[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF HOUSTON]

THE IDENTIFICATION OF ALCOHOLS. I. DERIVATIVES OF SOME C_5 AND C_6 ACYCLIC ALCOHOLS[1]

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When a new compound is synthesized, all too often no simple functional derivatives of the compound which may be used for its future identification are reported; seldom, indeed, are enough such derivatives prepared to distinguish it from its homologs. When a new reagent for the identification of a given class of compounds is proposed, usually only the simpler, easily available members of the class are used for the preparation of the new derivatives. In the case of alcohols, for example, numerous derivatives are known for those contaning four or less carbon atoms and for the higher straight chain primary alcohols. As the number of its carbon atoms increases, the problem of distinguishing a given alcohol from its homologs (or from alcohols with similar boiling points) becomes increasingly difficult, not only because the number of homologs increases rapidly but because the number of derivatives reported in the literature decreases sharply. It is the purpose of this series of investigations to simplify the problem of the identification of alcohols by providing a wider choice of derivatives than previously has been available.

A number of previously unreported solid derivatives of several C_5 and C_6 acyclic alcohols have been prepared and the melting points and analyses of these compounds are given in Table I. The preparation of all of the C_7 acyclic alcohols and of a selected group of their derivatives is currently under investigation in this laboratory.

EXPERIMENTAL

2,2-Dimethyl-3-butanol was prepared by a modification of the method used by Drake and Cooke (3), for the synthesis of 3-methyl-2-butanol. Acetaldehyde (147 g., 3.33 moles) in ether was added to an ethereal solution of *tert*-butylmagnesium bromide which had been formed by the reaction of 479 g. (3.49 moles) of *tert*-butyl bromide with 95 g. (3.90 moles) of magnesium metal. The reaction temperature was maintained at 10 ± 1° throughout the addition and then raised to 25° for a 20-minute stirring period. Hydrolysis of the reaction mixture followed by fractionation of the ether layer gave 2,2-dimethyl-3-butanol, bp_{763} 120–121°, bp_{150} 74–75°. The *3,5-dinitrobenzoate* melted at 106.5° as compared to 107° found by Sutter (4).

3-Hexanol was prepared by a modification of the method used by Moyer and Marvel (5) for the synthesis of 3-ethyl-3-pentanol. Propionaldehyde (174 g., 3.0 moles) was added to an ethereal solution of *n*-propylmagnesium bromide formed from 365 g. (3.0 moles) of *n*-propyl bromide and 90 g. (3.7 moles) of magnesium metal. Hydrolysis of the resulting reaction mixture, extraction with ether, followed by the removal of the ether from the extracts by

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[2] Taken from M.S. theses presented to the Graduate School of the University of Houston by M. D. C., W. A. H., and E. R. W. Inquiries should be addressed to E. N. McElrath.

TABLE I

New Derivatives of Some C_5 and C_6 Acyclic Alcohols

ALCOHOL		DERIVATIVE				
Name	b.p.[a] of Sample, °C.	Name	M.p.,[a] °C.	Molecular Formula	Nitrogen Analysis	
					Calc'd	Found
2,2-Dimethyl-1-butanol	136.0–136.5[b]	Hydrogen 3-nitrophthalate	154.0–155.0	$C_{14}H_{17}NO_6$	4.75	4.66
		1-Nitroanthraquinone-2-carboxylate	167–168	$C_{21}H_{19}NO_6$	3.67	3.48
		N-*p*-Diphenylcarbamate	74.5–76.0	$C_{19}H_{23}NO_2$	4.71	4.85
2,3-Dimethyl-2-butanol	118.0–118.5[c]	*p*-Nitrobenzoate	82	$C_{13}H_{17}NO_4$	5.57	5.66
		N-*p*-Nitrophenylcarbamate	100.5	$C_{13}H_{18}N_2O_4$	10.52	10.48
2,2-Dimethyl-3-butanol	120.0–121.0[c]	*p*-Nitrobenzoate	98.5	$C_{13}H_{17}NO_4$	5.57	5.77
		N-*p*-Nitrophenylcarbamate	102	$C_{13}H_{18}N_2O_4$	10.52	10.55
		N-α-Naphthylcarbamate	128.0–128.5	$C_{17}H_{21}NO_2$	5.16	5.19
2-Ethyl-1-butanol	147.5–148.1[d]	Hydrogen 3-nitrophthalate	146.5–147.2	$C_{14}H_{17}NO_6$	4.76	4.91
		N-α-Naphthylcarbamate	60–61	$C_{17}H_{21}NO_2$	5.16	5.30
2-Hexanol	138.0–139.0[e]	Hydrogen 3-nitrophthalate	62–63	$C_{14}H_{17}NO_6$	4.75	4.40
		1-Nitroanthraquinone-2-carboxylate	132–134	$C_{21}H_{19}NO_6$	3.67	3.70
		N-*p*-Diphenylcarbamate	87.5–88.3	$C_{19}H_{23}NO_2$	4.71	4.85
3-Hexanol	133.5–135.5[c]	Hydrogen 3-nitrophthalate	127–128	$C_{14}H_{17}NO_6$	4.75	4.72
		1-Nitroanthraquinone-2-carboxylate	149–150	$C_{21}H_{19}NO_6$	3.67	3.82
		N-*p*-Diphenylcarbamate	136.3–136.7	$C_{19}H_{23}NO_2$	4.71	4.80
		N-α-Naphthylcarbamate	71.5–72.0	$C_{17}H_{21}NO_2$	5.16	5.12
1-Pentanol	137.0–138.0[d]	α-Naphthylamine complex with 3,5-dinitrobenzoate	88.5–89.2	$C_{22}H_{23}N_3O_6$	9.88	9.61
2-Pentanol	119.5[d]	*p*-Nitrobenzoate	24–25	$C_{12}H_{15}NO_4$	5.90	5.91
2-Methyl-1-pentanol	147.5–148.5[d]	Hydrogen phthalate	50.5–51.5	$C_{14}H_{18}O$	[f]	[f]
3-Methyl-1-pentanol	152–153[c]	Hydrogen 3-nitrophthalate	151.5–152.2	$C_{14}H_{17}NO_6$	4.76	4.76
4-Methyl-1-pentanol	151.5–152.5[c]	Hydrogen phthalate	47.5–48.5	$C_{14}H_{18}O$	[g]	[g]
		N-α-Naphthylcarbamate	58–59	$C_{17}H_{21}NO_2$	5.16	5.31

TABLE I—*Continued*

ALCOHOL		DERIVATIVE				
Name	b.p.[a] of Sample, °C.	Name	M.p.,[a] °C.	Molecular Formula	Nitrogen Analysis	
					Calc'd	Found
2-Methyl-2-pentanol	121[d]	*p*-Nitrobenzoate	69.5	$C_{13}H_{17}NO_4$	5.57	5.62
		N-α-Naphthylcarbamate	104.0–104.5	$C_{17}H_{21}NO_2$	5.16	5.18
3-Methyl-3-pentanol	122–123[e]	*p*-Nitrobenzoate	67	$C_{13}H_{17}NO_4$	5.57	5.75

[a] All boiling and melting points given are corrected. [b] Prepared by the method of Conant, Webb, and Mendum (1). Sample used is a central cut obtained by distillation of the crude product through a 10″ Vigreaux column. [c] See *Experimental.* [d] Sample obtained by fractional distillation of commercially available alcohol, using a vacuum-jacketed column containing thirty 20-mm. bubble plates. [e] Prepared by the method of Barrow and Atkinson (2). Sample used is a central cut obtained by distillation of the crude product through a 10″ Vigreaux column. [f] Calc'd: C, 67.20; H, 7.20. Found: C, 67.12; H, 7.16. [g] Calc'd: C, 67.20; H, 7.20. Found: C, 66.92; H, 7.30.

distillation gave 3-hexanol. The crude 3-hexanol was fractionated using a 45 x 1-cm. Vigreaux column and the 90 g. (30%) fraction distilling at 133.5–135.5° was collected as pure 3-hexanol. The *3,5-dinitrobenzoate* melted at 74–76° as compared with 77° found by Sutter (4).

3-Methyl-1-pentanol was prepared by a modification of the method used by Dreger (6) for the preparation of 1-hexanol. Ethylene oxide gas (200 g., 4.54 moles) was passed into the reaction flask containing an ether solution of the Grignard reagent formed from 425 g. (4.59 moles) of *sec*-butyl chloride and 140 g. (5.60 moles) of magnesium metal. Replacement of the ether solvent by benzene, hydrolysis, and steam-distillation followed by fractionation of the oil obtained gave a 137 g. (29.5%) sample of 3-methyl-1-pentanol. A vacuum-jacketed column containing thirty 20-mm. bubble plates was used for the fractionation. The *3,5-dinitrobenzoate* melted at 35.0–36.5° as compared with 38° found by Sutter (4).

4-Methyl-1-pentanol was prepared by a method that is essentially that used by Hickinbottom (7) for the synthesis of 2-methyl-1-butanol. Trioxymethylene (150 g., ≈ 5.0 moles of formaldehyde) was added to an ethereal solution of the Grignard reagent obtained from 450 g. (4.22 moles) of isoamyl chloride and 125 g. (5.2 moles) of magnesium metal. The resulting mixture was refluxed for 24 hours and hydrolyzed. The ethereal layer gave, on fractionation through the vacuum-jacketed column of thirty 20-mm. bubble plates, a 175.5-g. (40.6%) fraction boiling 151.5–152.5° which was 4-methyl-1-pentanol. The *3,5-dinitrobenzoate* melted at 70.5–71.5° as compared with 72° found by Sutter (4).

3-Methyl-3-pentanol was prepared by the method given by Adams and Johnson (8) for the preparation of 2-methyl-2-pentanol. Methyl ethyl ketone (288 g., 3.99 moles) was added to an ethereal solution of ethylmagnesium bromide formed from 436 g. (4.00 moles) of ethyl bromide and 97 g. (3.98 moles) of magnesium metal. Hydrolysis and removal of the ether from the organic layer gave crude 3-methyl-3-pentanol. Fractionation through a 2 x 90-cm. column packed with glass helices gave 225 g. (54%) of pure 3-methyl-3-pentanol, bp_{150} 79–80°, bp_{763} 122–123°. The *3,5-dinitrobenzoate* melted at 96° as compared with 96.5° found by Sutter (4).

p-Nitrobenzoates. The alcohol (2 g.), 3 g. of *p*-nitrobenzoyl chloride, and 6 ml. of pyridine were heated on a steam-bath for two hours. Then 20 ml. of ether was added and the ethereal solution was washed with 15 ml. of dilute hydrochloric acid followed by washings with two

25-ml. portions of 5% sodium hydroxide solution. The ether was removed under reduced pressure. The residue was washed with 15 ml. of dilute hydrochloric acid and then recrystallized twice from hot 95% ethanol.

1-Nitroanthraquinone-2-carboxylates were prepared by the method of Sah and Ma (9).

Hydrogen phthalates and 3-nitrophthalates. Phthalic anhydride or 3-nitrophthalic anhydride (2 g. of either) was refluxed for 30 minutes with 1 g. of the alcohol. After allowing the solution to cool, the ester was extracted with 50 ml. of boiling water. On cooling the ester separated as an oil which crystallized after standing for several days. The ester was recrystallized twice from hot water.

N-p-Nitrophenylcarbamates and N-α-naphthylcarbamates. The isocyanate (3 g.) and 2 g. of the alcohol were heated on the steam-bath for one hour. The mixture was allowed to crystallize in an ice-bath. The carbamate was extracted with 10 ml. of warm ligroin, and the resulting solution was heated with decolorizing charcoal, filtered, and cooled. The carbamate that deposited on cooling was recrystallized from hot ethanol.

N-p-Diphenylcarbamates. The directions of van Gelderen (10) for the preparation of N-*p*-diphenylcarbamates were followed.

α-Naphthylamine complex with n-amyl 3,5-dinitrobenzoate. The method of Reichstein (11) for the formation of complexes of naphthylamine with the esters of 3,5-dinitrobenzoic acid was employed.

SUMMARY

The melting points of twenty-six new solid derivatives of some C_5 and C_6 acyclic alcohols are reported.

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