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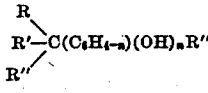
ALKYL PHENOLS

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No Drawing. Application December 29, 1931, Serial No. 583,704

7 Claims. (Cl. 260—154)

This invention relates to new alkylated hydroxy derivatives of aromatic hydrocarbons containing in the alkyl group a carbon atom attached to the aromatic nucleus and to not less than two other carbon atoms. These compounds comprise the secondary alkyl derivatives of phenols, cresols, resorcinols, and the like, and the tertiary alkyl derivatives of cresols, resorcinols, and similar substituted phenols. These compounds may be represented by the following formula:



In the above formula R and R' represent alkyl radicals, R'' represents either an alkyl radical or a hydrogen atom, R''' represents either an alkyl radical containing not more than four carbon atoms, or one of the hydrogen atoms normally attached to the aromatic nucleus, and n is an integer equal to 1 or more but not greater than the capacity of the aromatic nucleus permits, considering the alkyl constituents attached to the nucleus. The integer n is ordinarily 1 or 2. The total number of carbon atoms in the alkyl radicals is ordinarily not greater than 8. The secondary or tertiary carbon atom (C) in the above formula may be secondary in all cases satisfying the formula as already described, but is tertiary only in cases where n is greater than 1, or where R''' is an alkyl radical.

The alkyl radicals attached to the carbon atom (C) may also be attached to each other by carbon-to-carbon linkages, and cyclo-alkyl derivatives are contemplated as within the scope of this invention.

This invention relates both to the compounds as prepared by the ordinary methods by which are usually prepared mixtures of isomers, and to the compounds in their pure state.

These compounds may be prepared by reaction of unsaturated hydrocarbons and phenols in the presence of strong, preferably concentrated, sulfuric acid, as described in my co-pending application Serial No. 522,177, filed March 12, 1931. The process will be understood from the following description:

To the phenol there is added an equivalent or greater amount of moles of strong, preferably concentrated, H_2SO_4, and the unsaturated hydrocarbon is then added slowly with stirring. With higher secondary or with tertiary olefines such as the olefines containing more than three carbon atoms some cooling may be applied so as to keep the reaction mixture at or near room temperature while with lower boiling secondary olefines, such as propylene, gentle heating (up to 60°–70° C.) may be necessary for a practical speed of reaction. Any olefine of the aliphatic series above ethylene, or cyclo olefines, such as cyclo hexene, are satisfactory unsaturated hydrocarbons for this reaction. The phenols used in the reaction may be monohydric or polyhydric phenols, such as phenol, the cresols, resorcinol, or they may be hydroxyl compounds containing condensed nuclei, such as naphthol.

The sulfuric acid must be strong acid. Concentrated (93–97%) acid is preferable in most cases, although 90% or even more diluted acid will also be satisfactory. Similarly, stronger acid can also be used. The lower and upper limits of concentration of the sulfuric acid used may not be stated in definite figures because they depend on the nature of the olefine and phenol which take part in the reaction.

The following examples are specific illustrations of this process as applied to the preparation of secondary hexyl phenol and secondary hexyl resorcinol but it is understood that this process is applicable for the preparation of all the hydroxy aromatic derivatives of this invention:

1120 cc. hexene and 1000 cc. commercial cresol were mixed and then 670 cc. of 95% sulfuric acid added while the mixture was stirred and cooled with water. The stirring was continued for eight hours, then about three liters of water were added. The aqueous acid layer was drawn off and 1½ liters of water added to the upper layer. This mixture was then refluxed and distilled slowly at the same time whereby 30 cc. of hexene were recovered as overhead product. The refluxing was then interrupted, the aqueous layer removed and a liter of fresh water added, after which the refluxing was continued for a while. The mixture was then allowed to settle, the lower aqueous layer drawn off and the upper layer was subjected to distillation in vacuo under pressure of 3–1 mm. 1235 cc. of products distilled over below 192° C. (under 1–2 mm. pressure) and were recovered after condensation. These products were then treated with aqueous alkali and the alkylated phenolic products removed with aqueous alkali, then recovered after acidifying the alkali solution. There were thus finally obtained 816 cc. of aryl alkyl ethers and 293 cc. of alkylated phenols.

In another similar experiment with hexene the distillation was carried out at atmospheric pressure and the alkylated phenols were again removed from the aryl alkyl ether by means of aqueous alkali. The main body of the finally obtained alkylated phenolic product boiled between 260–270° C.

In another experiment 200 grams of resorcinol, 350 cc. of hexene and 110 cc. of 95% sulfuric acid were treated as in the preceding example, with the only difference that carbon tetrachloride was added to facilitate the stirring. After separation of the aqueous acid layer 2½ liters of water were added and the mixture refluxed and slowly

distilled. Some low boiling product came over and 465 grams residual crude product was obtained, which was submitted to distillation in vacuo under a pressure varying from 6–2 mm. The product boiled between the temperatures of 245–320° C., the main part of it coming over between 285–300° C. 25% of this final product was found to consist of alkylated phenols and was insoluble in water.

The secondary and tertiary alkyl phenols covered by this invention may also be prepared by other methods, and this invention is not to be limited to any particular method of preparing these compounds. These new phenolic compounds have very marked therapeutic properties being surprisingly powerful as antiseptics and germicides. The phenol coefficients of these compounds as tested with staphylococcus aureus range from about 50 to about 250 or higher. These secondary and tertiary alkyl phenols have the especially desirable feature of being oil soluble and lend themselves readily to the preparation of powerful oil soluble germicides. These compounds or their solutions in oil are of particular advantage for use in medicinal creams such as cold creams and other skin preparations, nasal and throat applications, heavy white oils to be taken internally, and in baby oils; in all of which compositions they are particularly valuable as disinfectants and germicides. These products may also be used in timber preserving oils and compounds in which they act as repellent and toxic agents against borers and similar insects and are of very great value as powerful fungicides.

Among the new secondary and tertiary alkyl phenols which may be obtained by the above methods are the following which are given together with their appearances, boiling points and refractive indexes:

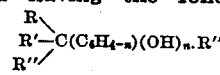
Compound	Appearance	Boiling point	Refractive index N_D
		°C.	°C.
Secondary amyl phenol $C_5H_{11}(C_6H_4)OH$.	Colorless liquid	238–244	1.5140 at 26.2
Secondary hexyl phenol $C_6H_{13}(C_6H_4)OH$.	do	250–260	1.5189 at 24.5
Secondary hexyl cresol $C_6H_{13}(C_6H_3)(OH).CH_3$.	do	259–263	1.5120 at 24.5
Secondary heptyl phenol $C_7H_{15}(C_6H_4)OH$.	do	270–285	1.5199 at 26.2
Tertiary amyl cresol $C_5H_{11}(C_6H_3)(OH).CH_3$.	do	207–251	1.5230 at 25.
Diisopropyl phenol $[(CH_3)_2CH]_2(C_6H_3)OH$.	do	231–242	1.5140 at 24.5
Secondary hexyl resorcinol $C_6H_{13}(C_6H_3)(OH)_2$.	do	155–180 at 1 mm. pressure	1.5233 at 27.2

The secondary hexyl resorcinols are especially powerful antiseptics, germicides and fungicides, and are greatly preferred over the normal hexyl resorcinols for these uses. The secondary hexyl resorcinols are substantially odorless and are more soluble in mineral oils than are the corresponding normal compounds.

This invention is a continuation in part of my co-pending application Serial No. 522,177 filed March 12, 1931.

I claim:

1. Alkylated hydroxy derivatives of aromatic hydrocarbons containing in the alkyl group a carbon atom attached to the aromatic nucleus and to not less than two other carbon atoms selected from the group consisting of secondary alkyl derivatives of phenols and substituted phenols, and tertiary alkyl derivatives of substituted phenols, and having the following formula:

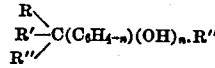


having not less than 5 nor more than 8 carbon atoms in the



alkyl radical, and having valuable therapeutic properties as antiseptics and germicides; R and R′ representing alkyl radicals, R″ representing a member of the group consisting of an alkyl radical and a hydrogen atom, R‴ representing a member of the group consisting of an alkyl radical containing not more than four carbon atoms and one of the hydrogen atoms normally attached to the aromatic nucleus.

2. Alkylated hydroxy derivatives of aromatic hydrocarbons containing in the alkyl group a carbon atom attached to the aromatic nucleus and to not less than two other carbon atoms selected from the group consisting of secondary alkyl derivatives of phenols and substituted phenols, and tertiary alkyl derivatives of substituted phenols, and having the following formula:

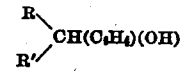


having more than 5 but less than 8 carbon atoms in the



alkyl radical, and having valuable therapeutic properties as antiseptics and germicides; R and R′ representing alkyl radicals, R″ representing a member of the group consisting of an alkyl radical and a hydrogen atom, R‴ representing a member of the group consisting of an alkyl radical containing not more than four carbon atoms and one of the hydrogen atoms normally attached to the aromatic nucleus.

3. Secondary alkyl phenols having the following formula:



having 6 carbon atoms in the alkyl radicals, and having valuable therapeutic properties as an antiseptic and germicide; R and R′ representing alkyl radicals.

4. Secondary amyl phenols, having the following formula:

$$C_5H_{11}(C_6H_4)OH$$

being colorless liquids boiling at 238 to 244° C., having a refractive index N_D=1.5140 at 26.2° C., and being a valuable therapeutic agent as an antiseptic and germicide.

5. Secondary hexyl phenols having the following formula:

$$C_6H_{13}(C_6H_4)OH$$

being colorless liquids boiling at 250 to 260° C., having a refractive index N_D=1.5189 at 24.5° C., and being a valuable therapeutic agent as an antiseptic and germicide.

6. Secondary heptyl phenols, normally liquid, boiling at about 270–285° C., having a refractive index N_D=1.5199 at 26.2° C. and having marked germicidal properties.

7. Composition of matter composed mainly of a hydroxylated aromatic nucleus with a carbon atom attached directly thereto and which is also directly attached to two other carbon atoms, forming a secondary alkyl group containing more than 4 but less than 7 carbon atoms.

HYYM E. BUC.

DISCLAIMER

2,104,412.—*Hyym E. Buc*, Roselle, N. J. ALKYL PHENOLS. Patent dated January 4, 1938. Disclaimer filed July 13, 1940, by the assignee, *Standard Oil Development Company*.

Hereby enters this disclaimer as to claims 3, 4, 5, and 7 and to that part of claims 1 and 2 which is within the scope of claims 3, 4, 5, and 7.

[*Official Gazette August 6, 1940.*]