

The Preparation of Derivatives of Stearophenone and Related Compounds

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Many investigators have shown that fatty-acid molecules can be tailored to meet requirements as surface-active agents, as auto-oxidation inhibitors or stabilizers, and as therapeutic agents.

The oldest surface-active agent is soap, whether made by saponification of fats with alkali or in more complex forms such as neutralization of fatty-acids with amines.

The addition of a hydrocarbon side chain and a sodium sulfonate group to an aromatic nucleus forms alkyl aryl sulfonates. In such compounds, one has a structure related to soap by a series of easy transitions. Benzene sulfonic acid shows some surface-active properties, toluenesulfonic acid more. Practically a longer side chain than the methyl radical is desirable to produce an adequate hydrocarbon character. The simplest form is a benzene derivative such as sodium kerylbenzenesulfonate, keryl meaning an aliphatic radical of the order of magnitude of that of the kerosene fraction.

This paper presents the results of a study in the preparation of compounds such as *n*-octadecylbenzene and *p*-chlorooctadecylbenzene which may be used as intermediates in the production of surface-active agents like sodium octadecylbenzenesulfonate and trimethyloctadecylbenzeneammonium chloride.

The procedures used in the synthesis of the halogenated octadecylbenzenes are illustrated by the equations

1. $\text{CH}_3(\text{CH}_2)_{16}\text{CH}_2\text{Cl} + \text{C}_6\text{H}_5\text{X} \rightarrow \text{CH}_3(\text{CH}_2)_{16}\text{CH}_2\text{C}_6\text{H}_4\text{X} + \text{HCl}$, or
2. a. $\text{CH}_3(\text{CH}_2)_{16}\text{COCl} + \text{C}_6\text{H}_5\text{X} \rightarrow \text{CH}_3(\text{CH}_2)_{16}\text{COC}_6\text{H}_4\text{X} + \text{HCl}$, and
b. $\text{CH}_3(\text{CH}_2)_{16}\text{COC}_6\text{H}_5\text{X} + 2\text{H}_2 / (\text{Zn}/\text{Hg}/\text{HCl}) \rightarrow \text{CH}_3(\text{CH}_2)_{17}\text{C}_6\text{H}_4\text{X} + \text{H}_2\text{O}$

It was found that the chlorooctadecylbenzenes prepared by the Friedel-Crafts reaction of *n*-octadecyl bromide with chlorobenzene do not have the same distilling range or melting point as the chlorooctadecylbenzenes prepared by the modified Clemenson reduction of the chlorostearophenones. This has led to the belief that the Friedl-Crafts reaction of *n*-octadecyl bromide with a halogenated benzene nucleus results in a

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secondary octadecyl radical being attached to the benzene nucleus instead of a *n*-octadecyl radical.

Ammonolysis of *p*-chlorooctadecylbenzene was carried out, using pressure, heat, and a catalyst, to form *p*-aminooctadecylbenzene. The amine is very unreactive, even to the formation of a hydrochloride.

Several derivatives of the various ketones synthesized, were made in order to characterize the individual ketones.

Experimental

A. Preparation of chlorooctadecylbenzene by the Friedel-Crafts reaction of *n*-octadecyl bromide with chlorobenzene

The *n*-octadecyl bromide was prepared by bubbling dry hydrogen bromide through molten *n*-octadecyl alcohol.

The *n*-octadecyl bromide so prepared was reacted with excess chlorobenzene in the presence of anhydrous aluminum chloride. Upon vacuum distillation of the resultant oil two separate fractions were identified. A fraction distilling at 205° C. (1 mm.) was proved to be *p*-chlorobenzoic acid. In a like manner a fraction distilling at 195° C. (1 mm.) was proved to be *o*-chlorooctadecylbenzene.

The theoretical molecular weight for both compounds is 365. The molecular weight for the fraction distilling at 205° C. (1 mm.) was found to be 360 and for the fraction distilling at 195° C. (1 mm.) 356.

B. Preparation of *p*-chlorooctadecylbenzene by the reduction of *n*-heptadecyl *p*-chlorophenyl ketone

The *n*-heptadecyl *p*-chlorophenyl ketone was prepared in the same manner as Claus and Hafelin¹ prepared *n*-heptadecyl phenyl ketone. The ketone was reduced to *p*-chloro-*n*-octadecylbenzene using the modified Clemenson method as suggested by Adams². Upon vacuum distillation of the resultant oil a fraction distilling at 220-225° C. (1 mm.) and melting at 42-43° C. was proved to be *p*-chloro-*n*-octadecylbenzene.

The theoretical molecular weight is 365. The molecular weight as determined was found to be 359.

¹ Claus and Hafelin, *J. Prakt. Chem.*, **54**:399 (1896).

² Adams, R., Buchmann, W. E., Fieser, L. F., Johnson, J. R., and Synder, H. R., "Organic Reactions", Vol. 1, John Wiley and Sons, Inc., New York (1942).

TABLE I.—Compounds Prepared

Compound	Dist. Range (1 mm.)	M. p., °C.
<i>n</i> -Octadecylbenzene	195-205°C. (4 mm.)	35-36
<i>n</i> -Heptadecyl Phenyl Ketone		63.5-64.5
<i>n</i> -Heptadecyl <i>o</i> -Chlorophenyl Ketone	230-235	63
<i>n</i> -Heptadecyl <i>p</i> -Chlorophenyl Ketone	250-260	76
<i>o</i> -Chloro- <i>n</i> -octadecylbenzene	210-215	36-37
<i>p</i> -Chloro- <i>n</i> -octadecylbenzene	220-225	42-43
<i>p</i> -Amino- <i>n</i> -octadecylbenzene	245-251	
	Detr. %N=4.01	Theor. %N=4.06
<i>p</i> -Bromo- <i>sec.</i> -octadecylbenzene	235	
<i>o</i> -Bromo- <i>sec.</i> -octadecylbenzene	195	
<i>n</i> -Heptadecyl <i>p</i> -Chlorophenyl Ketone		94
<i>n</i> -Heptadecyl <i>o</i> -Chlorophenyl Ketone		85
<i>n</i> -Heptadecyl <i>p</i> -Chlorophenol Ketoxime		42
<i>n</i> -Heptadecyl <i>p</i> -Chlorophenyl Ketone Semicarbazone		85
<i>n</i> -Heptadecyl <i>o</i> -Chlorophenyl Ketone Semicarbazone		66

Summary

The chlorooctadecylbenzenes prepared by the Friedel-Crafts reaction of *n*-octadecyl bromide with chlorobenzene do not have the same distilling range or melting points as the chlorooctadecylbenzenes prepared by the modified Clemenson reduction of the chlorostearophenones. This has led to the belief that the Friedel-Crafts reaction of *n*-octadecyl bromide with a halogenated benzene nucleus results in a secondary octadecyl radical being attached to the benzene nucleus instead of a *n*-octadecyl radical.

Ammonolysis of *p*-chlorooctadecylbenzene was carried out using pressure and heat, to form *p*-aminooctadecylbenzene.

Several derivatives of the various ketones were made in order to characterize the individual ketones.