem. J.*, **37**, 34 (1907).

[4] Nef, *Ann.*, **335**, 220 (1904).

115° and decomposing at 128–130°. A third group[5] described the powder as being converted to a viscous mass upon heating to temperatures between 80–110°; the solubilities were the same as those recorded above. No attempt ever has been made[6] to characterize any of the acrolein polymers.

A series of samples of the solid was prepared under widely varying conditions. They gave an immediate precipitate with Tollens' reagent, a definite although delayed test with Schiff's reagent, and an immediate precipitate of manganese dioxide with neutral aqueous permanganate at room temperature. The samples did not possess sharp melting points; decomposition temperatures were noted as low as 80° and as high as 125°.

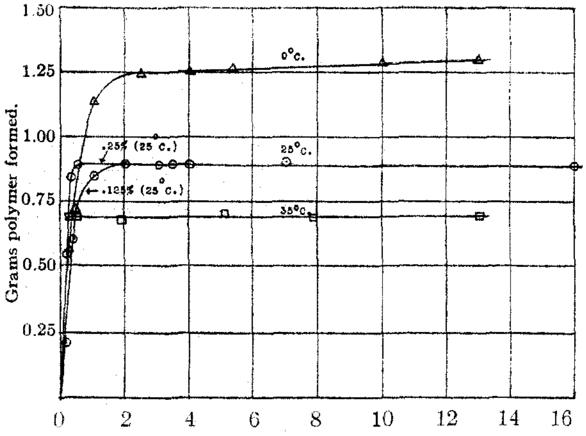
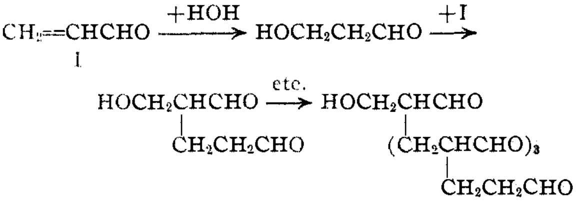


Fig. 1.

Analyses upon specimens variously prepared checked one another in being 4% lower in carbon than calculated for $(CH_2{=\!=}CHCHO)_n$; the hydrogen was slightly higher than calculated. By analogy to the type of product similarly obtained from α-methylacrolein, it was concluded tentatively that the polyacrolein was a hydroxypolyaldehyde formed from five acrolein molecules and one water molecule. This was established by the preparation of a monoöxime (in the cold), and by the preparation of a tetra-2,4-dinitrophenylhydrazone (in the hot). A polyacrylic acid also was obtained by cautious oxidation with permanganate in the cold—followed by dehydration. Direct determinations of the molecular weight in freezing dioxane gave values which fell between one and two times the calculated molecular weight. Molecules possessing hydroxyl groups and such high densities of strongly polar aldehyde groups might be expected to associate.

Acrolein polycondenses by a Michael reaction in a manner similar to α-methylacrolein. The addition of water to acrolein yields hydracrylic aldehyde, the active methylene group of which condenses with acrolein by a Michael reaction producing a new active methylene group which again condenses by the Michael reaction with another acrolein molecule. These reactions are known to be catalyzed by alkalies; the reaction would continue until the formation of the pentamer. These steps are summarized in the equations



$$\underset{\text{I}}{CH_2{=\!=}CHCHO} \xrightarrow{+HOH} HOCH_2CH_2CHO \xrightarrow{+I}$$

$$\begin{array}{l} HOCH_2CHCHO \\ \qquad\quad | \\ \qquad\quad CH_2CH_2CHO \end{array} \xrightarrow{\text{etc.}} \begin{array}{l} HOCH_2CHCHO \\ \qquad\quad | \\ \qquad\ (CH_2CHCHO)_3 \\ \qquad\qquad\quad | \\ \qquad\qquad\quad CH_2CH_2CHO \end{array}$$

The above structure of the pentamer (containing acrolein units) would allow the formation of acrolein observed by McLeod[3] during thermal depolymerization.

A series of reaction velocity curves was obtained for the formation of the polymer under varying conditions to determine whether or not its mode of formation is consistent with the Michael mechanism advanced above. The values obtained are recorded in Table I; some of these are plotted in Fig. 1. The following conclusions were drawn from an examination of these

TABLE I

YIELD OF ACROLEIN POLYMER OBTAINED UNDER VARYING CONDITIONS

Percentages refer to strength of catalyst solution added.

Hrs. 0.125%	G. 25°	Hrs. 0.25%	G. 25°	Hrs. 1.0%	G. 25°
0.40	0.596	0.25	0.843	0.20	0.767
1.00	.850	.50	.890	.50	.857
2.00	.890	3.50	.891	3.00	.893
4.20	.862	4.00	.894	7.00	.913
17.25	.870	7.00	.906	16.00	.887
0.25%	**0°**	**0.25%**	**35°**	**165 hrs.**	**25°**
0.25	0.572	0.25	0.697	0.125%	0.210
.50	.721	.50	.703	.25%	.538
1.00	1.138	1.88	.671	1.0%	.839
2.50	1.250	5.12	.700		
4.00	1.258	7.82	.682		
5.33	1.275	13.00	.694		
10.00	1.285				
13.00	1.297				

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(5) C. Moureu and C. Dufraisse, *Chemistry & Industry*, **40**, 858A (1921).

(6) C. Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corporation, New York, N. Y., 1935, p. 502.

data: (1) the reaction is an equilibrium type, since the curves become straight and parallel to the x-axis; (2) the rapidity with which equilibrium is reached depends upon the concentration of the alkaline catalyst (at a given temperature), although the position of the equilibrium point depends upon the temperature alone; (3) the equilibrium point is shifted to the left by a rise in temperature. It has been shown[7] that these phenomena are characteristic of the Michael reaction. It has also been shown[8] that substituents tend to hinder the Michael reaction. Thus acrolein yields a pentamer by the Michael polycondensation, while α-methylacrolein yields principally a trimer.

Experimental

The acrolein was used as received from Eastman Kodak Co.; it contained about 0.1% hydroquinone.

In determining the points for the velocity curves, the following procedure was employed. Two cubic centimeters of acrolein was dissolved in 20 cc. of distilled water. The stopper of the flask was then wired down securely. It was attached to the rotator of an isothermal bath (constant to within 0.03°), and was then rotated for fifteen minutes to attain the desired temperature. It was unstoppered quickly and 1 cc. of aqueous sodium hydroxide of specified strength was added. The flask was restoppered immediately and rotated for the desired time, after which it was removed from the bath. One cubic centimeter of dilute sulfuric acid was added to stop the reaction. The white precipitate was filtered on weighed filter paper, washed thoroughly with distilled water, and dried *in vacuo* for fifteen hours over concentrated sulfuric acid to constant weight. The data reported in Table I were obtained in this way.

The polymer is a white fluffy powder which cannot be crystallized; it was found to be soluble in alcohols, ketones and in dioxane, but insoluble in hydrocarbons and in water. These observations are in accord with previous work.[3-5]

Included among the specimens subjected to analysis were the following: (1) samples made by the addition of aqueous catalyst of the following strengths: 0.25, 0.5, and 1.0%; (2) samples made with 0.25% catalyst at 11, 25 and 40°; (3) white samples which had been filtered immediately, and those allowed to become yellow from longer exposure to the alkaline reaction medium; (4) specimens which had been reprecipitated from acetone by the addition of benzene. Nine samples were analyzed; the value cited below is the average from which no single analysis varied more than ±0.25%.

Anal. Calcd. for $C_{15}H_{22}O_6$: C, 60.40; H, 7.38. Found: C, 60.48; H, 7.37. (Calcd. for $(CH_2{=}CHCHO)_n$: C, 64.28; H, 7.14.) One sample prepared with 0.125% alkali analyzed to the tetramer. Calcd. for $C_{12}H_{18}O_5$: C, 59.50; H, 7.42. Found: C, 59.62; H, 7.50. These values were unchanged after reprecipitation from acetone with benzene.

The method of Oxford[9] was used for determining the molecular weights. The dioxane was dried and distilled over sodium, and the method was checked at intervals against naphthalene. Calcd. for the pentamer: mol. wt., 298. Found: mol. wt., 370, 376, 388, 472, 443, 485, 440, 582, 580. The same values were obtained at different concentrations.

Preparation of the Tetra-2,4-dinitrophenylhydrazone of the Polymer.—The method employed was essentially that suggested by Shriner and Fuson.[10] One equivalent of dinitrophenylhydrazine was employed for each aldehyde group. A brick-red solid was obtained upon cooling the reaction mixture. The crude product was fractionally crystallized from 250 cc. of 95% ethyl alcohol. The first crop was dried *in vacuo* for twelve hours over concentrated sulfuric acid. It decomposed at about 120° upon heating.

Anal. Calcd. for $C_{39}H_{38}N_{16}O_{18}$: C, 46.1; H, 3.74; N, 22.0. Found: C, 46.2; H, 3.55; N (Dumas), 21.63.

Preparation of the Monoöxime of the Polymer.—Two grams (0.007 mole) of the polymer was dissolved in 30 cc. of methyl alcohol. Two and one-half grams of hydroxylamine hydrochloride (0.36 mole) dissolved in methanol was added, and 2.9 g. (0.36 mole) of finely powdered sodium acetate also. The flask was sealed tightly and shaken vigorously at room temperature for three hours. The solution was then filtered free of sodium chloride and evaporated in a vacuum desiccator. During the evaporation more salt separated which was filtered. The solution was taken to dryness, and the white residue was thoroughly triturated with four fresh portions of distilled water. It was then dried *in vacuo* over concentrated sulfuric acid. Upon heating the oxime softened at 68° (uncorr.).

Anal. Calcd. for $C_{15}H_{23}NO_6$: C, 57.5; H, 7.35; N, 4.47. Found: C, 57.3; H, 7.20; N (Kjeldahl), 4.45.

Oxidation of the Polymer to Polyacrylic Acid.—One and seven-tenths grams (0.006 mole) of polymer was suspended in 50 cc. of distilled water; the suspension was cooled in an ice-bath. A solution of 3.2 g. (0.02 mole) of potassium permanganate and 0.4 g. of sodium hydroxide (0.01 mole) in 200 cc. of water was then added dropwise to the cooled suspension. Thorough mixing was ensured by the use of a stirring motor. The precipitation of manganese dioxide commenced almost immediately. Stirring was continued for about fifteen minutes after the addition was completed. The manganese dioxide was filtered by suction and thoroughly washed with three 20-cc. portions of hot water. The filtrate (placed in a large crystallizing dish) was put under vacuum over concentrated sulfuric acid. The solution was acidified after evaporation to a small volume. Since no precipitate formed, the evaporation was continued to dryness; a light brown resin separated. This was extracted thoroughly with four 30-cc. portions of boiling acetone and the acetone solution then filtered. Upon the addition of benzene, white flocks separated which were filtered and dried *in vacuo.* A white powder was obtained, yield 0.4 g. Upon heating it did not show a definite melting point, but began to sinter at about 70°. It was insoluble in dioxane and in hydrocarbons.

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(7) Ingold, *J. Chem. Soc.*, **119**, 1976 (1921).

(8) Cooper, Ingold and Ingold, *ibid.*, **129**, 1869 (1926).

(9) Oxford, *Biochem. J.*, **28**, 1325 (1934).

(10) Shriner and Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1935, p. 148.

Anal. Calcd. for $(CH_2{=}CHCOOH)_x$: C, 50.0; H, 5.56. Found: C, 50.0; H, 5.39.

Summary

Acrolein polycondenses in the presence of dilute alkalies by a Michael mechanism to give a hydroxypentaldehyde. The rate of polymerization was measured under varying conditions.

NEW HAVEN, CONN. RECEIVED JUNE 7, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON]

The Condensation of *n*-Butyraldehyde with 2-Butanone. II[1]

BY S. G. POWELL AND DONALD A. BALLARD

In a previous paper[2] it was shown that *n*-butyraldehyde reacts with 2-butanone under the influence of dilute potassium hydroxide solution to form a ketol which yields 3-methyl-3,2-heptenone (I) upon dehydration. Eccott and Linstead[3] carried out a similar series of reactions with *n*-butyraldehyde and acetone and obtained 3,2-heptenone (A). When, however, they treated a mixture of the aldehyde and acetone with a strong solution of sodium hydroxide they obtained as a direct product of the reaction a substance which they concluded was a geometrical isomer of (A). The present investigation was undertaken in an attempt to prepare in a similar manner the isomeric forms of 3-methyl-3,2-heptenone.

When *n*-butyraldehyde was added to a mixture of 2-butanone and a strong solution of sodium hydroxide we obtained a substance (II) which gave the analytical figures for $C_8H_{14}O$. The semicarbazone of (II) after recrystallization from dilute methanol melted constantly at 141–142°, whereas that of (I) melts at 168°. The semicarbazone of α-ethyl-α-hexenal, which results from the condensation of two molecules of *n*-butyraldehyde, melts at 152°.[4]

The substance (II) was almost completely soluble in a solution of sodium sulfite and sodium bicarbonate, showing it to be an α,β-unsaturated ketone or aldehyde.

Upon reduction with sodium and moist ether (II) gave 3-methyl-2-heptanol, although in small yield. This led to the belief that the substance was in fact the isomer of (I), which also yields 3-methyl-2-heptanol upon reduction. In order to determine the configuration of their two substances Eccott and Linstead prepared a 3,2-heptenone from an α-hexenoic acid of known configuration. Following the same procedure we prepared a 3-methyl-3,2-heptenone from α-methyl-α-hexenoyl chloride and methyl zinc iodide and found it to be identical with (I). On oxidation with sodium hypobromite, (I) gave this same α-methyl-α-hexenoic acid. However, the same acid was obtained when (II) was oxidized. At this point the semicarbazone of (II) was recrystallized carefully from dilute ethanol instead of methanol and the semicarbazone of α-ethyl-α-hexenal was isolated. It was also possible to isolate the 2,4-dinitrophenylhydrazone of α-ethyl-α-hexenal from the products of the reaction between (II) and 2,4-dinitrophenylhydrazine. A current of air was then passed through a sample of (II) for several hours to oxidize part of the aldehyde. From the residue, after washing with alkali, it was possible to prepare the semicarbazone of (I). The substance (II) was therefore merely a mixture of (I) and α-ethyl-α-hexenal.

As α-ethyl-α-hexenal might also exist in two modifications, it was prepared both by the action of alkali upon *n*-butyraldehyde and by the dehydration of *n*-butyraldol with iodine. Both products gave the same semicarbazone.

In view of the foregoing it seemed advisable to study further the reaction between *n*-butyraldehyde and acetone. By following the procedure of Eccott and Linstead we obtained the substance (A) which gave a semicarbazone melting at 152°, as reported by these authors. However, this was found to be identical with the semicarbazone of α-ethyl-α-hexenal. As a further check we treated (A) with 2,4-dinitrophenylhydrazine and isolated the 2,4-dinitrophenylhydrazone of α-ethyl-α-hexenal and also one that was identical with that obtained from the 3,2-heptenone produced by dehydrating the ketol.

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(1) This paper is an extract from a thesis presented by Donald A. Ballard in partial fulfilment of the requirements for the doctorate at the University of Washington.

(2) Powell, THIS JOURNAL, **46**, 2514 (1924).

(3) Eccott and Linstead, *J. Chem. Soc.*, 911 (1930).

(4) Batalin and Slavina, *J. Gen. Chem.* (U. S. S. R.), **7**, 202 (1937).