

**197.** *The Preparation of a Series of ( $\pm$ )-n-Eicosanols and n-Eicosanones.*

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The preparation and properties of the ( $\pm$ )-n-eicosanols ( $C_{20}H_{42}O$ ) and n-eicosanones ( $C_{20}H_{40}O$ ) having the polar groups in the 2-, 4-, 6-, 8-, and the 10-position are described.

IN the course of a programme of research into the dielectric properties of long-chain alcohols (Meakins and Sack, *Nature*, 1949, **164**, 798) and ketones (Meakins, *Nature*, 1948, **162**, 994; 1949, **163**, 840) it was desired to determine the effect of varying the position of the polar group in a normal paraffin chain. Eicos-2-, 4-, 6-, 8- and -10-ol and -one now described were prepared for that purpose. Of these compounds, only the n-eicosan-2-ol and n-eicosan-2-one have been reported previously (Pangborn and Anderson, *J. Amer. Chem. Soc.*, 1936, **58**, 10; Morgan and Holmes, *J. Soc. Chem. Ind.*, 1925, **44**, 108; Stenhagen and Stenhagen, *Arkiv Kemi., Mineral., Geol.*, 1945, **18**, A, No. 19).

The n-eicosanols were obtained by the Grignard reaction between alkylmagnesium iodides and the appropriate aldehydes, the product being separated from the hydrocarbon by-product by vacuum distillation, recrystallisation, or adsorption on alumina, according to chain-length. The yields varied from 20 to 55%, the higher yields being obtained with the alkyl halides of shorter chain-length. Pure, fresh-cut magnesium (99.95%) was used throughout.

EXPERIMENTAL.

(All m. p.s are uncorrected.)

( $\pm$ )-n-Eicosan-2-ol.—The Grignard reagent was prepared from magnesium (9.5 g.), octadecyl iodide (119 g.), and ether (350 ml.), the mixture being heated under reflux during the addition of the iodide and

for a further one hour. After the solution had cooled to room temperature, a solution of acetaldehyde (14 g.) in dry ether (15 ml.) was added slowly, with stirring. After being heated under reflux for a further 2 hours, the Grignard complex was decomposed with water (50 ml.), and 5*N*-hydrochloric acid (200 ml.) was added to dissolve the excess of magnesium. The ethereal layer was then separated, filtered to remove *n*-hexatriacontane, and washed with water, dilute sodium thiosulphate solution, and again several times with water, and dried ( $\text{Na}_2\text{SO}_4$ ), and the ether distilled off.

The residual solid was dissolved in benzene and chromatographed on a column of alumina (1,100 g.), 5 cm. in diameter. Elution with benzene (1 l.) removed the hydrocarbon by-products and the crude ( $\pm$ )-*n*-eicosan-2-ol was then obtained by elution with ether. Recrystallisation from light petroleum gave a product (11.7 g.) in the form of well-defined crystalline plates, m. p. 59–60°. A portion of this was distilled under vacuum and the second of three fractions (b. p. 208–212°/7 mm.), having the smallest melting-point range, was recrystallised from alcohol. This gave ( $\pm$ )-*n*-eicosan-2-ol as a microcrystalline powder (well-defined plates from benzene), m. p. 58.5–59.0° (Lit., m. p. 52.0–52.7° for the ( $\pm$ )-compound; m. p. 62–63° for the (+)-form) (Found: C, 80.5, 80.3; H, 13.9, 13.8. Calc. for  $\text{C}_{20}\text{H}_{42}\text{O}$ : C, 80.5%; H, 14.1%).

( $\pm$ )-*n*-Eicosan-4-ol.—This was similarly prepared from magnesium (2.5 g.) in dry ether (30 ml.), cetyl iodide (30 g.) in dry ether (50 ml.), and butyraldehyde (6.1 g.). The material obtained by elution of the chromatograph column with ether was recrystallised from light petroleum (b. p. 60–80°) then benzene, giving microcrystalline needles (7.7 g.), m. p. 54.0–54.5°. A portion of this product was distilled under vacuum and the second (b. p. 190–192°/3 mm.) of three fractions recrystallised from alcohol, giving ( $\pm$ )-*n*-eicosan-4-ol as microcrystalline needles (poorly defined), m. p. 55.0–55.3° (Found: C, 80.5, 80.5; H, 13.8, 13.9.  $\text{C}_{20}\text{H}_{42}\text{O}$  requires C, 80.5; H, 14.1%).

( $\pm$ )-*n*-Eicosan-6-ol.—This was prepared from magnesium (9.0 g.) in dry ether (200 ml.), tetradecyl iodide (100 g.) in dry ether (200 ml.), and hexanal (25.8 g.). The *n*-octacosane by-product was not precipitated, and was therefore contained in the solid mixture obtained by evaporation of the ether solution. This mixture was dissolved in light petroleum (b. p. 60–80°) and chromatographed on a column of alumina (1,500 g.), 5 cm. in diameter. Elution with light petroleum eliminated the hydrocarbons, and the eicosanol was then obtained by elution with benzene. Recrystallisation from light petroleum gave a product (24.1 g.), m. p. 55–57°, which was vacuum-distilled. The second fraction (b. p. 189°/2.7 mm.) was recrystallised from alcohol, giving ( $\pm$ )-*n*-eicosan-6-ol as a microcrystalline powder (needles from benzene), m. p. 57.7–57.8° (Found: C, 80.5, 80.5; H, 13.9, 13.8%).

( $\pm$ )-*n*-Eicosan-8-ol.—The scale of the preparation was the same as that described for ( $\pm$ )-*n*-eicosan-6-ol. The mixture obtained from the ether solution was partly distilled under a vacuum to remove *n*-dodecane and the residue recrystallised from light petroleum (900 ml.; b. p. 60–80°), giving a product (62 g.), m. p. 57–59°. A portion of this was distilled under a vacuum and the second (b. p. 192°/3 mm.) of three fractions recrystallised from alcohol, giving ( $\pm$ )-*n*-eicosan-8-ol as microcrystalline plates (short needles from benzene), m. p. 57.7–57.9° (Found: C, 80.6, 80.4; H, 14.1, 13.8%).

( $\pm$ )-*n*-Eicosan-10-ol.—The reaction product from the ether layer was recrystallised from light petroleum (500 ml.; b. p. 60–80°), giving a product, m. p. 62.5–64°. A portion of this was distilled under a vacuum and the second (b. p. 214°/7 mm.) of three fractions recrystallised from alcohol, giving ( $\pm$ )-*n*-eicosan-10-ol as microcrystalline plates (well-defined needles from benzene), m. p. 65.3–65.6° (Found: C, 80.5, 80.5; H, 14.0, 13.8%).

*The Preparation of the n-Eicosanones.*—A solution of the *n*-eicosanol (5 g.) in benzene (250 ml.) was added to a solution of sodium dichromate (7 g.) in acetic acid (5 ml.), sulphuric acid (9 ml.), and water (30 ml.), and the mixture shaken mechanically for 6 hours. The aqueous layer was removed, and the benzene layer washed with water, 0.5*N*-potassium hydroxide, and again several times with distilled water. The *n*-eicosanone was then obtained by evaporation of the benzene solution, and recrystallisation of the product twice from alcohol. The yield of pure product was, in each case, about 90%.

*n*-Eicosan-2-one formed crystalline flakes, m. p. 59.3–59.7° (lit. m. p. 58°) (Found: C, 81.0, 80.7; H, 13.5, 13.6; O, 5.6. Calc. for  $\text{C}_{20}\text{H}_{40}\text{O}$ : C, 81.1%; H, 13.5; O, 5.4%). 2:4-Dinitrophenylhydrazone: orange-yellow crystalline plates, m. p. 94.5–94.8°.

*n*-Eicosan-4-one was obtained as crystalline flakes, m. p. 54.0–54.5° (Found: C, 80.7, 80.8; H, 13.8, 14.0; O, 5.6%). 2:4-Dinitrophenylhydrazone: brick-red microcrystalline plates, m. p. 70.1–70.4°.

*n*-Eicosan-6-one formed crystalline flakes, m. p. 53.8–54.1° (Found: C, 81.4, 81.3; H, 13.8, 14.0; O, 5.6%). 2:4-Dinitrophenylhydrazone: yellow powder, m. p. 40.4–47.4°.

*n*-Eicosan-8-one formed crystalline flakes, m. p. 53.2–53.5° (Found: C, 81.0, 81.3; H, 13.8, 13.6; O, 5.7%). 2:4-Dinitrophenylhydrazone: yellow needles, m. p. 29.6–30.0°.

*n*-Eicosan-10-one was obtained as crystalline flakes, m. p. 53.7–54.0° (Found: C, 80.9, 81.0; H, 13.3, 13.4; O, 5.6%). The 2:4-dinitrophenylhydrazone was a yellow liquid at room temperature.

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