The remainder of the purification was similar to that described above for the purification of the bromides from the thermal equilibrium experiments. The results of these experiments are included in Table I, which also contains a summary of previous experiments with standard procedures.

The authors are indebted to Professors Linus Pauling and Howard J. Lucas and Mr. Saul Winstein for valuable discussions during the preparation of the manuscript.

Summary

A mechanism is proposed to account quantitatively for the differences in composition of the butenyl bromide mixtures which are observed when crotyl alcohol and methylvinylcarbinol are allowed to react with hydrogen bromide by standardized methods under controlled conditions.

The reaction is considered to be composed of two simultaneous processes. Process 1, involving resonance, gives the same mixture of bromides from both alcohols. Process 2, a normal substitution reaction without resonance, gives only primary bromide from the primary alcohol and secondary bromide from the secondary alcohol. The net result is a difference of 3–12% in the primary bromide content of the butenyl bromide mixtures prepared from the two alcohols by the standard methods.

Mathematical equations have been developed which make it possible to calculate (1) the percentage of alcohol which reacts by processes 1 and 2; (2) the refractive index, n_r, and hence the composition, P_r, of the bromide mixture produced due to a reaction by process 1. The calculated and experimentally determined values of n_r and P_r agree within experimental error for cases reported.

The use of a saturated solution of hydrogen bromide in glacial acetic acid in the preparation of butenyl bromide mixtures is described.

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[CONTRIBUTION FROM THE MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

alpha-Naphthaldehyde and Certain of its Derivatives

BY HAROLD W. COLES[1] AND MARY L. DODDS[2]

Most of the numerous methods reported in the literature for the preparation of α-naphthaldehyde were found to be too inconvenient and too costly for the preparation of relatively large quantities required for another project. It was found that the treatment of α-chloromethylnaphthalene with hexamethylenetetramine in 60% alcohol solution was most satisfactory in giving constant yields of 59–60% α-naphthaldehyde.[3] The necessary α-chloromethylnaphthalene was prepared in 68–70% yields by treating naphthalene with 40% formaldehyde solution and hydrochloric acid followed by treatment with concentrated sulfuric acid.[4] The modification of this method suggested by Rupe and Brentano[3c] (no details are given) together with several important precautions stressed in the experimental part have resulted in a trustworthy procedure for preparing α-chloromethylnaphthalene.

A number of α-naphthaldehyde derivatives prepared in the course of this work are listed in the table. These were prepared according to the usual methods. Dioxane was used in cases of difficult solubility.

The authors are grateful for the interest and advice of Dr. George D. Beal, Assistant Director of Mellon Institute.

Experimental Part

Preparation of alpha-Chloromethylnaphthalene.—For this reaction, 256 g. of naphthalene, 250 cc. of 30% formaldehyde solution and 424 cc. of concentrated hydrochloric acid were combined in a three-necked Pyrex round-bottomed flask equipped with an efficient stirrer and dropping funnel. The temperature of the flask contents was brought up to 60° by means of a water-bath and was held at that temperature for seven hours, during which time 278 cc. of concentrated sulfuric acid was added with constant efficient stirring. The heating and stirring were continued for another twenty hours, the naphthalene gradually disappearing. The naphthalene which collected about the top of the flask was frequently shaken down. The flask was placed in ice water and the contents diluted

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[1] Senior Industrial Fellow, E. R. Squibb and Sons Industrial Fellowship, Mellon Institute.

[2] Industrial Fellow, E. R. Squibb and Sons Industrial Fellowship, Mellon Institute.

[3] (a) Sommelet, *Compt. rend.*, **157**, 852 (1913); (b) Mayer and Stieglitz, *Ber.*, **55**, 1846 (1922); (c) Rupe and Brentano, *Helv. Chim. Acta*, **19**, 581 (1936).

[4] I. G., German Patent 533,132; *Frdl.*, **18**, 586. See also Sprague and Johnson, THIS JOURNAL, **59**, 1837 (1937).

with an equal volume of cold tap water. An extraction with ether was then carried out and the ether extract shaken twice with sodium carbonate and twice with distilled water to remove all traces of acid. The ether extract was then allowed to stand overnight over anhydrous sodium sulfate and finally filtered. The ether is removed by distillation and may be reused.

The chloromethylnaphthalene must be distilled *in vacuo* with great care. Precautions include the use of an oil-bath for even heating, a capillary tube to aid the distillation and the avoidance of too rapid distillation. Care should also be taken to use a flask which has no spots or focal points where decomposition can start. The yield is 238–250 g. (67–70%). There is some naphthalene that distils before the α-chloromethylnaphthalene, which collects in the condenser and must be washed out with benzene.

alpha-Chloromethylnaphthalene distils at 291–292°. Other temperatures are: 134°(3 mm.), 150°(9 mm.), 149.4–150.4°(11 mm.), 150–152°(13 mm.), 158–159°(14 mm.), and 173–174°(35 mm.). A small amount of liquid was distilled over at 170–200°(10–12 mm.), and this liquid crystallized in the receiver.[5] The crystals contain halogen, are insoluble in ether and melt sharply at 125°.[6] alpha-Chloromethylnaphthalene itself polymerizes fairly easily to a chlorine-free polymer,[5] accompanied by changes in physical state and in solubility. The cream-colored polymer melts around 200°.

Preparation of alpha-Naphthaldehyde.—The literature directions[3] for the preparation of this aldehyde are adequate and require no comment. The aldehyde, isolated through the bisulfite compound, is pure enough to employ without a final distillation. It should be stored in the dark and under nitrogen.

TABLE I

ALPHA-NAPHTHALDEHYDE DERIVATIVES

Derivatives	M. p., °C.	Nitrogen, %[a] Calcd.	Found
Oxime[b]	98	...	...
4,4-Diphenylsemicarbazide	197	11.50	11.82
p-Nitrophenylhydrazone	237	14.43	14.29
Semicarbazide	219	19.71	19.75
Thio-semicarbazide	217	18.33	18.00
as-Diphenylhydrazone	100.5	8.69	8.48
2,4-Dinitrophenylhydrazone	254	16.66	16.44
β-Naphthylhydrazone	174–175	9.46	9.18
p-Bromophenylhydrazone	136–137	8.72	8.52
Phenylhydrazone	82	11.38	11.30
2,5-Dichlorophenylhydrazone	114	8.88	8.70
Acetone[c]	130	...	...
Anilide	172	6.08	6.24
o-Toluidide	172.5	5.73	5.98

[a] Many of the analyses (micro-Dumas) by Saul Gottlieb, Columbia University. [b] Hinkel, Ayling and Beynon, *J. Chem. Soc.*, 339 (1936). [c] Calcd. for $C_{26}H_{18}O$: C, 89.78; H, 5.43. Found: C, 89.92; H, 5.30.

Summary

An improved method for the preparation of α-chloromethylnaphthalene is described. The properties of α-chloromethylnaphthalene are discussed.

The melting points are given for certain new derivatives of alpha-naphthaldehyde.

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(5) This compound when tested on spayed rats exhibited no oestrogenic properties. The authors are indebted to the Biological Laboratories, E. R. Squibb & Sons, New Brunswick, N. J., for these tests.

(6) All melting points are corrected for stem exposure.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Dimethyl Acetal of *d*-Glucose

BY M. L. WOLFROM AND S. W. WAISBROT

The dimethyl acetals of the pentamethyl ethers of *d*-glucose and of several other hexoses have been reported by Levene and Meyer.[1] In the unsubstituted sugar structures, acetals of the small carbon atom sugars, glycolaldehyde[2] and glyceraldehyde[3] have long been known. Hudson and co-workers[4] have prepared the dimethyl acetal of *d*-arabinose by a series of reactions discovered by them for the arabinose structure.

In 1895 Emil Fischer[5] concluded that the impure sirup obtained by treating glucose at room temperature with methanol containing 1% of hydrogen chloride, consisted essentially of glucose dimethyl acetal. This conclusion was a reasonable one since he had previously prepared the thioacetal of glucose.[6] A more thorough investigation of this same methanol reaction product made at a later date caused Emil Fischer[7] to characterize the substance as a new methyl glucoside rather than as a dimethyl acetal. By an extension to glucose of the procedure previously reported from

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(1) P. A. Levene and G. M. Meyer, *J. Biol. Chem.*, **69**, 175 (1926); *ibid.*, **74**, 695 (1927).

(2) A. Pinner, *Ber.*, **5**, 147 (1872); E. Fischer and G. Giebe, *ibid.*, **30**, 3053 (1897).

(3) A. Wohl, *ibid.*, **31**, 1796 (1898); A. Wohl and F. Momber, *ibid.*, **47**, 3346 (1914).

(4) Edna M. Montgomery, R. M. Hann and C. S. Hudson, THIS JOURNAL, **59**, 1124 (1937).

(5) E. Fischer, *Ber.*, **28**, 1145 (1895).

(6) E. Fischer, *ibid.*, **27**, 673 (1894).

(7) E. Fischer, *ibid.*, **47**, 1980 (1914).