picrate separated. This was crystallized once from benzene, giving 0.7 g. melting at 202–204°. The hydrocarbon was regenerated from the picrate by means of ammonia, giving approximately 0.2 g. This was recrystallized three times from acetone, once from acetone and a small amount of decolorizing carbon and finally from acetone alone, when it melted at 166–167°.

Anal. Calcd. for $C_{26}H_{28}$: C, 91.71; H, 8.29. For $C_{28}H_{30}$: C, 91.75; H, 8.25. Found: C, 91.67, 91.66; H, 7.85, 8.13.

A portion of the hydrocarbon was converted into the picrate which after one recrystallization from benzene melted at 209–210° with decomposition.

Anal. Calcd. for $C_{38}H_{34}O_{14}N_6$: C, 57.13; H, 4.29. For $C_{40}H_{36}O_{14}N_6$: C, 58.23; H, 4.40. Found: C, 56.84; H, 4.06.

The trinitrobenzenate melted at 219–220° but was insufficient for analysis.

Hydrocarbon, $C_{25}H_{20}$.—The residue from the dioxane extraction was heated very gradually in a flask with a wide low side arm and slowly distilled at 0.1 to 0.3 mm. With the bath at 300° a red liquid distilled which crystallized to a yellow solid in the cooler portion of the side arm. After washing with a little hot pyridine and crystallizing three times from a mixture of pyridine and methyl alcohol and three times from pyridine, a white product melting at 292–293° was obtained. Although not quite pure, it showed no depression in melting point when mixed with a specimen of the $C_{25}H_{20}$ hydrocarbon obtained from sumaresinolic acid, m. p. 296–297°.

Anal. Calcd. for $C_{25}H_{20}$: C, 93.69; H, 6.31. Found: C, 93.42; H, 5.95.

The writer wishes to thank Professor L. Ruzicka and Dr. H. Hösli for their invaluable advice during the course of this work.

Summary

Echinocystic acid on dehydrogenation with selenium yields the 1,2,3,4-tetramethylbenzene, 2,7-dimethylnaphthalene, 1,2,7-trimethylnaphthalene, 1,2,7-trimethylnaphthol, 1,2,5,6-tetramethylnaphthalene and the hydrocarbon, $C_{25}H_{20}$, which have previously been obtained by the dehydrogenation of other triterpenoids. The hydrocarbon, $C_{25}H_{24}$, m. p. 141.5°, could not be detected but instead a new hydrocarbon, m. p. 166–167°, has been isolated.

STANFORD UNIVERSITY, CALIF.   RECEIVED APRIL 9, 1934

Rearrangement of Alkyl Phenyl Ethers on Heating at Moderate Temperatures. Synthesis of Tertiary Amyl, Tertiary Butyl and Diisobutyl Phenols

BY SAMUEL NATELSON

Although the author and subsequently others[1] have shown that saturated alkyl phenyl ethers will rearrange in the presence of catalysts, the rearrangement of these compounds in the absence of these catalysts had not been clearly demonstrated.

It was observed that the boiling range and refractive index of *s*-amyl phenyl and cresyl ethers increased with each distillation at atmospheric pressure. In the case of the tertiary octyl phenyl ether (diisobutyl phenyl ether) rearrangement is so rapid that one distillation at atmospheric pressure is capable of bringing about a high conversion to the substituted phenol.[1a]

The substituted phenols are becoming of increasing value and importance as antiseptics and for the preparation of oil soluble resins. Since these alkyl phenyl ethers can be prepared readily by heating alkali with molten phenols and then adding the alkyl halide, this procedure is inexpensive in operation, considering the availability of chlorinated hydrocarbons. If the substituted phenol is desired, the ether need not be isolated but heating may be continued at elevated temperatures until conversion to the substituted phenol has taken place.

Diisobutyl, tertiary amyl and tertiary butyl phenols were therefore prepared by condensing the corresponding alkyl halide with potassium phenolate, adjusting the time of heating and the temperature so as to isolate the substituted phenols. The *t*-amylphenol obtained was identical with *p*-amylphenol, para rearrangement predominating in this case.

The method of preparing ethers by condensing unsaturated hydrocarbons with phenols with the aid of sulfuric acid could also be used to prepare substituted phenols by varying conditions. The poor yield of ethers previously obtained[2] was due

(1) (a) Samuel Natelson, Ph.D. Thesis, New York University, 1931; (b) Niederl and Natelson, THIS JOURNAL, **53**, 272, 1932 (1931); **54** 1063 (1932); (c) Sowa, Hinton and Nieuwland, *ibid.*, **55**, 3406 (1933); (d) Smith, *ibid.*, **55**, 3720 (1933).

(2) Niederl and Natelson, *ibid.*, **53**, 272 (1931).

to simultaneous formation of substituted phenol. Subsequently this method was varied to yield the substituted phenol as the main product of the reaction.[3]

In the light of the above understanding of the rearrangement of the alkyl phenyl ethers the procedure was again varied to give high yields of the substituted phenols rapidly. Condensation of the unsaturated hydrocarbon and the phenol was carried on at a low temperature to form the ether without sulfonation. The temperature was then raised to give a high yield of substituted phenol with a very short reaction time. The resultant phenol exists partly as the sulfuric acid ester and has to be hydrolyzed by vigorous stirring in water for maximum yield.

In the presence of sulfuric acid, boron trifluoride, aluminum chloride, zinc chloride and other acids or acidic salts, rearrangement is rapid but is more complex in nature than in the absence of such reagent. The author and other experimenters in this field have shown the complexity which the rearrangement of isopropyl phenyl ethers attains in the presence of acidic rearranging agents.[1b,c,d]

The postulation that the rearrangement of these ethers is bimolecular in that the isopropyl group is seen to shift from the phenol residue to a foreign benzenoid ring in the mixture in the presence of aluminum chloride[4] is not complete in that aluminum chloride will labilize and cause shifting of alkyl radicals in the absence of a phenolic group. Aluminum chloride will convert diethylbenzene to an equilibrium mixture of mono- and diethylbenzene in the presence of benzene.[5] If the case is intermolecular, as postulated, substituted diphenyl ethers should be isolated when diphenyl ether is added to an alkyl phenyl ether which is rearranged by heat alone. Adding diphenyl ether to diisobutyl phenyl ether and heating produced a high yield of diisobutylphenol and no diisobutyl diphenyl ether. The formation of substituted benzenes could be well explained by splitting of the ether and alkylation of benzene in the presence of aluminum chloride after the method of Friedel and Crafts.

If one considers these rearrangements as analogous to quinoid–benzenoid tautomerism, these rearrangements can be explained simply and the widely spread cases of phenyl ether rearrange-

ments, phenomena observed on preparation of substituted phenols by condensation with alcohols, halides, olefins, acids, acid chlorides, aldehydes and ketones, and the stripping of groups from the phenolic nucleus can be harmonized.
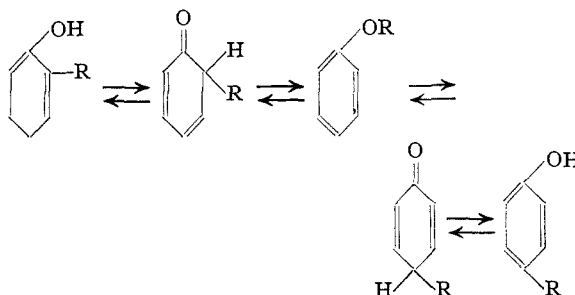
From the observations of numerous other investigators and from the experience of the author this equilibrium must be a dynamic one at elevated temperatures and the following conclusions are drawn.

1. All alkyl or cyclohexyl phenyl ethers will form equilibrium mixtures of ether and substituted phenol at higher temperatures and/or in the presence of catalysts.

2. The higher the molecular weight of the alkyl residue the more the equilibrium is shifted to the formation of substituted phenol.

3. If the ether forming carbon of the alkyl group is tertiary, the equilibrium is shifted so as to favor the formation of substituted phenol more than if secondary, than if primary.

4. Negative groups attached to the ether-forming carbon of the alkyl group shift the equilibrium so as to favor the formation of substituted phenols.[6]

5. The equilibrium of the mono-ethers of polyhydroxyphenols and naphthols is in the direction of the formation of substituted phenols. The greater the number of hydroxyl groups the greater the ease of rearrangement. Secondary and tertiary long chain ethers of resorcinol or pyrogallol can hardly be obtained.

6. Substituting a group in the phenyl nucleus of the alkyl phenyl ether throws the equilibrium in the direction of ether formation. Diisobutyl, diisobutyl phenyl ether did not rearrange readily.

7. The equilibrium can be shifted completely to ether formation if the ether is continuously removed by splitting. Hence nitric acid, phosphorus pentoxide, phosphorus pentachloride and

(3) Niederl, Natelson and Beekman, THIS JOURNAL, 55, 2571 (1933).

(4) Smith, ibid., 56, 717 (1934).

(5) Samuel Natelson, Ind. Eng. Chem., 25, 1391 (1933).

(6) Kolbe and Lautemann, Ann., 115, 203 (1860); Bucherer and Grolee, Ber., 39, 986 (1906); Van Alphen, Rec. trav. chem., 46, 287 (1927); Niederl and Storch, THIS JOURNAL, 55, 284 (1933).

similar reagents will strip alkyl groups from substituted phenols, forming trinitro phenol or cresols or esters of phenol or cresol, respectively.[7]

8. Equilibrium mixtures of ortho and para substituted phenols are obtained on rearrangement. In the case of isopropyl phenyl ethers the ratio is approximately 33% ortho and 66% para.[1b] As the alkyl radical increases in weight or becomes tertiary, the yield of para substituted product is increased so that in the case of t-amylphenol all the phenol obtained is the para substituted product.

Experimental

Preparation of Diisobutyl, t-Amyl and t-Butyl Phenols; (a) from the Halides; (b) from the Unsaturated Hydrocarbon.—(a) A mixture of one mole of powdered potassium hydroxide and one mole of phenol or cresol or guaiacol is heated at 65–100° in a metal bath until solution is complete. A mole of halide is then added drop by drop at about 75° until the reaction is complete. Potassium chloride separates out. The temperature of the bath is raised to 125°, kept there for three to four hours, raised to 180° and kept there for about one hour. After cooling, the potassium chloride is dissolved in water and the separated crystalline or oily product either recrystallized from ligroin or taken up in ether and distilled *in vacuo*. Low temperatures favor the formation of ethers, high temperatures the formation of substituted phenols.

(b) To a mixture of one mole of phenol and one mole of unsaturated hydrocarbon with vigorous stirring at 0°, one mole of concd. sulfuric acid is added drop by drop keeping the temperature below 10°. (In the case of isobutylene, the gas generated from the action of phosphorus pentoxide on isobutyl alcohol was bubbled into a mixture of phenol and concd. sulfuric acid at 0° until the desired increase in weight had been observed.) With the first few drops of sulfuric acid a vigorous reaction takes place and the mixture becomes homogeneous. (As little as $1/50$ mole of sulfuric acid will bring the reaction to completion. The

or means to fix the gas in solution.) After complete addition the mixture is allowed to come to room temperature, stirring vigorously as the material becomes more viscous. The mixture is then warmed to 65° with stirring for from one half to one hour. The reaction mixture poured into two liters of crushed ice is stirred as the substituted phenol separates as a white crystalline or sometimes partially oily mass which is filtered off. If a gummy, tacky oil separates with the precipitate and makes separation difficult, keeping the substituted phenol in colloidal suspension, the mixture of water, sulfuric acid and phenol is warmed to 40° and stirred with 300–500 cc. of warm ligroin. The ligroin dissolves the oil and the warm water hydrolyzes the last traces of sulfuric ester, leaving the crystalline substituted phenol, which is filtered off. This residue may be further purified by recrystallization from ligroin or by vacuum distillation. The ligroin in the filtrate is evaporated to recover more of the substituted phenol. The yields are usually in the neighborhood of 90% of the theoretical.

Diisobutyl Phenyl Ether.—To 23 g. of sodium dissolved in 350 cc. of 95% ethyl alcohol, 94 g. of phenol is added and the mixture is refluxed for a few minutes; 145 grams of diisobutyl chloride, prepared by the action of dry hydrogen chloride on cold diisobutylene is added and the mixture is gently refluxed for from one to two hours. The alcohol is evaporated off under slight vacuum and water is added to dissolve the salt. The oil which separates is washed with sodium hydroxide and water several times and then dried over calcium chloride. It is used directly for rearrangement without distilling.

Rearrangement of Diisobutyl Phenyl Ether.—Twenty-five grams of diisobutyl phenyl ether prepared as above was placed in a sealed tube and heated at 250° for two hours. On cooling in an ice-bath the whole mass crystallized and was recrystallized from ligroin–diisobutyl phenol, m. p. 84°. Twenty-five grams of diisobutyl phenyl ether was added to 10 g. of diphenyl ether in a sealed tube and heated to 250° for two hours. On cooling and fractionally crystallizing from ligroin, 9.5 g. of unchanged diphenyl ether was recovered and no evidence of formation of alkyl substituted diphenyl ether was observed.

TABLE I

Substance	Formula	M. p., °C.	B. p., °C.
Diisobutylphenol[a]	$(CH_3)_3CCH_2C(CH_3)_2C_6H_4OH$	84	.....
Diisobutyl-o-cresol[b]	$(CH_3)_3CCH_2C(CH_3)_2C_6H_3(CH_3)OH$	54	.....
Diisobutylguaiacol[c]	$(CH_3)_3CCH_2C(CH_3)_2C_6H_3(CH_3)OH$	..	295–298 38–44 (4 mm.)
t-Amylphenol[d]	$CH_3CH_2C(CH_3)_2C_6H_4OH$	93	260–265
t-Butylphenol[e]	$CH_3C(CH_3)_2C_6H_4OH$	98	235–238
Diisobutyl phenyl ether[c]	$(CH_3)_3CCH_2C(CH_3)_2OC_6H_5$	..	250–260 (partial rearrangement)
t-Butyl phenyl ether	$CH_3C(CH_3)_3OC_6H_5$	..	195–201 (partial rearrangement)

[a] *Anal.* Calcd. for $C_{14}H_{22}O$: C, 81.55; H, 10.68. Found: C, 80.99; H, 10.57.
[b] *Anal.* Calcd. for $C_{15}H_{24}O$: C, 81.82; H, 10.91. Found: C, 81.70; H, 10.71.
[c] Natelson, Ph.D. thesis, New York University (1931).
[d] A mixed melting point with pure commercial t-amylphenol showed no depression.
[e] *Anal.* Calcd. for $C_{10}H_{14}O$: C, 80.00; H, 9.66. Found: C, 79.49; H, 9.47.

greater amount of sulfuric acid speeds up the reaction and in the case of a gas the extra sulfuric acid acts as a solvent

(7) Engelhardt, *Latschinow-Zeit. für Chemie*, 621 (1869); Southworth, *Ann.*, **168**, 268 (1873); Tiemann and Schotten, *Ber.*, **11**, 769 (1878); Vongerichten, *ibid.*, **10**, 125 (1877); Armstrong and Rennie *Chem. News*, **47**, 115 (1883); **84**, 23 (1901).

Summary

1. t-Alkyl phenyl ethers rearrange to form substituted phenols on heating.

2. A method for the preparation of substituted

phenols from alkyl halides and alkali phenolates in good yields is demonstrated.

3. The method for the preparation of substituted phenols by the condensation of olefins with phenols by means of sulfuric acid is improved to give high yield with a shortened reaction time.

4. Rearrangement of alkyl ethers, condensa-

tions of unsaturated compounds, alcohols, acids, alkyl halides, acid chlorides, aldehydes and ketones with phenols, and a stripping of alkyl groups from the phenol nucleus are considered as special cases of a quinoid–benzenoid dynamic equilibrium which may be shifted in either direction by varying conditions.

[Contribution from the Laboratory of Organic Chemistry of the State University of Iowa]

Benzoxazolone Formation in the Attempt to Prepare Certain Mixed Diacyl Derivatives of o-Aminophenol

By L. Chas. Raiford and Gerald O. Inman

When two different acyl radicals are introduced into o-aminophenol the positions taken by these groups are determined by a number of factors.[1] If the acyls are $R—\overset{|}{C}{=}O$ and $R'—\overset{|}{C}{=}O$,[2] the heaviest and most acidic radical is usually found attached to nitrogen, regardless of the order of introduction.[3] To meet this requirement the migration of acyl from nitrogen to oxygen must occur in one of these reactions. When the acyls are $R—\overset{|}{C}{=}O$ and $R—O—\overset{|}{C}{=}O$ the latter is most frequently[4] found on nitrogen. If one of these radicals is $Ph—\overset{|}{\underset{||}{S}}{=}O$ no rearrangement takes place[5] regardless of the structure of the other radical or the order of introduction of the two groups.

In previous work with the $R—O—\overset{|}{C}{=}O$ radical, R has always been represented by alkyl. In the present study we have examined the behavior of derivatives in which R is aromatic. To do this a number of aryl chlorocarbonates were prepared and converted into the N-carboaryloxy derivatives of o-aminophenol and several of its substitution products, following the method of Groenvik.[6] When these compounds were mixed with caustic alkali solution for the purpose of acylating them[7] they were converted into

the corresponding benzoxazolones[8] while the required phenols were eliminated.

It is now shown that warming 2-N-carboaryloxyaminophenol with pyridine and with acetic anhydride, respectively, causes ring closure, and that in the latter instance N-acetylbenzoxazolone[9] is obtained. Likewise, when 2-benzoylaminophenol, in caustic soda or in pyridine solution, is treated with phenyl chlorocarbonate, phenol is liberated and N-benzoylbenzoxazolone is obtained in yields of 95 and 86%, respectively. No diacyl derivatives could be isolated.

The behavior of derivatives of 2-methylaminophenol was examined. Acylation of the base with phenyl chlorocarbonate gave 2-carbophenoxymethylaminophenol, m. p. 146°. This reacted with dilute caustic alkali solution to give 2-methylbenzoxazolone, m. p. 87.5°, which was also obtained by alkylation of benzoxazolone

(1) Raiford and Clark, This Journal, 48, 483 (1926). This paper gives important references to other work.

(2) R and R' may be aliphatic or aromatic.

(3) Exceptions have been noted by Raiford and others [This Journal, 46, 2308 (1924)]; Nelson and co-workers [ibid., 53, 997 (1931)]; Bell [J. Chem. Soc., 2962 (1931)].
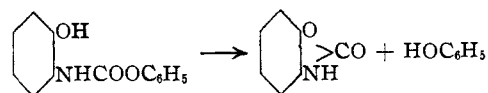
(4) Ransom and Nelson, This Journal, 36, 393 (1914); Nelson and others, loc. cit.

(5) Raiford and Lankelma, ibid., 47, 1123 (1925); Raiford and Grosz, ibid., 53, 3425 (1931).
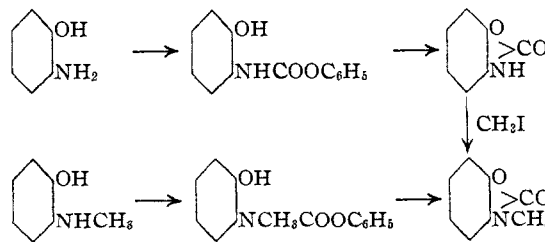
(6) Groenvik, Bull. soc. chim., [2] 25, 177 (1876).

(7) Schotten-Baumann, Ber., 17, 2544 (1884); 19, 3218 (1886).

(8) In previous work the formation of benzoxazolone from an acyl derivative of o-aminophenol has, with a single exception, been noted only in those cases where the starting material was heated to temperatures of 150 to 250°. Groenvik, Bull. soc. chim., [2] 25, 178 (1876); Kalckhoff, Ber., 16, 1828 (1883); Bender, ibid., 19, 2269 (1886); Ransom, ibid., 31, 1063 (1898), and Am. Chem. J., 23, 19 (1900).

(9) Kalckhoff, Ber., 16, 1828 (1883).