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

The Condensation of 2-Butanone with Normal Aliphatic Aldehydes[1]

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In a previous paper[2] it was shown that when 2-butanone reacts with *n*-butyraldehyde the condensation takes place through the methylene group of the ketone. This is also the case in its reaction with formaldehyde[3] and acetaldehyde.[4] On the other hand Thoms and Kahre[5] have shown that the reaction between 2-butanone and isobutyraldehyde yields 2-methyl-3-heptene-5-one, $(CH_3)_2CHCH{=}CHCOC_2H_5$. In view of this difference in behavior it seemed desirable to investigate the reaction between 2-butanone and other aldehydes.

It was found that the condensation of 2-butanone with propionaldehyde, *n*-valeraldehyde and *n*-heptaldehyde takes place through the methylene group of the ketone. From these results and those previously obtained in the cases of formaldehyde, acetaldehyde and *n*-butyraldehyde, it appears that the normal aliphatic aldehydes in general react in this manner with 2-butanone. As Thoms and Kahre have shown that the branched-chain isobutyraldehyde brings about a different reaction, an investigation of the reaction between 2-butanone and other branched-chain aldehydes is now under way.

The constitution of the condensation product was determined in each case by dehydration of the aldol to the unsaturated ketone and reduction of this to the corresponding saturated alcohol. In the case of propionaldehyde this saturated alcohol was found to be identical with the 3-methyl-2-hexanol described by Bjelouss[6] and on oxidation yielded a ketone identical with the 3-methyl-2-hexanone obtained by the hydrolysis of ethyl methyl-*n*-propyl-acetoacetate. The structures of the alcohols obtained from *n*-valeraldehyde and *n*-heptaldehyde were determined by oxidation and identification of the resulting acids as *n*-valeric and enanthic acids, respectively.

The condensation, dehydration, reduction to the saturated alcohol, and oxidation of this to the saturated ketone were carried out as described in the previous paper.[2]

In Table I are listed the new compounds prepared.

Identification of the Acids Obtained by Oxidizing 3-Methyl-2-octanol and 3-Methyl-2-decanol.—The alcohols were oxidized by boiling with a

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

[3] U. S. Patent 981,668.

[4] Salkind, *J. Russ. Phys.-Chem. Soc.*, **37**, 484 (1905).

[5] Thoms and Kahre, *Arch. Pharm.*, **263**, 241 (1925).

[6] Bjelouss, *Ber.*, **45**, 625 (1912).

TABLE I

	B. p., °C.	Mm.	n_D	d_4	Yield, %	Analyses, % Calcd. C	Analyses, % Calcd. H	Analyses, % Found C	Analyses, % Found H
$C_2H_5CHOHCH(CH_3)COCH_3$	94–96	20	1.435 (24°)	0.939 (22°)	61	64.57	10.84	64.00	10.95
$C_4H_9CHOHCH(CH_3)COCH_3$	98	16	1.4404 (29°)	.9167 (29°)	35	68.31	11.47	68.46	11.61
$C_6H_{13}CHOHCH(CH_3)COCH_3$	147	23	1.4425 (21°)	.889 (22°)	50	70.90	11.91	70.53	12.07
$C_3H_7CH(CH_3)COCH_3$	142–145		1.409 (24°)	.828 (25°)	57	73.61	12.37	73.53	12.60
$C_6H_{11}CH(CH_3)COCH_3$	64–65	18	1.424 (27°)	.832 (27°)	52	75.98	12.75	75.36	12.39
$C_7H_{15}CH(CH_3)COCH_3$	121	20	1.431 (20°)	.823 (20°)	43	77.57	13.03	77.20	12.84
$C_5H_{11}CH(CH_3)CHOHCH_3$	75	15	1.437 (27°)	.831 (27°)	47	75.00	13.88	74.91	13.98
$C_7H_{15}CH(CH_3)CHOHCH_3$	125	19	1.440 (21°)	.834 (23°)	43	76.65	14.05	76.10	13.36

mixture of sodium dichromate and sulfuric acid. The water-insoluble acid obtained from 3-methyl-2-octanol boiled at 183° (uncorr.); b. p. of *n*-valeric acid is 185°. Titration with standard alkali gave equivalent wt. 102; calcd. for valeric acid, 100.

The water-insoluble acid obtained from 3-methyl-2-decanol boiled at 220° (corr.); b. p. of enanthic acid is 224°. The amide, obtained by treatment with thionyl chloride and then ammonia, melted at 95° as did a mixture of it with enanthamide.

The water-soluble acid in each case was identified as acetic acid by conversion into the *p*-bromophenacyl ester by the method of Reid and Judefind.[7]

Summary

1. 2-Butanone has been found to react with propionaldehyde, *n*-valeraldehyde and *n*-heptaldehyde through the methylene group.

2. Several new derivatives of 3-methylhexane, 3-methyloctane and 3-methyldecane have been prepared.

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[7] Reid and Judefind, THIS JOURNAL, **42**, 1083 (1920).