[CONTRIBUTION FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

THE PREPARATION AND PROPERTIES OF SOME HIGHER PHENOLS AND THEIR ETHERS.

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In a recent publication from this laboratory,[1] was described a practical method of introducing alkyl groups into the benzene nucleus of mono- and polyhydric phenols. It was shown that this can easily be accomplished by reduction of acyl derivatives of phenols (ketone-phenols) to their corresponding alkyl derivatives, by digestion with zinc-amalgam and hydrochloric acid. That the latter reagents may be employed for the reduction of the ketone group was observed by Clemmensen[2] and the method was applied by him successfully for the reduction of the following aliphatic and aliphatic-aromatic ketones, namely, acetophenone, $C_6H_5COCH_3$, ethylphenylketone, $C_6H_5COCH_2CH_3$, propylphenylketone, $C_6H_5COCH_2CH_2CH_3$, methylbenzylketone, $C_6H_5CH_2COCH_3$, methylphenylethylketone, $C_6H_5CH_2CH_2COCH_3$, methyl-α-naphthylketone, $C_{10}H_7$-$COCH_3$, methylnonylketone, $CH_3COC_9H_{13}$, methylheptadecylketone, $CH_3COC_{17}H_{35}$ and stearone, $(C_{17}H_{35})_2CO$. Since the publication of our paper, Clemmensen has contributed two more papers on this reaction and has applied it successfully for the reduction of several varieties of ketones and also of aldehydes.[3] In fact, the results obtained in those cases examined have been so satisfactory, that the reaction may be considered as one of general application.

In our first paper we described the behavior, on reduction, of the lower acyl derivatives of some phenols and their ethers. No aliphatic grouping larger then CH_3CH_2CO- (propionyl) was studied, but in every case examined the reduction was smooth and the yield of alkyl derivative was excellent. In no case did we observe the formation of pinacones. We have found, however, since the completion of this work, that pinacones are formed in some cases.[4] During the progress of our work it became of especial interest to us, for several reasons, to investigate further certain properties of new phenols of the above type, especially those which contain long aliphatic side chains in the benzene nucleus. We had reason to believe, for example, that such phenols would exhibit unique chemical properties and, furthermore, that certain ones might very probably prove to be of immediate, biochemical interest. Several phenol compounds of this character have now been synthesized, and a description of their preparation and properties is recorded in the experimental part of this paper.

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[1] Johnson and Hodge, THIS JOURNAL, **35**, 1014 (1913).

[2] *Orig. Comm. 8th Intern. Congr. Appl. Chem.*, **7**, 68–80 (1912).

[3] *Ber.*, **46**, 1837 (1913); **47**, 51 (1914).

[4] These experiments will be discussed in a future paper (T. B. J.).

In September, 1913, the writer announced[1] the fact, that veratrol and myristyl chloride interact smoothly, in the presence of aluminium chloride, forming the ketone—*myristylveratrol* (I). It was also shown

$$C_6H_4(OCH_3)_2 + CH_3(CH_2)_{12}COCl = HCl + \underset{(I)}{CH_3(CH_2)_{12}CO.C_6H_3(OCH_3)_2}.$$

that the latter undergoes reduction, when digested with zinc-amalgam and hydrochloric acid, forming a veratrol derivative, $CH_3(CH_2)_{13}.C_6H_3(OCH_3)_2$, which is isomeric with the dimethyl ether of *hydrourushiol*, $(CH_3O)_2.C_6H_3.C_{14}H_{29}$. The latter substance is a definite crystalline product which is easily obtained by catalytic reduction of the corresponding ether of *urushiol*, a natural component of Japanese lac and first identified by the Japanese investigator, Majima.[2] No conclusion could be drawn at that time, however, regarding the actual identity of the compounds, because we did not have, in our possession, any of Majima's natural substance for comparison. Fortunately, however, soon after the announcement of our work, we received from Professor Majima a sample of his substance and established the fact that the two ethers were only isomeric and not identical. This interesting observation would have been published in THIS JOURNAL several months ago, but for the fact that it has purposely been held back to avoid misunderstandings, and as assurance that we have no intention of interfering with the work of other investigators in this field. Since a reasonable time has now been given for others to conclude their work, it is not necessary for us to delay longer the publication of our results.

In a recent paper entitled: "Eine neue Synthese von höheren Phenolen," Majima and Nakamura[3] have described several alkyl derivatives of veratrol, which were made by the reduction of ketones with zinc-amalgam. Among those synthesized is the tetradecylveratrol, $CH_3(CH_2)_{13}.C_6H_3(OCH_3)_2$, which was described by us. These investigators state that this compound melts at 49–50°, and confirm our observation that it is not identical with the dimethyl ether of hydrourushiol. The latter melts at 38–39°. They apparently failed, however, to recognize an unique property of their synthetical ether. We find that this veratrol is a dimorphic compound and can exist in two modifications, which melt at 37–38.5° and 49°, respectively. Majima and Nakamura were dealing with the stable modification. It is an interesting fact that the melting point of our unstable modification in practically identical with that of the dimethyl ether obtained from *urushiol* (m. p. 38–39°). The unique behavior of our compound is described in the experimental part of this paper.

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[1] Paper presented before Organic Chemistry Section, 48th meeting Am. Chem. Soc., Rochester, N. Y., September 8–12, 1913.

[2] *Ber.*, **40**, 4390 (1908); **42**, 1418, 3664 (1910); **45**, 2427 (1913).

[3] *Ibid.*, **46**, 4089 (1914).

We have now investigated the action of zinc-amalgam on the following higher phenol derivatives, which are represented by formulas (II), (III), (IV), (V), (VI) and (VII):

Palmitylethoxybenzene, $C_2H_5OC_6H_4.CO(CH_2)_{14}.CH_3$
(II)

Palmitylveratrol, $(CH_3O)_2.C_6H_3.CO(CH_2)_{14}.CH_3$
(III)

Myristylveratrol, $(CH_3O)_2.C_6H_3.CO(CH_2)_{12}.CH_3$
(IV)

Myristylethoxybenzene, $C_2H_5O.C_6H_4CO(CH_2)_{12}CH_3$
(V)

Dimethylether of myristylhydroquinone, $(CH_3O)_2C_6H_3.CO(CH_2)_{12}CH_3$ (VI)
and myristylphenol, $HO.C_6H_4.CO(CH_2)_{12}CH_3$
(VII)

Every one of these ketones, with the exception of the phenol (VII), underwent reduction smoothly with formation of their corresponding alkyl derivatives. These are represented by formulas (VIII), (IX), (X), (XI) and (XII), respectively.

$C_2H_5O.C_6H_4.(CH_2)_{15}CH_3 \longrightarrow HO.C_6H_4.(CH_2)_{15}CH_3$
(Hexadecylethoxybenzene) (Hexadecylphenol)
(VIII) (XIII)

$(CH_3O)_2.C_6H_3.(CH_2)_{15}CH_3$
(Hexadecylveratrol)
(IX)

$(CH_3O)_2C_6H_3.(CH_2)_{13}CH_3$
(Tetradecylveratrol)
(X)

$C_2H_{50}.C_6H_4(CH_2)_{13}CH_3 \longrightarrow HO.C_6H_4.(CH_2)_{13}CH_3$
(Tetradecylethoxybenzene) (Tetradecylphenol)
(XI) (XIV)

$(CH_{30})_2C_6H_3.(CH_2)_{13}CH_3$
(Dimethylether of tetradecylhydroquinone)
(XII)

The ketone-phenol (VII), was extremely stable and only a trace of the phenol (XIV), was obtained after digesting with zinc-amalgam and hydrochloric acid for 46 hours. The ketone (III) and the corresponding alkyl derivative (X), have been described by Majima and Nakamura.[1] The two ethers, (VIII) and (XI), were easily converted into the corresponding phenols (XIII) and (XIV), by heating with hydriodic acid.

Especially interesting are the facts that the two higher phenols represented by formulas (XIII) and (XIV) are insoluble in aqueous alkali. While it is a very general rule that mono-substituted phenols of this type are

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[1] *Loc. cit.*

soluble in alkali, these compounds, on the other hand, possess practically no acidic properties and approach the aliphatic alcohols in chemical nature. Both phenols, however, react normally with Millon's reagent giving the characteristic test for a phenol group.

It is our opinion that this insolubility is not to be explained by the fact that these higher phenols are differently constituted than the lower members of the series. Their neutral character is very probably due to the influence of the positive alkyl chain, in the *para* position of the ring, on the phenolic hydroxyl group. This assumption is supported by the interesting fact that the solubility of the mono substituted phenols, in alkali, apparently grows less as the length of the side chain is increased. An inspection of Table I will reveal these interesting relationships so far as can be brought out from what is known regarding the members of the series. A comparison of other classes of phenol compounds has also revealed similar relationships. A synthesis of the missing representatives of the series would be of interest in order to determine the limit of solubility in alkali.

TABLE I.

Empirical formula.	Phenol compound, $HO.C_6H_4.R$.	Solubility in alkali.
C_6H_6O	Phenol	Soluble
C_7H_8O	(*o*-, *m*-, *p*)-$HO.C_6H_4.CH_3$	Soluble
$C_8H_{10}O$	(*o*-, *m*-, *p*)-$HO.C_6H_4CH_2CH_3$	Soluble
$C_9H_{12}O$	(*o*-, *m*-, *p*)-$HO.C_6H_4(CH_2)_2CH_3$	Soluble
	(*o*-, *m*-, *p*)-$HO.C_6H_4.CH(CH_3)_2$	Soluble
$C_{10}H_{14}O$	(*p*)-$HO.C_6H_4.CH(CH_3)(C_2H_5)$	Soluble
	(*p*)-$HO.C_6H_4.C(CH_3)_3$	Soluble
$C_{11}H_{16}O$	(*p*)-$HO.C_6H_4.(CH_2)_2CH(CH_3)_2$	Soluble
$C_{12}H_{18}O$	None described	
$C_{13}H_{20}O$	$HO.C_6H_4.CH(C_3H_7)_2$	?
$C_{14}H_{22}O$	$HO.C_6H_4CH(CH_3)(CH_2)_5CH_3$	?
$C_{15}H_{24}O$	Cynanchocerin or cynanchin[1](?)	Insoluble
$C_{16}H_{26}O$	None described	
$C_{17}H_{28}O$	None described	
$C_{18}H_{30}O$	None described	
$C_{19}H_{32}O$	None described	
$C_{20}H_{34}O$	(*p*)-$HO.C_6H_4.(CH_2)_{13}.CH_3$	Insoluble
$C_{21}H_{36}O$	None described	
$C_{22}H_{38}O$	(*p*)-$HO.C_6H_4(CH_2)_{15}.CH_3$	Insoluble
$C_{23}H_{40}O$	None described	

The variations in degree of acidity of the phenolic group OH— in this series in undoubtedly due to the same influence as that observed by Solonina[2] in the case of alkali soluble derivatives of benzene sulfonamide. For example, he found that only the lower mono-alkyl substitution products of this sulfonamide, $C_6H_5SO_2NHR$, possess strong acidic properties.

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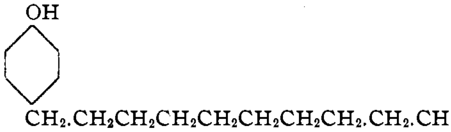
[1] Hesse, *Ann.*, **182**, 163; **192**, 183.

[2] *Chem. Centr.*, **2**, 867 (1899).

If alkyl groups containing more than six carbon atoms were substituted in the amide grouping the $SO_2.NH$ group lost its acidic properties and the resulting alkyl amides were absolutely insoluble in alkalies. Benzenesulfonheptylamide, $C_6H_5SO_2NH.(CH_2)_6CH_3$, benzene-sulfoncamphylamide $C_6H_5SO_2NH.C_{10}H_{17}$ and their corresponding *p*-bromobenzenesulfon- and *m*-nitrobenzenesulfonderivatives are examples of insoluble sulfonamides obtained. The benzenesulfonderivative of 2-aminoundecan was also insoluble. In other words, these higher alkyl groups apparently exert the same influence here on the acidity of the $—SO_2.NH—$ grouping as that of the corresponding radicals on the acid OH group in the above phenols.

Hesse[1] observed that *cynanchocerin* and *cynanchin*, two isomeric substances of unknown constitution, which he obtained from the sap of swallow-wort (*Cynanchum acutum*), are both insoluble in alkali and interact with sulfuric acid giving violet solutions (röthlich violett). It is of especial interest, now, to note that these two compounds are listed in Beilstein's Handbuch under phenols and the conclusion made that they are phenol ethers because of their insolubility in alkali. From what has already been shown it is not improbable that these substances may be true phenols, but contain long side chains which neutralize the acidic properties of the hydroxyl group.



$CH_2.CH_2CH_2CH_2CH_2CH_2CH_2CH_2.CH_2.CH_3$

Our investigations on phenols will be continued.

Experimental Part.

1,4-Hexadecylethoxybenzene. $C_2H_5O.C_6H_4.(CH_2)_{15}.CH_3$.—This benzene derivative was prepared by the reduction of 1,4-palmitylethoxybenzene.[2] Eleven and four-tenths grams of the ketone, an excess of amalgamated zinc and 300 cc. of hydrochloric acid (1 vol. concentrated acid to 2 vols. of water) were digested on a sand bath for about 15 hours, when the reduction was apparently complete and 11.5 g. of the crude ether were obtained. After crystallizing from alcohol this product melted at 40–54°, indicating that it was a mixture of the ketone and reduced ether. The mixture was again digested with zinc-amalgam for 8 hours, a little alcohol being added to aid solution of the ketone. After this second treatment we obtained the ether as a colorless, cystalline substance which separated from hot alcohol in globules of oil that immediately solidified on cooling. The ether melted at 43–45° to a clear oil. The yield of purified material was 6.5 g.

Calc. for $C_{24}H_{42}O$: C, 83.15; H, 12.2; found: C, 82.19; H, 11.85, 11.83.

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[1] *Loc. cit.*

[2] Krafft, *Ber.*, **21**, 2270 (1888).

p-Hexadecylphenol, $CH_3(CH_2)_{15}.C_6H_4.OH$.—This phenol was obtained by heating the above ether with hydriodic acid in a pressure tube at 150–180°. It was insoluble in water and was purified by crystallization from petroleum ether. It separated from this solvent in needles which melted at 78–79°. The phenol crystallizes from alcohol in clusters of radiating prisms. This phenol is absolutely insoluble in sodium hydroxide solution. It gives Millon's test.

Calc. for $C_{22}H_{38}O$: C, 82.9; H, 12.0; found: C, 82.26; H, 11.84.

This compound has previously been described by Krafft,[1] and was prepared by fusion of the *p*-sulfonic acid derivative of cetylbenzene, $CH_3(CH_2)_{15}.C_6H_4.SO_3H$, with potassium hydroxide at 250°. He assigned the temperature of 77.5° as its melting point. Later Krafft and Göttig[2] described its ethylether (above), which was prepared by heating the phenol in alcoholic potash with methyl iodide. They found this to melt at 43–44°, practically the same temperature as observed by us (43–45°).

Palmitylveratrol, $CH_3(CH_2)_{14}CO.C_6H_3(OCH_3)_2$.—This ketone has recently been described by Majima and Nakamura.[3] We prepared it by application of Friedel and Crafts' reaction with veratrol and palmitylchloride in carbon disulfide solution. It was purified by distillation under diminished pressure and recrystallization from alcohol. It melted at 78–79°. Majima observed that his product melted at 79–80°.

Calc. for $C_{24}H_{40}O_3$: C, 76.53; H, 10.71; found: C, 76.43; H, 10.73.

Hexadecylveratrol, $CH_3(CH_2)_{15}.C_6H_3(OCH_3)_2$.—This ether was formed quantitatively by reduction of the above ketone with zinc-amalgam and hydrochloric acid. It crystallized from alcohol in plates which melted at 55° to an oil.

Calc. for $C_{24}H_{42}O_2$: C, 79.48; H, 11.68; found: C, 79.90; H, 11.73.

Myristylveratrol, $CH_3(CH_2)_{12}CO.C_6H_3(OCH_3)_2$.—Majima and Nakamura[3] prepared this ketone by the action of myristyl chloride on veratrol in the presence of aluminium chloride. No diluent was used. From 10.7 g. of the acid chloride and 17 g. of the veratrol they obtained 3.5 g. of the pure ketone. We find that a much better yield of the ketone can be obtained if the reaction is applied in the presence of petroleum ether. Our procedure was as follows: Twenty-seven grams of the acid chloride were dissolved in 25 g. of petroleum ether and 15 g. of aluminium chloride suspended in the solution. Fifteen grams of veratrol were then added in portions, the mixture being cooled to —5°. On adding the veratrol under these conditions, a precipitate was obtained, but there was no appreciable amount of hydrochloric acid generated. After all the veratrol had been added, 50 cc. of petroleum ether were then added and the mix-

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[1] *Ber.*, **19**, 2984 (1886).

[2] *Ibid.*, **21**, 3181 (1888).

[3] *Loc. cit.*

ture allowed to stand at a temperature of 30–40° for fully 21–22 hours. Under these conditions the reaction proceeded smoothly, and hydrochloric acid gas was copiously evolved. In order to isolate the ketone, the reaction mixture, which had separated in two layers, was poured into a large volume of cold water, when a double aluminium chloride compound separated in the form of a grayish brown solid. This was then transferred to hydrochloric acid and the mixture warmed on the steam bath when the ketone was finally obtained as an oil which soon solidified on cooling. The yield of crude material was 40 g., or practically a theoretical yield. The ketone was purified by crystallization from alcohol and separated, on cooling, in aggregates of colorless needles melting at 73–75°. The yield of purified ketone was 32 g. A red color is produced when this ketone is mixed with concentrated sulfuric acid.

Calc. for $C_{22}H_{36}O_3$: C, 75.79; H, 10.19; found: C, 75.48; H, 10.12.

Tetradecylveratrol, $CH_3(CH_2)_{13}.C_6H_3(OCH_3)_2$.—This ether has recently been described by Majima,[1] and was obtained by catalytic reduction of tetradecenylveratrol and also by reducing the above ketone with zinc-amalgam. Only 2.5 g. of the ketone, however, were reduced by the latter method and no statement is made regarding the yield obtained.

We have now prepared this same ether by reducing the ketone with zinc-amalgam and hydrochloric acid and have obtained some interesting data which contribute to our knowledge of the properties of this compound.

Eleven grams of the above ketone and 25 g. of amalgamated zinc were suspended in 100 cc. of hydrochloric acid (1 vol. of concentrated hydrochloric acid to 2 vol. of water) and the mixture digested for 5 hours. Under these conditions the ketone had undergone practically no reduction and melted at 71.5–73°. Twenty-five grams of amalgam and 25 cc. of concentrated hydrochloric acid were then added and the digestion continued for 9 hours. After this treatment, the ketone was still only partially reduced and melted at 60–67°.

One hundred grams of zinc-amalgam and 150 cc. of hydrochloric acid were then added and the digestion continued for 7 hours longer when the melting point had been lowered to 45°. This melting point, however, was not sharp, the product beginning to melt as low as 39°. Therefore, 30 cc. of concentrated hydrochloric acid were added and the reduction continued for 6.5 hours when the reaction was apparently complete. The compound was purified by crystallization from boiling alcohol. It separated in prismatic crystals, on cooling, which melted at 47–49°. Majima and Nakamura[1] give 49–50° as the melting point. We found, however, that this compound can be made to melt at a much lower temperature. In fact, it is apparently capable of existing in two modifications—one melting at 37–38.5°, and the other melting at 47–49°. The lower modification

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[1] *Loc. cit.*

slowly undergoes transformation into the higher melting isomer at ordinary temperature. Especially striking is the change of the lower melting form into the higher. If the compound is melted in a capillary tube and the latter suddenly cooled by plunging into ice water, it then melts sharply at 37–38.5° to an oil. Almost immediately, however, after this change, crystals begin to appear in the fluid and finally the whole mass solidifies and then melts at 47–49°. This lower melting modification was also obtained by crystallization from alcohol. It is an interesting fact that the dimethylether of hydrourushiol[1] melts at 38–39°, or practically at the same temperature as the melting point of our unstable modification.

Calc. for $C_{22}H_{38}O_2$: C, 78.95; H, 11.46; found: C, 78.67; H, 11.18.

1,4-Myristylethoxybenzene, $CH_3(CH_2)_{12}CO.C_6H_4.OC_2H_5$.—This ketone was prepared by application of Friedel and Crafts' reaction with 52 g. of myristyl chloride and 100 g. of phenetol in the presence of 72 g. of aluminium chloride. After heating for two days at 60–70° the mixture was then poured while warm into warm, dilute hydrochloric acid and the crude ketone extracted with ether. After drying over calcium chloride, the ketone was subjected to distillation under diminished pressure and that fraction saved which boiled from 260–320° at 27–35 mm. This weighed 29 g. and was purified by crystallization from alcohol. It separated from this solvent in colorless blocks which melted at 66–67° to an oil.

Calc. for $C_{22}H_{36}O_2$: C, 79.44; H, 10.92; found: C, 79.02; H, 10.72.

1,4-Tetradecylethoxybenzene, $CH_3(CH_2)_{13}.C_6H_4.OC_2H_5$.—This compound was easily obtained by reduction of the above ketone with zinc amalgam and hydrochloric acid. It was purified by crystallization from alcohol and melted at 36–36.5° to an oil.

Calc. for $C_{22}H_{38}O$: C, 82.94; H, 12.03; found: C, 82.52; H, 11.83.

1,4-Tetradecylphenol, $CH_3(CH_2)_{13}.C_6H_4.OH$.—This phenol was obtained by heating the ethyl ether (above) with glacial acetic acid, saturated at 0° with hydrochloric acid, for 2–3 hours at 150–160°. It was insoluble in water and was purified by crystallization from petroleum ether and separated in stout prisms, which melted at 73–74°. The phenol is insoluble in aqueous sodium hydroxide solution. It gives Millon's test.

Calc. for $C_{20}H_{34}O$: C, 82.67; H, 11.81; found: C, 82.25; H, 11.87.

The phenol is also formed smoothly by heating the ether in a pressure tube with hydriodic acid and a trace of phosphorus at 155–156°.

1,4-Myristylphenol, $CH_3(CH_2)_{12}CO.C_6H_4.OH$.—Twenty-five grams of myristyl chloride and 13 g. of phenetol were dissolved in 150 cc. of dry carbon disulfide. Thirty-five grams of aluminium chloride were then added, in small portions at a time (2 g.) to avoid too violent action, and the solution

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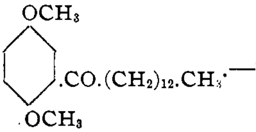
[1] Majima, *Ber.*, **45**, 2729 (1912).

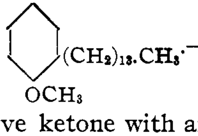
finally heated to boiling for 5 hours. The mixture was then poured into dilute hydrochloric acid and finally heated on the steam bath to expel the carbon bisulfide. The ketophenol was then obtained as a heavy, black oil which dissolved immediately in cold dilute sodium hydroxide solution. In order to purify the phenol for analysis the alkaline solution was digested with bone coal and the phenol then precipitated by addition of hydrochloric acid. It separated as a brown powder and was purified further by crystallization from a large volume of petroleum ether. It separated in the form of a pink powder and melted at 74–74.5° to an oil. The yield was poor.

Calc. for $C_{20}H_{32}O_2$: C, 78.86; H, 10.60; found: C, 78.96; H, 10.81.

An attempt to reduce this ketone to the corresponding tetradecylphenol with zinc-amalgam was unsuccessful. Only a mere trace of this phenol was obtained after digesting 11 g. of the ketone with amalgam and hydrochloric acid for 46 hours. The reduced product was easily separated from the ketone by treatment of the raw reduction product with dilute sodium hydroxide solution. The tetradecylphenol was insoluble in the alkali and was identified by its melting point (73–74°).

Dimethylether of Myristylhydroquinone, —This compound was easily obtained by application of Friedel and Crafts' reaction with 15 g. of hydroquinone dimethylether, 26 g. of myristyl chloride and 16 g. of aluminium chloride. Petroleum ether was used as a diluent. The reaction was extremely smooth and the yield of crude material was 37 g. The ketone was purified by crystallization from alcohol and separated in plates, which melted at 51–52° to an oil. The compound was insoluble in aqueous sodium hydroxide solution and did not give Millon's test. It dissolved, however, in a cold alcoholic solution of sodium hydroxide while, on the other hand, the reduction product (below) was insoluble in this same solvent.

Calc. for $C_{22}H_{36}O_3$: C, 75.79; H, 10.42; found: C, 75.58; H, 10.83.

Dimethylether of Tetradecylhydroquinone, —This compound was obtained by reduction of the above ketone with amalgamated zinc and hydrochloric acid. It is very soluble in cold ether, petroleum ether and difficultly soluble in cold alcohol. The compound boiled at 260–275° under 25–35 mm. pressure and crystallized from petroleum ether in aggregates of short needles which melted at 65° to an oil.

Calc. for $C_{22}H_{38}O_2$: C, 78.94; H, 11.45; found: C, 78.52; H, 11.10.

The Action of Nitric Acid on Tetradecylveratrol.—This ether apparently does not interact smoothly with nitric acid. Two grams of the veratrol were suspended in 12 cc. of concentrated nitric acid (sp. gr. 1.42) and the acid warmed sufficiently to melt the ether. This was then left in contact with the acid for about 10 minutes and then washed free from acid by pouring into cold water. The nitro compound was finally purified as follows: It was extracted with ether and dried over calcium chloride. After spontaneous evaporation of the ether, the nitro compound was purified further by crystallization from petroleum ether when it separated in the form of flakes which melted at 91–93°. The yield was small. A nitrogen determination agreed with the calculated value for a mononitro derivative—$CH_3(CH_2)_{13}.C_6H_2(NO_2)(OCH_3)_2$.

Calc. for $C_{22}H_{37}O_4N$: N, 3.69; found: N, 3.8.

Majima and Nakamura[1] observed that the mononitro derivative of the dimethylether of hydrourushiol melts at 72–73°.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI.]

ELECTROMERS AND STEREOMERS WITH POSITIVE AND NEGATIVE HYDROXYL.

BY LAUDER WILLIAM JONES.

Received March 9, 1914.

Although hydroxylamine is one of the simplest inorganic compounds containing nitrogen, it has not escaped speculative controversy concerning the structural formula best suited to represent it. Two formulas have been proposed:

$$H_2N—OH \quad (I) \qquad\qquad H_3N{=}O \quad (II)$$

Many of its reactions in organic chemistry, as well as some of its physical constants,[2] seemed to justify the formula which the name, hydroxylamine, implies. Some of the reactions, however, and especially the dual role which hydroxylamine plays as an oxidizing agent and as a reducing agent, have inclined other investigators to support the second formula.

One of the earliest statements of this view was made by Kolotow,[3] who heated hydroxylamine with ammonia at 100°, but could not find a trace of hydrazine. From this vague experiment, he concluded that hydroxylamine did not react as a hydroxyl compound, and that the formula, $H_3N{=}O$ was consequently the more probable. Haber[4] found that hydroxyl-

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[1] *Loc. cit.*

[2] Brühl preferred the formula, $H_2N—OH$, as more consistent with his spectrochemical findings. *Ber.*, **32**, 566 (1899).

[3] Kolotow, *Ber.*, **26**, 761 (1893).

[4] Haber, *Ibid.*, **29**, 2444 (1896).