methane was purified by treatment for thirty minutes with 85% sulfuric acid and was then distilled in a current of steam. The product gave no color with concentrated sulfuric acid until the mixture was warmed or allowed to stand for several hours.

Summary

1. Curves are presented for the absorption spectra of diphenylmethane, tetraphenylethane and triphenylmethane in solution in a mixture of sulfuric acid and dimethyl sulfate.

2. It has been shown that the color produced when triphenylmethane is dissolved in sulfuric acid is caused by the formation of triphenylcarbinol sulfate due to the oxidation of some of the triphenylmethane to triphenylcarbinol.

3. Sulfuric acid solutions of diphenylmethane give absorption spectra which are very similar to the spectra of sulfuric acid solutions of *sym*-tetraphenylethane. Whether this is due to the oxidation of diphenylmethane to a derivative of tetraphenylethane or to a cleavage of the tetraphenylethane to a diphenylmethane derivative cannot be demonstrated at present.

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Tertiary Aliphatic Alcohols Containing an Adjacent Tertiary Hydrogen, the Related Chlorides and Dehydration Products

BY FRANK C. WHITMORE AND W. L. EVERS[1]

The need for more knowledge about tertiary alcohols in connection with studies on rearrangements prompted this work.[2] The group of alcohols selected may be represented by the formula, $R(CH_3)(iso\text{-}C_3H_7)COH$, in which R is ethyl, *n*-propyl, *n*-butyl and *n*-amyl. Two adjacent carbons hold tertiary hydroxyl and tertiary hydrogen. These are readily removed to give a tetrasubstituted olefin. That the dehydration does not follow this course alone has been shown repeatedly with the first member of the series in which R is methyl.[3] The dimethylisopropylcarbinol gave the expected tetramethylethylene and amounts of 2,3-dimethylbutene-1 varying with the conditions of dehydration. The second member of the

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(1) Submitted in partial fulfilment of the requirements for the Ph.D. degree.

(2) (a) Whitmore, THIS JOURNAL, **55**, 3274 (1932); (b) Whitmore and Woodburn, *ibid.*, **55**, 361 (1933); (c) Whitmore and Williams, *ibid.*, **55**, 406 (1933).

(3) Henry, *Compt. rend.*, **144**, 552 (1907); Couturier, *Bull. soc. chim.*, [4] **9**, 898 (1911); Lindner, *Monatsh.*, **32**, 403 (1911); Kishner and Chonin, *Chem. Zentr.*, I, 1496 (1914); *J. Russ. Phys.-Chem. Soc.*, **45**, 1770 (1913).

series, methylethylisopropylcarbinol, gave two olefins but these were not identified.[4]

The four carbinols in the present study, when dehydrated by Hibbert's iodine method, gave mainly the tetrasubstituted olefins with lesser amounts of the olefins formed by the loss of hydrogen from the R group. No evidence was found that the methyl group was involved.[2c] The structure of the olefins was determined by ozonolysis. With the *n*-butyl and *n*-amyl compounds, the olefinic products were carefully fractionated. A study of the refractive index–distillate curve indicated that the dehydrations involving the tertiary and secondary hydrogens took place in about the ratio 2:1.

The tertiary chlorides were prepared and were found to be at least as stable as the related chlorides containing normal propyl instead of isopropyl groups.[2h,c] Thus the adjacent tertiary hydrogen had little or no greater effect than an adjacent secondary hydrogen. This is probably because the controlling step in the loss of hydrogen chloride is the removal of the chlorine with its complete octet.[2a]

Experimental

The carbinols were prepared from methyl isopropyl ketone (b. p. 91.5–92.3° (733 mm.)), n^{20}_{D} 1.3880, prepared in 60% yield by the hydrolysis and rearrangement of trimethylethylene dibromide prepared from tertiary amyl alcohol)[5] and the proper Grig-

TABLE I

THE TERTIARY CARBINOLS, $R(CH_3)(iso\text{-}C_3H_7)COH$ AND THEIR CHLORIDES

Carbinols

R	Wt. made, g.	Yield %	B. p., °C. (mm.)	n^{20}_{D}	d^{20}_{4}
C_2H_5	540	59	39– 38 (7) 44– 45 (14) 136–137 (740)[b]	1.4287	0.833
n-C_3H_7	130	35	42– 43 (6)[c]	1.4300	
n-C_4H_9	480	61	56– 57 (5) 42 (2)	1.4365	.8395[d]
n-C_5H_{11}	420	60	69– 70 (5)	1.4380	.8401

Chlorides

R	Wt. made, g.	Yield %	B. p., °C. (mm.)	n^{20}_{D}	d^{20}_{4}	Analysis, % Cl Calcd.	Analysis, % Cl Found
C_2H_5	20	50[a]	133–138			26.3	24.3 24.4[a]
n-C_3H_7	24	81	41– 43 (12)	1.4350	0.8869	23.9	23.3 23.4
n-C_4H_9	56	86	54 (8)	1.4391	.885[e]	21.8	21.2 21.8
n-C_5H_{11}	33	77	53– 55 (3)	1.4420	.8818	20.1	20.1 19.8

[a] The low yield and the low chlorine content were due to a slight decomposition during the distillation at atmospheric pressure. [b] Chavanne and de Graef (Ref. 4b) give b. p. 42–43° (11 mm.), and 139.4–139.9° (760 mm.). [c] Clarke [THIS JOURNAL, **33**, 528 (1911)] gives b. p. 158–158.2° (758 mm.). [d] d^{21}_{4} 0.8383. [e] Calcd. from d^{23}_{4} 0.8809.

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(4) (a) Pariselle and Simon, *Compt. rend.*, **173**, 86 (1921); (b) Chavanne and de Graef, *Bull. soc. chim. Belg.*, **33**, 366 (1924).

(5) Supplied by the Sharples Solvents Corp. of Philadelphia.

nard reagents. The halides used for their preparation were *n*-amyl bromide, b. p. 126.5–128° (740 mm.), prepared in 58% yield from *n*-amyl alcohol[5] and constant boiling hydrobromic acid; *n*-butyl bromide, b. p. 99–100° (740 mm.); *n*-propyl bromide, b. p. 68.5–70° (730 mm.) and ethyl bromide (Dow Chemical Co.).

The ethyl compound was also made from isopropyl bromide (b. p. 58–59° (740 mm.), prepared in 78% yields from 98% isopropyl alcohol[6] and constant boiling hydrobromic acid) and methyl ethyl ketone, b. p. 79–79.5° (739 mm.), prepared by dehydrogenating, with a brass catalyst, secondary butyl alcohol[6] (b. p. 97.7–98.7° (733 mm.)). The yield of tertiary carbinol was only 33%, probably due to the condensing action of the isopropyl Grignard on the ketone.[4a,7]

The tertiary chlorides were prepared from the carbinols in the usual way with dry hydrogen chloride at 0°. This treatment gave colorless or slightly yellow crude chlorides in sharp difference from the behavior of the corresponding *n*-propyl compounds, which gave deep colors.[2b,c]

The results on the tertiary carbinols and halides are summarized in Table I.

The carbinols were dehydrated by refluxing with a few crystals of iodine under a 50 × 1.5 cm. column. The olefin and water were distilled as formed. The olefin was washed with 10% sodium thiosulfate, dried over 10 g. of calcium chloride and finally over sodium. The product was then distilled through a short column.

TABLE II

DEHYDRATION OF THE CARBINOLS $R(CH_3)(iso\text{-}C_3H_7)COH$

R	Wt., g.	Water formed, g.	Olefin b. p. range, °C. (mm.)	Olefin, g.	Yield, %
C_2H_5	223	30	89–93.5 (732)	130	70
n-C_3H_7	65	7	108–115 (733)	28	50
n-C_4H_9	72	7	135–140 (742)	46	74
n-C_5H_{11}	474	46	159–166 (747)	325	77

The olefins were ozonized in about 0.3-mole lots in 250 cc. of 5–35° saturated hydrocarbons[8] at 0° in the usual way.[9] The ozonides were decomposed with zinc and hot water.[9] The results appear in Table III.

The ozonolysis products indicate that the dehydration took place exclusively from the isopropyl and R groups with the former predominating about 2:1. The carbinols gave the following pairs of olefins: ethylmethylisopropylcarbinol, 2,3-dimethylpentene-2 and -3; *n*-propylmethylisopropylcarbinol, 2,3-dimethylhexene-2 and -3; *n*-butylmethylisopropylcarbinol, 2,3-dimethylheptene-2 and -3; *n*-amylmethylisopropylcarbinol, 2,3-dimethyloctene-2 and -3.

Two of the pairs of olefins, those from the *n*-butyl and the *n*-amyl carbinols, were carefully fractionated through a 130 × 1.5 cm. adiabatic, total condensation variable reflux packed column,[10] using a reflux ratio of about 20:1.

The distillation of 320 g. of the olefins from *n*-butylmethylisopropylcarbinol gave 32 fractions of which the principal ones were 3–11, 112 g., b. p. 135.4° (743 mm.) to 137.1° (741 mm.), n^{20}_{D} 1.4232 to 1.4236; and 19–23, 42.5 g., b. p. 138.2–139.0° (741 mm.), n^{20}_{D} 1.4246–1.4257. These results taken with the ozonolysis results and the studies of Boord and his co-workers[11] indicate that the olefin formed in larger amount is the heptene-2 derivative. Measurements on the middle fractions of the olefins gave the follow-

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(6) Supplied by Stanco, Inc., New York City.

(7) Conant and Blatt, THIS JOURNAL, **51**, 1227 (1929).

(8) Supplied by the Viking Corp. of Charleston, W. Va.

(9) See Whitmore and Church, THIS JOURNAL, **54**, 3712 (1932).

(10) Table III, Ref. b.

(11) Schmitt and Boord, THIS JOURNAL, **54**, 751 (1932).

Table III

Ozonolysis of Olefins from the Carbinols, $R(CH_3)(iso\text{-}C_3H_7)COH$

R	Olefin used, g.	Substance in trap[a]	Substance in water layer	Oil layer, g.	No. of fractions	Fractionation of oil layer[b] chief fractions No.	B. p., °C.	g.	Substances identified	M. p., °C.
						1	−30	1.2	Acetaldehyde	
C_2H_5	49	CH_3CHO[c]	Acetone[e]	25	11	2	55–65	1	Acetone[e]	
		No HCHO				7–8	90–94	5	Methyl isopropyl ketone semicarbazone	113–114.5
$n\text{-}C_3H_7$	28	No HCHO	Propionaldehyde	20	7	1	46–49	0.5	Propionaldehyde (skatol)[d]	
			Acetone			3	76–94	5.0	Methyl isopropyl ketone semicarbazone	111–112
						4	94–104	4.5	Methyl propyl ketone semicarbazone	105–106
$n\text{-}C_4H_9$	31	No HCHO	Acetone	25	8	4	90–93	2	Methyl isopropyl ketone semicarbazone	112–112.4
						7	125–130	2	Methyl *n*-butyl ketone semicarbazone	117.5–118
$n\text{-}C_5H_{11}$	42	No HCHO	Acetone	36	14	1–2	32–55	1.5	Acetone[e]	
			higher aldehyde			6–7	89–94	4.5	Methyl isopropyl ketone semicarbazone	112–113
						8–10	94–103	10	*n*-Valeraldehyde oxime	50.7–51.5
						12–14	144–152	8.5	Methyl *n*-amyl ketone semicarbazone	121–122.5

[a] A trap containing dry ether kept at 0° was placed at the end of the apparatus to catch any formaldehyde.

[b] The fractionation was by means of a 60 × 1.2 cm. adiabatic total condensation variable take-off column packed with 5 × 5 mm. glass rings; *cf.* Whitmore and Lux, This Journal, **54,** 3451 (1932).

[c] Caught in 0° trap during decomposition of ozonide. Identified by conversion to ethylidene β-naphthol oxide, m. p. 172–174°.

[d] Tested with phenylhydrazine according to Mulliken.

[e] Acetone was tested with sodium nitroprusside according to Mulliken using blank tests.

ing properties: 2,3-dimethylheptene-2, b. p. 136.2–136.8° (743 mm.); n_D^{20} 1.4233, d_4^{20} 0.742; 2,3-dimethylheptene-3, b. p. 138.4–138.8° (740.5 mm.), n_D^{20} 1.4250, d_4^{20} 0.747.

Similarly 325 g. of the mixture of olefins from *n*-amylmethylisopropylcarbinol was distilled in 34 fractions of which the chief ones were 1–8, 72 g., b. p. 157.6° (731 mm.) to 160.2° (737.5 mm.), n_D^{20} 1.4280 to 1.4282; and 14–18, 45 g., b. p. 161.0° (739 mm.) to 161.8° (739.6 mm.), n_D^{20} 1.4289 to 1.4292. The lower boiling olefin was taken as the octene-2 derivative. The middle fractions gave the following properties: 2,3-dimethyloctene-2, b. p. 158.4–158.8° (733 mm.), n_D^{20} 1.4280; 2,3-dimethyloctene-3, b. p. 161.2–161.4° (739 mm.), n_D^{20} 1.4290.

Summary

1. Aliphatic alcohols containing tertiary hydroxyl and tertiary hydrogen on adjacent carbon atoms have been prepared and dehydrated. In each case a pair of olefins was formed. These were identified by ozonolysis.

2. The new tertiary alcohols prepared and studied were 2,3-dimethylhexanol-3, 2,3-dimethylheptanol-3 and 2,3-dimethyloctanol-3.

3. These alcohols were converted to the corresponding tertiary chlorides, 3-chloro-2,3-dimethyl-hexane, -heptane and -octane.

4. The four olefins, 2,3-dimethylheptene-2 and -3 and 2,3-dimethyloctene-2 and -3 have been prepared and studied.

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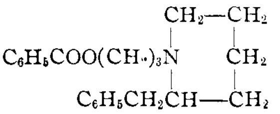
Piperidine Derivatives. XII. Local Anesthetics Derived from Reduction Products of Beta-Acetylpyridine

BY FRANK M. STRONG AND S. M. MCELVAIN

Two constructions that markedly enhance the action of the aminoalkyl benzoate type of local anesthetics on mucous surfaces have been shown to be (a) the phenylalkyl group attached to nitrogen[1] (preferably the nitrogen atom of the piperidine ring) and (b) a substituent methyl group in the alkylene group that joins the nitrogen atom to the benzoyloxy group.[2] These two types of structure are illustrated by I and II. It was the purpose of the work reported in the present paper to prepare and submit for pharmacological study a series of compounds of type III in which the two above-mentioned structures might be combined in a single molecule.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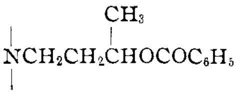
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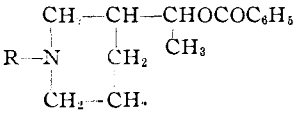
III

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[1] (a) Bailey and McElvain, THIS JOURNAL, **52**, 1639 (1930); (b) Bolyard and McElvain, *ibid.*, **51**, 927 (1929).

[2] Thayer and McElvain, *ibid.*, **50**, 3354 (1928).