

of the lower boiling ester. The attempted saponification of this lower boiling ester gave *i*-butyr-aldehyde as the only definitely characterized product. The rearrangement of a chloro alcohol of the type of III to an aldehyde is an orthodox reaction.

All three of the possible chloro-*s*-butyl alcohols have been reported, but solid derivatives have not been prepared nor the physical properties of the alcohols carefully defined. 3-Chlorobutanol-2, b. p. 138–139° (753 mm.), was prepared by the addition of hypochlorous acid to butene-2.¹⁰ 4-Chlorobutanol-2, b. p. 70° (13 mm.), has been prepared from methylmagnesium iodide and β -chloropropionaldehyde.¹¹ 1-Chlorobutanol-2, b. p. 52° (15 mm.), has been prepared by the reaction of chloroacetaldehyde and ethylmagnesium bromide.¹²

The 3-chloro alcohol would be the lowest boiling of the isomers, and would be the more unstable. It therefore seems probable that the lower boiling of the monochloro esters derived from *s*-butyl ester would be an ester of the 3-chloro isomer. All attempts to saponify this ester gave products such

(10) Henry, *Compt. rend.*, **145**, 499 (1907).

(11) Krassuski, *ibid.*, **145**, 763 (1905).

(12) Fourneau and Ramart-Lucas, *Bull. soc. chim.*, [4] **25**, 367 (1919).

as would correspond to *sym*-dimethylethylene oxide. This is a not unexpected result for the ester of such an alcohol. It should be noted that the ester of similar structure from *i*-butyl trichloroacetate also failed to give a chloro alcohol upon saponification.

There is no adequate basis for deciding whether the chlorobutanol-2 isolated was the 1- or 4-chloro compound. The boiling point is close to that reported for the 1-chloro compound. It would appear that the 4-chloro compound boils somewhat higher.¹⁰ The low yield of alcohol obtained by saponification also suggests the 1-chloro isomer since the 4-chloro alcohol would have a structure similar to 3-chloro-2-methylpropanol-1, which was obtained in excellent yield from its trichloroacetate.

Summary

The *n*-, *i*- and *s*-butyl trichloroacetates have been chlorinated and in each case two monochlorobutyl trichloroacetates have been separated as the major products of chlorination. The corresponding monochlorobutyl alcohols have been obtained in four cases by saponification of the esters while in two cases attempts at saponification failed to yield the alcohols.

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Relative Oxidation Potentials of Ketones

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Ketones may be arranged in a series according to their strength as oxidizing agents, *i. e.*, of their oxidation potentials. A ketone high in the series will oxidize rather completely the alcohol corresponding to a ketone low in the series. In such a comparison the quinones will be at the top and the dialkyl ketones at the bottom of the series. For example, diphenoquinone is probably one of the most powerful oxidizing agents among the ketones while di-*i*-propyl ketone is one of the weakest. The quinones have been compared with each other by virtue of the fact that the reduction of a quinone to a hydroquinone is a strictly reversible process, and that an aqueous solution containing appreciable quantities of these two substances, and having a fixed hydrogen-ion concentration, estab-

lishes a definite and accurately determinable potential on a platinum electrode. A comparison of the oxidation potential may be expressed in volts, as for example 0.95 for diphenoquinone, 0.71 for *p*-benzoquinone, 0.48 for α -naphthoquinone and 0.15 for 9,10-anthraquinone.²

The present paper is concerned with the comparison of several ketones which are much weaker as oxidizing agents than the quinones referred to above. It is not possible as yet to express quantitatively their oxidation potentials. It must suffice to state their strength as oxidizing agents in terms of a standard ketone. However, it is hoped that the gap in the series of ketones between the quinones and benzophenone may be bridged by the study of ketones of intermediate oxidation po-

(1) Procter and Gamble Fellow, 1938–1939.

(2) Fieser in Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, p. 96.

tentials. It will then be possible to express the oxidation potentials of all members of the series in the same units.

The comparisons here reported are based upon the fact that a ketone and a secondary alcohol may be equilibrated, in the presence of aluminum *t*-butoxide, against the alcohol corresponding to the ketone and the ketone corresponding to the alcohol³



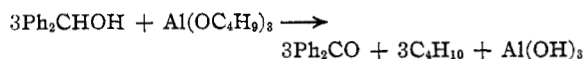
The general procedure for equilibration was as follows. Equimolecular amounts (0.01 mole) of a ketone and an alcohol were weighed into a test tube with a constricted neck. Fifteen ml. of toluene containing 2.5 g. of aluminum *t*-butoxide (0.01 mole) was added, the tube sealed off and suspended in a thermostat held at 100°. After a period of twenty to 620 hours a sample from the reaction mixture was analyzed by means of a polarograph.

In order to utilize the polarographic method of analysis at least one of the two ketones in the mixture must be unsaturated since saturated ketones do not show a depolarization potential. In the majority of cases benzophenone was the ketone upon which the analysis was based, while in other instances phenyl ketones carrying an ethyl, *n*-propyl, *i*-propyl, *n*-butyl or *n*-amyl group were used. Equilibrium in the reaction mixtures was always attained from both directions.

In the majority of cases approximately the same concentration of ketones was present after 150 to 200 hours no matter from which direction the reaction was run. For example, in the equilibration of benzophenone against phenyl *i*-propyl ketone, the concentration of benzophenone present after 150 hours was about 47.7 mole per cent. (the maximum deviation from the average being 1.8%) no matter whether the original reaction mixture contained Ph_2CO and *i*-PrCHOHPh or Ph_2CHOH and *i*-PrCOPh. However, in some cases equilibrium was not attained after 150 to 200 hours so that the period of reaction was prolonged to over 600 hours. For example, the concentration of benzophenone present in a reaction mixture varied as much as 7.6% after 200 to 250 hours, depending upon whether the reaction mixture originally contained Ph_2CO and *i*-BuCHOHPh or Ph_2CHOH and *i*-BuCOPh. However, after 600 hours the maximum deviation was 1.4%. After many comparisons had been made, it was

found that while the concentration of a ketone was independent, after a suitable interval, of the direction from which the reaction proceeded, it was not independent of the time of reaction. For instance, in the comparison of benzophenone and phenyl *i*-propyl ketone there were variations from a value of 47.6% after 150 to 200 hours, to values of 53.3% after 200 to 250 hours, and 39.3% after 380 to 430 hours. It should be emphasized that each of these values could be duplicated within 1 or 2% from either direction, if the time interval was constant.

It is apparent that a side reaction was occurring which modified the concentration of ketones. This side reaction could not be a condensation for it will be shown in another paper that the ketones under consideration do not undergo such a reaction with aluminum *t*-butoxide. It is probable that the side reaction was of the type



The formation of aluminum hydroxide and butane was indicated by the fact that reaction mixtures in some cases became gelatinous and considerable pressure was developed within the tubes after a few hundred hours.

In order to test the oxidation of alcohols by aluminum *t*-butoxide a few experiments were made in which various phenyl carbinols (0.01 mole) were allowed to react with an equimolecular amount of aluminum *t*-butoxide in 15 ml. of toluene at 100° in a sealed tube for 132 hours. Ketones were produced to the following extent, based upon polarographic analysis, Ph_2CO 4%, EtCOPh 5.5%, *n*-PrCOPh 1%, *i*-PrCOPh 2.4%, *n*-BuCOPh 1.2%, *n*-AmCOPh 4.3%. None of the polarographical non-reducible ketones were studied from this standpoint because of the lack of a convenient method of analysis for the ketones, but it must be assumed that any of the alcohols might undergo oxidation to the extent of a few per cent. within one hundred hours.

In order to minimize the effect of the side reaction upon the concentration of ketones in the reaction mixture, the procedure was modified so that equilibrium would be reached in a shorter time. The reaction mixtures were made up containing both ketones and both alcohols under comparison, the concentrations in one set of reaction mixtures being somewhat to the "right" of the probable equilibrium concentrations, while the

(3) Adkins and Cox, *THIS JOURNAL*, **60**, 1151 (1938).

other set was somewhat to the "left." For example, the earlier work suggested that the concentration of benzophenone in equilibrium with diethyl ketone would be about 33 to 34% if it were not modified by a side reaction. Reaction mixtures were therefore made up which contained in one case 0.0025 mole of Ph_2CO , 0.0075 Ph_2CHOH , 0.0075 Et_2CO and 0.0025 of Et_2CHOH , and in the second case 0.0040 Ph_2CO , 0.0060 Ph_2CHOH , 0.0060 Et_2CO and 0.0040 Et_2CHOH , respectively. The first set of mixtures after ninety-six hours gave 32.3, 31.7 and 30.6% benzophenone, while the second set gave values of 30.7 and 32.2.

In only three cases in these later studies did the average of the values from reaction in one direction differ by more than about 1% from the average of the values attained from the other. Thus, equilibrium approximately was attained after a maximum of ninety-six hours and in many cases in much shorter lengths of time. In three mixtures containing di-*i*-propyl or di-*i*-butyl ketones reaction was so slow that even after ninety-six hours the values were from 2.5 to 6% apart. In calculating the relative reactivity of the ketones the average of the values from one direction with that from the other was taken as the true concentration of the ketones at equilibrium.

There is presented in Table I a summary of the experimental data upon which the relative reactivities given in Table II are based. For purposes of comparison the value of 1.00 is assigned to di-*i*-propyl ketone. All the other ketones studied, with possibly one exception, are stronger oxidizing agents than is the standard ketone. That is to say, in an equilibrium mixture there would be a higher concentration of the di-*i*-propyl ketone than of any of the other twelve ketones. Stated in another way, it may be said that di-*i*-propylcarbinol has the greatest tendency to be oxidized as compared with the various carbinols investigated, while cyclohexanol has the least tendency to be oxidized. It may be said that cyclohexanone has the highest oxidation potential, *i. e.*, it is endowed with more power as an oxidation agent than any of the other ketones investigated.

The first four columns of figures in Table II give the relative reactivity values as calculated from the experimental comparisons. The "relative reactivity" values are obtained, for example, by dividing the mole per cent. of benzophenone

(24.1%) at equilibrium by the mole per cent. of di-*i*-propyl ketone (75.9%) to give a value of 0.32 for benzophenone.

In the case of the dialkyl ketones, which could not be equilibrated against di-*i*-propyl ketone because of the lack of a convenient and accurate method of analysis, the relative reactivities were calculated indirectly; *i. e.*, for diethyl ketone against benzophenone the ratio of diethyl ketone to benzophenone in the equilibrium mixture is 68.5/31.5, which when multiplied by the ratio of benzophenone to di-*i*-propyl ketone, 24.1/75.9, gives a value of 0.69 for the relative reactivity of diethyl ketone on the basis of di-*i*-propyl ketone being 1.00.

For ten of the ketones experimental comparisons have been made against two different ketones while diethyl ketone was equilibrated against four different ketones. In general it would appear that the oxidizing power of a ketone, relative to the standard ketone, is independent of the particular ketone with which it is compared in experiment. One exception is that the value for diethyl ketone against phenyl *n*-amyl ketone is 0.63, while the other three values for diethyl ketone are 0.69, 0.68 and 0.70. However, if the value for diethyl ketone is calculated through the benzophenone equilibria with diethyl ketone and with phenyl *n*-amyl ketone, then the value is 0.67, which is in excellent agreement with the other values. In a similar manner the value for dibutyl ketone may be raised from 0.92 to 0.96, which is in agreement with that expected for a dialkyl ketone.

The values given in the last column of Table II may thus be taken as fairly accurately depicting the relative tendency of a given ketone to oxidize an alcohol corresponding to one of the other ketones. The values for cyclohexanone and di-*i*-butyl ketone have been enclosed in parentheses to indicate that they are less certain than for the other ketones. The difficulty with di-*i*-butyl ketone is that it is reduced so slowly and di-*i*-butylcarbinol is oxidized so slowly that equilibrium was not obtained within the time limits used in the case of the other ketones and alcohols. The amount of di-*i*-butyl ketone present was 78% when equilibrium was approached from one direction and 72% when approached from the other. The average of these values, 75%, was assumed to be the concentration of the ketone at equilibrium.

TABLE I
 COMPOSITION OF REACTION MIXTURES

Ketone A	Ketone B	Time, hrs.	(From B side)		(From A side)		Av. % A	Max. dev., %	Av. dev., %
			% Ketone A	Av.	% Ketone A	Av.			
Ph ₂ CO	PrCOPh	48	33.1	33.7	33.7	33.7	33.7	0.6	0.4
		96	34.3						1.2
Ph ₂ CO	<i>i</i> -PrCOPh	48	43.8	44.3	46.1	45.6	45.0	2.2	0.9
		96	44.7		45.0				2.0
Ph ₂ CO	EtCOPh	61	38.0	38.5	37.9	39.0	38.8	1.3	0.8
		94	38.9		40.1				2.1
Ph ₂ CO	<i>n</i> -BuCOPh	62		34.9	36.1	36.4	35.7	1.1	0.8
		91			36.8				2.2
		92	35.2		36.6				
		92	34.6		36.2				
		92							
Ph ₂ CO	<i>n</i> -AmCOPh	61	36.7	36.9	38.0	37.9	37.4	0.7	0.5
		94	37.0		37.8				1.3
Ph ₂ CO	Et ₂ CO	91		31.5	30.7	31.5	31.5	0.9	0.7
		96	32.3		32.3				2.2
		96	31.7						
		96	30.6						
Ph ₂ CO	<i>n</i> -Pr ₂ CO	38	24.6	24.9	25.0	25.1	25.0	1.8	0.8
		92	25.1		23.2				3.2
		92			26.5				
		92			25.7				
		92							
Ph ₂ CO	<i>i</i> -Pr ₂ CO	38	21.2	21.9	27.7	26.2	24.1	3.6	2.2
		62	22.9		26.3				9.1
		91	21.5		23.9				
		91	22.1		26.9				
		91							
Ph ₂ CO	<i>n</i> -Bu ₂ CO	38	23.7	24.3	23.5	23.7	24.0	0.9	0.5
		62	24.9		23.9				2.1
EtCOPh	<i>i</i> -Pr ₂ CO	91	33.2	32.2	35.0	33.9	33.1	1.9	1.1
		91	31.2		32.7				3.3
<i>n</i> -PrCOPh	Et ₂ CO	91	48.7	47.2	47.8	46.7	47.0	1.7	1.3
		91	45.6		45.6				2.8
<i>n</i> -PrCOPh	<i>n</i> -Pr ₂ CO	91	39.9	39.8	36.2	38.2	39.0	2.8	1.4
		91	39.6		40.2				3.6
<i>n</i> -PrCOPh	<i>i</i> -Pr ₂ CO	60	36.0	36.4		38.5	37.5	1.5	1.1
		60	36.8		38.5				2.9
		107			38.5				
<i>n</i> -PrCOPh	<i>n</i> -Bu ₂ CO	91	40.3	39.6	39.6	39.3	39.5	0.8	0.5
		91	38.9		38.9				1.3
<i>i</i> -PrCOPh	Et ₂ CO	48	33.9	35.6	34.5	36.3	36.0	3.1	2.0
		48	37.3		38.0				5.6
<i>i</i> -PrCOPh	<i>i</i> -Pr ₂ CO	60	27.8	27.6		28.5	28.1	0.9	0.5
		60	27.3		28.0				1.8
		107			29.0				
<i>i</i> -PrCOPh	<i>t</i> -BuCOMe	91	38.3	37.8		38.0	37.9	0.6	0.4
		91	37.3		38.0				1.1
<i>n</i> -BuCOPh	<i>i</i> -Pr ₂ CO	91	33.8	33.3	36.1	35.8	34.6	1.8	1.2
		91	32.8		35.4				3.5
<i>n</i> -AmCOPh	<i>i</i> -Pr ₂ CO	91		33.6	32.4	33.3	33.5	1.1	0.7
		96	34.1		34.1				2.1
		96	33.0						
<i>n</i> -AmCOPh	Et ₂ CO	96	44.0	44.1	44.4	44.6	44.4	0.4	0.3
		96	44.1		44.8				0.7
Ph ₂ CO	<i>t</i> -BuCOMe	62	35.3	33.8		35.2	34.5	2.2	1.3
		91	32.4						
		96	34.3		36.7				3.8
		96	33.1		33.6				

TABLE I (Concluded)

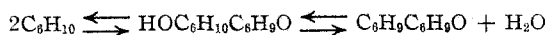
Ketone A	Ketone B	Time, hrs.	(From B side)		(From A side)		Av. % A	Max. dev., %	Av. dev., %
			% Ketone A	Av.	% Ketone A	Av.			
Ph ₂ CO	<i>i</i> -Bu ₂ CO	24	23.0		29.0		26.5		
		24	23.1	23.1	30.8	29.9			
		72	21.2	22.1	27.0	26.9	24.5		
		72	22.9		26.8				
<i>i</i> -PrCOPh	<i>i</i> -Bu ₂ CO	24	23.2		36.3		29.8		
		48	21.4	22.0	27.7	27.9	25.0		
		110	21.5		28.1				
		110	23.0						
Ph ₂ CO	Cyclohexanone	24	58.9		65.6		62.3		
		48	63.0		58.4		60.7		
		92	56.8	56.3	55.6	56.4	56.4		
		92	55.7		57.2				
<i>i</i> -PrCOPh	Cyclohexanone	21	65.8		70.4		68.1		
		48	57.2		59.2		58.7		

TABLE II

RELATIVE REACTIVITIES OF VARIOUS KETONES

Ketone	Other ketone in equilibrium mixture					Av. Value
	<i>i</i> -Pr ₂	Ph ₂	<i>n</i> -PrPh	<i>i</i> -PrPh	<i>n</i> -AmPh	
Cyclohexanone	(0.19)			(0.18)		(0.19)
Ph ₂ CO	0.32					.32
<i>i</i> -PrCOPh	.39	.39				.39
EtCOPh	.50	.51				.51
<i>n</i> -AmCOPh	.50	.53				.52
<i>n</i> -BuCOPh	.53	.57				.55
<i>n</i> -PrCOPh	.60	.63				.62
<i>i</i> -BuCOPh		.63		.64		.64
Et ₂ CO		.69	0.68	.70	0.63	.68
<i>i</i> -Bu ₂ CO		(.93)		(.92)		(.93)
<i>n</i> -Pr ₂ CO		.95	.94			.95
<i>n</i> -Bu ₂ CO		1.01	.92			.97
<i>i</i> -Pr ₂ CO	1.00	1.00	1.00	1.00	1.00	1.00

The difficulty with cyclohexanone is that it so readily undergoes condensation



Cyclohexylidene-cyclohexanone, the final condensation product, apparently was not formed, since this compound would show up on a polarographic analysis, but it is possible that the hydroxy ketone first formed would modify the oxidation reduction equilibrium. Possibly the value 0.19 assigned in the table to cyclohexanone is a little too low, but it certainly is not higher than 0.24.

An examination of the data in the last column of Table II reveals several general tendencies rather clearly. The diaryl ketones are better oxidizing agents than the alkyl aryl ketones and they in turn are better oxidizing agents than the majority of the dialkyl ketones. However, there are marked differences among the aliphatic ketones. The *t*-butyl group has an effect markedly similar to an aryl group, for pinacolone and butyrophenone have the same value when they are

compared against benzophenone. Diethyl ketone is a stronger oxidizing agent than are dipropyl and dibutyl ketones. The difference between alkyl groups is also shown by the fact that *i*-propyl phenyl ketone has a value of 0.39, while the corresponding *n*-propyl phenyl ketone has a relative reactivity of 0.60 or more.

Most striking of all is the fact that the saturated ketone, cyclohexanone, has an oxidation potential higher than any other ketone, even than the highly unsaturated ketone, benzophenone.

In general there is a parallelism between the depolarization potential or "reduction potential" as measured on a polarograph and the strength of a ketone as an oxidizing agent as determined by equilibration. That is, the aliphatic ketones have a high depolarization potential and a low oxidation potential while the quinones have a very low depolarization potential and a high oxidation potential.² However, the depolarization potential cannot be safely used as a guide in predicting the strength of a ketone as an oxidizing agent. For example, the propyl phenyl ketones give practically identical values for depolarization potentials (1.60 to 1.61 volts) while they are quite different as oxidizing agents as noted in a preceding paragraph. An even greater discrepancy is found in the case of cyclohexanone, whose depolarization potential is so high that it cannot be measured, yet it is a stronger oxidizing agent than any of the alkyl aryl ketones, all of which show depolarization potentials.

It must be kept clearly in mind that the oxidation potential of a ketone cannot be considered apart from the reducing power of the alcohol corresponding to it. In this paper for the sake of simplicity reference has been made particularly

to the oxidation potential of a ketone rather than to the reduction potential of the alcohol, but in reality one cannot measure the one tendency without the other. In the systems under investigation the alcohols are present at least in part as aluminum alkoxides and the ketones as addition products with aluminum alkoxides. Tendencies to form these compounds probably vary among the alcohols and ketones under consideration so that the relative reactivities of the ketones as oxidizing agents may be thus modified.

Preparation of Ketones and Alcohols.—The various alkyl phenyl ketones were made by the Friedel and Crafts synthesis, using the proper acid chloride (100 to 150 g.) in excess benzene (130 to 340 ml.) with aluminum chloride (122 to 312 g.). The yields were of the order of 80% of the theoretical amount. Di-*n*-butyl ketone was made as by Breise and McElvain.⁴ Benzophenone and pinacolone were made as described in "Organic Syntheses."⁵

All of the six phenyl carbinols as well as methyl-*t*-butylcarbinol, di-*i*-butylcarbinol and di-*n*-butylcarbinol were made by hydrogenation of the corresponding ketones dissolved in ethanol, over Raney nickel or copper chromite. The reaction was stopped after one mole of hydrogen per mole of ketone had been absorbed in the case of the phenyl ketones, otherwise hydrogenolysis of the hydroxy group will occur. The hydrogenations were made under 200 to 300 atm. at temperatures between 95 and 150°. From one-half to three hours were required, using 1 to 2 g. of catalyst per 0.5 mole of ketone. The yield of alcohols averaged 87% of the theoretical amount.

i-Propylphenylcarbinol was also made by reduction of the ketone with aluminum *i*-propoxide, but the yield was only 60%. Both of the propyl phenyl carbinols were also made by the Grignard reaction, the yields being about 88% of the theoretical amount.

The ketones and alcohols not referred to above were obtained from the Eastman Kodak Company.

The reaction mixtures were analyzed as follows. A sample (0.7 ml.) from the reaction mixture was pipetted into a weighed 25-ml. Erlenmeyer flask and weighed. The sample was diluted to approximately 25 ml. with 92.5% isopropyl alcohol and again weighed. The mixture was shaken thoroughly and allowed to stand for several hours during which time it was repeatedly shaken. A sample (1 ml.) of the clear, supernatant liquid was withdrawn and added to a polarographic cell containing 3 ml. of 92.5% isopropyl alcohol and 1 ml. of a 0.84 *N* solution of tetramethylammonium hydroxide.

Three polarographic curves were then made for the solution, and the average wave height computed by the Borchardt "b" method.⁶ Comparing the wave heights so obtained to a graph giving the relationship of wave height to concentration (from Table III) gave the moles, *C*, of the reducible ketone in the polarographic cell. From *C* was

calculated the percentage, *K*, of the polarographically reducible ketone in the equilibrium mixture by means of the following relationship

$$K = \frac{C \times 5}{1000} \cdot \frac{V}{d} \cdot \frac{W}{S} \cdot \frac{100}{B}$$

where *V* is the weight of the sample plus the weight of the isopropyl alcohol added; *W* is the total weight of the materials placed in the sealed tube; *S*, the weight of the 0.7-ml. sample; *B*, the moles of the ketone possible of existing in the reaction mixture (0.01 mole in the experiment as carried out above); and *d*, the density of the isopropyl alcohol solution of the sample. The constant "5" represents the volume of liquid in the polarographic cell, "1000," the number of ml. in a liter, and "100" is the factor for converting to percentage. For all practical purposes the value of *d* may be considered to be the same as that for the density of the isopropyl alcohol solution used in the dilution.

In the cases where there were two polarographically reducible ketones in the reaction mixture, the older "ratio of wave heights" method was employed in the analysis,⁶ the single ketone method being useful as an alternate method for verifying the value obtained by the ratio method.

The reaction mixtures always contained one of the six phenyl ketones listed in Table III. There are given in Table III the measured wave heights for two or three polarograms for each of three concentrations for each of the six ketones. The data show very clearly the reproducibility of the polarograms and the constancy of the relationship of wave height to concentration of any of the

TABLE III
RELATIONSHIP OF WAVE HEIGHTS TO CONCENTRATION OF VARIOUS KETONES

Concn. of ketone	Wave heights in cm.		
	3.2×10^{-3}	2.0×10^{-3}	0.8×10^{-3}
Ph ₂ CO	15.78	9.96	3.97
	15.80	9.88	3.98
	15.75	9.90	3.94
EtCOPh	15.76	10.12	3.97
	15.89	10.18	3.98
<i>n</i> -PrCOPh	15.78	9.86	3.84
	15.66	9.70	3.84
	15.60	9.72	3.96
<i>i</i> -PrCOPh	15.80	9.95	3.92
	15.91	9.95	3.92
	15.80	9.82	3.97
<i>n</i> -BuCOPh	15.78	9.98	4.00
	16.03	9.98	3.97
	15.78	9.98	3.98
<i>n</i> -AmCOPh	15.69	9.70	4.00
	15.62	9.70	4.03
			4.00
Av. value for six ketones	15.79	9.92	3.96
Max. dev. in cm.	0.24	0.22	0.12
Av. dev. in cm.	.09	.11	.04
Av. dev. in %	.6	1.1	.9
Ratio of wave heights	3.99	2.50	1.00
Ratio of concns.	4.00	2.50	1.00

(4) Breise and McElvain, *THIS JOURNAL*, **55**, 1697 (1933).

(5) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, pp. 89 and 451.

(6) Borchardt, Meloche and Adkins, *THIS JOURNAL*, **59**, 2173 (1937).

six ketones. As noted in the earlier paper, acetophenone shows an anomalous behavior.

The relationship of wave height to concentration of ketone was found to be independent of the presence of toluene, *t*-butyl alcohol, aluminum hydroxide, and another ketone, or alcohol such as was known to be present in the reaction mixtures. However, the relationship is not independent of the concentration of water or tetramethylammonium hydroxide in the polarographic cell. The relationship is not independent of the characteristics of the particular capillary electrode.

Summary

Thirteen representative ketones have been compared with each other as oxidizing agents. A numerical statement of the result of the comparison is given in the last column of Table II. The comparisons were made by equilibrating two ketones against each other in the presence of aluminum *t*-butoxide and the alcohols corresponding to the ketones. The concentration of the ketones at equilibrium was determined by means of a polarograph.

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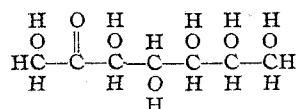
[CONTRIBUTION FROM THE LABORATORY OF BIOLOGICAL CHEMISTRY, LOYOLA UNIVERSITY SCHOOL OF MEDICINE]

The Reduction Products of *d*-Glucoheptulose¹

BY FRED L. HUMOLLER, STANLY J. KUMAN AND FRED H. SNYDER

In 1928 Bertrand and Nitzberg² prepared *l*-glucoheptulose (designated by them as α -glucoheptulose) by the action of *Bact. xylinium* on α -glucoheptitol. In their studies on the structure of this ketoheptose they subjected it to the action of sodium amalgam. From the reaction products they isolated α -glucoheptitol and a substance which they named α -glucoheptulitol. This new substance melted at 144° and showed a specific rotation of -2.24° .³ Later Khouvine and Nitzberg⁴ repeated the work of Bertrand and Nitzberg and also obtained α -glucoheptulitol as one of the reduction products of *l*-glucoheptulose. They assumed, though not without reservations, that α -glucoheptulitol was either β -*d*-glucoheptitol or β -*l*-glucoheptitol.

In 1930 Austin⁵ prepared *d*-glucoheptulose by the rearrangement of α -*d*-glucoheptose in lime water. Because of its method of preparation and because of the identity of its osazone with that obtained from α -*d*-glucoheptose, Austin assigned to *d*-glucoheptulose the formula



From its formula it can be seen that *d*-glucoheptulose should yield upon reduction of its ketone group α -glucoheptitol or β -*d*-glucoheptitol, or both, provided the structure which Austin assigned to this ketose is correct.

However, when Khouvine and Nitzberg⁶ reduced *d*-glucoheptulose with sodium amalgam, they obtained α -glucoheptitol and the enantiomorph of α -glucoheptulitol but not β -*d*-glucoheptitol as predicted by Austin's formula. This new substance, which they called α -*d*-glucoheptulitol, melted at 143–143.5° and showed a specific rotation of $+2.10^\circ$. From their studies on the structure of this substance they came to the conclusion that it was not identical with either β -*d*-glucoheptitol or β -*l*-glucoheptitol, but that it might be a heptitol of unknown structure. They suggested that the glucoheptulitols might be formed by the local concentration of alkali during the reduction with sodium amalgam. This view was strengthened by the fact that when they reduced *d*-glucoheptulose catalytically no α -*d*-glucoheptulitol was obtained but only the two glucoheptitols predicted by Austin's formula.⁷

In view of the findings of the French workers it seemed desirable to us to extend their studies on the structure of the glucoheptulitols. For that purpose *d*-glucoheptulose was prepared by the rearrangement of α -*d*-glucoheptose, using Austin's method⁵ with some modifications. These modifications were introduced in the separation of the

(1) These studies, a portion of which was reported on the program of the meeting of the American Chemical Society in Milwaukee, September, 1938, were abstracted in part from a dissertation submitted by Mr. Kuman to the Graduate School of Loyola University in partial fulfillment of the requirements for the degree of Master of Science.

(2) Bertrand and Nitzberg, *Compt. rend.*, **186**, 925 (1928).

(3) Bertrand and Nitzberg, *ibid.*, **186**, 1172 (1928).

(4) Khouvine and Nitzberg, *ibid.*, **196**, 218 (1933).

(5) Austin, *THIS JOURNAL*, **52**, 2106 (1930).

(6) Khouvine and Nitzberg, *Compt. rend.*, **198**, 985 (1934).

(7) Khouvine, *ibid.*, **204**, 983 (1937).