

TABLE I
 ANALYSES AND SOLUBILITIES OF SALTS

Anion	Na salt				K salt				
	% Metal calcd.	% Metal found ^a	Soly. at 30°, g./100 g. H ₂ O ^b	Soly., milli-moles/100 g. H ₂ O	% Metal calcd.	% Metal found ^a	Soly. at 30°, g./100 g. H ₂ O ^b	Soly., milli-moles/100 g. H ₂ O	Soly. Na salt/soly. K salt
2-Chloro-3-nitro- <i>p</i> -xylene sulfonate	8.95	8.90	93.4	325	14.32	14.24	9.21	30.4	10.7
Methyl picrate	8.68	8.61	3.15	11.8	13.91	13.93	3.78	13.4	0.88
Chloropicrate	8.06	8.04	31.2	110	12.94	12.94	1.82	6.03	18
Styphnate	8.61	8.72	8.43	31.5	13.81	13.76	1.54	5.42	5.8
Flavianate ^c	12.83	12.91	9.8	27	19.12 ^d	19.22	1.03	2.5	10.8
Picrate	8.55 ^d	8.62	5.58 ^e	20.8	14.61	14.53	0.755 ^f	2.84	7.3
Nitranilate	16.79	16.92	0.724	2.64	25.54	25.62	.567	1.85	1.4
Picolonate	8.01	8.04	0.285	1.00	12.90	12.97	.338	1.12	0.89
Dipicrylamide ^g	4.96	5.05	11.6	25.2	8.20	8.17	.146 ^h	0.304	83
Diliturate	11.79	11.80	1.034	5.31 ⁱ	18.52	18.69	.086	0.40 ^j	13

^a Average of two values with a mean deviation of 0.3%. ^b Average of two or three values with a mean deviation of 1.4%. ^c Dibasic. ^d Monohydrate. ^e Perhaps the best literature value is given by Fischer, *Z. physik. Chem.*, **92**, 581 (1918), as 4.30 at 25°. ^f Fischer gives 0.645 at 25°. ^g There is disagreement on the names for salts of dipicrylamine; this one is sometimes called "potassium dipicrylamine." We prefer the name "potassium dipicrylamide" as best indicating the structure of a substituted potassium amide. ^h Kiehlend, *Ber.*, **71**, 220 (1938), gives the solubility as 0.0025 molar at 25°, which is equivalent to 0.12 g./100 g. H₂O. Kolthoff and Bendix (ref. 16) give the value 0.088 for the same temperature. ⁱ Fredholm (ref. 15) gives the value as 0.049 molar at 18°. ^j Fredholm gives 0.0022 molar at 18°.

determined. The most sensitive reagents in the group were dipicrylamine and dilituric acid. Introduction of additional groups into the molecules of such potassium reagents as picric acid,

dilituric acid, and 2-chloro-3-nitrotoluene-5-sulfonic acid is more likely to decrease than to increase their value.

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[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Hydrogenation of 1,3-Diketones to Ketols

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Sprague¹ obtained the ketol (CH₃)₃CC(O)CH₂-CHOHCH₃ in 68% yield by the hydrogenation of (CH₃)₃CC(O)CH₂C(O)CH₃. This rather unexpected result was no doubt due to the relative resistance to hydrogenation of a carbonyl group adjacent to a tertiary butyl group. The study reported herewith was directed toward finding conditions under which other ketols, less resistant to hydrogenation, could be obtained by the partial hydrogenation of the corresponding 1,3-diketones.

Eight diketones, in which R was methyl, ethyl, a propyl or a butyl radical in compounds of the formula RCOCH₂COCH₃, were prepared and subjected to hydrogenation over Raney nickel under various conditions in attempting to obtain the optimum yield of the various ketols.

Hydrogenation at 100° over Raney nickel of the diketones dissolved in methanol gave in general the highest yield of ketols. The yields of ketol

were where R was methyl 35%, ethyl 51%, *n*-propyl 58%, isopropyl 50%, *n*-butyl 66%, isobutyl 49%, *s*-butyl 64%. Hydrogenation of the diketone dissolved in ether, dioxane or ethanol gave in several cases lower yields, though this difference may have been due more to differences in the losses during isolation rather than to the effect of the solvent upon the rate or course of hydrogenation. The differences between solvents were in most cases negligible, as for example where R was *t*-butyl the yields of the ketol were 66, 68 and 70% in methanol, ether and ethanol, respectively. The 68% yield in ether confirms the yield reported by Sprague referred to above.

The most important consideration, for a given diketone, in determining the yield of ketol is the amount of hydrogen which is absorbed before the reaction is stopped. In order to obtain the yields given above, the shaking of the reaction vessel was stopped after 0.9 to 1.0 mole of hydrogen per

(1) Sprague and Adkins, *This Journal*, **56**, 2669 (1934).

mole of diketone had been absorbed. Since the hydrogenation proceeds rapidly it is not always easy to stop the reaction when the proper amount of hydrogen has been taken up.

Improved yields have been obtained by making use of the technique recently described for the partial hydrogenation of phenanthrene.² In this procedure the hydrogenation is carried out under nitrogen with a limited amount of hydrogen. The diketone, methanol and catalyst were placed in the reaction vessel and nitrogen added to a pressure of about 100 atmospheres. One mole of hydrogen per mole of diketone was then added. The mixture was then shaken at 100° until the pressure was constant. The pressure of nitrogen kept the contents of the bomb in the liquid phase even after all the hydrogen had reacted. This procedure enables exactly the proper amount of hydrogen to be added to the diketone and in the three cases in which it was tried raised the yields by 4, 20 and 17%, respectively. The method was tried where R was methyl, *i*-butyl and *s*-butyl. The hydrogenations required about one hundred and ten minutes due to the low pressure of hydrogen, as compared with about twenty minutes under 125 atmospheres of hydrogen.

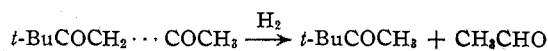
Hydrogen did not react at the carbonyl next to R until the carbonyl next to the methyl group had been hydrogenated, as the ketols obtained were in each case methylcarbinols, *i. e.*, RCOCH₂CHOHCH₃. The structure of the ketols was ascertained by dehydrating each one over oxalic acid³ to the corresponding unsaturated ketone RCOCH=CHCH₃, which was then hydrogenated to RCOCH₂CH₂CH₃. Solid derivatives of the ketone so prepared were compared by mixed melting points with derivatives of a sample of a ketone of known structure.

The 2,4-dinitrophenylhydrazones of the unsaturated ketones were prepared in six cases. The same derivative was obtained from the ketol as from the unsaturated ketone since the ketol is dehydrated during the process of forming the hydrazone.

The hydrogenation of 1,3-diketones may be continued beyond the ketol stage to give good yields of the glycols of the type RCHOHCH₂CHOHCH₃.¹ Glycols where R is ethyl, *n*-propyl, *n*-butyl or *s*-butyl have been prepared for the first time in yields of 92, 94, 94 and 80%, respec-

tively. These hydrogenations were made at 100 to 125° during the course of one and a half to three hours under approximately 100 atm. of hydrogen over 4 g. of Raney nickel. Approximately 25 g. of the diketone was dissolved in 80 ml. of dry methanol and the glycols obtained by fractionation after hydrogenation.

Sprague noted that the hydrogenation of certain 1,3-diketones resulted in the cleavage of the chain with the formation of ketones and aldehydes, *i. e.*



The splitting was ascribed to cleavage by hydrogen of the carbon to carbon linkage indicated by the dots in the formula. It seemed possible that hydrogenation of the carbonyl group, rather than hydrogenolysis of the carbon to carbon linkage, might have taken place to give a ketol, which might then undergo disproportionation to give the ketone and aldehyde, *i. e.*



The disproportionation might have occurred in the reaction vessel under the conditions of hydrogenation or during the separation and purification of the products. To test this hypothesis the ketol indicated just above was heated in ether solution at 60° in the bomb in the presence of Raney nickel for twelve hours. No disproportionation products were formed and the ketol was recovered unchanged. Since alkali would tend to facilitate disproportionation during the process of working up the reaction products after a hydrogenation, Sprague's procedure was modified in that potassium carbonate was not used for drying the solution of the products before fractionation. Ethylbenzoylacetylmethane, C₆H₅CO⋯CH(Et)COCH₃, was subjected to hydrogenation as by Sprague but the products were isolated without drying them over potassium carbonate. The results showed a 27% cleavage at the linkage indicated by dots in the formula. Ethylbenzoylacetylmethane was used in this experiment in preference to *t*-BuCOCH₂COCH₃ because the former undergoes cleavage to a greater extent according to Sprague's results.

There is therefore no evidence that the cleavage observed by Sprague was due to disproportionation of a ketol, but rather it may be regarded as dependent upon hydrogenolysis of the diketone.

The 1,3-diketones were made by condensing ethyl acetate with the proper ketone using sodium

(2) Durland and Adkins, *THIS JOURNAL*, **60**, 1501 (1938).

(3) Pastreau and Zamenhof, *Compt. rend.*, **182**, 323 (1926).

ethoxide as the condensing agent. The procedure was essentially that previously described and labeled "B."⁴ Methyl *i*-propyl⁵ and methyl *t*-butyl ketones⁶ were made by the methods described in "Organic Syntheses." Methyl ketones containing *n*-propyl, *n*-butyl and *s*-butyl groups were made through the use of acetoacetic ester, the hydrolysis being made as given in "Organic Syntheses."⁷ The other monoketones used were commercial products.

Hydrogenations were carried out in various reaction vessels but all those reported herewith were made in a steel bomb having a void of 270 ml. The general procedure was as follows. The diketone (0.15 to 0.35 mole) dissolved in 40 to 80 ml. of dry methanol was placed in the reaction vessel with 3 to 5 g. of Raney nickel. Hydrogenation under a pressure of 100 to 200 atmospheres was allowed to proceed at 100° until one mole of hydrogen per mole of diketone had been absorbed. The time of reaction was in general from five to thirty minutes. The reaction vessel was then cooled to room temperature, the excess hydrogen released, the vessel opened and the reaction mixture and washings filtered. The solvent was then distilled through a fractionating column at atmospheric pressure and the products separated by fractional distillation at a convenient pressure. Both a Widmer and a modified Widmer column were used.⁸ The modified Widmer containing a spiral 15 cm. in length with 12 turns of the helix was preferable. Since all the yields reported were isolated by fractionation they represent minimum rather than maximum values. In particular the mechanical losses in the case of the viscous glycols were relatively large.

The ketols (10 to 20 g.) were dehydrated to the unsaturated ketones by slow distillation through the modified Widmer column from a flask containing 0.3 to 0.6 g. of oxalic acid. The water layer in the distillate was discarded, the ketone dried over sodium sulfate and fractionated through the modified Widmer column. The yields were 70 to 90% of the theoretical quantity. The unsaturated ketone (4 to 9 g.) was then hydrogenated over Raney nickel at 30–40° under 100

atm. of hydrogen in a small steel reaction vessel.⁹

The 2,4-dinitrophenylhydrazones of the ketones and ketols were made by the method of Allen¹⁰ or Brady.¹¹ When R was ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl or *t*-butyl the ketol gave the same derivative as the corresponding unsaturated ketone. The bisphenylurethans of the glycols were prepared as by Tessmer.¹²

The colors of the 2,4-dinitrophenylhydrazones of ketones, after recrystallization from the indicated solvent were as follows: hexene-4-one-3 and heptene-2-one-4, red needles from dry ethanol; 2-methylhexene-4-one-3, orange needles from methanol; octene-2-one-4, orange needles from 95% alcohol; 6-methylheptene-2-one-4, red plates from 95% alcohol; and 2,2-dimethylhexene-4-one-3, yellow needles from a methanol-water mixture. The melting points and analytical data for these and other derivatives are given in Table I.

TABLE I
MELTING POINTS AND ANALYSES OF VARIOUS DERIVATIVES

Compound	M. p., °C.	Nitrogen, %	
		Calcd.	Found
Hexene-4-one-3 ^a	164–165	20.14	20.40
Heptene-2-one-4 ^a	142–143	19.18	19.29
2-Methylhexene-4-one-3 ^a	140–141	19.18	19.28
Octene-2-one-4 ^a	108–109	18.30	18.48
6-Methylheptene-2-one-4 ^a	101–101.5	18.30	18.56
2,2-Dimethylhexene-4-one-3 ^a	135–135.5	18.30	18.51
3-Methylheptanone-4 ^b	106–107	22.69	22.78
6-Methylheptanone-4-ol-2 ^c	111–113	11.86	11.93
Heptanediol-2,4 ^d	101–101.5	7.56	7.67
5-Methylhexanediol-2,4 ^d	134–135	7.56	7.60
Octanediol-2,4 ^d	126–127	7.29	7.42
6-Methylheptanediol-2,4 ^d	143–143.5	7.29	7.30
5-Methylheptanediol-2,4 ^d	129–130	7.29	7.45

^a 2,4-Dinitrophenylhydrazone.

^b Semicarbazone.

^c Phenylhydrazone. ^d Bisphenylurethan.

The saturated ketones, obtained as the result of dehydration of the ketols followed by hydrogenation, all proved to be of the type $n\text{-C}_3\text{H}_7\text{COR}$ where R was a methyl, ethyl, a propyl or a butyl radical. They were identified by solid derivatives as follows: ethyl *n*-propyl ketone, b. p. 123–124°, as a 2,4-dinitrophenylhydrazone, m. p. 136°¹⁰; dipropyl ketone, b. p. 145–147°, as the semicarbazone, m. p. 131–132°¹³; *i*-propyl *n*-propyl ketone, b. p. 132–134°, as the semicarbazone, m. p. 119–120°¹⁴; *n*-butyl *n*-propyl ketone,

(9) Adkins, *THIS JOURNAL*, **55**, 4272 (1933).

(10) Allen, *ibid.*, **52**, 2955 (1930).

(11) Brady, *J. Chem. Soc.*, 756 (1931).

(12) Tessmer, *Ber.*, **18**, 969 (1885).

(13) Sherrill, *THIS JOURNAL*, **52**, 1990 (1930).

(14) Michael, *ibid.*, **41**, 418 (1919).

(4) Sprague, Beckham and Adkins, *THIS JOURNAL*, **56**, 2665 (1934).

(5) "Organic Syntheses," John Wiley and Sons, New York, N. Y. 1933, Vol. XIII, p. 68.

(6) *Ibid.*, John Wiley and Sons, New York, N. Y. 1932, Coll. Vol. I, p. 451.

(7) "Organic Syntheses," John Wiley and Sons, New York, N. Y. 1932, Coll. Vol. I, p. 343.

(8) Martha E. Smith and Adkins, *THIS JOURNAL*, **60**, 862 (1938).

TABLE II
 PHYSICAL CONSTANTS AND ANALYTICAL DATA

Compound	B. p., °C.	Mm.	n_D^{20}	d_4^{20}	MR		H, %		C, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
Hexanone-3-ol-5	75-78	12	1.4280	0.950	31.44	31.44	10.42	10.51	62.03	62.04
Pentanone-2-ol-4 ¹⁹	93-95	43	1.4238							
Heptanone-4-ol-2	101	24	1.4300	.930	36.06	36.15	10.84	10.91	64.58	64.47
2-Methylhexanone-3-ol-5	72-73	9	1.4278	.929	36.06	36.01	10.84	11.03	64.58	64.43
Octanone-4-ol-2	91	8	1.4333	.920	40.68	40.73	11.19	11.29	66.62	66.41
6-Methylheptanone-4-ol-2	86	9	1.4294	.914	40.68	40.67	11.19	11.30	66.62	66.48
2,2-Dimethylhexanone-3-ol-5 ¹	72-74	10	1.4243							
5-Methylheptanone-4-ol-2	113-114	36	1.4318	.921	40.68	40.57	11.19	11.22	66.62	66.69
Hexene-4-one-3 ²⁰	136-139	740	1.4345	.851	29.45	30.04				
2-Methylhexene-4-one-3	147-148.5	739	1.4345	.843	34.07	34.69	10.79	10.96	74.95	74.79
Heptene-2-one-4 ²⁰	156-162	740	1.4383	.852	34.07	34.56				
Octene-2-one-4	178	740	1.4393	.852	38.69	38.96	11.18	11.22	76.14	75.95
6-Methylheptene-2-one-4	168-170	741	1.4388	.841	38.69	39.45	11.18	11.13	76.14	75.97
5-Methylheptene-2-one-4	170	740	1.4400	.848	38.69	39.19	11.18	11.26	76.14	76.04
2,2-Dimethylhexene-4-one-3 ¹	153-154	740	1.4380	.843	38.69	39.27				
3-Methylheptanone-4	152-154	740	1.4103	.817	39.16	38.91	12.58	12.68	74.94	74.93
Heptanediol-2,4	107-108	8	1.4386	.926	37.58	37.47	12.20	12.21	63.59	63.54
Octanediol-2,4	117-118	8	1.4422	.918	42.19	42.14	12.41	12.29	65.70	65.74
5-Methylheptanediol-2,4	111-112	8	1.4449	.928	42.19	41.91	12.41	12.46	65.70	65.64

b. p. 168-171°, as the semicarbazone, m. p. 100-101°¹⁵; *s*-butyl *n*-propyl ketone, b. p. 152-154°, as the semicarbazone, m. p. 106-107°; *i*-butyl *n*-propyl ketone, b. p. 153-155°, as the semicarbazone, m. p. 122-123°¹⁶; *t*-butyl *n*-propyl ketone, b. p. 143-144°, as the semicarbazone, m. p. 153-154.5°, and oxime, m. p. 77.5-78.5°.¹⁷ The ketol CH₃CHOHCH₂COCH₃ was characterized by its phenylhydrazone, m. p. 103-104°.¹⁸

Summary

Ketols of the type RCOCH₂CHOHCH₃ have been prepared in yields averaging above 50% by the hydrogenation over Raney nickel of 1,3-di-

ketones where R is a methyl, ethyl, a propyl or a butyl group. In order to obtain good yields of the ketols it is necessary to interrupt the hydrogenation after the absorption of one mole of hydrogen per mole of ketone. This is most satisfactorily accomplished by having in the reaction vessel no more than the required amount of hydrogen, and adding a sufficient amount of nitrogen to obtain the desired pressure. All of the eight ketols obtained were methylcarbinols, showing that hydrogenation proceeds to completion at the acetyl group before it begins at propionyl, butyryl or valeryl groups.

Evidence is presented that the cleavage of diketones previously reported is really a hydrogenolysis and not a disproportionation of a ketol subsequent to hydrogenation.

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(15) Bouveault and Locquin, *Bull. soc. chim.*, [3] **33**, 47 (1905).

(16) Fournier, *ibid.*, [4] **7**, 839 (1910).

(17) Haller and Bauer, *Compt. rend.*, **150**, 568 (1910).

(18) Claisen, *Ann.*, **306**, 325 (1899).

(19) Perkin, *J. Chem. Soc.*, **65**, 825 (1894).

(20) Blaise, *Bull. soc. chim.*, [3] **33**, 47 (1905).