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.

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[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).

Experimental

The Direct Condensation of 2-Butanone with *n*-Butyraldehyde.—One hundred and forty-four grams of *n*-butyraldehyde was added in a slow stream to a mixture of 144 g. of 2-butanone and 1000 cc. of a 2.5% sodium hydroxide solution. The reaction was allowed to proceed until the first vigorous reaction had subsided and then the mixture was shaken for fifty-six hours. The upper layer was separated, washed with water and distilled. The fraction of b. p. 72–74° (20 mm.), 117 g., was shaken for fifteen hours with a mixture of 234 g. of sodium sulfite heptahydrate, 78 g. of sodium bicarbonate and 660 cc. of water. The aqueous solution was made alkaline with 40 g. of sodium hydroxide and distilled with steam. The oily portion of the distillate was separated, dried with calcium chloride and distilled; b. p. 77–78° (25 mm.); yield 77 g.

Anal. Calcd. for $C_8H_{14}O$: C, 76.12; H, 11.11. Found: C, 76.13; H, 11.30.

The semicarbazone was prepared in the usual manner from 1 g. of semicarbazide hydrochloride, 1.5 g. of sodium acetate and 0.8 g. of the ketone. The crude product melted at 137–140° and after recrystallization from dilute methanol at 141–142°.

Anal. Calcd. for $C_9H_{17}ON_3$: N, 22.94. Found: N, 22.9, 23.0.

Twenty-two grams of the condensation product was hydrogenated partially by passage with hydrogen over nickel at 200°. The partially reduced product (17 g.) was mixed with 100 cc. of ether and 250 cc. of water and treated with 7 g. of sodium. The material was worked up in the usual manner, yielding 10 g. of product, b. p. 70–90° (20 mm.). This was oxidized with a solution of 10 g. of sodium dichromate and 14 g. of sulfuric acid in 75 cc. of water, keeping the temperature below 50°. After stirring for several hours the mixture was steam distilled. The oily portion of the distillate was separated, dried with calcium chloride and distilled, yielding, beside high boiling substances, 2.5 g. of material, b. p. 57–62 (20 mm.). The semicarbazone of this melted at 82–84° after recrystallization from dilute methanol, as did a mixture of it with the semicarbazone of 3-methyl-2-heptanone.

3-Methyl-3,2-heptenone.—A solution of 12 g. of α-methyl-α-hexenoyl chloride in 20 cc. of dry benzene was added to the methyl zinc iodide prepared from 25 g. of methyl iodide and the resulting ketone isolated in the usual manner. The crude ketone (10 g.) was shaken for five hours with a mixture of 10 g. of sodium sulfite heptahydrate, 8 g. of sodium bicarbonate, and 60 cc. of water.[5] The mixture was extracted with ether and the aqueous portion made alkaline with 4 g. of sodium hydroxide and distilled with steam. The resulting ketone yielded a semicarbazone melting at 166–168°, identical with that obtained from the 3-methyl-3,2-heptenone formed by dehydrating the ketol.[2]

The α-methyl-α-hexenoyl chloride was prepared by the action of phosphorus trichloride on α-methyl-α-hexenoic acid, which in turn was prepared by the method of Kon, Linstead and McLennan.[6,7] The 2,4-dinitrophenylhydrazone, orange crystals, m. p. 137°, was prepared by the method of Allen.[8]

Anal. Calcd. for $C_{14}H_{18}O_4N_4$: N, 18.3. Found: N, 18.4, 18.5.

Oxidation of 3-Methyl-3,2-heptenone.—A solution of 55 g. of sodium hydroxide in 470 cc. of water contained in a one-liter flask was cooled to 0° and 80 g. of bromine added with constant stirring, keeping the temperature below 10°. The solution was again cooled to 0°, 21 g. of 3-methyl-3,2-heptenone (obtained by dehydration of the ketol) added, and the mixture stirred for four hours. The bromoform and carbon tetrabromide were then distilled off with steam. The residue was cooled to 60°, 67 cc. of sulfuric acid added, the mixture distilled with steam, and the distillate extracted three times with ether. The combined extracts were dried with calcium chloride, the ether removed, and the residue distilled, yielding 5 g. of acid, b. p. 127–130° (20 mm.); neut. equiv. calcd. 128; found 129.5.

***p*-Toluidide.**—The acid chloride was prepared and dissolved in benzene. Two equivalents of *p*-toluidine was added and the mixture heated to boiling for a few minutes. The benzene layer was washed with water, dilute hydrochloric acid, dilute sodium hydroxide, and finally with water again. The benzene was evaporated off and the residue recrystallized from petroleum ether, m. p. 85–88°.

Anal. Calcd. for $C_{14}H_{14}ON$: N, 6.45. Found: N, 6.37, 6.26.

A sample of the *p*-toluidide prepared in the same manner from the acid obtained by the method of Kon, Linstead and McLennan was found to be identical.

Oxidation of the Direct Condensation Product.—This was oxidized in the same manner as the 3-methyl-3,2-heptenone, yielding an acid b. p. of 130–135° (25 mm.); neut. equiv. 130; m. p. of the *p*-toluidide, 85–88°.

α-Ethyl-α-hexenal.—A solution of 12 g. of sodium hydroxide in 65 cc. of water was placed in a flask fitted with a reflux condenser and mechanical stirrer, and 72 g. of *n*-butyraldehyde rapidly added. Stirring was continued for thirty minutes, the oil separated, dried with calcium chloride and distilled; b. p. 75–82° (24 mm.); yield 40 g. The semicarbazone melted at 152° after recrystallization from dilute methanol.

α-Ethyl-α-hexenal was also prepared by heating 15 g. of *n*-butyraldol (prepared by the method of Grignard and Vestermann[9]) with a few crystals of iodine; yield 11 g., b. p. 71–74° (30 mm.). The semicarbazone melted at 152°. The 2,4-dinitrophenylhydrazone melted at 124–125°.

Anal. Calcd. for $C_{14}H_{18}O_4N_4$: N, 18.3. Found: N, 18.4, 18.2.

Isolation of the Components of the Direct Condensation Product.—A stream of air was drawn through 60 g. of the product for twelve hours. It was then shaken with dilute sodium hydroxide solution, dried with calcium chloride, and again treated with air for twelve hours. The treatment with sodium hydroxide was repeated and then air drawn through the residue for thirty-six hours. At the end of this time the material was again shaken with sodium hydroxide solution and the residual oil dried and distilled, yielding 22 g., b. p. 70–90° (20 mm.), and 7 g., b. p. 90–

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(5) Tiemann and Tigges, *Ber.*, **33**, 561 (1900).

(6) Kon, Linstead and McLennan, *J. Chem. Soc.*, **2453** (1932).

(7) The authors are indebted to Dr. T. R. Liston for the preparation of the necessary α-methyl-α-hexenoic acid and also for many valuable suggestions during the course of this investigation.

(8) Allen, THIS JOURNAL, **52**, 2956 (1930).

(9) Grignard and Vestermann, *Bull. soc. chim.*, **37**, 420 (1925).

140° (20 mm.). On redistillation the first fraction gave 10 g. of material of b. p. 70–75° (20 mm.). The crude semicarbazone of this fraction melted at 150–160°. After recrystallization it melted at 163–167° as did a mixture of it and the semicarbazone of 3-methyl-3,2-heptenone obtained by the dehydration of the ketol.

The sodium hydroxide extracts were combined and extracted with ether. The aqueous portion was acidified with dilute sulfuric acid and extracted with ether. The ether solution was dried, the ether removed, and the residue distilled. The acid boiled at 136–137° (20 mm.); neut. equiv., 145. The neutral equivalent of α-ethyl-α-hexenoic acid is 142.

The Direct Condensation of *n*-Butyraldehyde with Acetone.—This was carried out according to the directions of Eccott and Linstead.[3] The crude product was fractionated, yielding the following fractions: up to 90° (21 mm.), 62 g.; 90–130° (21 mm.), 17 g.; 130–180° (18 mm.), 43 g.; residue 30 g. The first fraction was carefully redistilled through a Podbielniak column, yielding 3 fractions.[10] The semicarbazones and 2,4-dinitrophenylhydrazones of each fraction were prepared and their melting points are given in Table I.

TABLE I

	B. p., °C. (19 mm.)	Wt., g.	M. p. (°C.) of crude semicarbazone	M. p. (°C.) of crude 2,4-dinitrophenylhydrazone
1	–65	3	110–120	95–100
2	65–69	29	123–133	99–110
3	69–71	11	143–148	120–122

By repeated crystallization of the crude derivative in each case, we were able to isolate a semicarbazone melting at 152°, identical with that of α-ethyl-α-hexenal. Fraction 3 was apparently almost entirely α-ethyl-α-hexenal. In order to identify the other component of fractions 1 and 2, the crude 2,4-dinitrophenylhydrazones were dissolved in alcohol, and the solution cooled, when crystals of the 2,4-dinitrophenylhydrazone of α-ethyl-α-hexenal separated. The mother liquor was evaporated to dryness and the residue dissolved in warm gasoline. When the solution was cooled a further crop of the 2,4-dinitrophenylhydrazone of α-ethyl-α-hexenal was obtained. The mother liquor was evaporated to dryness and the residue recrystallized from alcohol. This substance melted at 125–126° but was not identical with the 2,4-dinitrophenylhydrazone of α-ethyl-α-hexenal, m. p. 124–125°, as a mixture of the two melted at 100–110°.

A sample of 3,2-heptenone was prepared by dehydrating the ketol with oxalic acid, according to the method of Eccott and Linstead, and converted into the 2,4-dinitrophenylhydrazone. This substance melted at 125–126° and was identical with that obtained above.

Anal. Calcd. for $C_{13}H_{16}O_4N_3$: N, 19.2. Found: N, 18.9, 19.0.

Summary

1. An unsuccessful attempt was made to prepare *cis* and *trans* forms of 3-methyl-3,2-heptenone. An unsuccessful attempt was also made to prepare the *cis* and *trans* forms of 3,2-heptenone as described by Eccott and Linstead.

2. The 2,4-dinitrophenylhydrazones of α-ethyl-α-hexenal, 3,2-heptenone, and 3-methyl-3,2-heptenone were prepared.

3. The *p*-toluidide of α-methyl-α-hexenoic acid was prepared.

SEATTLE, WASH.

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[10] Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **3**, 179 (1931).

[CONTRIBUTIONS FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

Researches on Nitrogenous Glucosides. IV. Some New Attempts to Synthesize Pyrimidine Glucosides

BY TREAT B. JOHNSON AND WERNER BERGMANN

The authors desire to report in this paper new data resulting from some special experiments applied in their researches on nitrogenous glucosides, which do not find their proper place in other papers to be published on this subject. The first contribution of importance from this Laboratory was made in 1930 when Hilbert and Johnson[1] synthesized successfully 3-glucosidouracil by interaction of 2,6-dimethoxypyrimidine with tetraacetylbromoglucose. The resulting acetyl derivative gave the desired nucleoside on hydrolysis. Later Hilbert[2] applied a similar reaction using 2-methoxy-6-aminopyrimidine and tetraacetylbromoglucose in order to obtain the corresponding glucoside of cytosine, but without success. It is of interest to note here that E. Fischer also failed in his attempts to prepare glucosides of both uracil and cytosine by the action of tetraacetylbromoglucose on the silver salts of these two pyrimidines.[3] Recognizing the limitations of this method of approach to practical methods of synthesizing nitrogenous glucosides, we next turned our attention to the study of techniques based on the use of sugar isocyanates and corresponding ureas as starting points. The only

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[1] Hilbert and Johnson, THIS JOURNAL, **52**, 4489 (1930).

[2] Hilbert, *ibid.*, **56**, 190 (1934).

[3] E. Fischer, *Ber.*, **47**, 1377 (1914).