reaction product when worked up in a customary manner gave about 0.5 cc. of a clear, pleasant smelling liquid. This was definitely identified as 2-methylfuran by converting it to 5-methyl-2-chloromercurifuran by means of mercuric chloride and sodium acetate. A mixed melting point determination with an authentic specimen melting at 132° showed no depression.

Summary

The first complete series of di-substituted furans, particularly useful as reference or standard compounds in studies on orientation of nuclear substituents of furan, has been made available by the synthesis of 5-methyl-3-furoic acid.

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Aliphatic Tertiary Alcohols and Chlorides Containing the Normal Amyl Group and the Related Olefins and their Ozonolysis

BY FRANK C. WHITMORE AND F. E. WILLIAMS[1]

The primary purpose of this research was to supply intermediates for the preparation of certain complex pinacolyl alcohols for use in rearrangement studies.[2] The series of tertiary alcohols chosen contained combinations of the five normal alkyls up to amyl with each alcohol containing at least one amyl group. The *n*-amyl group was chosen because of the present availability of that alcohol in large quantity.[3] Twelve of the fifteen possible alcohols of this type have been prepared in this study. Of these only four have been prepared elsewhere. These are dimethylamylcarbinol,[5] methylethylamylcarbinol,[3] diethylamylcarbinol[3,4] and triamylcarbinol.[6] The triamylcarbinol was kindly supplied by Dr. Marvel. The twelve carbinols were prepared by means of the Grignard reagent in yields of 40–75%. The chief difficulty was in the distillation of the carbinols. All traces of acid had to be removed before distillation and a suitably low pressure was necessary.

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[1] Presented in partial fulfilment of the requirements for the Ph.D. degree at the Pennsylvania State College. This study was finished in August 1930.

[2] (a) Whitmore, THIS JOURNAL, **54**, 3274, 3431 (1932); (b) Whitmore and Woodburn, *ibid.*, **55**, 361 (1933).

[3] The alcohol used in this work was generously supplied by the Sharples Solvents Corporation of Philadelphia.

[4] Masson, *Compt. rend.*, **132**, 483 (1901); V. Braun and Sobecki, *Ber.*, **44**, 1927 (1911).

[5] Davies, Dixon and Jones, *J. Chem. Soc.*, **131**, 468 (1930).

[6] Moyer and Marvel, "Organic Syntheses," Vol. XI, 1931, p. 100.

The alcohols were all colorless sirupy liquids. The higher ones were entirely odorless. Dimethylamyl and methylethylamyl carbinols had pronounced camphor odors and methylpropylamylcarbinol had a slight odor of similar nature. As the number of simple aliphatic tertiary alcohols is increased[2b] regularities in physical properties are appearing. These will be discussed in a later paper.

The chlorides were prepared by hydrogen chloride in the usual way.[2b] The higher members could not be distilled without decomposition even at pressures below 1 mm. These were successfully purified by shaking with cold concentrated sulfuric acid.

The only one of the alcohols which had been previously converted to an olefin is dimethylamylcarbinol,[7] whose chloride was distilled with solid potassium hydroxide to give 2-methylhexene-2. Of the eleven other carbinols, ten were successfully dehydrated by Hibbert's iodine method. The triamylcarbinol carbonized so badly that its study was abandoned. The alcohols fell in two groups according to their ease of dehydration, (1) those easily dehydrated, methylethylamyl, methylbutylamyl, diethylamyl, ethyldiamyl, and butyldiamyl carbinols, and (2) those which required longer heating, methylpropylamyl, methyldiamyl, propyldiamyl and dipropylamyl carbinols. The fact that the second group contains only alkyls with odd numbers of carbon atoms may or may not be fortuitous. Ozonolysis of the olefins gave ketones which could be isolated and identified but great difficulty was experienced with the aldehyde products.[8] The carbinols, $R(CH_3)(C_5H_{11})COH$, formed olefins which gave as their chief ozonolysis product methyl amyl ketone, indicating that the dehydration involved mainly the ethyl, propyl or butyl group rather than the methyl or amyl group. The olefin from diethylamylcarbinol gave ethyl amyl ketone. Similarly propyl amyl ketone was obtained from dipropylamylcarbinol. Ethyldiamylcarbinol gave ethyl amyl ketone. No products were identified from dibutylamyl, propyldiamyl or butyldiamyl carbinol. Thus the chief dehydration products identified are as follows: methylethylamylcarbinol, 3-methyloctene-2; methylpropylamylcarbinol, 4-methylnonene-3; methylbutylamylcarbinol, 5-methyldecene-4; methyldiamylcarbinol, 6-methylundecene-5; dipropylamylcarbinol, 4-propylnonene-3; ethyldiamylcarbinol, 6-ethylundecene-5.

Experimental

The bromides used in the syntheses of the tertiary alcohols were prepared by the methods of Kamm and Marvel[9] with the following properties and yields: *n*-propyl bromide, b. p. 70–70.3° (740), 70%; *n*-butyl bromide (stirring and refluxing for eight

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[7] Henry, *Compt. rend.*, **143**, 103 (1906).

[8] This problem has been studied intensively and successfully by J. M. Church in this Laboratory since 1930 and will be reported on shortly.

[9] Kamm and Marvel, "Organic Syntheses," Vol. I, 1921, p. 5.

hours), b. p. 99–101° (730), 75%; *n*-amyl bromide (from Sharples *n*-amyl alcohol, b. p. 135–136.5° (748)), b. p. 127–128° (736 mm.), 50%. Ethyl caproate was prepared in 53% yield from the acid and alcohol and dry hydrogen chloride, b. p. 163–164° (733). Methyl *n*-amyl ketone (b. p. 148–151° (738), yield 67%) was prepared from ethyl *n*-butylacetoacetate[10] supplied by the Mallinckrodt Chemical Works.

The Grignard reagents were prepared in the usual way.[11] The reactions with the carbonyl compounds involved no unusual features except that the reaction product was decomposed by pouring on ice and only a *slight* excess of dilute sulfuric acid. The last traces of acid were removed from the ether extracts by standing with solid anhydrous sodium carbonate. The alcohols were distilled at 15 mm. or below using a barostat to control the pressure. Heat for the distillations was supplied by an oil-bath. The study of the carbinols is summarized in Table I.

TABLE I

TERTIARY CARBINOLS

	Source		Yield		Analyses						
	Carbonyl				Calcd.		Found		B. p., °C.		
Carbinol	cpd.	Halide	%	g.	C	H	C	H	(mm.)	n_D^{20d}	d_4^{25d}
Me_2Am	$AmCO_2Et$	MeCl	61	158					66.5–68.5 (15) 162–164 (235)	1.4240	0.8136
MeEtAm	MeCOAm	EtBr	76	650	74.9	14.0	74.9 74.6	14.4 14.5	80–81 (15)[a]	1.4315	.8258
MePrAm	MeCOAm	PrBr	70	660	75.9	14.0	75.9 76.2	14.6 14.2	92–93 (15)	1.4338	.8245
MeBuAm	MeCOAm	BuPr	66	680	76.7	14.0	76.4 76.5	14.1 14.2	106–107 (15)	1.4369	.8262
$MeAm_2$	MeCOOEt	AmBr	75	420	77.3	14.1	77.7 77.8	13.7 14.1	80–83 (2.0)	1.4392	.8271
Et_2Am	AmCOOEt	EtBr		175	75.9	14.0	75.4 75.1	14.2 14.0	89.5–91.5 (15)	1.4390	.8361
Pr_2Am	AmCOOEt	PrBr	40	250	77.3	14.1	77.3 77.1	14.1 14.2	75–76 (1.4)[b]	1.4406	.8324
Bu_2Am	AmCOOEt	BuPr	76	490	78.4	14.1	78.2 78.0	14.1 14.3	90–92 (1.2)	1.4450	.8345
$EtAm_2$	EtCOOEt	AmBr	40	240	77.9	14.1	77.9 77.9	14.2 14.3	87–89 (2.0)	1.4438	.8348
$PrAm_2$	PrCOOEt	AmBr	58	220	78.4	14.1	78.9 79.1	14.4 14.1	81–82 (0.4)	1.4452	.8336
$BuAm_2$	BuCOOEt	AmBr	59	200	78.9	14.1	78.7 78.4	14.1 14.0	99–102 (1.0)	1.4460	.8344
Am_3	Et_2CO_3	AmBr			79.2	14.1	79.4 79.4	14.1 14.2	115–117 (1.5)	1.4470	.8293[c]

[a] Barostat set at 15 mm. [b] Pressures of 2.0 mm. and lower were measured with a McLeod gage; *cf.* Gross and White, *Ind. Eng. Chem.*, **13**, 702 (1921). [c] This low value is unexplained. [d] For methods used see Reference 2b.

The tertiary chlorides were prepared from the carbinols and hydrogen chloride gas.[2b] All the alcohols darkened in the process but this was especially noticeable with diethylamyl- and methylpropylamylcarbinol. This phenomenon has not been explained. Most of the chlorides were distilled at pressures of about 1 mm. (McLeod gage). In several cases this was impossible because of decomposition even at these pressures. Such chlorides were treated as follows. The dissolved hydrogen chloride was removed at room temperature and low pressure. The crude chloride was then washed with one-half volume of concentrated C. P. sulfuric acid. After separating the acid, the cloudy chloride layer was centrifuged until clear. The chloride layer was removed and allowed to stand at 0° for twelve hours with anhydrous sodium sulfate

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[10] Johnson and Hager, "Organic Syntheses," Vol. VII, 1927, p. 60.

[11] Gilman, Zoellner and Dickey, THIS JOURNAL, 51, 1576 (1929).

and carbonate. Filtration gave a clear colorless odorless liquid. The analyses of chlorides purified in this way indicated a higher purity than that obtained in the other chlorides which were distilled. The crude chlorides are stable at 0° but at room temperature slowly decompose with the evolution of hydrogen chloride and with darkening. The purified chlorides underwent little or no change in two years. The chlorides are summarized in Table II.

TABLE II

TERTIARY CHLORIDES

Carbinyl chloride	Yield %	Yield g.	Chlorine analyses Calcd.	Chlorine analyses Found	B. p., °C. (mm.)	n_D^{20}	d_4^{25}	Stability[b]
Me_2Am	73	27	23.9	23.7	[a]	1.4257	0.8568	*c, d, e*
MeEtAm	72	68	21.8	21.6	72.7–74 (15)	1.4347	.8680	*c, d, e*
MePrAm	85	75	20.1	20.0	43–45 (1.0)	1.4375	.8663	*e, f, g*
MeBuAm	84	81	18.6	18.5	52–54 (0.75)	1.4404	.8645	*c, d, e*
$MeAm_2$	33	29	17.3	17.1	63–65 (0.75)	1.4426	.8623	*c, d, e*
Et_2Am	72	64	20.1	20.1	42–43 (0.5)	1.4423	.8792	*c, e, g*
Pr_2Am	79	70	17.3	17.3	60–62 (0.65)	1.4460	.8699	*c, d, e*
Bu_2Am	76	65	15.3	15.2		1.4490	.8666	*e, f, g*
$EtAm_2$	61	54	16.2	16.0	74–76 (0.65)	1.4474	.8698	*c, d, h*
$PrAm_2$	67	60	15.3	15.2		1.4490	.8676	*e, f, g*
$BuAm_2$	83	45	14.4	14.4		1.4507	.8649	*c, d, e*
Am_3	70	75	13.6	13.6		1.4511	.8637	

[a] Halides for which no boiling points are given decomposed on heating even below 1 mm. and so were purified by the sulfuric acid method. [b] The samples of chlorides were examined after having stood for two years in ordinary glass bottles in the laboratory. The chlorides proved to be surprisingly stable. The changes on standing follow: [c] Still colorless. [d] No odor of hydrogen chloride. [e] Change in refractive index not over 0.0004. [f] Color changed to yellow. [g] Odor of hydrogen chloride. [h] Increase in refractive index of +0.0008.

TABLE III

OLEFINS

Olefin	Parent carbinol	Yield %	Yield g.	Analyses, calcd. C, 85.6; H, 14.4 Found C	Found H	B. p., °C. (mm.)	n_D^{20}	d_4^{25}
3-Methyloctene-2	MeEtAm	79	100	83.4	14.6	143–145 (734)	1.4247	0.7409
4-Methylnonene-3 and -4	MePrAm	67	94			58–59 (15) 161–163.5 (734)	1.4293	.7483
5-Methyldecene-4	MeBuAm	64	66	83.2 85.0	14.7 15.1	75–76 (15)	1.4333	.7578
6-Methylundecene-5	$MeAm_2$	59	100	85.8 86.1	14.5 14.8	90–92 (15)	1.4368	.7647
3-Ethyloctene-2	Et_2Am	68	48	84.7 85.0	14.9 14.7	57–59 (15)	1.4303	.7545
4-Propylnonene-3	Pr_2Am	82	74	85.6 85.3	14.6 14.7	84–87 (15)	1.4362	.7643
$C_{14}H_{28}$[a]	Bu_2Am	65	95	85.1 85.3	14.6 14.7	113–115 (15)	1.4414	.7748
6-Ethylundecene-5	$EtAm_2$	72	45	86.0 86.1	14.7 14.5	102–105 (15)	1.4401	.7701
$C_{14}H_{28}$[a]	$PrAm_2$	50	80	85.0 85.1	14.6 14.8	111–114 (15)	1.4411	.7749
$C_{15}H_{30}$[a]	$BuAm_2$	63	57	85.9 86.0	14.6 14.7	126–129 (15)	1.4436	.7781

[a] The ozonolysis products of these olefins gave mixtures of semicarbazones which could not be separated or identified.

The carbinols were dehydrated by heating at 100° with a trace of iodine.[12] The best method for removing traces of iodine was treatment with mercury. The product was distilled under reduced pressure. The results on the olefins are summarized in Table III.

TABLE IV

OZONOLYSIS OF OLEFINS FROM THE TERTIARY CARBINOLS

Parent carbinol	Olefin used, g.	Ozonide obtained, g.	Oil from ozonide, cc.	Main fractions B. p., °C.	Main fractions cc.	Low fractions, cc.	High fractions, cc.	Semicarbazone isolated	M. p., °C.	Mixed m. p., °C.
MeEtAm	25	33	15	145–153	7	4	3	$CH_3COC_5H_{11}$	121–122	121–123
MePrAm	25	31	19	97–101	5	4	4	$CH_3COC_3H_7$(?)		
				145–155	6			$CH_3COC_5H_{11}$	121–122	122–123
MeBuAm	25	31	12	144–154	3.5	5	3	$CH_3COC_5H_{11}$	120–121	121–122
MeAm$_2$	25	31	11	146–152	5	4	2	$CH_3COC_5H_{11}$	121–123	121–123
Et$_2$Am	25	32	14	165–168	7	5	2	$C_2H_5COC_5H_{11}$[a]	116–117	
Pr$_2$Am	25	32	15	71–81 (15)	5.5	6	3	$C_3H_7COC_5H_{11}$[b]	72–73	
Bu$_2$Am	25	31	12	58–95 (15)	6.5	3	1	[c]	58–60	
EtAm$_2$	25	32	15	98–112 (13)	4	9	1	$C_2H_5COC_5H_{11}$(?)	111–112.5	
PrAm$_2$	25	31	13	80–92 (15)	4	2	1	[d]		
				92–105 (15)						
				105–120 (15)						
BuAm$_2$	25	32	19	89–95 (13)	5	2	1	[e]		
				95–105 (13)	7					
				105–118 (13)	4					

[a] Bouveault and Locquin, *Bull. soc. chim.*, [3] **31**, 1158 (1904), give 117–117.5° as the m. p. of the semicarbazone of ethyl *n*-amyl ketone.

[b] They give 73–74° for the corresponding derivative of *n*-propyl *n*-amyl ketone.

[c] The semicarbazone obtained did not correspond to any known substance.

[d] Each fraction gave mixtures of semicarbazones which could not be separated by repeated crystallizations.

[e] The first two fractions gave impure semicarbazones.

The ozonization of the olefins was performed in 29–35° ligroin at −15° with ozonized oxygen.[13] The ozonides, freed from solvent, were surprisingly stable even to boiling water. They were finally decomposed by boiling water and zinc dust.[14] All attempts to identify aldehyde or acid products failed. The ketones could be identified, however, as their semicarbazones. These were confirmed by mixed melting point determinations with known materials. The ozonolysis results are summarized in Table IV.

Summary

1. A series of twelve aliphatic tertiary alcohols of the general types, $R(CH_3)(n\text{-}C_5H_{11})COH$, $R_2(n\text{-}C_5H_{11})COH$ and $R(n\text{-}C_5H_{11})_2COH$, in which R is methyl, ethyl, *n*-propyl, *n*-butyl and *n*-amyl, has been synthesized and studied.
2. The tertiary chlorides have been made from the alcohols.
3. The alcohols have been dehydrated.

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

[13] *Cf.* Henne, *ibid.*, **51**, 2676 (1929); Smith, *ibid.*, **47**, 1844 (1925). Full details of the ozonolysis technique as used in this Laboratory will be published shortly by J. M. Church.

[14] *Cf.* Noller and Adams, *ibid.*, **48**, 1077 (1926).

4. Six of the resulting olefins have been identified by their ozonolysis products. These are 3-methyloctene-2, 5-methyldecene-4, 6-methyl undecene-5, 3-ethyloctene-2, 4-propylnonene-3 and 6-ethylundecene-5. In addition a mixture of 4-methylnonene-3 and -4 was identified.

5. Alcohols of the type, $R(CH_3)(n\text{-}C_5H_{11})COH$, were dehydrated chiefly through the R group.

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Solubility Relationships among Optically Isomeric Salts. III. The Mandelates and Alpha-Bromocamphor-Pi-Sulfonates of Alpha-Phenylethylamine and Alpha-Para-Tolylethylamine

BY A. W. INGERSOLL, S. H. BABCOCK AND FRANK B. BURNS

The following five types of optically isomeric salts represent all the possible combinations of active and inactive acid and base ions.

(*d*B*d*A or *l*B*l*A); (*d*B*l*A or *l*B*d*A); *dl*B*dl*A; (*d*B*dl*A or *l*B*dl*A); (*dl*B*d*A or *dl*B*l*A)

The stabilities and relative solubilities of these types of salts determine which of them can exist in solution, and the order in which the stable salts can be separated from a mixture by fractional crystallization It has been shown in previous papers[1] that these factors are of primary importance for a method of complete optical resolution in which mixtures containing several varieties of isomeric salts may be encountered. It was shown that not more than three of the nine varieties of salts represented above can result from the evaporation of a solution, no matter what proportions of active and inactive acid and base ions may have been introduced originally. Nevertheless, it was pointed out that there are some twenty[2] different orders in which these coexistent salts may separate during fractional crystallization. At present it seems impossible to predict the stabilities and relative solubilities of the salts of a particular acid and base. Hence numerous groups of isomeric salts are being studied for the purpose of gaining a comprehensive knowledge of these factors. Five such groups of salts have already been described and classified. This paper describes a similar study of the four additional groups of salts named in the title.

The salts previously described illustrated two instances each of Cases 4[1a] and 7[1b,1d] and one of Case 8.[1c] The salts described in this paper were found to illustrate the previously unobserved cases (1) and (6), another instance of Case 8, and an instance of either Case 4 or 7, depending on the

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[1] (a) Ingersoll, THIS JOURNAL, **47**, 1168 (1925); (b) **50**, 2264 (1928); (c) Ingersoll and White, *ibid.*, **54**, 274 (1932); (d) Ingersoll and Burns, *ibid.*, **54**, 4712 (1932).

[2] Only eight orders (Cases 1–8) are possible in the mixtures resulting from the usual procedure for complete resolution. All of the cases were described and numbered in Part I.[1c]