Ethers of B Napthol as Perfumes.

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by

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Index.

Preface.

This thesis as the name suggest represents the work of the author on the ethers of B Napthol, in order that he might produce a ether that would produce a fragrant odor suitable for a perfume.

Work was first done on some known ethers such as nerolin and the ethyl ether of B Napthol. This was done inorder to compare the ethers. The work that followed was original work.

Most of the work on these ethers had never been performed before or had not been done in the hope of getting a ether that would produce a fragrant odor.

The idea that the ethers of B Napthol might have a fragrant odor originated from the fact that the ethyl and methyl ethers of B Napthol do have a pleasing odor. The methyl ether of B. Napthol known to commerce as nerolin has been considerably used as a perfume in soap making. The ethers were prepared in much the same way as nerolin is prepared.

Commercially. The B Napthol was dissolved in potash yielding the metallic derivatives. The metallic derivatives like those of the alcohols react

with alkyl halogen compounds and with acid Chlorides yielding substances analogous to the ethers and esters respectively.

The author wishes to acknowledge his indebtedness to Dr. F. B. Dains for his interest in the work and for his helpful suggestions.

FWS/SDS

Ethers of B Napthol as Perfumes.

The synthesis of flower oils have showed great progress in the last few years and have resulted in a lowered cost until today the most meager toiler may revel in amber scents of odorous perfumes that were once secluded to the adornment of the roralty. The chemist has been able to take the extract of Civit cat and masquerade it as the delicate perfume of a spring Nosegay. Through the effort of the chemist we need no longer depend upon cow dung or the vomit of the whale as the source of ambergris, but ambrein, the odor constituent of ambergris in a fine state of perfection is now produced in the laboratory and from substances that have a very different effect upon our gustatory functions.

One of the first synthetic materials to find successful application in perfumery was vanillin-- the flavoring constituent of vanilla bean. In 1876, Tumann took out his first patent on a process to produce this nethyl ether of protoratechan aldehyde by means of acetylation of eugenol and its subsequent oxidation. The first vanillin sold for nearly $800. per pound. Through advance in chemical discovery, improved manufacturing processes, increased consumption and opposition of rival patentees this price has been gradually reduced

until today vanillin can be bought for less than one-onehundreth of the inductory price.

Tuman furthered the industry of synthetic perfumery by preparing an artificial violet perfume which he called ionone. Ionone was formed by condensing the olefinic aldehyde citral with acetone. The olefinic ketone in the presence of alkalies formed pseudoconone of the formula C_{15} H_{20} C. By inversion with dilute acid pseudoconone was converted into ionone. This methyl ketone a straw colored oil has such a powerful violet odor that one pound of it was equal to the perfume contained in all the violets one could pack in a fair sized room. In rapid succession one discovery followed another until today perfumers can choose from several hundred aromatic chemicals and produce thousands of fine combinations satisfying to the most fastidious. Synthetics have made possible theperfection of many old perfumes and enabled the perfumer to produce new scents undreamed of heretofore.

As mere traces of impurities will seriously alter the basic odor of a synthetic perfume, it must besides being chemical pure respond to the olefactory test. While the sense of smell in man is inferior to that developed in animals it is nevertheless marvelously delicate.

To pass the cultivated nose great care is exercised by the chemist to free his laboratory creations of detrimental impurities.

Few of the natural flower oils are not made up of a single aromatic substance,but are very complex, some oils have upward of half a hundred individual constitutents. Some of these constitutents have decided effect upon characterof the completed odor, are present in minute traces only, making recognition exceedingly difficult.

A perfume must not only have a fragrant odor but must have a good carrying power and lasting property. This is one of the reasons for the use of the extract from the civit cat.

Just as the chemist has found the delightful fragrance of new mown hay to be crystalline lactone courmarin so in time he will discover and synthesize the refreshing odor of the sea born breeze, the exhilarating fragrance abounding in the forests after a warm rain and the many charming odors that prevail at different seasons.

Methyl Ether of B. Napthol.

This either was made by dissolving ten grams of napthol in 5 c c c of alcohol that had been freed of pyridene and adding 5 grams of methyl iodide and 2.5 grams of potassium hydroxide. The contents were heated using a reflux condenser for several hours. The alcohol was evaporated off and the product recrystallized from alcohol.

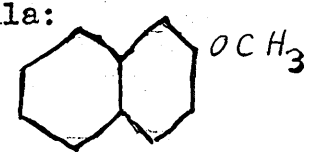
$C_{10}H_7CH$ plus KCH $=$ $C_{10}H_7OK$ plus H_2C

$C_{10}H_7OK$ plus CH_3I $=$ $C_{10}H_7CCH_3$ plus KI

Properties melting point 72 degrees. Brownish solid, volatile in steam.

Remarks: Has a odor of orange blossoms.

Formula:



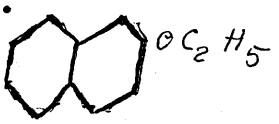
Ethyl Ether of B Napthol.

This ether was made much like the methyl ether of B Napthol. It was made by dissolving ten grams of B napthol in 50 cc. of ethyl alcohol that had been freed from pyridine and adding five grains of ethyl iodide and 2.5 grams of potassium hydroxide. The contents were heated using a reflex condenser for several hours. The alcohol was evaporated off and the product recrystallized from alcohol.

Properties melting point 32 degrees. Brownish solid, volatile in steam.

Remarks: Has a odor of pineapples.

Formula.

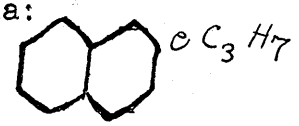


Propyl Ether of B Napthol.

The potassium salt of B Napthol was first made by dissolving ten grams of B Napthol in thirty cubic centimeters of a 20% solution of potassium hydroxide and evaporating the water off. To this salt was added ten grams of iso-propyl iodide. The mixture was now heated on a sand bath with a reflux condenser for four hours. At the end of this period the ether was distilled with steam and separated from the water with a separating funnel. The liquid was cooled down to 0 C in a bath of brine and the crystals placed on a porus plate and dried.

Properties: White solid. Melting point 38 degrees. No odor.

Formula:



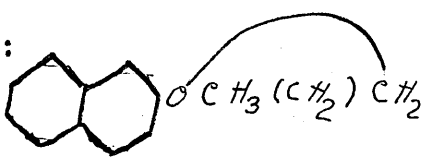
Nor Batyl Ether of B Napthol.

The B napthol was first dissolved in Nor batyl alcohol and then 6 grams of potassium hydroxide was added. To this mixture was added about nine and five tenths grams of Nor. batyl bromide. The mixture was heated on the sand bath for a couple of hours and then cooled in a bath of brine to the freezing point when the ether crystalized out. The product was washed and distilled.

Properties: Boiling point 302 degrees C. Long Yellowish needles in soluble in water. Very disagreeable strong odor with good carrying properties.

Remarks: Ethyl alcohol was first used as a solvent in place of batyl alcohol and same results were obtained. The ether was distilled under reduced pressure in the hope of bettering the odor but no change was noticed. There was not much trouble in getting the product.

Formula:

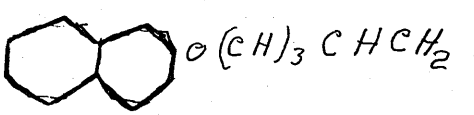


Iso-Butyl Ether of B Napthol.

The B Napthol was first dissolved in iso-butyl alcohol and then thirty c.c of twenty percent potassium hydroxide solution. To this mixture was added about nine and five tenths grams of iso-butyl bromide. The mixture was heated on a sand bath for a couple of hours and then cooled in a bath of brine to the freezing point when the ether crystallized out. The product was washed and distilled.

Properties: Long brownish needles soluble in water alcohol bath. Disagreeable odor.

Remarks: The iso-butyl ether was more difficult to prepare than the nor-butyl ether as it was harder to crystallize out.

Formula: 

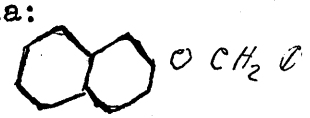
Benzyl Ether of B Napthol.

The potassium salt of B napthol was first made by dissolving 10 grams of B napthol in 30 c c of twenty percent solution.of potassium hydroxide, and boiling most of the water off. To this mixture was added 10 grams of benzyl chloride. The mixture was heated on a sand bath with reflex condenser for a couple of hours. The resulting crystals were filtered and washed.

Properties: White solid with little odor.

Remarks: Mostly a oily substance was formed.

Formula:



Ethylene Ether of B Napthol.

The potassium salt of B napthol was first made by dissolving 10 grams of B napthol in 30 c. c. of 20 percent solution of potassium hydroxide and boiling most of the water off. To this was added 15 grams of ethylene bromide. The mixture was heated on a sand bath with a reflex condenser a couple of hours. The resulting crystals were filtered and washed and dried.

Properties: Melting point 217 degrees. White solid difficultly soluble in ether and chloroform. No odor.

$C_{10}H_7O - CH_2$
$C_{10}H_7O \quad CH_2$

Allyl Ether of B Napthol

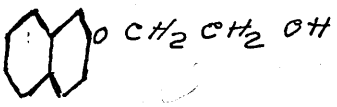
The B Napthol was first dissolved in ethyl acetate and thirty cubic centimeters of a 20 per cent hydroxide solution and ten grams of allyl bromide was added. The mixture was refluxed on a water bath for four hours. No results were obtained as the allyl bromide used was considered too impure. For further information concerning allyl ether of B napthol see Chemical Abstracts Vol. 7, page 1016.

Hydrine Ether of B Napthol.

The potassium salt of B napthol was first made by dissolving 10 grams of B napthol in 30 c. c. of 20 percent solution of potassium hydroxide and boiling most of the water off. To this mixture was added 5 grams of chlorhydrine. The mixture was heated on a sand bath with reflux condenser for a couple of hours. The resulting crystals were filtered and washed.

Properties: White solid. Melting point 76 degrees C. No odor.

Formula:



Nitro Methyl Ether of B Napthol.

Ten grams of neroline were dissolved in about thirty cubic centimetersof acetic acid. To this mixture was added five grams of concentrates nitric and slowly keeping the mixture cold. The resulting crystals were poured into a liter of water and filtered and washed.

Properties: Melting point 86 degrees. Yellow crystals, no odor.

Remarks: This ether was first tried by using chloroform as a solvent for the neoline with no results.

Bromo Methyl Ether of B Napthol.

The nerolin was dissolved in chloroform. To the solution was added the calulated amount of bromine slowly keeping the solutions cool. No results were obtained by this method. The next time the bromine was added directly without dissolving in the ether with no further results.

Conclusion.

The work performed on this thesis has showed that the ethers of B Napithol worked with have no pleasant odor with the exception of the methyl and ethyl ether. Because I have not gotten a perfume from the ethers of B Napthol does not mean that there are not perfumes that can be gotten from the ethers of B Napthol. Very often the slightest change in the formula will change a highly odoriferous substance into one that is odorless, and vice versa. If one was going to work further on this subject I would suggest that they try substituting in the Napthaline group.

Summary.

Compound	Odor.
$C_{10}H_7OCH_3$	Orange blossom
$C_{10}H_7OC_2H_5$	Pineapple
$C_{10}H_7OC_3H_7$	None
$C_{10}H_7OCH_3(CH_2)_2CH_2$	Strong unpleasant
$C_{10}H_7O(CH_3)_2CHCH_2$	Strong unpleasant
$(C_{10}H_7)_2C_2H_4$	None
$C_{10}H_7OCH_2O$	None
$C_{10}H_7OCH_2CH_2CH_2OH$	None
$NO_2C_{10}H_6OCH_3$	None