H, 14.83; molecular weight, 380; melting point, 59°.[3]

The fraction soluble in warm methanol was recrystallized repeatedly from ethyl acetate. The final melting point was 52–54° (uncorrected). Analysis gave: C, 85.07; H, 15.08%. Calcd. for pentacosane ($C_{25}H_{52}$): C, 85.37; H, 14.63; melting point, 54°.[3]

It is not certain whether this fraction consists of a pure hydrocarbon, or a mixture of two or more hydrocarbons. On crystallizing from ethyl acetate on a microscope slide it has the form of homogeneous hexagonal plates.

Besides the solubilities mentioned above, these fractions are very soluble in chloroform and benzene, soluble in hot and insoluble in cold acetone and ethanol, and insoluble in water and alkali.

They contain no nitrogen or phosphorus, have no acid or saponification number, do not reduce Fehling's solution, and do not absorb bromine from chloroform solution. They have been found to have no oestrogenic activity.

The procedure outlined above was applied to eight liters of non-pregnant female urine which had been aged for two weeks. From the petroleum ether was obtained 3.8 mg. of an impure waxy substance from which it was not possible to isolate any crystalline material melting below 120°.

The same procedure was also applied to two samples of male urine of eight liters each. One of these was a year old; the other had been aged two weeks. Like the non-pregnant female urine each yielded a few milligrams of impure waxy substance from which no crystalline material melting below 120° could be isolated. If these hydrocarbons occur in non-pregnant female, and male, urine they must do so in an amount far less than in urine of pregnancy. The physiological source of these hydrocarbons during pregnancy raises many interesting speculations.

The authors regret that factors beyond their control have prevented an extension of this investigation. They wish to thank Dr. F. R. Eldred, Director of Research, of Reed and Carnrick, for his kind permission to publish this work, and Dr. J. B. Niederl of Washington Square College, New York University, for the micro analyses and molecular weight determinations.

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[3] Hildebrand and Wachter, THIS JOURNAL, **51**, 2487 (1929).

A CONTRIBUTION FROM THE
LABORATORIES OF REED AND CARNRICK
JERSEY CITY, N. J.

RECEIVED OCTOBER 25, 1935

Preparation of Alpha-Naphthoic Acid

BY D. J. LODER[1] AND F. C. WHITMORE

During some work which demanded the preparation of a considerable amount of pure alpha-naphthoic acid, all of the regular methods of preparing this substance were tried with only mediocre success. At the same time some studies were being carried out on the preparation of tertiary alcohols by the action of the Grignard reagent with diethyl carbonate and it had been observed that when the Grignard reagent was "sterically hindered" the reaction could be stopped at the ketone stage or even at the ester stage. Consequently, alpha-naphthylmagnesium bromide (5 moles in 2.5 liters of absolute ether) was added slowly to a solution of ethyl carbonate (7.5 moles in 500 cc. of dry ether). Treatment of the mixture with a slight excess of 30% sulfuric acid, separation of the ether layer and isolation in the usual way gave a 70% yield of redistilled ethyl alpha-naphthoate boiling at 143–144.5° at 3 mm. Hydrolysis of the ester gave over a 90% yield of pure alpha-naphthoic acid.

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The Mechanism of the Addition of Halogens to Ethylenic Linkages

BY RICHARD A. OGG, JR.

The addition in solution of halogens to an ethylenic linkage is assumed by Ingold[1] to proceed through the formation of an intermediate positive carbonium ion, as $\mathrm{RCHBr{-}C^{+}HR}$, which subsequently adds a halide ion. Experiment indicates positive carbonium ions to be configuratively unstable,[2,3] and hence this mechanism would lead one to expect identical products (*i. e.*, a mixture of meso and *dl* dihalides) from *cis–trans* isomers, in contradiction to experimental fact.

Carothers[4] has proposed that addition reactions of ethylenic linkages are initiated by an internal ionization of the double bond, followed by addition of the reagent molecule at the positive end,

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[1] C. K. Ingold, *Chem. Reviews*, **15**, 225 (1934).

[2] E. S. Wallis and F. H. Adams, THIS JOURNAL, **55**, 3838 (1933).

[3] E. Bergmann and M. Polanyi, *Naturwissenschaften*, **21**, 378 (1933).

[4] W. H. Carothers, THIS JOURNAL, **46**, 2227 (1924).