nane-3β,17α,20β-triol 20-sulfate (XI). The analytical sample melted at 133–141°.

Anal. Calcd. for $C_{21}H_{35}NaO_6S$: C, 57.51; H, 8.05; S, 7.31. Found: C, 57.29; H, 8.34; S, 7.57.

Solvolysis of Sulfate XI with Hydrochloric Acid.—A solution of 10 mg. of 5α-pregnane-3β,17,20β-triol 20-sulfate (XI) in 8 ml. of 1 *N* hydrochloric acid was heated on the steam bath for 1 hr. It was then extracted with ethyl acetate, washed with base and water, and dried over sodium sulfate; the solvent was evaporated to give 6 mg. of product. Preparative thin layer chromatography of the product on silica gel G with cyclohexane–ethyl acetate (1:1) gave materials with R_f of 0.4 and 0.2. Acetylation of substance with R_f 0.4 yielded 3β-acetoxy-17α-methyl-D-homo-5α-androstan-17a-one (IV). Recrystallizations from methanol gave 0.5 mg. of the D-homo ketone IV, m.p. 165.5–167.5°; the infrared spectrum in potassium bromide dispersion was identical with that of the authentic sample.

The substance with R_f 0.2 on acetylation yielded 5α-pregnane-3β,17α,20β-triol 3,20-diacetate verified by its infrared spectrum.

Solvolysis of Sulfate XI in Moist Acidic Ethyl Acetate.—A solution of 6.6 mg. of sulfate XI in 10 ml. of 0.1 *N* sulfuric acid solution and 2.5 g. of sodium chloride was extracted with 40 ml. of ethyl acetate. The moist acidic ethyl acetate solution was incubated at 37° for 24 hr. and washed with base and water; the solvent was evaporated to give 3 mg. of 5α-pregnane-3β,17α,20β-triol, m.p. 185–197°. No trace of the D-homo 17a-ketone could be detected.

Treatment of Sulfate XI with Base.—A solution of 8 mg. of sulfate XI in 1 ml. of methanol and 4 ml. of 5% sodium hydroxide solution was refluxed for 2 hr. It was extracted with ethyl acetate, washed with water, and dried over sodium sulfate; the solvent was evaporated to give 3.5 mg. of product. Acetylation with pyridine–acetic anhydride yielded 4 mg. of 17α,20α-oxido-5α-pregnan-3β-ol 3-acetate (VI), R_f 0.67, on a thin layer of silica gel G with ethyl acetate–cyclohexane (1:1). Recrystallization from methanol yielded oxide VI, m.p. 167–169°; the infrared spectrum in potassium bromide dispersion was identical with that of the authentic sample.

Acknowledgment.—We wish to acknowledge the interest and support of Dr. T. F. Gallagher throughout this investigation. We are grateful to Mrs. Beatrice S. Gallagher for the determination and interpretation of the infrared spectra.

Tetranonacontane[1]

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A general method of synthesis for high molecular weight *n*-paraffin hydrocarbons has been applied to the synthesis of tetranonacontane. The viscosities and densities at three temperatures of this hydrocarbon are reported.

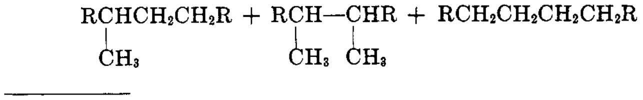
Very high molecular weight *n*-paraffins are of interest because they provide model systems for studying and relating the properties of linear polymers to their molecular weights.[3,4] In addition, a number[5,6] of empirical and theoretical correlations of physical properties as a function of molecular weight have been proposed for these "simplest" hydrocarbons and it is important to determine whether such correlations are valid, particularly at the higher molecular weights where many configurations are possible in both the liquid and solid state. However, only a few syntheses of *n*-paraffins larger than C_{50} have been reported and physical property data are almost nonexistent.

All of the syntheses in the literature have a Wurtz reaction as a key step. Carothers[7] synthesized *n*-pentacontane ($C_{50}H_{102}$), *n*-hexacontane ($C_{60}H_{122}$), and *n*-heptacontane ($C_{70}H_{142}$) by a bifunctional Wurtz reaction from decamethylene dibromide and finely divided sodium in dry ether. The hydrocarbons $C_{20}H_{42}$, $C_{30}H_{62}$, and $C_{40}H_{82}$ represented 25% of the product and were separated by fractional crystallization. The remainder was separated by molecular distillation into fractions of $C_{50}H_{102}$, $C_{60}H_{122}$, $C_{70}H_{142}$, and a residue thought to consist of higher polymers. No properties but the melting points were reported. Doolittle and Peterson[8] prepared *n*-tetrahexacontane from 1-bromodotriacontane (derived from the C_{32}-alcohol of carnauba wax) and sodium sand in dry ether. In addition to the melting point these authors determined the densities and viscosities over a range of temperatures.

The pioneering syntheses of *n*-dooctacontane ($C_{82}H_{166}$) and *n*-hectane ($C_{100}H_{202}$) were accomplished by Ställberg, Ställberg-Stenhagen, and Stenhagen[9] who used the Wurtz reaction to couple, in the case of *n*-hectane, two 1-iodopentacontane ($C_{50}H_{101}I$) molecules. Melting points and certain crystal data were obtained.

This paper reports a relatively large-scale (100 g.) synthesis of *n*-tetranonacontane. The synthetic route used avoids the Wurtz reaction and is applicable to the preparation of other high molecular weight *n*-paraffins. In addition, the densities and viscosities of *n*-C_{94} over a range of temperature are reported and compared with similar data for previously studied straight-chain hydrocarbons.

Synthesis.—The synthetic route used in the present work is outlined in Scheme I. The Wurtz coupling reaction was avoided because it has been observed in this laboratory[10] and elsewhere that the formation of branched-chain products frequently accompanies the formation of the desired straight-chain compounds.



$$RCH_2CH_2X + Na \longrightarrow \underset{CH_3}{RCH}CH_2CH_2R + \underset{CH_3}{RCH}\text{—}\underset{CH_3}{CHR} + RCH_2CH_2CH_2CH_2R$$

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(1) Abstracted from a thesis submitted by R. R. Reinhard in partial fulfillment of the requirements for the Ph.D. degree, 1961.

(2) To whom inquiries should be made.

(3) M. G. Broadhurst, *J. Chem. Phys.*, **36**, 2578 (1962).

(4) M. Kuratee and S. Iside, *ibid.*, **23**, 1126 (1955).

(5) M. G. Broadhurst, *J. Res. Natl. Bur. Std.*, **A66**, 241 (1962), and references therein.

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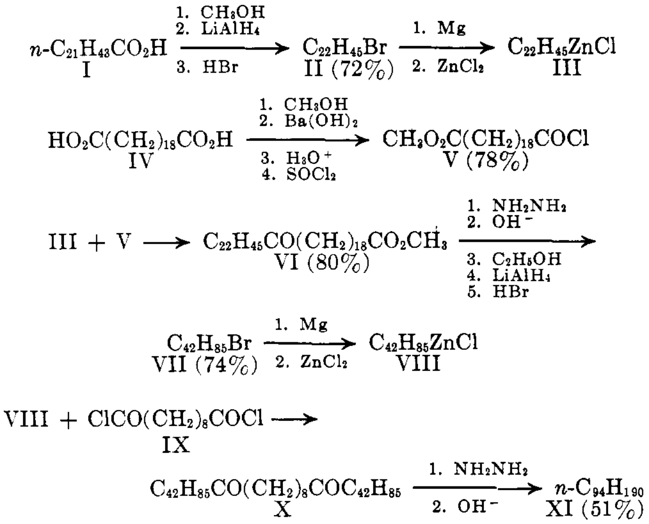
(8) A. K. Doolittle and R. H. Peterson, *ibid.*, **73**, 2145 (1951).

(9) G. Ställberg, S. Ställberg-Stenhagen, and E. Stenhagen, *Acta Chem. Scand.*, **6**, 313 (1952).

(10) S. G. Clark, II, and R. W. Schiessler, unpublished results.

SCHEME I



$$\underset{\text{I}}{n\text{-}C_{21}H_{43}CO_2H} \xrightarrow[\text{3. HBr}]{\substack{\text{1. CH}_3\text{OH}\\ \text{2. LiAlH}_4}} \underset{\text{II (72\%)}}{C_{22}H_{45}Br} \xrightarrow[\text{2. ZnCl}_2]{\text{1. Mg}} \underset{\text{III}}{C_{22}H_{45}ZnCl}$$

$$\underset{\text{IV}}{HO_2C(CH_2)_{18}CO_2H} \xrightarrow[\substack{\text{3. H}_3\text{O}^+\\ \text{4. SOCl}_2}]{\substack{\text{1. CH}_3\text{OH}\\ \text{2. Ba(OH)}_2}} \underset{\text{V (78\%)}}{CH_3O_2C(CH_2)_{18}COCl}$$

$$\text{III} + \text{V} \longrightarrow \underset{\text{VI (80\%)}}{C_{22}H_{45}CO(CH_2)_{18}CO_2CH_3} \xrightarrow[\substack{\text{3. C}_2\text{H}_5\text{OH}\\ \text{4. LiAlH}_4\\ \text{5. HBr}}]{\substack{\text{1. NH}_2\text{NH}_2\\ \text{2. OH}^-}}$$

$$\underset{\text{VII (74\%)}}{C_{42}H_{85}Br} \xrightarrow[\text{2. ZnCl}_2]{\text{1. Mg}} \underset{\text{VIII}}{C_{42}H_{85}ZnCl}$$

$$\text{VIII} + \underset{\text{IX}}{ClCO(CH_2)_8COCl} \longrightarrow$$

$$\underset{\text{X}}{C_{42}H_{85}CO(CH_2)_8COC_{42}H_{85}} \xrightarrow[\text{2. OH}^-]{\text{1. NH}_2\text{NH}_2} \underset{\text{XI (51\%)}}{n\text{-}C_{94}H_{190}}$$

Such impurities are extremely difficult to remove at the higher molecular weights.

During the research preceding the synthesis it was found that many classical reactions which proceeded readily with lower molecular weight reagents gave poor yields at C_{50} and above. The insolubility of reaction intermediates or of reagents tended to stop the desired reaction or to so decrease its rate that undesirable competing reactions became dominant.

For example, the higher molecular weight dialkylcadmium reagents[11] reacted sufficiently slowly with acid chlorides that the competing reaction of acyl halide attack on ether became competitive.[12] As a result the yields of the desired ketones, VI and X, were low. Replacement of the dialkylcadmium reagent by the corresponding alkylzinc reagent[13,14] overcame this difficulty.

In addition, certain reactions were abandoned when it was found very difficult to purify the necessary high molecular weight reagents, reagents whose lower molecular weight homologs may be readily purified by fractional distillation or sublimation.

The purification of the tetranonacontane by chromatography on alumina and crystallization from heptane yielded a product containing some ketone. All attempts to remove this impurity by crystallization or chromatography failed. Treatment with concentrated sulfuric acid at 125° as suggested by Ställberg, *et al.*,[9] gave a pure product.

Properties.—The melting points and solid-phase behavior of the tetranonacontane whose preparation is described here, and other straight-chain paraffins have been discussed elsewhere.[3,5,6,15]

The viscosities and densities of the C_{94}-compound at three temperatures are listed in Table I and the changes of the properties with increasing molecular weight may be seen in Table II.

TABLE I

VISCOSITY AND DENSITY OF n-$C_{94}H_{190}$

Temp., °C.	Viscosity, cp.	Density, g./ml.
115	39.29 (117°)	0.7833
125	33.95	0.7774
135	28.38	0.7714

TABLE II

VISCOSITIES AND DENSITIES OF n-ALKANES

No. of carbon atoms	135°		Ref.
	Density, g./ml.	Viscosity, cp.	
12	0.6520	0.3769	*a*
20	0.7113	0.919	*a*
35	0.7436	2.569	*b*
44	0.7514	3.910	*c*
64	0.7654	9.7	*d*
94	0.7714	28.3	This work

[a] F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953. [b] Unpublished work, this laboratory. [c] R. W. Schiessler and F. C. Whitmore, *Ind. Eng. Chem.*, **47**, 1660 (1955). [d] Ref. 8. Viscosity at 135° estimated from data at other temperatures.

It may be noted that the trends in viscosity and density as functions of molecular weight that are established at the lower molecular weights continue into the area of molecular weight 1300 and beyond. Thus, one can make valid predictions of these properties by interpolation for any n-paraffin of interest between C_{44} and C_{94}.

Experimental[16]

Docosanoic acid (I) was Eastman Kodak practical grade material.

1-Docosanol.—The docosanoic acid was converted to the methyl ester by conventional procedures and fractionally distilled to yield material which had the correct elemental analysis and analysed 99.5% by g.c. The ester was reduced with lithium aluminum hydride in ether solution. The yield of material purified by repeated crystallization from hexane was 86.5%, m.p. 70.9–71.3° (lit.[17] m.p. 70.8°).

Anal. Calcd.: C, 80.9; H, 14.2. Found: C, 81.4; H, 14.1.

1-Bromodocosane (II).—Hydrogen bromide gas (Matheson Chemical Co.) was bubbled through the alcohol at 120° for 22 hr. The usual procedure for working up such products was followed by crystallization from pentane and fractional distillation, m.p. 43.6–44.0° (lit.[18] m.p. 44°).

Anal. Calcd.: Br, 20.5. Found: Br, 20.4.

Monomethyl Hydrogen Eicosanedioate.—Eicosanedioic acid, generously furnished by the Shell Chemical Co., was converted to the dimethyl ester by the usual procedures, fractionally distilled, and crystallized from methanol, m.p. 66.0–66.4° (lit.[19] m.p. 65.6–66.0°).

Anal. Calcd.: C, 71.3; H, 11.4. Found: C, 71.8; H, 11.3.

Treatment of the diester with barium hydroxide in methanol[20] for 24 hr. at 50° followed by crystallization from acetone gave a 90% yield of the half-ester, m.p. 83.5–84.0°.

Anal. Calcd. for $C_{21}H_{40}O_4$: C, 70.74; H, 11.31; neut. equiv., 356.5. Found: C, 70.75; H, 11.41; neut. equiv., 354.

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[11] J. Cason and F. S. Prout, "Organic Syntheses," Coll. Vol. III, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, p. 601.

[12] D. A. Shirley, *Org. Reactions*, **8**, 28 (1954).

[13] R. G. Jones, *J. Am. Chem. Soc.*, **69**, 2350 (1947).

[14] The preparation of anhydrous ethereal solutions of zinc chloride was found to be a critical step in the preparation and use of the alkylzinc reagent. By fusing the zinc chloride under high vacuum and adding the anhydrous ether to the evacuated system, water-white solutions were obtained. These solutions were stable if kept at room temperature in an ether atmosphere.

[15] F. A. Khoury, Meeting of the American Physical Society, Baltimore, Md., March 1962.

[16] Analyses were by Dr. Alfred Bernhardt, Max-Planck Institute, Mülheim, Germany, Mr. James Rigas, Brooklyn, N. Y., and Midwest Microlab, Inc., Indianapolis, Ind.

[17] F. Francis, J. E. Collins, and S. H. Piper, *Proc. Roy. Soc.* (London), **A158**, 691 (1937).

[18] J. v. Braun, W. Teuffert, and K. Weissbach, *Ann.*, **472**, 132 (1929).

[19] P. Chuit and J. Hausser, *Helv. Chim. Acta*, **12**, 856 (1929).

[20] H. Hunsdiecker and C. Hunsdiecker, *Ber.*, **75**, 291 (1942).

Methyl 19-Chloroformylnonadecanoate (V).—Monomethyl hydrogen eicosanedioate (243.6 g., 0.68 mole), 125 ml. of thionyl chloride (200.0 g., 1.68 moles), and 500 ml. of anhydrous benzene were refluxed until no more hydrogen chloride fumes were evolved (5 hr.). The benzene and excess thionyl chloride were distilled under vacuum. Benzene (100 ml.) was added to the residue and then distilled under gradually increasing vacuum to 0.1-mm. pressure. The residue was dissolved in 1 l. of hot anhydrous hexane, the solution was filtered while hot, and the filtrate was allowed to crystallize at 0°. The solids were filtered and washed with cold pentane to give 246.9 g. (96.7%), m.p. 59.4–60.8°. The acid chloride was stored under nitrogen in the refrigerator, but hydrogen chloride fumes were always noted upon opening the bottle.

The infrared spectrum of V exhibited two strong peaks in the carbonyl region, at 1795 and 1740 cm.$^{-1}$, assigned to acid chloride and ester functions, respectively. No peak corresponding to the acid carbonyl was detected.

Methyl 20-Oxodotetracontanoate (VI).—Three preparations of the C_{42} keto ester were run in 77.7, 80.8, and 81.0% yields using the same method. Only one of the preparations will be described. 1-Bromodocosane (229.8 g., 0.59 mole) and excess magnesium turnings were allowed to react in ether under nitrogen to give a 90% yield of Grignard reagent. The warm Grignard solution was pumped through a glass-wool plug into a dry, nitrogen-filled dropping funnel.

Zinc chloride (65.4 g., 0.48 mole) was weighed into a 500-ml. suction flask, the arm of which was closed off with a clamped 4-in. length of Tygon tubing. The mouth of the flask was fitted with a one-hole stopper containing a 4-in. length of glass tubing topped by a 2-in. section of pressure tubing and clamp. The tip of a 250-ml. dropping funnel was inserted into the pressure tubing and the top of the funnel was connected to a vacuum pump. A glass-covered magnetic stirring bar was held off the bottom of the suction flask by an external permanent magnet. The system was evacuated to full pump vacuum and flame dried. The zinc chloride was slowly fused to a clear melt with a Bunsen flame. After cooling the flask to room temperature under vacuum, the dropping funnel stopcock was closed, the vacuum pump line was removed, and 200 ml. of anhydrous ether was added to the funnel. The funnel was immediately stoppered. The stopcock was opened to allow ether to flow into the evacuated suction flask. The stopcock was closed just before the last bit of ether passed through to prevent air from entering the suction flask. The mixture in the closed system was stirred magnetically until the fused zinc chloride had dissolved. The ether solution became red on first stirring with the solid zinc chloride, but after 4 hr. of stirring the solution became colorless.

To this solution the Grignard reagent was added rapidly. A thick, gray paste formed very quickly with considerable refluxing. The mixture was stirred for 20 min. before distilling out 900 ml. of ether over a 2-hr. period. Anhydrous benzene (100 ml.) was added to the gray, pasty mixture. A negative Gilman test was obtained.

Methyl 19-chloroformylnonadecanoate (V; 133.9 g., 0.357 mole) in 800 ml. of benzene was added to the stirred organozinc reagent over a period of 15 min. Near the end of this addition the reaction mixture became a very dark but nearly transparent solution. This solution was stirred and refluxed for 3 hr. under nitrogen.

The reaction mixture was hydrolyzed with 2 *N* hydrochloric acid (vigorous reaction) and the benzene was distilled. The resulting white solid residue was filtered, washed with water, crushed with a pestle, and continuously extracted with ether in a Soxhlet extractor for 12 hr. The cup residue was dried and crystallized from benzene to give 187.6 g. (81.0%) of VI, m.p. 95.0–96.0°.

Anal. Calcd. for $C_{43}H_{84}O_3$: C, 79.91; H, 13.04. Found: C, 80.15; H, 12.84.

Dotetracontanoic Acid.—The Huang-Minlon[21] modification of the Wolff–Kishner reaction was used to prepare the *n*-C_{42} acid. After crystallization from toluene and recrystallization from heptane there was obtained 264.7 g. (90%) of the acid, m.p. 106.0–107.0°.

Anal. Calcd. for $C_{42}H_{84}O_2$: C, 81.22; H, 13.63; neut. equiv., 621. Found: C, 81.29; H, 13.53; neut. equiv., 624, 628.

1-Dotetracontanol.—Small pilot reactions involving the direct reduction of the *n*-C_{42} acid with lithium aluminum hydride in tetrahydrofuran showed that the reduction of the acid was incomplete. However, reduction of the ethyl ester was found to give a 91% yield of the desired alcohol, m.p. 101–102°.

Anal. Calcd. for $C_{42}H_{86}O$: C, 83.09; H, 14.28. Found: C, 83.13; H, 14.22.

1-Bromodotetracontane (VII).—Hydrogen bromide was bubbled through the above alcohol at 120° for 36 hr. The usual work-up procedure was followed by passage of a heptane solution of the bromide through a column of silica gel and crystallization from the same solvent. The yield of product was 96.8%, m.p. 85.0–85.3°.

Anal. Calcd. for $C_{42}H_{85}Br$: C, 75.28; H, 12.79; Br, 11.93. Found: C, 74.96; H, 12.79; Br, 11.98.

43,52-Tetranonacontanedione (X).—Two preparations of 43,52-tetranonacontanedione were performed in 63.5 and 64.8% yields. The procedure was very similar to that for the preparation of methyl 20-oxodotetracontanoate (VI). The diketone was purified by crystallization three times from toluene, continuous 4-hr. extractions with tetrahydrofuran, and crystallization from heptane. The yield of diketone melting at 124.5–125.5° was 64.8%.

Anal. Calcd. for $C_{94}H_{168}O_2$: C, 83.72; H, 13.90. Found: C, 84.20; H, 13.89.

The dioxime melted, after recrystallization from toluene, at 97.5–98.0°.

Anal. Calcd. for $C_{94}H_{188}N_2O_2$: N, 2.03. Found: N, 2.11.

***n*-Tetranonacontane.**—Small pilot experiments indicated that reduction of the C_{94} diketone to the C_{94} paraffin was incomplete using the Huang-Minlon[21] modification of the Wolff–Kishner reaction. The standard conditions gave only 35% reduction to the hydrocarbon. The addition of mechanical stirring increased the yield to 45%. Since the difficulty apparently arose from the low solubility of the C_{94} diketone in triethylene glycol, a better solvent system, such as the one suggested by Schiessler,[22] was tried.

43,52-Tetranonacontanedione (X; 52.7 g., 0.039 mole), 50 ml. of hydrazine hydrate (50 g., 1 mole), 5 ml. of glacial acetic acid, and 1 l. of 1-octanol (Humphrey–Wilkinson Chemical Co.) were refluxed at 120–193° for 9 hr. while slowly distilling excess hydrazine and water. The solution was homogeneous at all times.

A solution of sodium octylate (17.7 g., 0.75 mole of sodium in 400 ml. of 1-octanol) was added to the cooled hydrazone solution. This mixture was refluxed at 190–197° for 20 hr. and worked up in the usual fashion. After chromatography on alumina, the hydrocarbon was stirred with 200 ml. of concentrated sulfuric acid for 1 hr. at 123°.[9] There was appreciable charring. The mixture was poured onto ice and the hydrocarbon was isolated by extractions with hot heptane. After rechromatography on alumina and two crystallizations from heptane, 16.9 g. (33%) of high purity tetranonacontane was obtained, m.p. 114.07–114.47°.[23]

Anal. Calcd. for $C_{94}H_{190}$: C, 85.50; H, 14.50. Found: C, 85.51; H, 14.48.

A second portion of the diketone X was reduced and purified similarly except that two additional recrystallizations and two treatments with activated alumina were substituted for the sulfuric acid treatment. The melting point of this material was essentially identical with the other product, but it was shown by infrared analyses[24] to contain a small quantity of ketone. To date the only method for removing this impurity appears to be treatment with concentrated sulfuric acid. One carbonyl group in a chain of 90 methylene groups makes a very small difference in the solubility, adsorptability, etc.

Acknowledgment.—The support of this work by the American Viscose Corporation and the American Petroleum Institute is gratefully acknowledged. The

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[21] Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

[22] R. W. Schiessler, Ph.D. Thesis, The Pennsylvania State University, 1945.

[23] Determined in a premelted sample in a sealed capillary, using a thermometer calibrated by the National Bureau of Standards.

[24] We are indebted to Dr. John Y. Beach of the California Research Corporation for his very careful determination and analysis of the infrared spectrum. The very small carbonyl adsorptions due to minor amounts of the C_{94} ketone are readily missed in a routine infrared analysis.

large sample of eicosanedioic acid was very generously furnished by the Shell Chemical Company. The determinations and analyses of the infrared spectra of samples of tetranonacontane obtained at various stages during the purification by Dr. John Y. Beach of the California Research Corporation is gratefully acknowledged. The viscosities and densities were determined by George H. Neff.

Oxidation of Alkylarenes with Aqueous Sodium Dichromate. A Useful Method for Preparing Mono- and Polyaromatic Carboxylic Acids[1]

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Mono- and polyalkyl-substituted polycyclic aromatic hydrocarbons are generally oxidized conveniently and in excellent yields to their corresponding polynuclear carboxylic acids by aqueous sodium dichromate at 225–250° in metal equipment. Selective conversion of hydrocarbons such as 1- and 2-methylnaphthalenes, 1,2- and 2,6-dimethylnaphthalenes, 4-methylphenanthrene, 2-methyltriphenylene, 6-methylcrysene, 3-picoline, and 3-methylthiophene to their aromatic or heterocyclic carboxylic acids illustrates the utility of sodium dichromate as an oxidant. Typical procedures for effecting oxidation in various types of equipment are described; the effects of excess oxidant and of buffers on the stoichiometry, selectivity, and rates of oxidation of various hydrocarbons have been investigated. Oxidations of benzene and naphthalene derivatives containing halogen, methoxyl, and nitro groups in various positions have been studied; general limitations of the oxidation method imparted by substituents and their positions have been defined.

Aromatic mono- and polycarboxylic acids are important intermediates in chemistry and considerable effort has been expended into developing methods[3] for their preparation. A particularly attractive method is the oxidation of side chains of mononuclear hydrocarbons[4] such as toluene to benzoic acid and *p*-xylene to terephthalic acid, etc. The oxidants usually used are air,[5a] acid or alkaline permanganate,[5b] chromic acid,[5c] nitric acid,[5d] potassium ferricyanide,[5e] and more recently sulfur and some of its oxidized derivatives.[5f] With the possible exceptions of potassium ferricyanide, the sulfur processes, and air oxidation, all of the aforementioned reagents are generally unsuccessful when applied to alkylated polynuclear aromatic systems because they result in extensive ring degradation. For example, 2-methylnaphthalene is oxidized by chromic acid to 2-methylnaphthoquinone[6a]; this reaction involves only nuclear oxidation. Similarly, anthracene is oxidized to anthraquinone[6b] and phenanthrene to phenanthraquinone,[6a,b] etc.

The problem of oxidizing 2-methylnaphthalene to 2-naphthoic acid is formidable. The common oxidizing agents[7a,b] either (a) completely destroy the compound, (b) attack the nucleus, or (c) effect electrophilic substitution.[7b,d] Potassium ferricyanide[7c] will slowly oxidize 2-methylnaphthalene to 2-naphthoic acid but the yield is poor and the product is accompanied by phthalic acid. These difficulties are common to all aromatic polycyclic systems.

The objective of the present investigation was to develop a general method for oxidation of alkylarenes to their corresponding acids. Oxidation of toluene,[8a] chlorotoluenes,[8b] xylenes,[8b] acenaphthene,[8b,c] and 3-picoline[8e] to their corresponding acids by aqueous sodium dichromate at elevated temperatures and pressures has been reported. Large excesses and high concentrations of sodium dichromate resulted in excessive nuclear destruction in oxidation of acenaphthene[8d]; yields of 1,8-naphthalic acid greater than 85% were obtained, however, at 200–210° using a 50% excess of 15–25% aqueous sodium dichromate.[8d]

A number of representative polynuclear hydrocarbons were thus subjected to 30% aqueous sodium dichromate at 250° for 15–18 hr. to determine their resistance to nuclear oxidation. Naphthalene, biphenyl, *o*-, *m*-, and *p*-terphenyls, phenanthrene, fluoranthene, and picene are essentially completely resistant under these conditions. *The stabilities of these hydrocarbons to aqueous sodium dichromate are quite remarkable in view*

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(1) (a) Abstracted in part from the Ph.D. Dissertations of L. Friedman, The Ohio State University, 1959, and D. L. Fishel, The Ohio State University, 1959; (b) presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, Abstracts, p. 66U, and in part of the 136th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1959, Abstracts, p. 22P.

(2) From whom reprints may be obtained: Department of Chemistry, Case Institute of Technology, Cleveland, Ohio 44106.

(3) The preparation of carboxylic acids has been reviewed in "Methoden der Organischen Chemie" [Vol. VIII, part 3, E. Muller, Ed., George Thieme Verlag, Stuttgart, 1952].

(4) H. Henecka, ref. 3, pp. 384–400.

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