was kept between 80 and 90°. Data for the acids obtained are given in Table III.

TABLE III

SUBSTITUTED 1,5-DIPHENYLPYRAZOLE-3-CARBOXYLIC ACIDS (COLORLESS PRISMS FROM ALCOHOL)

Substituted phenyl in position 5	Formula	M. p., °C.	Analyses, nitrogen, % Calcd.	Found
4-Methoxy-	$C_{17}H_{14}O_3N_2$	196–197[a]	9.52	9.46
4-Ethoxy-	$C_{18}H_{16}O_3N_2$	163–164	9.09	8.91
4-Dimethylamino-	$C_{18}H_{17}O_2N_3$	141–142[b]	13.68	13.50

[a] This product was further identified by comparison with the acids obtained by oxidation of 1-phenyl-3-(4-methoxystyryl)-5-(4-methoxyphenyl)-pyrazoline, first obtained by Straus [*Ber.*, **51**, 1471 (1918)]. A mixture of one of them, shown to be anisic acid, m. p. 184°, with the product here in question, had a melting range of 140–145°; with the other one, m. p. 196–197°, no depression was noted; with 1,5-diphenylpyrazole-3-carboxylic acid, m. p. 185°, the range was 160–165°. [b] This acid was also obtained by oxidation of 1-phenyl-3-methyl-5-(4-dimethylaminophenyl)-pyrazoline.

Summary

1. Several unsymmetrical dibenzalacetones containing substituents not regarded as "acid-forming" have been subjected to the action of phenylhydrazine and the products studied.
2. A hydrazone was obtained from styryl 4-dimethylaminostyryl ketone. In other cases rearrangement occurred so rapidly that the pyrazoline only could be isolated.
3. Oxidation of these products with permanganate gave, in the greater number of cases, the acids expected if the closing of the pyrazoline ring took place in the direction of the phenyl radical containing the "non-acidic" group. This is opposite that observed when ketones with "acid-forming" substituents were employed.
4. Further work is in progress.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Ozonolysis of Purely Aliphatic Olefins.[1] The Behavior of the Five Simplest Normal Alkyl Radicals in the Dehydration of Tertiary Alcohols

BY JAMES M. CHURCH WITH F. C. WHITMORE AND R. V. MCGREW

Although the first application of ozone to organic compounds was made in 1855[2] and in spite of the classical studies of Harries and his co-workers, detailed and specific directions for the *quantitative* isolation of the ozonolysis products of purely aliphatic olefins of low molecular weight are lacking. A surprisingly small amount of Harries' work dealt with such compounds.[3] The ozonolysis products of ethylene, propylene and butylene have been determined with precision.[4] Little exact work has been done on the methods of decomposing the ozonides. Among the methods used are treatment with zinc and acetic acid,[5] potassium ferrocyanide,[6] sodium bisulfite,[7] and catalytic hydrogenation.[8]

The present study of ozonolysis was undertaken to make available methods for the determination of mixtures of isomeric olefins as obtained by the dehydration of tertiary alcohols.[9]

In the present work the ozonides were prepared from solutions of the olefins in a mixture of paraffin hydrocarbons of boiling range 0–30°.[10] In some cases the ozonides were decomposed in the presence of the solvent. Usually, however, the low-boiling solvent was removed at low pressures, leaving the sirupy ozonides which were handled with proper precautions because of the danger of explosions. Most of the ozonides obtained in this work showed little explosibility. The ozonides of the highly branched and heavier olefins were most unstable to light and heat.

The best method for decomposing the ozonides was by treatment with water and zinc in the presence of traces of silver and hydroquinone.[1a] The catalysts[4] diminished the oxidation of the aldehydes by the hydrogen peroxide formed. This technique was adopted only after extensive studies of other methods of decomposing ozonides including those already mentioned and new meth-

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(1) *Cf.* Whitmore and Church (a) THIS JOURNAL, **54**, 3710 (1932); (b) *ibid.*, **55**, 1119 (1933).

(2) Schönbein, *J. prakt. Chem.*, **66**, 282 (1855).

(3) Harries and co-workers, *Ber.*, **37**, 845 (1904); **41**, 3098 (1908); **42**, 3305 (1909); *Ann.*, **343**, 311 (1905); **390**, 238 (1912).

(4) Briner and co-workers, *Helv. Chim. Acta*, **12**, 154, 181, 529 (1929); **14**, 794 (1931).

(5) (a) Harries and Haarmann, *Ber.*, **48**, 32, 231 (Witt) (1915); (b) Noller and Adams, THIS JOURNAL, **48**, 1074 (1926).

(6) Harries, *Chem. Zentr.*, IV, 292 (1920).

(7) Briner and Schnorf, *Helv. Chim. Acta*, **12**, 179 (1929).

(8) Fischer and co-workers, *Ann.*, **464**, 69 (1928); *Ber.*, **65**, 1468 (1932).

(9) *Cf.* Whitmore and Williams, THIS JOURNAL, **55**, 406 (1933).

(10) Supplied by the Viking Corporation of Charleston, W. Va.

ods involving the action of acetic anhydride, propionic anhydride, liquid ammonia and hydrazine hydrate solution. Each of these methods gave satisfactory results in certain cases but no one of them was as generally satisfactory as the water–zinc–catalysts system finally adopted.

Detailed studies were made to find the best methods for isolating and estimating the carbonyl compounds expected from the olefins to be studied. These expected compounds included the five *n*-aldehydes containing one to five carbons and the fifteen ketones containing all possible pairs of *n*-alkyl groups from methyl to amyl. In preliminary studies several of the pure carbonyl compounds were mixed with hydrogen peroxide and the various reagents normally used in a particular method of ozonolysis, and the percentage recovery of the carbonyl compounds gave an indication of the possibilities of that method. In general the methods for isolating the carbonyl compounds were those already published.[1]

The olefins here employed in developing an improved technique of ozonolysis were obtained by the dehydration of certain aliphatic tertiary alcohols, and this report deals not only with the technique of ozonolysis but with the behavior of certain alkyl groups in the dehydration of tertiary alcohols. Some twenty-two tertiary alcohols containing various combinations of normal alkyl groups from methyl to amyl were dehydrated and the structures of the resulting olefins were determined. If the alcohol contains two or three different alkyl groups, two or three different olefins normally result. But in all cases these alcohols dehydrated without rearrangement.

Many of the alcohols had previously been made and dehydrated.[11] In general the results have been made much more accurate. The earlier conclusions as to the effect of odd and even alkyl groups and the difficulty in dehydrating tri-*n*-amylcarbinol[11b] have been corrected.

The tertiary alcohols were all prepared by condensing Grignard reagents with carbonyl compounds and hydrolyzing. In addition to being prepared from the alcohols, several of the olefins related to the symmetrical carbinols R_3COH were prepared by direct heating of the Grignard complexes. In every case the olefins prepared by the two methods appeared to be identical. The process of heating the Grignard complex was shorter, but the yields were not quite as good as when the alcohol was isolated.

The alcohols studied were of the types R_3COH, $R'R_2COH$ and $R'R''RCOH$. The technique of ozonolysis and identification of the carbonyl compounds was developed with the first type because of the simplicity of the products. The resulting technique was then applied to the more difficult mixtures from the other two classes of carbinols.

The dehydration of the tertiary alcohols by iodine[12] was dependent on the temperature used. Thus *tert*-amyl alcohol refluxing at 102° is not dehydrated by iodine. Increase of the pressure to two atmospheres and the boiling point to 128° gave a ready dehydration. By heating tri-*n*-amylcarbinol[11b] with iodine under reduced pressure to give a refluxing temperature of about 170°, a 95% yield of 6-*n*-amylundecene-5 was easily obtained.

The symmetrical tertiary alcohols, R_3COH, included those in which R was ethyl, *n*-propyl, *n*-butyl and *n*-amyl. Their dehydration products, 3-ethylpentene-2, 4-*n*-propylheptene-3, 5-*n*-butylnonene-4 and 6-*n*-amylundecene-5 were ozonized according to the various procedures being studied. The yields of isolated ozonolysis products were 18–98% for the aldehydes and 57–68% for the ketones, as based on the amount of ozonide taken for decomposition. Propionaldehyde offered the greatest difficulty because of its low boiling point and the absence of any suitable derivative for its quantitative estimation.

The study of the dehydration products of the alcohols $R'R_2COH$ and $R'R''RCOH$ containing normal alkyl groups from methyl to *n*-amyl was most difficult and interesting because of the mixture of isomeric olefins formed in each case. With the alcohols $R'R_2COH$ the yields of the two possible aldehydes were 25–95% and of the two ketones were 40–88%. With the $R'R''RCOH$ compounds, the yields of the separated and identified carbonyl compounds were 30–50% for the three aldehydes and 50–60% for the three ketones. All these yields are based on the weight of ozonide used. The yield of ozonides from the olefin mixtures was usually 90–100%.

By summarizing the results of all the dehydrations the conclusion is reached that the decreasing order of ease of supplying the hydrogen to go with the hydroxyl is as follows: ethyl, *n*-propyl,

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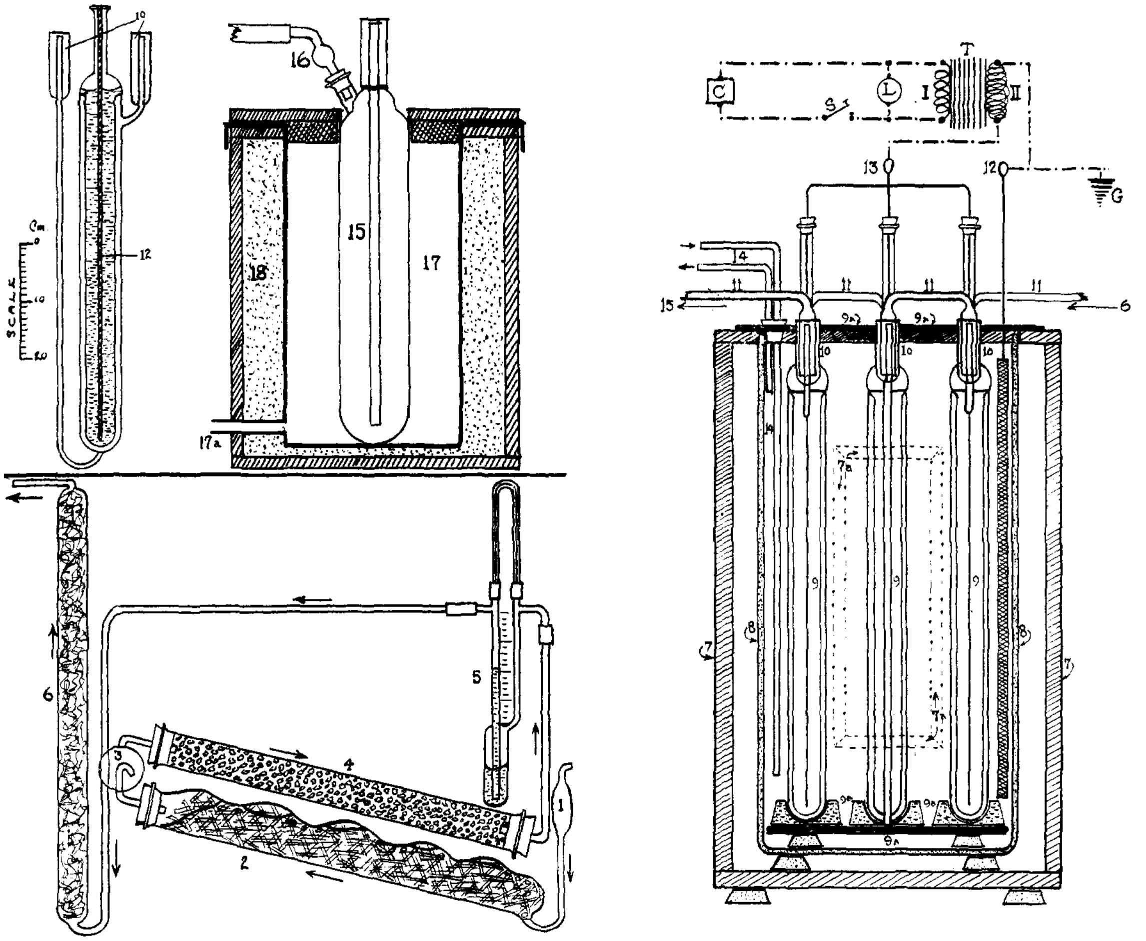
[11] (a) Whitmore and Woodburn, THIS JOURNAL, **55**, 361 (1933); (b) Whitmore and Williams, *ibid.*, **55**, 406 (1933).

[12] Hibbert, *ibid.*, **37**, 1748 (1915).

n-butyl, *n*-amyl, methyl. Slight exceptions occur only with the carbinols $R'R_2COH$, and only when the alkyls involved are adjacent in the list. In some cases in which R contained one more carbon than R′ the amount of dehydration from the R groups was slightly more than twice that from the R′ group. In certain carbinols the dehydration involving the *n*-butyl group is only little different from that of the *n*-amyl group.



1, Trap; 2, special sulfuric acid drying tube containing short pieces of glass tubing; 3, spray; 4, drying tube containing activated alumina; 5, flow meter containing butyl phthalate; 6, tower full of glass wool to catch spray; 7, insulated wooden case; 8, tall Pyrex battery jar; 9, soft glass ozonizer tube; 10, mercury wells for connections; 11, glass connections fitted to mercury wells; 12, inner electrode of twisted No. 6 copper wire, two strands; 13, connection for inner electrodes; 14, tubes for circulating cooling water; 15, five hundred cc. ozonizing bottle with sealed in bubble tube and mercury cup joints; 16, trap and rubber tube connected with ventilation; 17, copper cans for ice–salt cooling mixture; 18, wooden box insulated with ground cork and having a felt insulated lid.

Experimental

The Technique of Ozonolysis.—The preferred method of ozonolysis employed in this Laboratory has already been described,[1a] and is referred to in this report as the zinc-water-catalysts method. But because of the lack of details in the literature on other methods of ozonolysis, especially with reference to the yields of the carbonyl products, it seems desirable to describe briefly certain other methods which have been studied, some of which give almost equally good results with certain types of olefins.

In all cases the ozone was prepared from dried oxygen by passing it through the silent electric discharge in ozonizing tubes of the Berthelot type (Fig. 1). Soft glass tubes were found more permanent than Pyrex. The entire apparatus was placed in a well-ventilated hood with shatter-proof glass doors.[13] The ozonized oxygen was passed into a solution of the olefin in a low-boiling paraffin hydrocarbon solvent (boiling range 0–30°),[10] kept at about −10° in an ice–salt mixture. About 300 cc. of solvent was used for 0.5 mole of olefin. The solid ozonides of some of the higher olefins were not soluble in this solvent, in which case glacial acetic acid was used instead. Ethyl bromide also was used as the solvent in a few cases. The ozoniza-

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(13) One apparatus of this type exploded violently in this Laboratory, for reasons still undetermined.

tion was continued as long as the ozone was completely absorbed (usually about sixteen hours for 0.5 mole). Small amounts of the olefins were lost by volatilization during the process, but in no case was any unchanged olefin found remaining at the end. In most cases the solution of the ozonide was next transferred to a tared dropping funnel with a heavy wire screen jacket and the solvent removed at room temperature by applying suction. The weight of the colorless or yellow liquid ozonide was determined (the yield was usually at least 90% of the theoretical) and it was then decomposed by the chosen method as soon as possible.

A few ozonides explode spontaneously at room temperature, and the explosions are of considerable violence. Hence, the worker should wear goggles and gloves and should always have the apparatus containing the ozonide surrounded by shields of shatterproof glass. This applies not only during the hydrolysis of the ozonide but also during the fractional distillation of the products, for occasionally a small amount of undecomposed ozonide may steam distil out of the hydrolysis mixture and leave an explosive residue during the fractionation.

To avoid the formation of hydrogen peroxide, the decomposition of ozonides by a few non-aqueous reagents was tried. (It is of course possible that other strong oxidizing agents might be formed in these cases.) Thus, the ozonides of a few simple known olefins (those from triethyl, tri-*n*-propyl, tri-*n*-butyl and tri-*n*-amyl carbinols) were added to boiling acetic anhydride containing a few drops of concentrated sulfuric acid. The products were steam distilled from the excess acetic anhydride and the oil layer of the distillate dried and fractionated. The expected ketones were thus obtained in the following yields: diethyl ketone 88%, di-*n*-propyl ketone 62%, di-*n*-butyl ketone 36%, di-*n*-amyl ketone 48%. The aldehydes were present as their *diacetates*, which were collected in the following yields from the fractionations: acetaldehyde 23%, propionaldehyde 18%, butyraldehyde 31%, valeraldehyde 52%. In a blank experiment where a mixture of acetaldehyde and diethyl ketone was added instead of the ozonide, 90% of the ketone was recovered, boiling at 101–102° (740 mm.), and 83% of the aldehyde was recovered as ethylidene diacetate, boiling at 167–169°. Attempts to hydrolyze the diacetates and further identify the aldehyde products were unsuccessful. The boiling points and other physical constants of the diacetates would scarcely be enough to identify some aldehydes, so for the present this method cannot be used as a general one for unknown olefins. In addition, the yields were by no means all that could be desired.

Propionic anhydride was tried instead of acetic anhydride with very similar results. The aldehydes were isolated as their dipropionates, but could not be otherwise identified.

Liquid ammonia was tried as another non-aqueous reagent for decomposing ozonides. The liquid ozonide was dropped into an excess of liquid ammonia in a Dewar flask. Considerable reaction seemed to occur and the gases were allowed to escape. Ether was then added, the excess ammonia allowed to evaporate, the last of it removed by extraction with dilute acid, and the ether solution finally fractionated. The expected ketones were obtained in the following yields: diethyl ketone 57%, di-*n*-propyl ketone 49%, di-*n*-butyl ketone 53%, di-*n*-amyl ketone 71%. The crystalline ammonia compound of acetaldehyde was isolated in 83% yield. The higher aldehydes, however, gave insoluble resinous oils, the amounts of which corresponded to a 23% yield for propionaldehyde, 40% for butyraldehyde and 29% for valeraldehyde. Acid hydrolysis of these resins gave sufficient amounts of the free aldehydes to permit the preparation of the usual derivatives for identification. An accurate estimation of the proportion of two aldehydes in the resin would probably be impossible, however.

Thus, none of these methods for decomposing ozonides in non-aqueous systems is promising for the quantitative determination of aldehyde products, though all the methods permitted the isolation of the ketones in fair yields. A further study was therefore made of methods for decomposing ozonides in aqueous systems.

F. E. Williams[14] of this Laboratory investigated the methods suggested in the literature for decomposing ozonides by means of concentrated potassium bisulfite solution[15] or dilute sodium bisulfite solution.[8] He was able to isolate the aldehyde products in only very small yields, however, so these methods were not further investigated.

The decomposition of ozonides in the presence of hydrazine was studied. It was thought that this reducing agent might destroy the hydrogen peroxide, while an excess of it might form hydrazones of the aldehydes and ketones. The ozonide of 3-ethylpentene-2 was dropped into a boiling 4-molar solution of hydrazine hydrate, to which a trace of potassium iodide had been added to catalyze the formation of hydrazones. The mixture was then acidified with sulfuric acid and steam distilled. Only a small amount of the expected diethyl ketone came over as an oil layer. Likewise, only a low yield of the acetaldehyde was obtained, by absorption in ether and precipitation as the ammonia compound. The hydrazine was recovered practically quantitatively as the sulfate. Blank experiments in which hydrogen peroxide and a mixture of the aldehyde and ketone were dropped into the hydrazine solution also gave very poor recovery of the aldehyde and ketone, while the hydrazine was recovered so nearly quantitatively that very little, if any, of it could have reacted with the hydrogen peroxide or the carbonyl compounds.

Another procedure tried was that of Noller and Adams[5b] for decomposing ozonides in acetic acid by the addition of much zinc dust and a little water. Only poor yields of the lower aldehydes could be isolated, however, and it was difficult to separate some of the ketones from the large amount of acetic acid. Blank experiments indicated that the conditions of this method were not very effective for destroying hydrogen peroxide.

Somewhat better results were obtained by dropping the ozonide or an acetic acid solution of it into a boiling mixture of zinc dust and 50% acetic acid. The oily products were removed by steam distillation and extraction with ether and fractionated. The expected ketones were thus isolated in the following yields: diethyl ketone 51%, di-*n*-propyl ketone 69%, di-*n*-butyl ketone 65%; while the

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(14) F. E. Williams, Thesis, The Pennsylvania State College, 1931, p. 98.

(15) Molinari and Barosi, *Ber.*, **41**, 2795 (1908).

aldehydes were isolated in poorer yields, namely: acetaldehyde 36%, propionaldehyde 16%, butyraldehyde 16%.

Similar experiments were tried with zinc and water alone, with no acetic acid. Blank experiments with this method gave unusually encouraging results. With actual ozonides, however, the yields of aldehydes still were unsatisfactory, as shown by the figures: acetaldehyde 36%, butyraldehyde 18%. The yields of ketones were only fair: diethyl ketone 40%, di-*n*-butyl ketone 46%.

Further details concerning this preferred method for decomposing ozonides by the zinc–water-catalysts method are to be found in the earlier paper. In some cases it may be desirable to add acetic acid to the system, but for most of the lower olefins it seems to do no good and it makes the isolation of the products a little more difficult. In case an easily oxidized aldehyde, such as trimethylacetaldehyde, is among the ozonolysis products, one may still expect to find part of it as the acid rather than the aldehyde.

Table I

Preparation and Dehydration of Tertiary Alcohols

		Source						Olefins produced		
	Carbinol	Carbonyl compound	Halide	Yield, %	Yield, g.	B. p., °C. (mm.)	n^{20}_D	Yield, %	B. p., °C. (mm.)	n^{20}_D
1	Et_3	CO_3Et_2	EtBr	80	48	138-140 (742)		96	96–97 (737)	1.4142
						.....		65^a	94–95 (730)	
2	Pr_3	CO_3Et_2	PrBr	69	196	89–90 (15)		91	65–96 (15)	
						.....		56^a	160–162 (734)	1.4386
3	Bu_3	CO_3Et_2	BuBr	81	484	118–120 (17)	1.4445	94	98–99 (15)	1.4419
						.....		63^a	108–109 (22)	1.4421
4	Am_3	CO_3Et_2	AmBr	55		163–165 (17)		85	135–137 (17)	
						.....		36^a	132–134 (15)	
5	Me_2Et	Commercial				101–102 (734)		75	35–38 (734)	1.3872
6	Me_2Bu	Me_2CO	BuBr	68		141–143 (730)	1.4186	76	91-93 (734)	1.4069
7	Me_2Am^b	$AmCO_2Et$	MeCl	64	108	155–156	1.4243	89	117–119 (740)	1.4138
8	Et_2Me	$MeCO_2Et$	EtBr	67	205	121–122 (740)		72	66–68 (735)	
9	Et_2Pr	$PrCO_2Et$	EtBr	61	159	158–160 (733)		79	118.5–119.5 (742)	1.4214
10	Et_2Bu	$BuCO_2Et$	EtBr	69	298	78–80 (18)	1.4362	79	142–143 (740)	1.4265
11	Et_2Am	$AmCO_2Et$	EtBr	73	231	83–85 (12)	1.4391	89	158–159 (726)	1.4306
						.....		53^a	160–162 (735)	1.4306
12	Pr_2Et	$EtCO_2Et$	PrBr	58	150	76–78 (17)		78	138–140 (743)	1.4250
13	Pr_2Am	$AmCO_2Et$	PrBr	44	163	88–90 (4)	1.4413	95	84–86 (15)	1.4370
14	Bu_2Et	$EtCO_2Et$	BuBr	73	250	100–102 (15)	1.4411	90	66–68 (12)	1.4345
15	Bu_2Pr	$PrCO_2Et$	BuBr	73	271	110–112 (12)	1.4427	89	84–86 (15)	1.4364
16	Bu_2Am^c	$AmCO_2Et$	BuBr	76	490	98–100 (2)	1.4450	87	109–111 (13)	1.4412
17	Am_2Me	$MeCO_2Et$	AmBr	75	280	117–120 (15)	1.4395	61	90–92 (15)	1.4375
						.....		37^a	68–70 (5)	1.4378
18	Am_2Et^c	$EtCO_2Et$	AmBr	40	240	104–106 (3)	1.4424	72	103–105 (15)	1.4401
19	Am_2Pr^c	$PrCO_2Et$	AmBr	50	220	135–138 (14)	1.4453	95	108–110 (12)	1.4418
20	Am_2Bu^c	$BuCO_2Et$	AmBr	58	200	109–110 (2)	1.4482	63	126–129 (15)	1.4437
21	$MeEtBu^b$	MeCOEt	BuBr	83	290	158–159 (731)	1.4238	93	119–120 (735)	1.4186
22	MeEtAm	MeCOAm	EtBr	77	665	78–79 (15)	1.4323	78	143–144 (727)	1.4260
23	MePrAm	MeCOAm	PrBr	70	332	84–86 (15)	1.4344	72	57–58 (15)	1.4350
24	MeBuAm	MeCOAm	BuBr	68	235	104–105 (15)	1.4373	87	74–75 (14)	1.4378

[a] Olefin obtained by heating the Grignard complex. Yield based on the starting materials. [b] Dehydrated with 5% by weight of 50% H_2SO_4. [c] Prepared by F. E. Williams of this Laboratory.

As pointed out in the previous publication,[1a] this method is greatly improved by the addition of catalysts to counteract the effect of the hydrogen peroxide. It was found that the addition of about 0.001 mole of silver nitrate (10% solution) or platinic chloride gave the finely divided metal which rapidly destroyed the hydrogen peroxide. About 0.001 mole of hydroquinone was also added, as an antioxidant catalyst, to retard the oxidation of the aldehydes. The effectiveness of these catalysts is shown by the following yields of carbonyl products isolated, which may be compared with those obtained by the other methods given above: acetaldehyde 38%, propionaldehyde 18%, butyraldehyde 27%, valeraldehyde 38%, diethyl ketone 57%, di-*n*-propyl ketone 61%, di-*n*-butyl ketone 65%, di-*n*-amyl ketone 63%.

As indicated in the above discussion, all of the carbonyl compounds except formaldehyde, acetaldehyde and part of the acetone were isolated in fairly pure form by distillation through efficient fractionating columns of the type previously described.[16] More than one distillation of certain fractions was necessary. The boiling point and refractive index indicated the composition of each main fraction. The fractions were identified by known derivatives, such as semicarbazones or 2,4-dinitrophenylhydrazones.

Formaldehyde was detected qualitatively by the various color tests. It was determined quantitatively by iodimetric titrations of the aqueous portions of the ozonolysis products. In case acetone or other substances were present that would interfere with the iodimetric determina

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[16] Whitmore and Lux, This Journal, **54**, 3448 (1932).

TABLE II

DATA ON OZONOLYSIS OF OLEFINS FROM TERTIARY ALCOHOLS

	Parent carbinol	Olefin, g.	Ozonide obtained, g.	Oil from ozonide, g.	Main fractions		Fractions		Products isolated		Derivatives		
					B. p., °C. (mm.)	g.	Low, g.	High, g.	Formula	Yield, %	Type	M. p., °C.	Mixed m. p., °C.
1	Et_3	49	67	32 cc.	99–102 (739)	22.6	2.2	1.8	Et_2CO	57	B	153	152
									MeCHO	38	C	89	
2	Pr_3	70	87	43 g.	45–50 (734)	4.8	0.6	0.9	EtCHO	18	B	155	154
					138–142	32.1	.9	1.1	Pr_2CO	61	A	133	132
3	Bu_3	91	105	100	70–74	8.9	3.8	7.7	PrCHO	27	B	121	
					180–186	42.5	10.4	11.2	Bu_2CO	65	A	90	
4	Am_3	112	129	101	99–104 (746)	12.2	2.6	3.4	BuCHO	38	B	98	
					90–95 (15)	52.0	3.4	5.3	Am_2CO	63	A	78	
5	Me_2Et	28[a]	33	9.5	75–80 (738)	3.9			MeCOEt	30	B	112	
									HCHO	14			
									MeCHO	4	C	87	
		28[b]	...	...	Qualitative		..	...	Me_2CO	..	D	111	
									MeCHO	..	C	89	
6	Me_2Bu	49	63	33.6	54–58 (742)	2.5	0.8	0.8	Me_2CO	16	D	110	
					72–76	8.4	.8	.9	PrCHO	27	B	120	121
					118–126	11.1	.9	.9	MeCOBu	26	A	118	120
									HCHO	35			
7	Me_2Am	45	58	44.7	55–60 (734)	2.2	..	0.6	Me_2CO	59	D	108	109
					98–103	3.1	0.6	1.6	BuCHO	10	B	96	97
					145–150	15.2	1.6	9.6	MeCOAm	42	A	118	120
									HCHO	10			
8	Et_2Me	57	72[c]	...	78–82 (742)	9.2	5.0	11.9	MeCOEt	31	A	135	
									MeCHO	51	C		
9	Et_2Pr	56	64	41.3	36–53 (740)	0.9	..	0.6	EtCHO	4	B	153	
					100–105	3.8	0.7	3.9	Et_2CO	11	A	136	
					120–124	15.3	2.0	1.8	EtCOPr	38	A	110	
									MeCHO	25	C		
10	Et_2Bu	42	46	37	72–74 (739)	0.8	0.5	0.8	PrCHO	4	B	119	117
					102–104	1.7	.9	1.1	Et_2CO	7	A	134	
					143–145	17.3	2.1	1.1	EtCOBu	56	A	102	104
									MeCHO	93	C	88	
11	Et_2Am	70	89	62	98–103	11.3	2.7	3.0	BuCHO	13	B	96	94
									Et_2CO	14	B	143	139
					164–168	29.1	3.1	5.3	EtCOAm	47	A	86	
									MeCHO	85	C	89	
12	Pr_2Et	32	35	27	48–53 (736)	1.3	1.1	1.5	EtCHO	6	B	155	
					120–123	16.6	1.6	1.8	EtCOPr	43	A	108	107
					140–143	12.2	1.9	3.1	Pr_2CO	28	A	132	133
									MeCHO	52	C	88	
13	Pr_2Am	84	82	73	46–50 (743)	3.8	1.2	0.7	EtCHO	17	B	154	
					100–105	6.3	0.7	1.0	BuCHO	19	B	97	
					140–145	12.8	1.1	3.8	Pr_2CO	30	A	133	
					182–187	31.4	3.8	...	PrCOAm	58	A	145	145
14	Bu_2Et	77	98	66	72–76 (743)	5.1	1.4	0.9	PrCHO	15	B	121	121
					144–147	22.6	1.0	1.5	EtCOBu	41	A	98	98
					180–185	19.3	1.6	1.3	Bu_2CO	27	A	89	88
									MeCHO	170	C	87	
15	Bu_2Pr	84	102	79	48–55 (740)	1.5	..	0.4	EtCHO	6	B	154	153
					73–75	7.2	0.4	1.5	PrCHO	22	B	121	120
					162–167	33.9	1.5	1.2	PrCOBu	61	A	96	
					180–185	14.2	1.2	1.1	Bu_2CO	21	A	89	88
16	Bu_2Am	79	97	78	72–75 (742)	4.2	1.6	0.7	PrCHO	15	B	121	121
					100–105	3.2	0.7	.5	BuCHO	10	B	97	96
					73–78 (14)	14.6	.6	1.2	Bu_2CO	26	A	89	88
					85–90 (14)	25.3	1.2	4.5	BuCOAm	41	A	69	

TABLE II (*Concluded*)

	Parent carbinol	Olefin, g.	Ozonide obtained, g.	Oil from ozonide, g.	Main fractions B. p., °C. (mm.)	Main fractions g.	Fractions Low, g.	Fractions High, g.	Products isolated Formula	Products isolated Yield, %	Derivatives Type	Derivatives M. p., °C.	Derivatives Mixed m. p., °C.
17	Am_2Me	84	97	73	98–103 (741)	14.1	1.3	1.7	BuCHO	35	B	98	
					146–151	24.8	1.8	5.7	MeCOAm	49	A	115	115
					98–103 (14)	4.8	5.8	1.6	Am_2CO ?	7	..		
									HCHO	4			
18	Am_2Pr	79	97	70.5	48–52 (727)	2.3	..	1.0	EtCHO	10	B	153	153
					98–103	6.9	1.1	1.8	BuCHO	20	B	98	97
					75–80 (15)	26.0	1.8	0.9	PrCOAm	46	A	143	143
					98–103 (15)	14.6	1.0	3.1	Am_2CO ?	22	..		
19	MeEtBu	112	140	100	70–75 (732)	11.1	3.2	0	PrCHO	23	B		
					75–80	14.2	0	3.1	MeCOEt	23	A		
					123–128	25.2	3.1	2.2	MeCOBu	39	A		
					143–148	4.1	2.1	7.5	EtCOBu	4	A		
									HCHO	6			
									MeCHO	7	C	92	
20	MeEtAm	63	73	56	77–82 (732)	3.7	1.3	0.7	MeCOEt	12	A	136	138
					98–103	3.1	0.6	2.0	BuCHO	9	B	96	98
					147–152	11.8	2.1	2.1	MeCOAm	25	A	114	114
					163–168	6.8	2.2	3.8	EtCOAm	13	A	88	85
									HCHO	8			
									MeCHO	15	C	89	
21	MePrAm	70	86	73	45–50 (741)	6.1	1.0	0.8	EtCHO	20	B	154	153
					98–103	10.6	0.9	0.7	BuCHO	13	B	92	90
									MeCOPr	13	B	95	103
					145–150	11.5	0.8	1.5	MeCOAm	22	A	112	113
					178–183	5.8	1.6	1.8	PrCOAm	12	A	66	
									HCHO	12			
22	MeBuAm	76	95	68	70–75 (735)	4.3	0.6	0.9	PrCHO	13	B	119	118
					98–103	5.8	1.0	1.3	BuCHO	14	B	97	98
					125–130	11.0	1.3	1.6	MeCOBu	23	B	105	105
					145–150	14.9	1.6	3.3	MeCOAm	28	A	114	115
					82–87 (12)	5.6	3.4	...	BuCOAm ?	8			
									HCHO	11			

A = Semicarbazone. B = 2,4-Dinitrophenylhydrazone. C = Acetaldehyde ammonia. D = Dibenzalacetone.

[a,b] The olefin mixture was separated by repeated fractionation into two main fractions: (*a*) b. p. 31.3–32.6 °, n^{20}_{D} 1.3803, 24%; (*b*) b. p. 36.0–37.3 °, n^{20}_{D} 1.3878, 76%. They were ozonized separately as indicated. The ozonide of *b* (trimethylethylene) was so unstable that only qualitative results could be obtained from it.

[c] Ozonide decomposed by the liquid ammonia method.

tion, it was determined by the hydrogen peroxide method. It was also found that the formaldehyde could be isolated in excellent yields by condensing it in a trap cooled in solid carbon dioxide and acetone. Acetaldehyde was usually absorbed in dry ether containing ammonia, and weighed as the crystalline aldehyde-ammonia compound. Part of the acetone was isolated by fractional distillation and identified by its dibenzal derivative, and part was determined iodimetrically in the aqueous solutions.

Preparation of Aliphatic Tertiary Alcohols.—All of the tertiary alcohols used in this investigation, except *tert*-amyl, were prepared in this Laboratory by condensation of suitable carbonyl compounds with Grignard reagents. Practically all of them had been synthesized previously by Woodburn or Williams,[11] or by other investigators.[17] The methods of preparation used in the present work are indicated in Table I, together with the yield, boiling point and refractive index of each alcohol. The starting materials as well as the final products were all carefully purified by the standard methods as well as by distillation, in every case, through efficient fractionating columns.[16]

Dehydration of the Tertiary Alcohols.—The standard method of dehydration consisted in refluxing the tertiary alcohol with a trace of iodine (Hibbert). The flask was connected to a fractionating column to permit the olefin and water to be distilled out as formed while the unchanged alcohol was held back. Under these conditions (with a 90-cm. fractionating column) *tert*-amyl alcohol did not dehydrate noticeably at atmospheric pressure (b. p. 102°), but at two atmospheres (b. p. 128°) it lost water slowly, 5 moles being about 75% dehydrated in five hours. The other comparatively low-boiling alcohols dehydrated but slowly at atmospheric pressure (five hours for 2 moles of methyldiethylcarbinol, b. p. 121–122°). The higher-boiling alcohols (permitting a higher reaction temperature) lost water more rapidy, often in less than thirty

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[17] (a) Masson, *Compt. rend.*, **132**, 483 (1901); (b) Von Braun and Sobecki, *Ber.*, **44**, 1927 (1911); (c) Davies, Dixon and Jones, *J. Chem. Soc.*, **131**, 468 (1930); (d) Moyer and Marvel, "Organic Syntheses," Vol. XI, 1931, p. 98.

minutes per mole. The highest-boiling alcohols examined, such as triamylcarbinol, dehydrated rapidly; and if the process was carried out under somewhat reduced pressure, so the olefin could be distilled out more easily, excellent yields were obtained.

The olefins of several of the simpler tertiary alcohols were also prepared by direct heating of the Grignard complexes. In this process, after the alkylmagnesium halide had been condensed with the carbonyl compound, the ether was removed by distillation on a water-bath and the residue was then strongly heated in a copper shot bath as long as any distillate would come over (under reduced pressure in the case of the higher olefins). The yields by this procedure were not quite as good as when the alcohol

TABLE III

RESULTS OF DEHYDRATION OF TRI-*n*-ALKYLCARBINOLS

	Carbinol	Dehydration products	Ozonolysis yields (aldehyde: ketone)	Extrapolated yields of dehydration products	Approximate order of preference of dehydration from groups
1	Triethyl	3-Ethylpentene-2	38:57	100	......
2	Tri-*n*-propyl	4-*n*-Propylheptene-3	18:61	100	......
3	Tri-*n*-butyl	5-*n*-Butylnonene-4	27:65	100	......
4	Tri-*n*-amyl	6-*n*-Amylundecene-5	38:63	100	......
5	Dimethylethyl	2-Methylbutene-1[a]	14:30	22	Ethyl:Methyl
		2-Methylbutene-2[a]	qual.	78	8:1
6	Dimethyl-*n*-butyl	2-Methylhexene-1	35:26	55	*n*-Butyl:Methyl
		2-Methylhexene-2	27:16	45	2:1
7	Dimethyl-*n*-amyl	2-Methylheptene-1	10:42	40	*n*-Amyl:Methyl
		2-Methylheptene-2	10:59	60	3:1
8	Diethylmethyl	2-Ethylbutene-1	0:0	trace	Ethyl:Methyl
		3-Methylpentene-2	51:31	mainly	mainly ethyl
9	Diethyl-*n*-propyl	3-Ethylhexene-2	25:38	80	Ethyl:*n*-Propyl
		3-Ethylhexene-3	4:11	20	2:1
10	Diethyl-*n*-butyl	3-Ethylheptene-2	93:56	90	Ethyl:*n*-Butyl
		3-Ethylheptene-3	4:7	10	5:1
11	Diethyl-*n*-amyl	3-Ethyloctene-2	85:47	85	Ethyl:*n*-Amyl
		3-Ethyloctene-3	13:14	15	3:1
12	Di-*n*-propylethyl	3-*n*-Propylhexene-2	52:28	50	Ethyl:*n*-Propyl
		4-Ethylheptene-3	6:43	50	2:1
13	Di-*n*-propyl-*n*-amyl	4-*n*-Propylnonene-3	17:58	60	*n*-Amyl:*n*-Propyl
		4-*n*-Propylnonene-4	19:30	40	4:3
14	Di-*n*-butylethyl	3-*n*-Butylheptene-2	17:29	40	Ethyl:*n*-Butyl
		5-Ethylnonene-4	15:41	60	4:3
15	Di-*n*-butyl-*n*-propyl	4-*n*-Butyloctene-3	6:21	25	*n*-Butyl:*n*-Propyl
		5-*n*-Propylnonene-4	22:61	75	7:5
16	Di-*n*-butyl-*n*-amyl	5-*n*-Butyldecene-4	15:41	60	*n*-Amyl:*n*-Butyl
		5-*n*-Butyldecene-5	10:26	40	4:3
17	Di-*n*-amylmethyl	6-Methylundecene-5	35:49	90	*n*-Amyl:Methyl
		2-*n*-Amylheptene-1	4:7	10	5:1
18	Di-*n*-amyl-*n*-propyl	6-*n*-Propylundecene-5	20:46	67	*n*-Propyl:*n*-Amyl
		4-*n*-Amylnonene-3	10:22	33	1:1
19	Methylethyl-*n*-butyl	2-Ethylhexene-1	6:4	15	Ethyl:*n*-Butyl:Methyl
		3-Methylheptene-2	7:39	55	4:2:1
		3-Methylheptene-3	23:23	30	
20	Methylethyl-*n*-amyl	2-Ethylheptene-1	8:13	20	Ethyl:*n*-Amyl:Methyl
		3-Methyloctene-2	15:25	50	5:3:2
		3-Methyloctene-3	9:12	30	
21	Methyl-*n*-propyl-*n*-amyl	2-*n*-Propylheptene-1	12:12	20	*n*-Propyl:*n*-Amyl:Methyl
		4-Methylnonene-3	20:22	50	5:3:1
		4-Methylnonene-4	13:13	30	
22	Methyl-*n*-butyl-*n*-amyl	2-*n*-Butylheptene-1	11:8	15	*n*-Butyl:*n*-Amyl:Methyl
		5-Methyldecene-4	13:28	45	9:8:3
		5-Methyldecene-5	14:23	40	

[a] Separated by distillation before ozonolysis.

was isolated and dehydrated with iodine (yields based on the carbonyl compound or Grignard reagent in both cases), but the process was shorter and the olefinic products appeared always to be the same by the two methods.

In a few cases the tertiary alcohols were dehydrated by sulfuric acid as well as by iodine. Again there was no rearrangement of the carbon skeleton and the products were the same by the two methods. The procedure with sulfuric acid was similar to that where iodine was used, except 5% by weight of 50% sulfuric acid was used instead of the iodine.

After the dehydrations by either iodine or sulfuric acid, the amount of water layer in the distillate was measured as a check on the completeness of the dehydration. The crude olefinic product was dried over anhydrous copper sulfate and then distilled through a fractionating column to remove any unchanged alcohol or other impurity. No attempt was made to separate the isomeric olefins in the product.

The dehydration data are summarized in Table I, including the yields, boiling points, and refractive indexes of the olefins produced from each tertiary alcohol. Except where otherwise indicated, the dehydration was performed with iodine.

Ozonolysis of the Olefins.—The olefinic product resulting from the dehydration of each alcohol was ozonized and the ozonide decomposed by the zinc–water-catalysts method described above. The products were determined as quantitatively as possible and identified by suitable derivatives. The significant ozonolysis data are given in Table II. The percentage yields of carbonyl products isolated are based upon the weight of ozonide taken for decomposition. The weights of only nearly pure fractions were used in calculating the yields, which would be somewhat higher if intermediate cuts were included.

The ozonolysis products recorded in Table II establish the structure of the olefins from which they were derived, and their amounts show the proportion in which the isomeric olefins were present in the material ozonized. The olefins produced from each alcohol are recorded in Table III together with their relative amounts as derived from the ozonolysis results. It is recognized that in many cases more nearly quantitative ozonolysis yields would be desirable. But the results given in Table III are sufficiently accurate, extensive and consistent to show that there is a marked difference in the ease with which different *n*-alkyl groups supply the hydrogen in the dehydration of tertiary alcohols. The ethyl group supplies it most easily, the propyl group next, then the butyl, then amyl, while the methyl group supplies it even less easily than the amyl group. The results indicate a few slight deviations from this order, usually involving butyl and amyl groups.

Summary

1. Methods of preparing and decomposing ozonides of aliphatic olefins have been studied.

2. Methods are described by which greatly improved yields of carbonyl compounds can be obtained from ozonides.

3. Ozonolysis has been used to determine the proportion of two or three olefins in a mixture.

4. The dehydration of twenty-two aliphatic tertiary alcohols, containing the *n*-alkyl groups from methyl to amyl, has been studied.

5. The ease of dehydration of these alcohols by iodine increases as the temperature (the boiling point of the alcohol) increases.

6. All of these tertiary alcohols are dehydrated by iodine without rearrangement.

7. The order of decreasing ease with which the different alkyl groups supply the hydrogen to form water in the dehydrations has been found to be: ethyl, *n*-propyl, *n*-butyl, *n*-amyl, methyl.

8. The same olefins were obtained by heating the Grignard complexes, from which alcohols would be obtained by hydrolysis, as by dehydrating the alcohols themselves.

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