is run in the following manner on batteries containing the separators to be tested:

1. Charge at 10 amperes for 6 minutes and 25 seconds.
2. Allow to rest for 3 minutes.
3. Discharge at a rate of 300 amperes for 5 seconds.
4. Allow to rest for 30 seconds.

This cycle is repeated continuously for 6 days. On the seventh day a capacity test is made on the battery and the battery is recharged. The cycle is again repeated continuously for 6 days, and the test is continued in the same manner as long as desired. As the battery attains a temperature of 110° to 120° F. (43.3° to 48.9° C.), the test becomes quite severe. Figure 3 shows sections of latex and of Port Orford cedar separators removed from standard thirteen-plate batteries after a life test of twelve thousand cycles. The battery containing the wood separators had failed, but the one containing the latex separator had not. Life tests of twenty-four thousand cycles have resulted in disintegration of the plates without failure of the latex separators.

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High-Molecular-Weight Alkyl-Aryl Ketones

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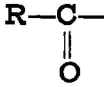
A number of ketones of the type  $R-\underset{\underset{O}{\|}}{C}-R'$**, where R is an aryl and R′ an alkyl radical, have been synthesized. Two general methods of preparation were employed—the Friedel-Crafts using the aliphatic acid chloride and the Grignard reaction employing the aliphatic nitrile. The ketones described are waxlike solids insoluble in water, alcohol, and acetone, and very soluble in solvents such as benzene, toluene, kerosene, and turpentine. Their properties are discussed and several uses indicated.**

ONLY a comparatively small number of high-molecular-weight alkyl-aryl ketones have been previously synthesized. The present paper describes the preparation and properties of a number of new compounds of this type. With the exception of those ketones which are liquid at room temperature, the new ketones are waxlike solids. When highly purified by repeated recrystallization they still retain their waxlike properties. All are characterized by low viscosities in the molten state, high flash and fire points, and resistance to oxidation when heated for prolonged periods at 350° F. These ketones have the property of adhering to metallic surfaces, forming permanent lubricating and protective films.

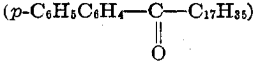
In reviewing the work of previous investigators, we find that Claus and Häfelin (*2*) prepared the following by the action of acid chlorides upon the corresponding hydrocarbons: phenyl heptadecyl ketone, *m*-xylyl heptadecyl ketone, *p*-xylyl heptadecyl ketone, *p*-tolyl pentadecyl ketone, and mesityl pentadecyl ketone. Krafft (*4*) prepared *p*-tolyl heptadecyl ketone, *m*-xylyl pentadecyl ketone, *p*-ethoxyphenyl pentadecyl ketone, and dimethylresorcyl pentadecyl ketone by a similar method. α-Naphthyl heptadecyl ketone was prepared by Ryan and Nolan (*6*) by the action of the corresponding Grignard reagent upon stearamide. The same authors also prepared α-naphthyl pentadecyl ketone and *p*-tolyl pentadecyl ketone using palmitamide. Rosenmund and Lohfert (*5*) prepared 3,4-dihydroxyphenyl heptadecyl ketone by heating catechol distearate with aluminum chloride, and Auwers (*1*) prepared *p*-hydroxyphenyl pentadecyl ketone by heating *p*-ethoxyphenyl pentadecyl ketone with aluminum chloride.

Methods of Preparation

The writers prepared a number of mixed ketones and investigated some of their chemical and physical properties. Two general methods of preparation, the Friedel-Crafts reaction and the Grignard synthesis, were employed and comparisons made to establish the identity of the products. The synthesis of diphenyl heptadecyl ketone is typical of the preparation of these compounds by the Friedel-Crafts reaction:

A 15.4-gram (0.1-mole) sample of diphenyl was dissolved in 200 cc. carbon disulfide and 30.2 grams (0.1 mole) stearyl chloride. This mixture was cooled in ice to approximately 10° C., and 13.3 grams (0.1 mole) aluminum chloride were added slowly over a period of one-half hour with constant stirring and refluxed until no further evolution of hydrochloric acid was observed.

TABLE I. ARYL-ALKYL KETONES PREPARED

Product	Method of Preparation	Starting Materials	Physical Properties	Other Observations
Diphenyl heptadecyl ketone  $(p\text{-}C_6H_5C_6H_4\text{—}\underset{\underset{O}{\Vert}}{C}\text{—}C_{17}H_{35})$	Friedel-Crafts	Diphenyl, stearyl chloride ($C_{17}H_{35}COCl$)	Wax, d_{20}^{20} 0.9384, m. p. 108–9° C.	Flash point 512° F. (266.7° C.), fire point 542° F. (283.3° C.)
	Grignard	Diphenylmagnesium bromide, stearonitrile	Wax, d_{20}^{20} 0.9380, m. p. 109° C.	Yield 67%
Diphenyl tridecyl ketone	Friedel-Crafts	Diphenyl, palmityl chloride ($C_{15}H_{31}COCl$)	Waxlike, m. p. 102–3° C.	....
	Grignard	Diphenylmagnesium bromide, palmitonitrile	M. p. 103° C.	....
Diphenyl undecyl ketone	Friedel-Crafts	Diphenyl lauryl chloride ($C_{11}H_{23}COCl$)	Waxlike, m. p. 97–8° C.	....
	Grignard	Diphenylmagnesium bromide	M. p. 97–8° C.	Yield 61.5%
p-Methyldiphenyl heptadecyl ketone	Friedel-Crafts	*p*-Methyldiphenyl, stearyl chloride	Waxlike, m. p. 105–6° C.	....
p-Chlorodiphenyl heptadecyl ketone	Friedel-Crafts	*p*-Chlorodiphenyl, stearyl chloride	Waxlike, m. p. 96–7° C.	....
Phenoxyphenyl heptadecyl ketone	Friedel-Crafts	Diphenyl ether, stearyl chloride	Lustrous wax, m. p. 68° C.	Expands on cooling, flash point 525° F. (273.9° C.), fire point 556° F. (291.1° C.)
	Grignard	Phenoxyphenylmagnesium bromide, stearonitrile	M. p. 68° C.	Yield 78.5%
Phenoxyphenyl tridecyl ketone	Friedel-Crafts	Diphenyl ether, palmityl chloride	Waxlike, m. p. 53.5–54.5° C.	....
Phenoxyphenyl undecyl ketone	Friedel-Crafts	Diphenyl ether, lauryl chloride	Soft wax, m. p. 45–6° C.	....
	Grignard	Phenoxyphenylmagnesium bromide, lauronitrile	M. p. 46° C.	Yield 80.0%
p-Methylphenoxyphenyl heptadecyl ketone	Grignard	*p*-Methylphenoxyphenylmagnesium bromide, stearonitrile	Waxlike, m. p. 77–8° C.	....
p-Nitrophenoxyphenyl heptadecyl ketone	Friedel-Crafts	*p*-Nitrodiphenyl ether, stearyl chloride	Hard wax, m. p. 177–8° C.	....
2-Furyl heptadecyl ketone	Friedel-Crafts	Furan, stearyl chloride	Soft wax, m. p. 56–7° C.	....
2-Furyl undecyl ketone	Friedel-Crafts	Furan, lauryl chloride	Waxy liquid, b. p. 165–6° C. at 5 mm.	....
	Grignard	2-Furylmagnesium iodide, lauronitrile	B. p. 167–8° C. at 5 mm.	....
5-Methyl-2-furyl heptadecyl ketone	Friedel-Crafts	2-Methylfuran, stearyl chloride	Soft wax, m. p. 68–9° C.	....
2-Dibenzofuryl heptadecyl ketone	Friedel-Crafts	Dibenzofuran, stearyl chloride	Lustrous wax, m. p. 83–4° C.	....
	Grignard	2-Dibenzofurylmagnesium bromide, stearonitrile	M. p. 83–4° C.	Yield 63%
2-Dibenzofuryl undecyl ketone	Friedel-Crafts	Dibenzofuran, lauryl chloride	Soft wax, m. p. 74–5° C.	....
	Grignard	2-Dibenzofurylmagnesium bromide, lauronitrile	M. p. 74–5° C.	Yield 52.5%
2-Stearylcarbazole	Fries (Friedel-Crafts)	Carbazole, stearyl chloride	Wax, m. p. 105–6° C.	....
2-Laurylcarbazole	Fries (Friedel-Crafts)	Carbazole, lauryl chloride	Soft wax, m. p. 101–2° C.	....
2,8-Distearylcarbazole[a]	Fries (Friedel-Crafts)	Carbazole, stearyl chloride	Wax, m. p. 161–2° C.	....
2,8-Dipalmitylcarbazole	Fries (Friedel-Crafts)	Carbazole, palmityl chloride	Wax, m. p. 162° C.	....
2,8-Dimyristylcarbazole	Fries (Friedel-Crafts)	Carbazole, myristyl chloride	Hard wax, m. p. 169° C.	....
2,8-Dilaurylcarbazole	Fries (Friedel-Crafts)	Carbazole, lauryl chloride	Hard wax, m. p. 176° C.	....
2-Stearylthiophene	Friedel-Crafts	Thiophene, stearyl chloride, stannic chloride	Soft wax, m. p. 48–9° C.	....
2-Myristylthiophene	Friedel-Crafts	Thiophene, myristyl chloride, stannic chloride	Colorless, b. p. 205–10° C. at 4 mm.	n_D^{25} 1.4961, d_{25}^{25} 0.9506
2-Laurylthiophene	Friedel-Crafts	Thiophene, lauryl chloride, stannic chloride	Colorless, b. p. 190–5° C. at 4 mm.	n_D^{25} 1.5019, d_{25}^{25} 0.9632
3-Stearyldibenzothiophene	Friedel-Crafts	Dibenzothiophene, stearyl chloride	Soft wax, m. p. 69–70° C.	....
α-Naphthyl heptadecyl ketone	Grignard	α-Bromonaphthalene, stearonitrile	Waxy, m. p. 53–4° C.	Yield 93.5%
α-Naphthyl undecyl ketone	Grignard	α-Bromonaphthalene, lauronitrile	Colorless, b. p. 240–5° C. at 5 mm.	Yield 80.0%

[a] For nomenclature, see Patterson, *J. Am. Chem. Soc.*, **47**, 543 (1925).

The reaction mixture was poured upon a mixture of ice and dilute hydrochloric acid to hydrolyze the complex aluminum compound formed. The hydrolyzed mixture was steam-distilled to remove the carbon disulfide and to complete the hydrolysis, after which the ketone was separated from the water layer by decantation. The ketone was recrystallized from benzene to constant melting point. The same general procedure has been used in large runs (100 moles).

When these ketones were prepared by the Grignard reaction, a standard procedure was employed. The magnesium complex was prepared and the corresponding nitrile added dropwise and refluxed until the Grignard reagent was used up, as evidenced by a negative color test (*3*). The reaction mixtures were hydrolyzed by 10 per cent hydrochloric acid. Satisfactory yields were obtained—for example, 67.0 per cent, in the synthesis of *p*-diphenyl heptadecyl ketone, and 61.5 per cent in the case of *p*-diphenyl undecyl ketone.

The ketones made from carbazole were prepared by the Fries rearrangement. 2-Stearylcarbazole, for example, was prepared by reacting *N*-stearylcarbazole with aluminum chloride, hydrolyzing the product, and subjecting the mixture to steam distillation. The ketones were purified by recrystallizing from carbon tetrachloride. Diketones of carbazole were prepared by using 2 moles of stearyl chloride.

Table I shows the ketones prepared, together with the method of synthesis, starting materials, and physical properties. Aluminum chloride was used as the condensing agent in the Friedel-Crafts reaction unless otherwise indicated.

Attempts to synthesize naphthyl ketones by the Friedel-Crafts reaction resulted in the formation of soft waxes or oils of complex composition. The high degree of unsaturation of naphthalene possibly accounts for its failure to give any substantial yields of definite products under these conditions. The reaction of anthracene under similar conditions was also complex; a reddish brown reaction product was obtained which did not yield readily to purification. A product (melting point, 48° C.) was finally obtained after repeated crystallization, from alcohol but it apparently still contained impurities.

The reaction of xylene with stearyl chloride in the presence of aluminum chloride gave a light yellowish liquid (boiling at 210–280° C. and 4 mm.). The physical characteristics of this mixture are of unusual interest. Its viscosity is 85 seconds Saybolt at 100° F. (37.8° C.), flash point 460° F. (237.8° C.), fire point 510° F. (265.6° C.), specific gravity 0.901 at 28° C., and refractive index 1.4930 at 20° C. It is extremely resistant to oxidation upon prolonged heating at 350° F. (176.7° C.). Commercial xylene consisting of *o*-, *m*-, and *p*-xylenes was used in its preparation, and six isomeric monosubstitution products are theoretically possible. In the presence of aluminum chloride there is a tendency for methyl groups to migrate, both inter- and intramolecularly, and it is believed that this partially accounts for the complexity of this product. It is of interest to note that Claus and Häfelin (*2*) found the melting point of *p*-xylyl heptadecyl ketone to be 50° C. and that of *m*-xylyl heptadecyl ketone, 39° C.

Solubilities

The ketones mentioned are, without exception, insoluble in water and glycerol, very slightly soluble in ethyl alcohol and acetone, slightly soluble in *n*-butyl alcohol, and very soluble in benzene, carbon tetrachloride, kerosene, toluene, chloroform, and turpentine. The solubilities of diphenyl heptadecyl ketone are typical, and are shown in Table II.

Ketones containing the phenoxyphenyl radical show interesting solubility phenomena. Instead of crystallizing from the solvent when their solubility is exceeded, very stiff gels are formed. This has been observed with solutions of phenoxyphenyl ketones in kerosene, benzene, carbon tetrachloride, toluene, and turpentine. The gels are stable and did not separate after standing several months.

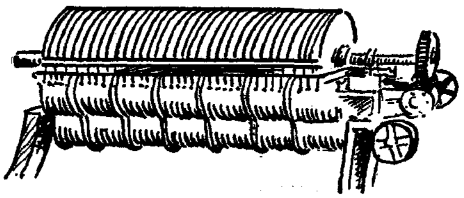


TABLE II. SOLUBILITIES OF DIPHENYL HEPTADECYL KETONE

Solvent	Temp. ° C.	Solubility Grams/ 100 cc.
Ethyl alcohol	27.0	0.082
Glycerol	50.0	0.000
Acetone	15.0	0.202
	24.0	0.400
n-Butyl alcohol	9.0	0.400
	45.0	1.00
	70.5	8.00
Benzene	26.0	4.00
	50.5	24.02
	61.0	80.04
Toluene	31.0	4.00
	48.0	20.00
	65.5	80.00
Carbon tetrachloride	24.0	4.01
	52.0	30.02
	80.0	80.00
Chloroform	20.0	8.00
	43.0	32.00
	54.0	64.00
Kerosene	30.0	1.00
	47.5	4.00
	75.0	48.00
Turpentine	22.0	1.00
	41.5	4.00
	73.5	60.00

Specific Properties and Industrial Uses

Some properties of these new ketones have been investigated. Because of their waxlike nature, resistance to chemical change, and relatively high melting points, their use as wax substitutes suggests itself. Tests show them to impart high permanent luster to wood surfaces. Preliminary tests, as yet not completed, indicate them to possess high insulating properties. Those prepared from diphenyl ether and also from carbazole show exceptional properties as to foam prevention in boilers operating under 200 pounds per square inch (14.1 kg. per sq. cm.) steam pressure. Their effect upon lubricants when added to the lubricant in small amounts has been extensively studied by the writers, as has also their use as lubricants per se or when blended with various proportions of other lubricating materials. When used in this connection they indicate the formation of a lubricating film which is exceedingly difficult to remove.

The effect of these ketones upon the viscosity index, pour point, and stability of lubricants has also been determined. The results will be reported later. They have been shown to be noncorrosive when exposed to metal surfaces, such as cadmium silver, for periods ranging from 12 to 30 hours at temperatures from room temperature to 350° F. (176.7° C.). Prolonged tests are now under way to ascertain their effectiveness in preventing corrosion of metal parts exposed to such conditions as salt brine and other corrosive substances. Other properties are being investigated, such as their plasticizing ability for oxidized oil films and nitrocellulose films.

Acknowledgment

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