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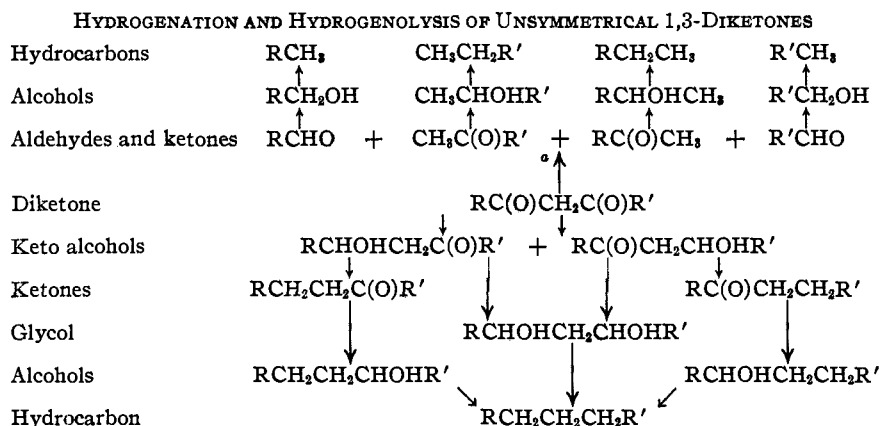
## Hydrogenation and Hydrogenolysis of 1,3-Diketones

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The cleavage by hydrogen of oxygen to carbon and of carbon to carbon linkages in  $\beta$ -keto esters and 1,3-diketones has been observed in a number of cases.<sup>1</sup> Since it was known that 1,3-glycols were cleaved under the same conditions, it was assumed in earlier papers from this Laboratory that the carbonyls were first reduced to carbinols and that the cleavage then ensued. In beginning a systematic study of the relationship of structure to the rate and mode of cleavage we intended to prepare a series of 1,3-glycols and then submit them to hydrogenolysis. It soon became evident that even under very mild conditions (50°) cleavage preceded hydrogenation and that the glycols were much more resistant to cleavage than the diketones, in fact the anomalous situation was encountered of obtaining aldehydes and ketones as the result of hydrogenation. Attention was then directed to the relationship of structure to the hydrogenation and hydrogenolysis of 1,3-diketones.

Products has actually been obtained from one or another of the 1,3-diketones submitted to study. The multiplicity of the possible products as well as the similarity of the physical properties of some of them makes it difficult to determine the effect of the structure of the diketone upon the ratio of the products, so that it was necessary to select conditions of hydrogenation that would minimize the complexity of the mixture of reaction products. The ratio of products is primarily a function of the structure of the diketone and of the amount of hydrogen which the reaction mixture is allowed to take up. The temperature of hydrogenation, the kind, activity and amount of catalyst, the nature of the reaction medium and other experimental factors probably also play a lesser role in determining the ratio of products. A considerable number of hydrogenations of various diketones under various conditions were made and attempts made to isolate and estimate the ratio of products. As a result of this experi-

TABLE I



\* The keto alcohols and the glycol may also undergo carbon to carbon cleavage but no products in addition to those indicated above can be formed.

There are outlined in Table I the steps by which twenty aldehydes, ketones, keto alcohols, a glycol, alcohols and hydrocarbons may be formed by the action of hydrogen upon a single unsymmetrical 1,3-diketone. An inspection of the experimental results summarized in Table II will show that a representative of each of these prod-

mentation, which it seems unnecessary to report in detail, a standard procedure was adopted for the comparisons.

The standard procedure was as follows. The diketone (0.15–0.50 mole) in dry ether (30–100 cc.), with Raney nickel<sup>2</sup> (4–8 g.), in a copper vessel contained in a steel bomb,<sup>3</sup> was submitted

(1) Connor and Adkins, *THIS JOURNAL*, **54**, 4678 (1932); Ellis, "Hydrogenation," 3d ed., D. Van Nostrand Co., N. Y., 1930, pp. 196–197.

(2) Covert and Adkins, *ibid.*, **54**, 4116 (1932).

(3) Adkins, *ibid.*, **55**, 4272 (1933).

TABLE II  
 HYDROGENATION OF 1,3-DIKETONES

( ) methane	Mole	Time, hrs.	Temp., °C.	Moles H <sub>2</sub> per mole diketone	Products	%	B. p., °C.	Mm.
Diacetyl	0.30	1	125	1.80	Ethanol, propanol-2	..	72-90	
					Unsaturated compound	..	.....	
					Pentanediol-2,4 <sup>4</sup>	80	195-199	
Isobutyrylacetyl-	.27	4	25	1.70	Ethanol (acetaldehyde)	..	77-84	
					Unsaturated compound	9.6	135-139	
					2-Methylhexanediol-3,5	73	210-214	
Isobutyrylacetyl-	.33	5	125	1.60	Ethanol	..	.....	
					Propyl isopropyl ketone <sup>5</sup>	30	132-136	
					2-Methylhexanediol-3,5	60	123-124	24
Trimethylacetylacetyl-	.32	6	100	1.12	Ethanol	..	76-84	
					Δ <sup>4</sup> -2,2-Dimethylhexanone-3	43.4	52-54	9
					2,2-Dimethylhexanediol-3,5	13.0	102-126	9
					High boiling product	(5.5 g.)	154	9
Trimethylacetylacetyl-	.28	10	60	1.60	Ethanol	..	76-80	
					Pinacolone <sup>6</sup>	5.4	101-105	
					Δ <sup>4</sup> -2,2-Dimethylhexanone-3	16.3	45-98	11
					2,2-Dimethylhexanone-3-ol-5	15.0	76-80	11
					2,2-Dimethylhexanediol-3,5	52.0	108-109	11
Trimethylacetylacetyl-	.40	12	60	1.00	Ethanol	..	.....	
					Pinacolone	6.7	102-108	
					Δ <sup>4</sup> -2,2-Dimethylhexanone-3	62.0	153-155	
					2,2-Dimethylhexanediol-3,5	17.0	105-110	10
Trimethylacetylacetyl-	.20	3	60	1.10	2,2-Dimethylhexanone-3-ol-5	68	87-90	21
					2,2-Dimethylhexanediol-3,5	18	105-108	11
Isovalerylacetyl-	.28	15	85	1.75	2-Methylheptanediol-4,6	77	124-126	14
Isovalerylacetyl-	.40	7	125	1.90	Ethanol	..	.....	
					Isobutyl propyl ketone <sup>7</sup>	42	151-154	
					2-Methylheptanediol-4,6	44	114-116	9
Cyclohexanoylacetyl-	.19	9	125	1.92	Cyclohexyl propyl ketone <sup>8</sup>	38	106-109	21
					1-Cyclohexylbutanediol-1,3	47	163-167	21
Furoylacetyl-	.50	11.5	125	4.0	1-Tetrahydrofuryl butanediol-1,3	73	160-163	24
Tetrahydrofuroylacetyl-	.22	8	125	1.72	1-Tetrahydrofuryl butanediol-1,3	92	160-163	24
<i>p</i> -Phenylbenzoylacetyl-	.15	5	125	4.66	1-( <i>p</i> -Cyclohexylphenyl)-butanol-3	57	140-144	1-2
2,4,6-Trimethylbenzoylacetyl	.14	10	125	1.93	<i>n</i> -Butylmesitylene <sup>9</sup>	79	121-124	7
					1-(2,4,6-Trimethylphenyl)-butanediol-1,3	12	173-178	7
Benzoylacetyl-	.30	1	125	3.00	<i>n</i> -Butylbenzene <sup>10</sup>	3.7	72-75	21
					1-Phenylbutanol-3 <sup>10</sup>	40	125-130	21
					1-Phenylbutanone-3			
					1-Phenylbutanediol-1,3 <sup>11</sup>	50	175-178	21
Ethylbenzoylacetyl-	.12	4	60	1.93	Benzaldehyde	25	63-67	14
					Methyl propyl ketone	43.7	99-101	
					Phenyl propyl ketone <sup>12</sup>	11.3	98-103	13
					1-Phenyl-2-ethylbutanediol-1,3	32.3	197-203	13

(4) Franke and Kohn, *Ber.*, **37**, 4730 (1904).(5) Michael, *This Journal*, **41**, 418 (1919).

(6) Semicarbazone m. p. 157°, Clarke, "Handbook of Organic Analysis," 1926.

(7) Fournier, *Bull. soc. chim.*, [4] **7**, 839 (1910).(8) Douris, *Compt. rend.*, **157**, 57 (1913).(9) Klages, *Ber.*, **35**, 2258 (1902).(10) Klages, *ibid.*, **37**, 2314 (1904).(11) Shoppee, *J. Chem. Soc.*, 2571 (1928).(12) Franke and Kohn, *Monatsh.*, **27**, 1115 (1906).(13) Von Braun and Deutsch, *Ber.*, **45**, 2181 (1912).

TABLE II (Concluded)

( ) methane	Mole	Time, hrs.	Temp., °C.	Moles H <sub>2</sub> per mole diketone	Products	%	B. p., °C.	Mm.
<i>n</i> -Butylbenzoylacetyl-	0.23	4	50	1.50	Acetaldehyde, ethanol	..	.....	
					Benzaldehyde	25	63-67	14
					Methyl <i>n</i> -amyl ketone <sup>14</sup>	35	149-152	
					Phenyl <i>n</i> -amyl ketone <sup>16</sup>	18	133-138	14
					1-Phenyl-2- <i>n</i> -butylbutanediol-1,3	40.5	186-191	14
<i>n</i> -Heptylbenzoylacetyl-	.15	5	50	1.53	Benzaldehyde	18	58-62	10
					Methyl <i>n</i> -octyl ketone <sup>5</sup>	20	85-88	8
					Phenyl <i>n</i> -octyl ketone <sup>16</sup>	20	163-168	8
					1-Phenyl-2- <i>n</i> -heptylbutane-diol-1,3	50	197-203	8
					Benzylbenzoylacetyl-	.22	6.5	50
Benzyl-1,3-diketone	.28	18	60	1.1	1-Phenylbutanone-3 <sup>10</sup>	48	75-80	3-4
					1,3-Diphenylpropanone-1 <sup>11</sup>	20.5	156-160	3
							M. p. 72-3	
					1-Phenyl-2-benzylbutanediol-1,3	30.5	182-187	1-2
					1-Phenylbutanone-3	40	123-126	20
Ethyldiacetyl-	.23	7	50	1.40	Unchanged diketone	12	118-124	3
					3-Benzylpentanediol-2,4	46	140-143	3
					Ethanol	..	.....	
					Methyl propyl ketone	10	98-102	
Ethyl-1,3-diketone	.10	7	50	1.84	Unsaturated compound	(9)	154-157	
					3-Ethylpentanediol-2,4	64	205-210	
					Benzaldehyde	14	36-40	3
					Phenyl propyl ketone	15	.....	
2,4,6-Trimethylbenzoyl-benzoyl-	.20	6	125	2.1	1,3-Diphenyl-2-ethylpropanediol-1,3	80	190-196	3
					Benzaldehyde	..	.....	
					Acetylmesitylene <sup>17</sup>	25	103-106	9
Furoylbenzoyl-	.25	11	125	4.0	$\beta$ -Phenylpropionylmesitylene	70.8	167-169	1.5
					Benzyl alcohol	..	83-86	8
					1-Tetrahydrofuryl-3-phenylpropanol-1	28	134-139	2
Methone <sup>20</sup>	.25	7	125	2.0	1-Tetrahydrofuryl-3-phenylpropanediol-1,3	30	170-171	2
					3,3-Dimethylcyclohexanol-1 <sup>18</sup>	3.8	175-181	
					5,5-Dimethylcyclohexanediol-1,3 (2 stereoisomers)	80	M. ps. 102-104 and 146	
Dibenzoyl <sup>21</sup>	.24	0.8	125	2.3	Acetophenone	..	.....	
					1,3-Diphenylpropane <sup>19</sup>	11	134-139	5
					1,3-Diphenylpropanol-1	20	168-174	5
					1,3-Diphenylpropanediol-1,3	51	210-220	6
						M. p. 93-97		

to the action of hydrogen at 150-200 atmospheres. The temperature selected for the reaction of the unalkylated diketones was 125° while for those bearing a substituent on the central carbon atom it was 50 to 60°. The unalkylated compounds in general required a higher temperature for a reasonably rapid rate of reaction. The temperatures selected appeared to give mixtures of products that, after drying over potassium carbonate,

(14) Sorge, *Ber.*, **35**, 1074 (1902).(15) Schroeter, *ibid.*, **40**, 1603 (1907).(16) Sabatier and Mailhe, *Compt. rend.*, **158**, 834 (1914).(17) Noller and Adams, *This Journal*, **46**, 1892 (1924).(18) Crossley and Renouf, *J. Chem. Soc.*, **107**, 604 (1915).(19) Straus and Grindel, *Ann.*, **439**, 246 (1924).(20) Vorländer, *Z. anal. Chem.*, **27**, 741 (1929).

(21) "Organic Syntheses," John Wiley and Sons, Inc., New York, 1932, Coll. Vol. I, p. 199.

could in most cases be separated by a careful fractionation through a Widmer column. The hydrogenation was in general stopped after 1.6 to 1.9 moles of hydrogen had been absorbed per mole of diketone. In the case of a number of the diketones (especially the alkylated) the absorption of hydrogen stopped at about that point while in most other cases the rate of hydrogenation became markedly slower.<sup>22</sup>

There are four linkages in 1,3-diketones which

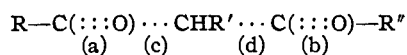
(22) It should be noted that, with one or two exceptions, all of the ketones and aldehydes isolated are, when pure, readily hydrogenated under the conditions of temperature, pressure of hydrogen and catalyst at which they were produced. They are not rapidly, if at all, hydrogenated when present in the mixture of reaction products; cf. Adkins, Cramer, Connor and Diwocky, *This Journal*, **51**, 3418 (1929); **52**, 5192 (1930); **53**, 1868 (1931).

TABLE III<sup>a</sup>  
RELATIVE SUSCEPTIBILITY TOWARD HYDROGEN OF FOUR LABILE LINKAGES IN 1,3-DIKETONES.  
R—C(::O)···CHR'···C(::O)—R''

R	Substituents R'	R''	(a)	(c)	(d)	(b)	Hydrogenation, %	Hydrogenolysis at oxygen, %	Hydrogenolysis at carbon, %	Enol, %
Me	H	Me			80					78 <sup>23</sup>
<i>i</i> -Pr	H	Me			73					84
<i>i</i> -Pr	H	Me			60		30(b)			..
<i>t</i> -Bu	H	Me (60°)			(52 + 31)			6(d)		60 <sup>25</sup>
<i>t</i> -Bu	H	Me (60°)			(18 + 68)					..
<i>i</i> -Bu	H	Me			44		42(b)			86
<i>i</i> -Bu	H	Me (85°)			77					..
(Cyclohexyl)	H	Me			47		38(b)			89
Furyl	H	Me			73					85
Tetrahydrofuryl	H	Me			92					64
Ph	H	Me			59		33(a)			100 <sup>26</sup>
Mesityl	H	Me			22		71(b)			102
Mesityl	H	Me			12		79(b)			..
<i>p</i> -Di-Ph	H	Me					57(a)			..
Mesityl	H	Ph					71(b)	25(d)		100 <sup>27</sup>
Ph	H	Ph			51		20 + 11	7(c and d)		100
Furyl	H	Ph			30		28(b)	20(d)		99
Ph	Et	Me (60°)			32			44(c) + 11(d)		3 <sup>24</sup>
Ph	<i>n</i> -Bu	Me (60°)			40			35(c) + 18(d)		3
Ph	<i>n</i> -C <sub>7</sub> H <sub>15</sub>	Me (60°)			50			20(c) + 20(d)		3
Ph	PhCH <sub>2</sub>	Me (60°)			30			48(c) + 20(d)		0 <sup>25</sup>
Me	Et	Me (60°)			64			10(c + d)		28 <sup>26</sup>
Me	PhCH <sub>2</sub>	Me (60°)			46			40(c + d)		60
Ph	Et	Ph (60°)			80			15(c and d)		0

<sup>a</sup> The figures in this table are the percentage yields of the indicated products actually isolated by fractionation, and represent, therefore, minimum rather than maximum values. Temperatures of reaction 125° unless noted otherwise.

are labile toward hydrogen under the conditions of this investigation. These are indicated by dotted lines in the type formula.



The oxygen to carbon linkages (a) and (b) may be hydrogenated (hydrogen added) while all four linkages (a), (b), (c) and (d) may undergo hydrogenolysis, *i. e.*, be cleaved by addition of hydrogen. The extent to which various diketones underwent these various reactions is given in Table III.

In the great majority of cases the major product of hydrogenation under the standard conditions was a glycol, *i. e.*, linkages (a) and (b) were both hydrogenated. In the case where R was *t*-butyl and R'' was methyl a keto alcohol was also obtained, *i. e.*, linkage (a) was not attacked while hydrogen added at (b). A large yield (68%) of keto alcohol was obtained by inter-

rupting the absorption of hydrogen in this latter case after 1.1 to 1.2 moles had been taken up at 60°. This result is indicative of the feasibility of the preparation of keto alcohols from 1,3-diketones by partial hydrogenations. Evidence of the formation of keto alcohols was obtained in the case of two other diketones.

An inspection of the yield of glycols recorded in column 4 of Table III shows that for the unalkylated diketones a yield of glycol of from 50 to 90% may be expected by hydrogenation of the corresponding diketone over Raney nickel. Even with the alkylated diketones the yield of glycol was, with one exception, 30% or higher.

In several cases considerable yields (30 to 79%) of monoketones were obtained which had the same number of carbon atoms as the original diketone, and which therefore resulted from the hydrogenolysis of one oxygen while the other carbonyl was not even hydrogenated. With two exceptions the (b) rather than the (a) linkage was broken. The groups effective in thus protecting the carbonyl group adjacent to it were isopropyl, isobutyl, cyclohexyl and mesityl.

(23) Weygand, *Ber.*, **62**, 574 (1929).

(24) Dieckmann, *ibid.*, **55**, 2470 (1922).

(25) Trotman, *J. Chem. Soc.*, **127**, 94 (1925).

(26) Conant and Thompson, *THIS JOURNAL*, **54**, 4039 (1932).

(27) Kohler and Barnes, *ibid.*, **55**, 692 (1933).

In the case where R was *p*-diphenyl or tetrahydrofuryl the carbinol corresponding to the monoketone was isolated in yields of 57 and 28%, respectively. It thus appears that the branched groups protect the carbonyl or carbinol adjacent to them.

The exceptions (benzoyl and *p*-phenylbenzoyl acetylmethanes) in which the (a) rather than the (b) linkage was broken are due to the well-known effect of the phenyl group in labilizing the elimination of the adjacent oxygen. The contrast between the mesityl and the phenyl group is further brought out by the fact that acetylmesitylene was stable toward hydrogen over Raney nickel at 150°, while acetylbenzene is rapidly hydrogenated to ethylbenzene at a much lower temperature. It is a striking fact that while phenyl is probably the most effective of all groups in facilitating the cleavage of oxygen to carbon in compounds of the type  $\text{Ph}-\overset{\text{O}}{\underset{|}{\text{C}}}\cdots\text{O}-$  the substitution of methyl groups in phenyl, as in mesityl, renders the groups perhaps the most protective of all groups.

A surprising result of this study was the discovery of the readiness of cleavage by hydrogen of the carbon to carbon linkages (c and d) in certain diketones. Eleven of the diketones submitted to hydrogenation gave measurable amounts of aldehydes and ketones so produced. In five cases this type of hydrogenolysis occurred to the extent of 40 to 68%. Four of the unalkylated diketones gave 6 to 25% of carbon to carbon cleavage while two alkylated diketones gave 10 to 15% cleavage.

The ease of cleavage of a carbon to carbon linkage,  $-\overset{|}{\text{C}}\cdots\overset{|}{\text{C}}-$  by hydrogen under the influence of a catalyst (as measured by the temperature required), is a function of the kind and number of substituents which the carbons bear. It is not easy to design an experimental method which will place quantitatively the substituents with respect to each other, but a study of the data available from several investigations indicates that among the common radicals the order of increasing effectiveness is:  $\text{Me} > \text{Et} > i\text{-Pr} > t\text{-Bu} > \text{Ph} \text{ or } \alpha\text{-furyl} > -\text{OH} > =\text{O} > -\text{CH}_2\text{OH} > \text{RCOH} > \text{RC}=\text{O}$ .

Pentaphenylethane was cleaved at 125° over nickel<sup>28</sup> but hydrogenolysis at temperatures below

(28) Zartman and Adkins, *THIS JOURNAL*, **54**, 1668 (1932).

125° has not been observed unless the carbon bond was simultaneously under the influence of a carbon and of an oxygen containing substituent. Substituents may thus exert their influence through labilizing the carbon to carbon linkage or (and) by protecting from hydrogenation or hydrogenolysis the very effective oxygen containing substituents. The protective action of *t*-butyl, mesityl and  $\alpha$ -furyl for carbonyls no doubt, in part at least, accounts for the rather considerable carbon to carbon cleavage observed in diketones containing these groups. The effectiveness of *t*-butyl and mesityl in protecting a carbonyl group has been illustrated above while it is well known that furfuraldehyde is hydrogenated less readily than acetaldehyde or acetone for example. The importance of the protective action of groups for oxygen in increasing carbon to carbon cleavage is further shown by the fact that this type of reaction was more than three times as important when R was mesityl as when R was phenyl.

The question arises as to whether there may not be a correlation between the enol content of a diketone and the ratio of reaction products. The four monoalkyl diketones which showed the highest proportion of carbon to carbon cleavage contain an almost negligible amount of the enol form. This is in accord with the view that the carbonyl is a more powerful labilizing group for carbon to carbon cleavages than is the carbinol. However, two diketones (R is mesityl or furyl, R' is phenyl) which showed 20-25% carbon cleavage are apparently completely enolized, while one ketone ( $\text{PhC}(\text{O})\text{CH}(\text{Et})\text{C}(\text{O})\text{Ph}$ ), which exists wholly in the diketone form gave only 15% cleavage with an 80% yield of glycol. These latter results may be rationalized upon the basis of the specific effects of the phenyl radical. However, it does not seem safe at the present time to draw a definite conclusion as to the relationship of enol content to carbon to carbon cleavage, although it seems probable that the diketone is cleaved more easily than the enol.

One of the objectives in determining the position of cleavage of unsymmetrical diketones by hydrogen was the comparison of the results with those obtained in cleavage of diketones with alcohol and water. Beckham showed that in alcoholysis the cleavage occurred from two to five times as rapidly at the (c) as at the (d) linkage in the case of the compounds where R was phenyl.

R<sup>m</sup> methyl and R' ethyl, *n*-butyl, *n*-heptyl or benzyl.<sup>29</sup> In these same cases the cleavage at the (c) linkage by hydrogen was from two to four times as great as at the (d) linkage. It thus appears that the relative weakness of bonds

flask containing Raney nickel. The products reported in Table II were in general characterized by standard methods, including analysis (see Table IV). The characterization of some of the less common compounds is outlined below.

TABLE IV  
PROPERTIES AND ANALYTICAL DATA FOR NEW COMPOUNDS

Compound	B. p. or m. p., °C. Mm.	Carbon, %		Hydrogen, %		n <sub>D</sub> <sup>20</sup>	Mol. wt. <sup>a</sup>		
		Calcd.	Found	Calcd.	Found		Calcd.	Found	
2-Methylhexanediol-3,5	123-124	24	63.57	63.48	12.20	12.30	1.4415	132	128
2,2-Dimethylhexanediol-3,5	108-109	11	65.68	65.64	12.41	12.44	....	146	149
	M. p. 61-62° uncorr.								
2-Methylheptanediol-4,6	114-116	9	65.68	65.72	12.42	12.33	1.4402	146	150
1-Cyclohexylbutanediol-1,3	163-167	21	69.76	69.78	11.76	11.57	1.4782	172	176
1-Tetrahydrofurylbutanediol-1,3	160-163	24	60.00	60.23	10.07	10.25	....	160	158
1-(2,4,6-Trimethylphenyl)-butanediol-1,3	177-179	7	75.00	75.21	9.68	9.67	....		
1-Phenyl-2-ethylbutanediol-1,3	170-173	12	74.18	74.15	9.34	9.16	1.5200	194	198
1-Phenyl-2- <i>n</i> -butylbutanediol-1,3	186-191	14	75.62	75.41	9.98	9.74	1.5124	222	222
1-Phenyl-2- <i>n</i> -heptylbutanediol-1,3	197-202	8	77.21	77.29	10.68	10.45	1.4995	264	267
1-Phenyl-2-benzylbutanediol-1,3	182-187	2	79.65	79.79	7.87	7.83	1.5650	256	261
3-Ethylpentanediol-2,4	205-210		63.59	63.20	12.20	11.97	....	132	124
1,3-Diphenyl-2-ethylpropanediol-1,3	190-196	3	79.70	79.84	7.88	8.15	....	256	261
1-Tetrahydrofuryl-3-phenylpropanediol-1,3	170-171	2	70.24	70.47	8.16	8.23	....	...	...
5,5-Dimethylcyclohexanediol-1,3	M. p. 102-104								
1-Tetrahydrofuryl-butanol-3	120.5-123	22	66.61	66.43	11.18	11.27	1.4541	...	...
	221-223	740							
1-Tetrahydrofuryl-3-phenylpropanol-1	128-130	1	75.68	75.74	8.80	8.72	1.5262	206	210
<i>n</i> -Butyrylmesitylene	132-136	10	82.02	82.09	9.54	9.55	1.5065	...	...
( $\beta$ -Phenylpropionyl)-mesitylene	168-172	1.5	85.66	85.45	7.99	8.23	1.5520	...	...
$\Delta^4$ -2,2-Dimethylhexanone-3	153-155		76.19	75.99	11.11	11.27	1.4380	...	...
2,2-Dimethylhexanone-3-ol-5	89-90	22	66.61	66.74	11.18	11.29	....	...	...
1-( <i>p</i> -Cyclohexylphenyl)-butanol-3	140-144	2	82.76	82.81	10.43	10.50	....	232	227
1,3-Diphenylpropanediol-1,3	214-218	4	78.91	78.98	7.07	7.20	....	...	...
	M. p. 94-98°								
3-Benzylpentanediol-2,4	140-143	2.5	74.23	74.40	9.35	9.53	....	...	...

<sup>a</sup> The molecular weight was calculated from the saponification equivalent of the acetate.

(c) and (d) toward hydrogenolysis is nearly the same as their relative weakness toward alcoholysis. It should be noted that the mechanism for cleavage which appears to rationalize the experimental findings on the alcoholysis of diketones also involves a cleavage adjacent to a carbonyl.

### Experimental

The diketones were prepared and had the properties described in a previous paper.<sup>30</sup> In many cases they were purified by distilling them from a

(29) Beckham and Adkins, *THIS JOURNAL*, **56**, 2676 (1934).

(30) Sprague, Beckham and Adkins, *ibid.*, **56**, 2665 (1934).

The "unsaturated compound" reported from the isobutyrylacetylmethane was probably  $\Delta^4$ -2-Me-hexanone-3. It gave no iodoform test, added bromine rapidly, formed a semicarbazone having a m. p. (with decomposition) of 180-190°. The corresponding unsaturated ketone  $\Delta^4$ -2,2-di-Me-hexanone-3 obtained from trimethylacetylmethane was identified definitely as follows: 0.00255 mole adsorbed 0.0024 mole of bromine in a carbon tetrachloride solution. The dibromide had the following properties: b. p. 102-104° (10 mm.), m. p. 31-32°;  $d_4^{25}$  1.5331,  $n_D^{25}$  1.5000;

M'R<sub>D</sub> calcd. 54.86, found 54.82; % bromine calcd. for C<sub>9</sub>H<sub>14</sub>Br<sub>2</sub>O, 55.93%, found (Parr bomb) 55.65%. Trimethylacetic acid (2.2 g.) was obtained by the oxidation with potassium permanganate of the unsaturated ketone (6 g.).

The unsaturated ketones were unquestionably produced by the dehydration during distillation of the keto alcohols. The pure keto alcohol obtained in another hydrogenation was found to be stable toward distillation at atmospheric pressure but to undergo dehydration when heated with a small amount of potassium carbonate.

1 (1-Cyclohexylphenyl)-butanol-3 was oxidized to terephthalic acid which shows that the end rather than the central benzenoid ring was hydrogenated.

*n*-Butyryl and  $\beta$ -phenylpropionylmesitylenes were converted to mesitylene and butyric acid or  $\beta$ -phenylpropionic acid by heating with sirupy phosphoric acid.<sup>31</sup>

Two stereoisomeric diols (m. p. 102–104 and 146°) were obtained by the recrystallization from benzene-acetone of the products from methone. They were partially soluble in the ether but were best removed from the catalyst by extraction with alcohol. They crystallized out when the alcohol-ether solution was concentrated and cooled. The mother liquor contained 3,3-di-Me-cyclohexanol-1, which was distilled and gave a phenyl urethan of m. p. 90–91°. This is a higher melting point for the urethan than previously reported. Only the higher melting of the diols has previously been obtained.<sup>32</sup>

It is not certain that the compound referred to as 1-tetrahydrofurfuryl-3-phenylpropanol-1 in Tables II and IV does not have the hydroxyl group in the 3 position. The latter isomer has been described previously<sup>33</sup> and also prepared in this Laboratory by Dr. Harold E. Burdick. All attempts to prepare solid derivatives (phenyl and

(31) Klages and Lickroth, *Ber.*, **32**, 1554 (1899).

(32) Zelinsky, *Ber.*, **46**, 1416 (1913); Crosley and Renouf, *J. Chem. Soc.*, **107**, 604 (1915).

(33) Adams and Kaufmann, *This Journal*, **45**, 3043 (1923).

$\alpha$ -naphthyl urethans, 3,5-dinitrobenzoates and acid phthalates) of these isomeric alcohols have failed. The compound reported in this paper is believed to have the hydroxyl adjacent to the tetrahydrofuryl group rather than next to the phenyl because a hydroxyl in the latter position is so readily eliminated by hydrogen over nickel.

The enol contents of the diketones as given in Table III were determined by bromine titration of the liquid diketones at  $-10^\circ$  as described by Conant and Thompson.<sup>26</sup> The values agree with those previously reported in the literature for the eight diketones whose enol content had been determined.

### Summary

Hydrogen over Raney nickel at 50–125° converts 1,3-diketones into a variety of products as indicated in Table I. The proportion of these products varies with the structure of the diketone and with the duration of hydrogenation. In most instances the glycol corresponding to the diketone has been obtained in quite satisfactory yields. It seems probable that the process may be interrupted and the  $\beta$ -keto alcohols obtained in similar yields.

Certain diketones underwent cleavage by hydrogen at either a carbon to oxygen or at a carbon to carbon linkage. Ketones or alcohols having the same carbon chain as the original diketone were formed by hydrogenolysis of oxygen, particularly in those compounds which had branched radicals adjacent to one carbonyl. The hydrogenolysis of the carbon chain occurred with the formation of aldehydes and ketones under quite mild conditions (50°) particularly in the case of the substituted 1,3-diketones. The relative lability

of the two bonds (c) and (d) 
$$\begin{array}{c} \text{O}=\text{C} \cdots \cdots \text{C} \cdots \cdots \text{C}=\text{O} \\ | \quad \quad \quad | \quad \quad \quad | \\ \text{(c)} \quad \quad \quad \text{(d)} \quad \quad \quad | \end{array}$$

in an unsymmetrical diketone seem to be approximately the same irrespective of whether the reaction is alcoholysis, hydrolysis or hydrogenolysis.