

Notes

A department for short papers of immediate interest.

Synthesis of Squalane

KARL J. SAX AND FRED H. STROSS

Received April 16, 1957

Squalane (the mixture of stereoisomers of 2,6,10,15,19,23-hexamethyltetracosane formed on hydrogenation of squalene) has been tested as a standard for several analytical procedures.¹ During this study a synthetic sample was prepared by a new route to compare its properties with those of hydrogenated squalene. The method of preparation is outlined in Fig. 1.

the synthetic sample and of hydrogenated squalene were superimposable.

EXPERIMENTAL

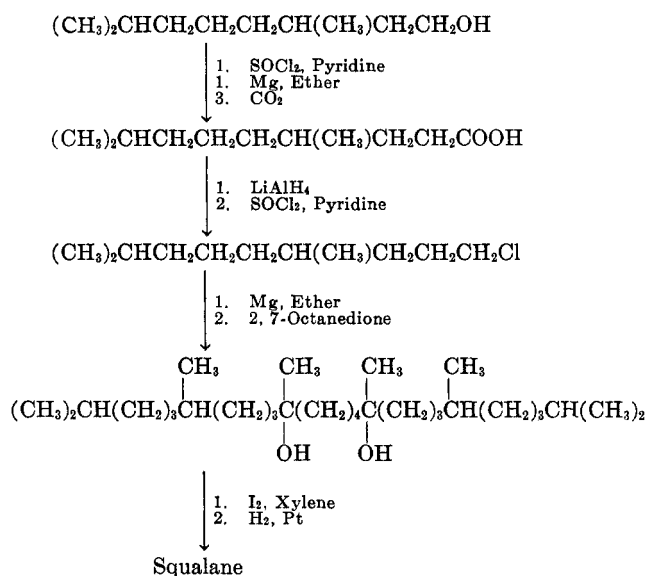
Tetrahydrogeraniol. Geraniol was hydrogenated with Raney nickel according to the method of Smith *et al.*⁷ The product had a b.p. 107°/10 mm., n_D^{20} 1.4379–1.4381 (reported⁷ n_D^{20} 1.4379).

Tetrahydrogeranyl chloride. Tetrahydrogeraniol was converted to the chloride with thionyl chloride and pyridine. Distillation in a packed column at 92–94°/13–15 mm. gave a 66% yield of product, n_D^{20} 1.4364.

Anal. Calcd. for C₁₀H₂₁Cl: C, 67.96; H, 11.98; Cl, 20.06. Found: C, 68.2; H, 12.0; Cl, 20.0.

4,8-Dimethylnonanoic acid. A Grignard reagent was pre-

FIGURE 1.



Although squalane has been prepared by the hydrogenation of both synthetic and natural squalene,^{2–6} the reported constants vary considerably. Four reference samples prepared in this work by the hydrogenation of squalene had identical physical properties.¹ The synthetic sample reported here differed slightly in refractive index and viscosity. Mass spectroscopy showed that it contained a small amount of impurity which may have caused the difference. The infrared spectra of

pared from 138.5 g. (0.784 mole) of tetrahydrogeranyl chloride and 19.1 g. (0.785 mole) of magnesium in anhydrous ether. The ether solution was poured onto crushed dry ice and the reaction complex was hydrolyzed with 40 ml. of concentrated sulfuric acid in 600 ml. of water. The ether layer was separated and the aqueous layer was re-extracted with ether. The combined ether extract was washed once with water and the acid was extracted with a solution of 70 g. of potassium hydroxide in 1 liter of water in two portions. The solution of the sodium salt was washed with ether several times, acidified, and the free acid was extracted with ether. The ether was evaporated and the product was distilled through a packed column at 126°/3.5 mm. Fractions with a neutralization equivalent of 186.0–186.5 (calcd. 186.3) were combined; wt. 75.0 g. (51%).

4,8-Dimethylnonanoic acid. A solution of 70.4 g. of 4,8-dimethylnonanoic acid in 200 ml. of anhydrous ether was added dropwise, during stirring, to a suspension of 16 g. of

(7) L. I. Smith, H. E. Ungnade, F. L. Austin, W. Pritchard, and J. W. Opie, *J. Org. Chem.*, **4**, 338 (1939).

- (1) K. J. Sax and F. H. Stross, *Anal. Chem.*, in press.
- (2) S. Trippett, *Chemistry and Industry*, **80** (1956).
- (3) M. Tsujimoto, *Ind. Eng. Chem.*, **8**, 889 (1916).
- (4) A. C. Chapman, *J. Chem. Soc.*, 56 (1917).
- (5) A. C. Chapman, *J. Chem. Soc.*, 769 (1923).
- (6) I. M. Heilbron, E. D. Kamm and W. M. Owens, *J. Chem. Soc.*, 1631 (1926).

lithium aluminum hydride in 300 ml. of anhydrous ether. The suspension was stirred overnight, refluxed for 1 hr. and the excess hydride was decomposed with methanol in ether solution. Water was added slowly and the pasty mass was acidified with hydrochloric acid. The aqueous layer was removed and extracted twice with ether. The combined ether extract was washed with dilute sodium hydroxide solution and water. The ether layer was dried over magnesium sulfate, filtered, and evaporated. The yield of product (64.2 g., n_D^{20} 1.4385) was 99%.

Anal. Calcd. for $C_{11}H_{24}O$: C, 76.67; H, 14.04. Found: C, 76.39; H, 13.99.

4,8-Dimethylnonyl chloride. A mixture of 94.0 g. (0.546 mole) of 4,8-dimethylnonanol-1 and 41.0 g. (0.519 mole) of pyridine was added slowly to 130 g. (1.09 mole) of thionyl chloride during cooling and shaking in an ice bath. The mixture was refluxed 1.5 hr., cooled, and the upper layer was separated and poured onto crushed ice. The aqueous layer was separated and the product layer was diluted with benzene, washed with water several times, 10% sodium carbonate solution twice and was dried over potassium carbonate. After filtration, the benzene was evaporated and the product was distilled in vacuum at 92–93°/7.5 mm; wt. 98.8 g. (95%). The product was redistilled in a packed column. The major portion boiled at 99°/10 mm., n_D^{20} 1.4396.

Anal. Calcd. for $C_{11}H_{23}Cl$: C, 69.26; H, 12.15; Cl, 18.6. Found: C, 69.29; H, 12.17; Cl, 18.8.

2,7-Octanedione. A Grignard reagent was prepared from 88.7 g. (0.62 mole) of methyl iodide, 15.2 g. (0.63 mole) of magnesium and 250 ml. of ether. The solution was cooled under nitrogen and treated with 62.5 g. of anhydrous cadmium chloride during stirring. A negative Gilman test was obtained after 0.5 hr. The ether was replaced with benzene by distillation until the distillate began to leave a deposit on evaporation.

The dimethylcadmium suspension was cooled and added slowly during stirring to a cooled solution of 49 g. (0.27 mole) of adipyl chloride (Distillation Products Inc.) in 300 ml. of benzene. The mixture was refluxed for 1 hr., cooled and treated with 500 ml. of saturated ammonium chloride. The benzene layer was separated and the aqueous residue was extracted twice with ether. The combined extract was washed with dilute sodium bicarbonate and water and dried over magnesium sulfate. After filtration, the benzene was evaporated and the product was crystallized from benzene-petroleum ether (30–60°). Fractional crystallization from benzene-petroleum ether gave 20.1 g., (53%) m.p. 39.5–40.5.

2,6,10,15,19,23-Hexamethyl-10,15-tetracosanediol. A Grignard reagent was prepared from 57.2 g. (0.3 mole) of 4,8-dimethylnonyl chloride and 7.3 g. (0.3 mole) of magnesium in about 250 ml. of ether at reflux. The solution was assayed by titration of an aliquot and 0.273 mole of Grignard reagent was found. A solution of 14.2 g. (0.1 mole) of 2,7-octanedione in 100 ml. of benzene was added to the ethereal Grignard solution during stirring under nitrogen. The mixture was placed on a steam bath and the ether was replaced with benzene by distillation over an hour's time. The mixture was allowed to stand under nitrogen for 2 days and 500 ml. of 20% sulfuric acid was added during cooling and stirring. The benzene layer was separated and washed with water and sodium bicarbonate until neutral. The aqueous layers were washed with benzene and the combined benzene extract was dried over magnesium sulfate, filtered, and concentrated in vacuum. The infrared absorption spectrum of the residue, 42 g. (92% based on diketone) indicated the presence of tertiary hydroxyl groups.

Anal. Calcd. for $C_{30}H_{62}O_2$: C, 79.22; H, 13.74. Found: C, 78.95; H, 13.65.

Octahydrosqualene. A solution of 30 g. of the above diol in 350 ml. of xylene was treated with 0.1 g. of iodine and was distilled slowly for 1 hr. Another 0.1 g. portion of iodine was added each hour for 12 hr. as the distillation was con-

tinued. The xylene was removed by distillation in vacuum and the residue was dissolved in petroleum ether and passed through a 170 × 66 mm. alumina column. A total of 29.0 g. was isolated in the first 500 ml. of petroleum ether eluate; a colored zone remained on the column. The product was heated at 100°/4 mm. for 0.5 hr. and 26.1 g. of product (94%) was obtained.

Anal. Calcd. for $C_{30}H_{58}$: C, 86.04; H, 13.96. Found: C, 86.0; H, 13.9.

Squalane. A mixture of 23.0 g. of octahydrosqualene was placed in a hydrogenation bottle with 0.5 g. of platinum oxide. The mixture was shaken under hydrogen until the theoretical amount of hydrogen was absorbed. Shaking was continued for several hours without further hydrogen uptake. The product was diluted with benzene and filtered. Evaporation of the benzene gave a residue of 17.5 g., n_D^{20} 1.45200. It was passed through a 20 × 200 mm. silica gel column with isopentane; 17.0 g., n_D^{20} 1.45195. Distillation in a molecular still gave about 1.0 g. of forerun, n_D^{20} 1.4511 and a main fraction, n_D^{20} 1.4520, viscosity at 100°F., 20.21 cs. The ultraviolet and infrared absorption spectra showed traces of a monosubstituted benzene. The product was passed through a twelve-foot column of silica gel with isopentane and the eluate was examined in an ultraviolet spectrophotometer. No absorption was noted. The cuts were combined and evaporated. The product, 7.0 g., n_D^{20} 1.45189 gave an infrared absorption spectrum identical with the reference curve. The viscosity was essentially unchanged.

Anal. Calcd. for $C_{30}H_{58}$: C, 85.22; H, 14.78. Found: C, 85.26; H, 14.76.

SHELL DEVELOPMENT CO.
EMERYVILLE, CALIF.

Vinyl Derivatives of the Metals. V. Free Radical Addition Reactions of Triethylvinyltin¹

DIETMAR SEYFERTH

Received May 27, 1957

In Part II of this series² it was shown that hydrogen bromide and mercaptans, which undergo free radical, peroxide-catalyzed addition to vinylsilicon compounds, cleave the vinyl-tin bond. The fact that even mercaptans reacted in this manner seemed to indicate that any reagent capable of electrophilic attack on the α -carbon atom of the vinyl group attached to tin would undergo this reaction in preference to the double bond addition reaction. Thus a rather severe limit was set on the types of compounds that could conceivably add to the vinyl-tin system.

The polyhalomethanes³ and hydrogenchlorosilanes⁴ are known to add to vinylsilanes. It would

(1) Part IV, D. Seyferth, *J. Am. Chem. Soc.*, **79**, 2738 (1957).

(2) D. Seyferth, *J. Am. Chem. Soc.*, **79**, 2133 (1957).

(3) (a) P. Tarrant, WADC Technical Report 55-220, August 1955; (b) A. F. Gordon, U. S. Patent 2,715,113 (August 1955); *Chem. Abstr.*, **50**, 7131 (1956); (c) A. D. Petrov, E. A. Chernyshev and M. Bisku, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1445 (1956).

(4) (a) C. A. Burkhard and R. H. Kriebel, *J. Am. Chem. Soc.*, **69**, 2687 (1947); (b) M. Kanazashi, *Bull. Chem. Soc. Japan*, **26**, 493 (1953); (c) D. Seyferth and E. G. Rochow, *J. Org. Chem.*, **20**, 250 (1955).