TABLE I

Cyanomethyl ester of	Method	Yield, %	B. p. °C.	B. p. Mm.	M. p., °C.	n^{25}D	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
Acrylic acid	A	17	60	4	..	1.4331	54.05	53.75	4.54	4.87	12.62	12.57
Methacrylic acid	A	58	90–91	10	..	1.4390	57.60	57.66	5.64	5.66	11.20	11.38
Crotonic acid	A	60	103–104	17	..	1.4482	57.60	57.81	5.64	5.90	11.20	11.38
β-Chlorocrotonic acid	A	53	116	16	..	1.4797	45.15	45.37	3.78	3.87	8.98	8.64
Cinnamic acid	A	73	164–165	4	63	....	70.57	70.69	4.84	4.75	7.48	7.63
	B	75										
α-Methylcinnamic acid	A	63	162–163	3	..	1.5669	71.62	72.36	5.52	5.73	6.96	6.87
Fumaric acid	B	45	.....	..	83	....	49.50	49.68	3.11	3.02	14.43	14.38
Mesaconic acid[a]	B	43	192–193	3	..	1.4815	51.92	52.50	3.87	3.98	13.46	13.42

[a] Prepared by Dr. W. Frederick Huber.

maryl and mesaconyl chlorides were made from maleic anhydride and phthalyl chloride.[8]

Glycolonitrile.—A modification of the cyanohydrin interchange method[9] was used for the preparation of glycolonitrile.

To a concentrated aqueous solution of 1040 g. of sodium bisulfite was added 720 g. (10.0 moles) of methyl ethyl ketone with stirring and cooling by addition of ice. A solution of 520 g. of 95% sodium cyanide was then added in a similar manner. The resultant supernatant oil was separated and mixed with 871 g. of 37% formalin, to which 5 g. of sodium cyanide had been added. After this solution had been stirred at 35° for two hours, 30 g. of phthalic anhydride was added and the material distilled. The regenerated ketone and water were removed at 100 mm. The product was then rapidly distilled at 20–30 mm. (slight decomposition), b. p. 100–120°. When the distillation was about two-thirds completed, the residue became very viscous. The flame had to be removed and the flask cooled immediately to avoid violent dissociation and polymerization caused by superheating. The crude product was refractionated without decomposition over 5 g. of phthalic anhydride, giving 228 g. (40% yield) of glycolonitrile, b. p. 99–100° (17 mm.), n^{25}D 1.4090.

Cyanomethyl Acrylate (Method A).—Acrylyl chloride (233 g., 2.6 moles) was added dropwise to a briskly stirred solution of 236 cc. (2.7 moles) of 37% formalin and 154 g. (2.9 moles) of 95% sodium cyanide in 300 cc. of water at 10°.

Stirring was continued for one hour after addition was complete, while the solution was allowed to rise to room temperature. The supernatant oil was taken up in several volumes of ether, washed with dilute solutions of sodium carbonate and hydrochloric acid. Distillation over hydroquinone of the dried ether solution gave 46 g. (17%) of cyanomethyl acrylate, b. p. 42–43° (1 mm.), and 50 g. of a compound, $C_6H_9O_3N$, b. p. 82–83° (1 mm.), n^{25}D 1.4248, which did not decolorize a carbon tetrachloride solution of bromine.

Anal. Calcd. for $C_6H_9O_3N$: C, 50.36; H, 6.34; N, 9.79. Found: C, 50.74; H, 6.27; N, 9.94.

Solid acid chlorides such as cinnamoyl chloride were dissolved in dioxane to facilitate dropwise addition to the aqeuous solution.

Cyanomethyl Cinnamate (Method B).—Glycolonitrile (28.5 g., 0.5 mole) was added slowly with stirring to a solution of 86 g. of cinnamoyl chloride (0.5 mole) and 60 g. of dimethylaniline (0.5 mole) in 100 cc. of anhydrous ether at 5–10°. The solution was allowed to warm to room temperature and stirred for two hours before dilution with two volumes of ether and washing with dilute solutions of sodium carbonate and hydrochloric acid. Evaporation of the ether gave 72 g. (75%) of crude cyanomethyl cinnamate, m. p. 57–60°. Three recrystallizations from dilute ethanol gave large colorless plates, m. p. 62.7–63.0°.

Summary

The reaction of an aqueous solution of sodium cyanide and formaldehyde with benzoyl chloride has been extended to the acid chlorides of monobasic α,β-unsaturated acids. The cyanomethyl esters of acrylic, methacrylic, crotonic, β-chlorocrotonic, cinnamic, α-methylcinnamic, fumaric and mesaconic acids are reported.

DAYTON, OHIO

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[8] Kyrides, This Journal, **59**, 207 (1937).

[9] Kung, U. S. Patent 2,259,167 (1941).

[Contribution from the Department of Chemistry, University of Washington]

The Condensation of Isobutyraldehyde with Aliphatic Ketones

By S. G. Powell and French Hagemann[1]

It has been shown that certain straight chain aliphatic aldehydes condense with methyl ethyl ketone through the methylene group of the ketone,[2] whereas homologous methyl ketones which contain six or more carbon atoms appear to condense through the methyl group.[3] On the other hand, the condensation of α-methylbutyraldehyde, α-ethylbutyraldehyde and α-ethylcaproaldehyde with various methyl ketones has been found to take place through the methyl group.[4]

The same alkaline condensing agents which bring about the above-mentioned reactions with aliphatic aldehydes cause aromatic aldehydes to react with the methyl group of the ketone, while acids bring about condensation with the methyl-

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[1] From the Ph.D. dissertation of French Hagemann.

[2] (a) Powell, *et al.*, This Journal, **46**, 2514 (1924); **55**, 1153 (1933); (b) Salkind, *J. Russ. Phys.-Chem. Soc.*, **37**, 484 (1905); (c) Merling and Köhler, U. S. Patent 981,668 (1901).

[3] Wickert and Freure, U. S. Patent 2,088,018 (1937), British Patent 461,662 (1937).

[4] (a) Powell and Baldwin, This Journal, **58**, 1871 (1936); (b) Wickert and Carter, U. S. Patent 2,088,017 (1937); (c) Carbide and Carbon Chemicals Corp., French Patent 782,835 (1935); (d) Ref. (3).

ene group.[5] No similar behavior seems to have been observed in the case of aliphatic aldehydes.

The course of the reaction between the simplest *alpha*-branched chain aldehyde, isobutyraldehyde and unsymmetrical methyl ketones has been established only in the case of methyl ethyl ketone, which Thoms and Kahre[6] found to condense through the methyl group. Therefore, it seemed desirable to investigate the reaction of isobutyraldehyde with other ketones.

Isobutyraldehyde was condensed with methyl *n*-propyl, methyl *n*-butyl, methyl isobutyl, methyl *n*-amyl and methyl *n*-hexyl ketones in the presence of dilute potassium hydroxide and the resulting ketol was dehydrated to the unsaturated ketone. The structure of the unsaturated ketone was determined by ozonolysis, and in each case the condensation was found to take place upon the methyl carbon atom. By repeated fractionation of the crude unsaturated ketone resulting from the reaction between isobutyraldehyde and methyl *n*-amyl ketone there was obtained a small fraction which consisted chiefly of the compound formed by methylene condensation. It is possible that similar small quantities of the methylene isomer may have formed in the other condensations.

When the ozonides were decomposed, the expected 1,2-dicarbonyl compounds were oxidized by the hydrogen peroxide to mixtures of acids which were identified.

$$(CH_3)_2CHCH{=}CHCOCH_2R = (CH_3)_2CHCHO + RCH_2COCHO + H_2O_2$$

$$RCH_2COCHO + H_2O_2 = RCH_2COOH + HCOOH$$

In the neutral fraction of the decomposition products, in addition to isobutyraldehyde, appreciable amounts of acetone and acetone peroxide were identified. The last two substances must have been formed by oxidation of the isobutyraldehyde by the hydrogen peroxide.

Further proof of the structure of the unsaturated ketones in the case of methyl *n*-amyl and methyl *n*-hexyl ketones was obtained by reducing them to the corresponding saturated ketones and oxidizing the latter to a mixture of acids which were identified. Also, the saturated ketone from the methyl *n*-amyl ketone condensation was found to be identical with *n*-amyl isoamyl ketone prepared by another method.

Thoms and Kahre gave the structure of the condensation product of di-ethyl ketone and isobutyraldehyde as $(CH_3)_2CHCH{=}CHCH_2COCH_2CH_3$, whereas Franke and Köhler[7] gave the structure as $(CH_3)_2CHCH{=}C(CH_3)COCH_2CH_3$. As no proof of structure was given in either case, this work was repeated. The unsaturated ketone was ozonized and the ozonide decomposed in the presence of hydroxylamine. Since methylethylglyoxime was identified as a product, the correct structure is that given by Franke and Köhler.

It was not possible to reduce completely some of the unsaturated ketones to the saturated alcohols with sodium and alcohol or moist ether, even though a large excess of sodium was used. 2-Methyl-3-decen-5-one, 2-methyl-3-undecen-5-one and 2,7-dimethyl-5-octen-4-one yielded products which were still unsaturated, but which gave the saturated alcohols upon hydrogenation with platinum oxide catalyst.

In order to explain this behavior, 2-methyl-3-decen-5-one was treated with sodium and ethyl alcohol. The analysis and the molar refraction of the product agreed closely with that calculated for an unsaturated alcohol, $C_{11}H_{22}O$. Ozonolysis established its formula as $(CH_3)_2C{=}CHCH_2CHOHCH_2CH_2CH_2CH_2CH_3$. Acetone, but no isobutyraldehyde, and an aldehyde which appeared to be unsaturated were found as ozonolysis products. The semicarbazone of the latter compound was prepared and found to melt at 169–170° (cor.); van Romburgh[8] reported the melting point of the semicarbazone of α-octenaldehyde as 163°. Analysis of the compound corresponded to octenaldehyde semicarbazone. α-Octenaldehyde would result from the dehydration of β-hydroxycaprylaldehyde which would be the primary ozonolysis product of this alcohol. Apparently in the presence of the alkaline reduction medium the double bond shifts from the α-β to the β-γ position. In the latter position the ethylenic bond is very resistant to reduction by sodium and alcohol or water.

Experimental Part

The physical properties and analyses of the ketones and alcohols prepared in the course of this investigation are collected in Table I. The melting points and analyses of the new derivatives prepared are listed in Table II.

Condensations.—All of the condensations were carried out by the addition of a mixture of one mole proportion of aldehyde and one-half mole of ketone to two and one-half moles of ketone and excess alcoholic potassium hydroxide as previously described.[2a] The rate of addition was regulated so as to keep the temperature below 35°.

Dehydrations.—The ketols were dehydrated by slow distillation at atmospheric pressure in the presence of a small amount of iodine.[9] The distillate was separated from water and the distillation repeated with fresh iodine. Drying over anhydrous magnesium sulfate and fractionation gave the desired unsaturated ketone.

The crude unsaturated ketone from the methyl *n*-amyl ketone condensation was put through a 28-plate fractionating column at atmospheric pressure. From 246 g. were obtained the following fractions: up to 205°, 15 g.; 205–223°, 45 g.; 223–224°, 85 g. A large viscous residue of about 100 g. remained in the pot, due to decomposition and resinification during the long-continued heating at high temperature. Refractionation of the 205–223° portion gave 28 g. of material boiling from 208–218°, which upon redistillation at reduced pressure yielded 14.2 g. boiling at 103–105° (24.5 mm.). This material gave a very strong positive iodoform reaction,[10] whereas the 223–224° fraction gave a negative reaction.

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(5) (a) Harries and Mueller, *Ber.*, **35**, 966, 3088 (1902); (b) Ryan and Cahill, *Proc. Roy. Irish Acad.*, **36B**, 334 (1924).

(6) Thoms and Kahre, *Arch. Pharm.*, **263**, 241 (1925).

(7) Franke and Köhler, *Ann.*, **433**, 314 (1923).

(8) Van Romburgh, *Rec. trav. chim.*, **57**, 494 (1938).

(9) Hibbert, THIS JOURNAL, **37**, 1748 (1915).

(10) Shriner and Fuson, "Identification of Organic Compound 2d ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 53

TABLE I

Compound	Yield, %	B. p. °C.; cor.	Mm.	d^{20}_4	$n^{20}D$	MD (obs.)	MD (calcd.)	Analyses, % Calcd. C	Calcd. H	Found C	Found H
7-Methyl-5-octen-4-one[a]	45	85–86	25	0.8520	1.4413	43.49	43.32[f]	77.08	11.50	76.96	11.73
2-Methyl-3-nonen-5-one	50	103–105	25	.8485	1.4438	48.27	47.94[f]	77.87	11.76	77.89	12.08
2,7-Dimethyl-5-octen-4-one	65	199–200	760	.8412	1.4399	48.31	47.94[f]	77.87	11.76	78.02	12.02
2-Methyl-3-decen-5-one	61	223–224	760	.8487	1.4457	52.84	52.58[f]	78.52	11.98	78.28	12.22
2-Methyl-3-undecen-5-one	35	135–136	28	.8502	1.4480	57.40	57.18[f]	79.06	12.16	78.77	12.44
4,6-Dimethyl-4-hepten-3-one[b]	49	176–178	760	.8499	1.4432	43.76	43.32[f]	77.08	11.50	76.77	11.68
7-Methyl-4-octanone[c]	62	177–179	760	.8239	1.4210	43.77	43.79	76.00	12.75	75.75	12.82
2-Methyl-5-nonanone	54	203–204	760	.8213	1.4239	48.54	48.41	76.86	12.90	76.78	13.14
2,7-Dimethyl-4-octanone	64	196–198	760	.8305	1.4280	48.41	48.41	76.86	12.90	76.76	12.65
2-Methyl-5-decanone	50	119–121	28	.8235	1.4279	53.19	53.03	77.58	13.02	77.48	13.25
2-Methyl-5-undecanone	47	126–128	23.5	.8268	1.4307	57.67	57.65	78.19	13.12	78.19	13.24
4,6-Dimethyl-3-heptanone[d]	57	170–173	760	.8208	1.4197	44.26	43.79	76.00	12.75	75.80	12.97
2-Methyl-5-nonanol	78	111.5–113	28.5	8215	1.4310	49.89	49.92	75.88	14.01	75.98	14.09
2,7-Dimethyl-4-octanol[e]	68	107–108	29.5	.8183	1.4297	49.94	49.92	75.88	14.01	75.91	14.02
2-Methyl-5-decanol	42	122.5–123	24	.8266	1.4351	54.40	54.54	76.67	14.04	76.55	13.87
2-Methyl-5-undecanol	50	132–133	24	.8266	1.4346	58.76	59.16	77.35	14.07	77.65	13.77

[a] Thoms and Kahre, ref. (5), gave b. p. 68–78° (24 mm.); d^{12} 0.9011; n_D 1.47477. [b] Thoms and Kahre, ref. (6) gave b. p. 171–184° (760 mm.), 73–77° (19 mm.); d^{19} 0.8628; n_D 1.44533 for the unsaturated ketone which they considered to be 7-methyl-5-octen-3-one. Franke and Köhler, ref. (7), gave b. p., 178–183° (760 mm.), 66–69° (16 mm.) for the unsaturated ketone which they reported to be 4,6-dimethyl-4-hepten-3-one. [c] Blaise, *Compt. rend.*, **133**, 1217 (19 1). reported the b. p. as 176–178°, and Douris, *ibid.*, **157**, 55 (1913), gave b. p. 177–179°, d^{21}_4 0.8205; semicarbazone, m. p. 144.5–145.5°. *Anal.* Calcd. for $C_{10}H_{21}N_3O$: N, 21.08. Found: N, 21.05. Blaise gave 102° and Douris, 107° as the m. p. of the semicarbazone. [d] Thoms and Kahre, ref. (6), gave for the corresponding saturated ketone considered to be 7-methyl-3-octanone, b. p. 180–185°; d^{20}_{20} 0.8353; n_D 1.43479. [e] Tuot, *Compt. rend.*, 202, 1339 (1936), gave b. p. 96° (18 mm.); d^{20}_{20} 0.8154; $n^{20}D$ 1.4280. [f] Calculated without exaltation for conjugation.

TABLE II

Hydantoin[a] of	M. p., °C. (cor.)	Analyses, % N Calcd.	Found
2-Methyl-3-nonen-5-one	149.5–150	12.49	12.65
2,7-Dimethyl-5-octen-4-one	176.5–177	12.49	12.52
2-Methyl-3-decen-5-one[f]	135–136	11.76	11.83
3-*n*-Butyl-5-methyl-3-hexen-2-one	175–176	11.76	11.65
2-Methyl-3-undecen-5-one	118.5–119	11.10	11.07
7-Methyl-4-octanone	175–175.5	13.20	13.14
2-Methyl-5-nonanone	192–192.5	12.38	12.39
2,7-Dimethyl-4-octanone	216–217	12.38	12.44
2-Methyl-5-decanone	192–192.5	11.66	11.70
2-Methyl-5-undecanone	175–175.5	11.02	11.02
4,6-Dimethyl-3-heptanone	186–186.5	13.20	13.23
Nitroguanylhydrazone[b] of			
2-Methyl-5-decanone	78–79.5 (d.)	25.81	25.97
2-Methyl-5-undecanone	84.5–86 (d.)	24.54	24.49
Semicarbazone[c] of			
2,7-Dimethyl-4-octanone	78–79	19.70	19.86
2,4-Dinitrophenylhydrazone[d] of			
4,6-Dimethyl-4-hepten-3-one	174–175	17.49	17.56
3,5-Dinitrobenzoate[e] of			
2-Methyl-5-nonanol	63.5–64.5	7.95	7.94
2,7-Dimethyl-4-octanol	81–82	7.95	8.10

[a] Ref. (11). [b] Whitmore, Revukas and Smith, THIS JOURNAL, **57**, 706 (1935). [c] Ref. (10), p. 142. [d] Ref. (10), p. 143. [e] Reichstein, *Helv. Chim. Acta*, **9**, 800 (1926). [f] This compound showed no depression in melting point when mixed with the hydantoin of *n*-amyl isoamyl ketone obtained by oxidation of *n*-amylisoamylcarbinol prepared by the Grignard method.

The 5,5-disubstituted hydantoin derivative[11] of the 223–224° fraction melted at 135–136° while that of the 103–105° (24.5 mm.) fraction melted at 175–176°. Ozonolysis showed that the latter fraction consisted chiefly of 2-*n*-butyl-5-methyl-3-hexen-2-one.

Reduction of Unsaturated to Saturated Ketones.—The unsaturated ketones were converted to the corresponding saturated ketones by vapor phase hydrogenation over supported nickel catalyst maintained at 200°.

Reduction of Saturated Ketones to Alcohols.—2-Methyl-5-nonanone and 2,7-dimethyl-4-octanone were reduced to the corresponding alcohols by dissolving 0.1-mole proportion in 100 ml. of absolute ethyl alcohol and adding 0.4 mole of sodium. After initial cooling, the reaction was completed upon the steam-bath. The solution was then diluted with 400 ml. of water, the insoluble layer separated, washed with water and steam distilled. Extraction of the distillate with ether, drying over potassium carbonate and removal of the ether yielded the desired alcohol.

Reduction of Unsaturated Ketones to Alcohols: (1) **Preparation of 2-Methyl-5-decanol.**—Four-tenths mole (67 g.) of 2-methyl-3-decen-5-one was dissolved in 500 ml. of ether and placed in a flask containing a suspension of 250 g. of sodium bicarbonate in 500 ml. of water. Sixty grams (2.6 moles) of sodium metal cut in narrow strips was added piece by piece. After completion of the addition, the ether layer was separated and dried over anhydrous sodium sulfate. There was obtained 34.5 g. of material boiling from 120–128° (24 mm.). Redistillation yielded a sample boiling at 124–126° (24 mm.) which upon analysis gave C. 76.75 and H. 13.61. Calcd. for $C_{11}H_{24}O$: C, 76.67; H. 14.04.

As the material was apparently still partially unsaturated, the reduction was completed by catalytic hydrogenation. Twenty-nine grams of the substance was dissolved in 150 ml. of 95% ethyl alcohol and treated with hydrogen at about three atmospheres pressure using 0.3 g. of platinum oxide as catalyst.[12] Upon redistillation the pure compound boiled at 122.5–123° (24 mm.).

(2) **Preparation of 2-Methyl-5-undecanol.**—Four tenths mole (74 g.) of 2-methyl-3-undecen-5-one was reduced with moist ether as above yielding 50 g. of material of b. p. 135–140° (27 mm.). A sample boiling at 135° (24 mm.) obtained by redistillation gave the following analysis: C, 77.84; H, 12.92. Calcd. for $C_{12}H_{26}O$: 77.35; H, 14.07.

Thirty grams of this material was reduced catalytically

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(11) Henze and Speer, THIS JOURNAL, **64**, 522 (1942).

(12) Gilman, "Organic Syntheses," Coll. Vol. 1, 1932, p. 452.

as above. Distillation of the alcohol gave 22 g. of material boiling from 129–134° (24 mm.). Upon redistillation the compound boiled at 132–133° (24 mm.).

(3) **Preparation of 2-Methyl-2-decen-5-ol.**—Twenty grams (0.12 mole) of 2-methyl-3-decen-5-one was dissolved in 200 ml. of absolute ethyl alcohol and 71 g. (0.75 mole) of metallic sodium added. After completion of the reaction the solution was diluted with water, the oily layer separated, washed with water and steam distilled. The distillate was extracted with ether and dried over potassium carbonate. Distillation gave 8.6 g. (42%) of colorless, rather viscous liquid, b. p. 129.5–131° (30 mm.); d^{20}_4 0.8422; n^{20}_D 1.4473; M_D (obs.), 54.05; M_D (calcd.), 54.07.

Anal. Calcd. for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.34; H, 13.27.

The 3,5-dinitrobenzoate was an oil which could not be made to crystallize.

Ozonolysis.—For production of ozone, a generator similar in design to that described by Henne[13] was used. The ozone content of the issuing gas was about 8% by weight at a flow of about 3 liters per hour.

(1) **Unsaturated Ketones Obtained from Methyl Ketones.**—Ozone was passed through the sample (0.1 to 0.15 mole), cooled by an ice–salt mixture, until the sudden liberation of iodine in a solution of potassium iodide serving as a trap for the exit gases indicated completion of the reaction. All of the ozonides were viscous yellow liquids possessing reeking odors. Decomposition was immediately carried out by adding the ozonide dropwise, with stirring, to a boiling mixture of 200 ml. of water, an excess of zinc, and a trace of hydroquinone and silver nitrate.[14] The volatile decomposition products were allowed to distill over during the addition of the ozonide, and, after addition was complete, distillation was continued until all steam-volatile products were removed, more water being added if necessary. The residue was then acidified with an amount of sulfuric acid equivalent to the zinc used and the mixture distilled with repeated additions of water until no more acid material came over. In each case an appreciable amount of white solid deposited on the walls of the condenser. This was identified as acetone peroxide by its melting point of 131.5–132.5°, both alone and when mixed with a known sample prepared by oxidation of acetone with Caro's acid.[15]

The distillate was neutralized with sodium hydroxide and the neutral material removed by distillation. In each case this was found to consist of isobutyraldehyde, identified as the 2,4-dinitrophenylhydrazone, acetone, identified by conversion to dibenzalacetone, and a high boiling fraction which was not investigated further.

The remaining solution was evaporated to dryness, an equivalent amount of dilute sulfuric acid added and the liberated acids distilled off by repeated additions of water. The distillate was extracted with ether, the ether solution was dried over calcium chloride, the ether was removed and the acids fractionated. The aqueous layer was neutralized with sodium hydroxide and evaporated to dryness. The sodium salts were treated with *p*-bromophenacyl bromide,[10] and in all but one case the product was the formic acid ester, m. p. 140–141°, alone and when mixed with an authentic sample. In the case of the small lower boiling fraction of the unsaturated ketone from the methyl *n*-amyl ketone condensation, the formic acid ester was found and in addition a larger quantity of the acetic acid ester, m. p. 84.5–85.5°, alone and mixed with a known sample.

Table III lists the acids which were found in the ether soluble fractions. In each case mixed melting point determinations with known samples of the derivatives were made to confirm the identity of the compounds.

TABLE III

Methyl ketone	Unsaturated ketone	Acid
	$(CH_3)_2CHCH=CHCO\cdot n$-propyl	
n-Propyl	$(CH_3)_2CHCH=CHCO$-*n*-propyl	*n*-Butyric[a]
n-Butyl	$(CH_3)_2CHCH=CHCO$-*n*-butyl	*n*-Valeric[b]
Isobutyl	$(CH_3)_2CHCH=CHCO$-isobutyl	Isovaleric[c]
n-Amyl	$(CH_3)_2CHCH=CHCO$-*n*-amyl	*n*-Caproic[d]
n-Amyl	$(CH_3)_2CHCH=C(n\text{-butyl})COCH_3$	*n*-Valeric[e]
		n-Caproic[f]
n-Hexyl	$(CH_3)_2CHCH=CHCO$-*n*-hexyl	*n*-Heptoic[g]

[a] Identified as the piperazonium salt, m. p. 119–120°; ref. (18). [b] Identified as the anilide, m. p. 62–63°; ref. (10). p. 132. [c] Identified as the piperazonium salt, m. p. 140.5 141.5°, and as the anilide, m. p. 110.5–111.5°. [d] Identified as the piperazonium salt, m. p. 112–113° and as the anilide, m. p. 96–97°. [e] Identified as the anilide, m. p. 61–62°, and the piperazonium salt, m. p. 109–110°. [f] By fractional crystallization from dilute methanol a small amount of anilide, m. p. 91–92.5°, was obtained from the least soluble portion. A mixed melting point determination with known *n*-caproanilide, m. p. 96–97°, gave m. p. 93–95°. With known *n*-valeranilide, m. p. 62–63°, the mixed melting point was 60–75°. [g] Identified as the piperazonium salt, m. p. 96–97°.

(2) **Unsaturated Ketone Obtained from Diethyl Ketone.**—Three-hundredths mole of 4,6-dimethyl-4-hepten-3-one was dissolved in 25 ml. of ethyl acetate and ozonized as above. The solution of ozonide was poured into 100 ml. of water containing 0.12 mole each of hydroxylamine hydrochloride and sodium acetate. The mixture was stirred for two hours, then distilled to remove ethyl acetate and other volatile material. To the residue was added 1 g. of ammonium chloride and ammonium hydroxide until alkaline to litmus. A solution of 3.7 g. of nickel acetate was then added and the mixture allowed to stand overnight. The orange-brown precipitate of nickel salt was filtered and dried; yield, 1.0 g. (18%).

The dry salt was shaken with 5% sulfuric acid and the solution extracted with ether. Evaporation of the ether left a white solid residue, which, after recrystallization from water, melted at 172–173°. A sample of methylethylglyoxime was prepared by treating isonitrosodiethyl ketone (prepared from diethyl ketone by treating with ethyl nitrite) with hydroxylamine hydrochloride and sodium acetate. The melting point was 172–173° and a mixed melting point with the above material was also 172–173°.

(3) **2-Methyl-2-decen-5-ol.**—Four and two-tenths grams of the alcohol was dissolved in 10 ml. of glacial acetic acid and ozonized as above. The colorless ozonide solution was diluted with 50 ml. of ether and decomposed by addition of 5 g. of zinc dust followed by dropwise addition of 5 ml. of water. The mixture was stirred and refluxed until a drop of the solution no longer gave a blue color when shaken with starch–iodide solution, then the sludge of zinc and zinc acetate was filtered off and washed with ether. The filtrate and washings was almost neutralized with powdered sodium bicarbonate, then shaken with sodium carbonate solution, washed with water and dried over anhydrous magnesium sulfate.

After removing the ether, about 3 g. of yellow liquid remained. The material appeared to decompose, splitting out water when distillation was attempted, so it was purified by means of steam distillation. A colorless liquid possessing a penetrating aromatic odor somewhat similar to that of *n*-heptaldehyde was obtained which readily gave a purple color with fuchsin-aldehyde reagent, and rapidly absorbed bromine in carbon tetrachloride solution without evolution of hydrobromic acid. The semicarbazone of this material melted, after two recrystallizations from dilute methanol, at 169–170°. The melting point of α-octenaldehyde semicarbazone was reported by van Romburgh[8] as 163°.

Anal. Calcd. for $C_9H_{17}N_3O$: C, 58.99; H. 9.35; N, 22.93. Found: C. 58.72; H, 9.14; N. 22.73.

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(13) Henne, THIS JOURNAL, **51**, 2676 (1929).

(14) Church, Whitmore and McGrew, *ibid.*, **56**, 176 (1934).

(15) Baeyer and Villiger, *Ber.*, **32**, 3625 (1899).

The ether which had been removed by distillation was found to contain acetone, identified by conversion to dibenzalacetone, m. p. 111.5–112.5°, both alone and when mixed with an authentic sample.

Oxidation of Saturated Ketones to Acids: (1) Methyl *n*-Amyl Ketone Condensation.—Five-hundredths mole of 2-methyl-5-decanone was oxidized with 0.15 mole of sodium dichromate, 0.6 mole of sulfuric acid and 250 ml. of water as previously described.[2a,16] Considerable carbon dioxide was evolved at the start and throughout the course of the oxidation. A total of 0.09 mole of acid was obtained. *n*-Caproic acid was identified in the water-insoluble acid fraction by conversion to the 2-alkyl benzimidazole,[17] m. p. 157–158°, which showed no depression when mixed with the known *n*-caproic acid derivative, m. p. 158–158.5°. Acetic acid was shown to be present in the water-soluble fraction by preparing the *p*-toluide, m. p. 146.5–147.5°, alone and when mixed with known aceto-*p*-toluide.

(2) **Methyl *n*-Hexyl Ketone Condensation.**—Five-hundredths mole of 2-methyl-5-undecanone, oxidized as above, gave 1.1 moles of total acids. *n*-Heptoic acid was identified in the water-insoluble fraction by conversion to the piperazonium salt,[18] m. p. 97–98°, which showed no depression when mixed with authentic piperazonium di-*n*-heptoate, m. p. 96–97°. Isovaleric acid was also shown to be present by preparing the piperazonium salt, m. p. 140–141°, alone and mixed with known piperazonium di-isovalerate, m. p. 140–141°. The presence of acetic acid in the water-soluble fraction was shown by preparing the *p*-toluide, m. p. 146.5–147.5°, which exhibited no depression when mixed with known aceto-*p*-toluide.

Preparation of 2-Methyl-5-decanone.—From 0.6 mole of isoamyl bromide, 0.6 mole of *n*-hexaldehyde and 0.6 mole of magnesium there was obtained 38 g. (37%) of 2-methyl-5-decanol boiling at 122–126° (28.5 mm.). Twenty-nine grams (0.17 mole) of the alcohol was oxidized to the ketone by adding dropwise, with stirring, to a mixture of 0.057 mole of sodium dichromate, 0.226 mole of sulfuric acid and 100 ml. of water. Rate of addition was controlled so that the temperature did not rise above 50°. The mixture was stirred for one hour longer, then the insoluble layer was separated, washed with sodium carbonate solution and water and dried over potassium carbonate. Distillation gave 21.5 g. (75%) of *n*-amyl isoamyl ketone, b. p. 113–118° (28.5 mm.); hydantoin, m. p. 193–194°.

Summary

1. It has been shown that isobutyraldehyde, in alkaline reaction medium, condenses through the alpha methyl carbon atom of the following methyl ketones: *n*-propyl, *n*-butyl, isobutyl, *n*-amyl and *n*-hexyl. A small fraction consisting chiefly of the unsaturated ketone resulting from methylene condensation was isolated in the methyl *n*-amyl ketone condensation.
2. Isobutyraldehyde condenses through the alpha methylene carbon atom of diethyl ketone.
3. Reduction of 2-methyl-3-decen-5-one with sodium and ethyl alcohol yielded 2-methyl-2-decen-5-ol.
4. The following new compounds have been prepared and characterized: 2-methyl-3-nonen-5-one, 2,7-dimethyl-5-octen-4-one, 2-methyl-3-decen-5-one, 2-methyl-3-undecen-5-one, 2-methyl-5-nonanone, 2,7-dimethyl-4-octanone, 2-methyl-5-decanone, 2-methyl-5-undecanone, 2-methyl-5-nonanol, 2-methyl-5-decanol, 2-methyl-5-undecanol, and 2-methyl-2-decen-5-ol.
5. The 5,5-disubstituted hydantoins of the following ketones have been prepared and characterized: 2-methyl-3-nonen-5-one, 2,7-dimethyl-5-octen-4-one, 2-methyl-3-decen-5-one, 3-*n*-butyl-5-methyl-3-hexen-2-one, 2-methyl-3-undecen-5-one, 7-methyl-4-octanone, 2-methyl-5-nonanone, 2,7-dimethyl-4-octanone, 2-methyl-5-decanone, 2-methyl-4-undecanone, and 4,6-dimethyl-3-heptanone.
6. The following new derivatives have been prepared and characterized: the nitroguanylhydrazones of 2-methyl-5-decanone and 2-methyl-5-undecanone; the 2,4-dinitrophenylhydrazone of 4,6-dimethyl-4-hepten-3-one; the semicarbazone of 2,7-dimethyl-4-octanone; the 3,5-dinitrobenzoates of 2-methyl-5-nonanol and 2,7-dimethyl-4-octanol.

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(16) Powell and Secoy, THIS JOURNAL, **53**, 765 (1931).

(17) Pool, Harwood and Ralston, *ibid.*, **59**, 178 (1937).

(18) Pollard, Adelson and Bain, *ibid.*, **56**, 1759 (1934).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

Electrolyte Catalysis in the Ammonolysis of 9-Phenyl-9-chlorofluorene by Liquid Ammonia[1]

BY P. M. WILLIAMSON,[2] ROBBIN C. ANDERSON AND GEORGE W. WATT

Studies on the ammonolysis of both esters and organic halogen compounds by liquid ammonia[3] have provided numerous examples of acceleration of the rates of these reactions by ammonium salts. Since ammonium salts behave as acids in liquid ammonia solutions,[4] it has been assumed that the observed catalytic effects are to be attributed to acid catalysis. Earlier work in these Laboratories,[5-7] has led to the suggestion[7] that catalysis by ammonium salts is fundamentally no different from similar effects produced by non-onium type salts. As a result of their studies on both ammonolytic and aminolytic reactions, Audrieth, Scott and Hill[8] have expressed tentatively this same opinion and have suggested the use of the term "electrolyte catalysis."

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(1) From the Ph.D. Dissertation of P. M. Williamson, The University of Texas, August, 1943.

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(3) For review and primary references see Fernelius and Bowman, *Chem. Revs.*, **26**, 3–48 (1940).

(4) Bergstrom, *J. Phys. Chem.*, **20**, 160 (1925).

(5) Lemons, Anderson and Watt, THIS JOURNAL, **63**, 1953 (1941).

(6) Lemons, Williamson, Anderson and Watt, *ibid.*, **64**, 467 (1942).

(7) Williamson, Anderson and Watt, *ibid.*, **65**, 49 (1943).

(8) Audrieth, Scott and Hill, *ibid.*, **64** 2498 (1942).