[CONTRIBUTION FROM SOCONY-VACUUM LABORATORIES (A DIVISION OF SOCONY-VACUUM OIL COMPANY, INC.) RESEARCH AND DEVELOPMENT DEPARTMENT]

# The Synthesis and Physical Properties of Tetraethylmethane

BY A. WESLEY HORTON

Tetraethylmethane has been synthesized in one previous investigation by the reaction of zinc diethyl with triethylcarbinyl iodide.[1] The following physical properties were reported: m. p. −41°, b. p. (Siwoloboff) 139.2°, $d^{20}_4$ 0.7522; $n^{18}_D$ 1.4205.

Two methods of calculating the physical properties of this nonane by analogy with hydrocarbons of similar structure have been published. In the first,[2] empirical equations were set up for the densities and refractive indices of the homologous series derived from neopentane by successive substitution of ethyl groups for methyl groups (2,2-dimethylpropane, 2,2-dimethylbutane, 3,3-dimethylpentane, 3-methyl-3-ethylpentane, 3,3-diethylpentane). The values calculated for tetraethylmethane (3,3-diethylpentane), $d^{20}_4$ 0.7520 and $n^{20}_D$ 1.4203, agree well with those reported by Morgan, *et al.* However, the boiling point, 139.2°, could not be checked by any method of calculation. It was estimated by Francis that the true boiling point should be approximately 147.6°.

A general method of calculation proposed recently[3] yields the following values of properties for tetraethylmethane: b. p. 149.4°, $d^{20}_4$ 0.7575, $n^{20}_D$ 1.4230. In obtaining these results, no account was taken of interactions between parts of the molecule not directly bound. The existence of such interactions would be indicated if the actual values of the properties differ markedly from those calculated by this method.

Further study in connection with the present synthesis has shown that it is possible to fit a simple cubic equation to the accepted experimental values[4] for the boiling points of the above homologous series $(CH_3)_{4-n}C(C_2H_5)_n$. Derived by the method of least squares,[5] the following equation

$$\text{b. p.} = 9.443 + 42.342n - 2.0225n^2 \qquad (1)$$

gives a calculated boiling point for tetraethylmethane of 146.45°. The agreement with the constants for the first four hydrocarbons of the series is within 0.02°.

The synthesis of the desired nonane was accomplished in three steps

$$(EtO)_2CO \xrightarrow{EtMgBr} Et_3COH \xrightarrow{HCl} Et_3CCl \xrightarrow{Et_2Zn} Et_4C$$

Purification of the product followed the usual procedure for paraffin hydrocarbons, percolation through finely divided activated silica gel, efficient fractional distillation, and washing with concentrated sulfuric acid.

The following values of properties were determined experimentally on the best sample of tetraethylmethane prepared in this investigation: m. p. −31.1°; b.p. (Cottrell) 146.4°; $d^{20}_4$ 0.7524; $n^{20}_D$ 1.4200. These constants were submitted to the National Bureau of Standards in May, 1943, and agree closely with the selected values for this nonane in the latest tables of the American Petroleum Institute Research Project 44.

The observed boiling point is in excellent agreement with the value calculated from equation (1). Further confirmation of the internal self-consistency of the homologous series $(CH_3)_{4-n}C(C_2H_5)_n$ is shown by the following equations developed for the densities and refractive indices

$$d^{20}_4 = 0.59585 + 0.05813n - 0.00475n^2 \qquad (2)$$

$$n^{20}_D = 1.34187 + 0.02942n - 0.00247n^2 \qquad (3)$$

Values calculated for the individual hydrocarbons check the accepted properties[4] to within 0.0001. Equations (2) and (3) are further useful as a direct means of calculation of the density and refractive index of liquid neopentane at a temperature, 20°, at which experimental measurement is made difficult by the superatmospheric vapor pressure of the hydrocarbon.

## Experimental

**Tetraethylmethane.**—In a typical run, 32 g. (0.26 mole) of zinc diethyl was prepared and dissolved in 52 g. of anhydrous tetralin.[6] To this solution 68 g. (0.5 mole) of triethylcarbinyl chloride (prepared by standard procedures[7,8]) in 48 g. of tetralin was added dropwise. The reaction proceeded readily at room temperature and the flask was cooled externally from time to time. After addition was complete the mixture was heated on the steam-bath for one-half hour and then hydrolyzed with dilute hydrochloric acid. The hydrocarbon layer was washed twice with concentrated sulfuric acid to remove olefins. After neutralization and drying it was percolated through finely divided activated silica gel to remove a trace of unreacted chloride. The colorless liquid was then distilled through a fractionating column with an efficiency of thirty theoretical plates. After removal of 18 g. of 3-ethylpentane boiling 90–95°, 16 g. of tetraethylmethane was collected boiling 145–147° (yield, 25% of theoretical).

The sample used to determine physical properties was further purified by shaking with equal volumes of warm concentrated sulfuric acid until it gave a constant melting point. Two acid washes were sufficient.

## Summary

A three-step synthesis of tetraethylmethane is described and the physical properties deter-

---

[1] G. T. Morgan, S. R. Carter and A. E. Duck, *J. Chem. Soc.*, **127**, 1252 (1925).

[2] A. W. Francis, *Ind. Eng. Chem.*, **35**, 447 (1943).

[3] W. J. Taylor, J. M. Pignocco and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 413 (1945).

[4] American Petroleum Institute Research Project 44, Tables 1a, 2a, 3a and 4a.

[5] Whittaker and Robinson, "The Calculus of Observations," Blackie and Sons, London, 1932, p. 211.

[6] C. R. Noller, THIS JOURNAL, **51**, 594 (1929).

[7] "Organic Syntheses," Vol. XI, p. 98.

[8] F. C. Whitmore and D. E. Badertscher, THIS JOURNAL, **55**, 1560 (1933).

mined experimentally on a carefully purified sample of the nonane are reported. Empirical equations relating molecular structure to boiling point, density, and refractive index for the symmetrical series $(CH_3)_{4-n}C(C_2H_5)_n$ are presented.

PAULSBORO, N. J. RECEIVED JUNE 27, 1946

# NOTES

## Attempted Asymmetric Synthesis in a Metathetical Grignard Reaction

BY WILLIAM A. BONNER

In connection with another problem it became desirable to investigate the possibility of producing an asymmetric synthesis in a metathetical replacement reaction involving the Grignard reagent. The reaction selected was the formation of ethyl α-phenylethyl ether by the action of phenylmagnesium bromide on ethyl α-chloroethyl ether. The replacement was carried out in the presence of a variety of optically active agents including methyl tetramethyl-α-D-glucoside, tetraacetylglucosyl chloride, brucine, and *d*-bromocamphor. In each instance the ethyl α-phenylethyl ether obtained showed no optical activity beyond experimental error.

The well known investigations of McKenzie and others, wherein asymmetric syntheses have been achieved via the Grignard reagent, have been confined to the addition of the Grignard to carbonyl groups in molecules *already* possessing asymmetric centers. Very few Grignard reactions have been conducted to test the possibility of asymmetric synthesis in the presence of *external* asymmetric molecules. Betti and Lucchi[1] claimed in 1940 to have prepared optically active α-phenylethanols by the action of Grignard reagents on aldehydes in the presence of dimethylbornylamine. Tarbell and Paulson[2] showed later, however, that the activity of the Betti and Lucchi alcohols was due to an active impurity, and were further unable to prepare active alcohols under a variety of conditions, even using an optically active ether as solvent. The present attempted asymmetric synthesis apparently fails for the same possible reason, namely, because the asymmetric center supposedly imparting an asymmetric bias to the reaction is present only externally, and not as part of the reacting molecule. Several instances of successful asymmetric synthesis in the presence of external optically active agents have been reported, but none of these employs the Grignard reagent.

### Experimental

**Ethyl α-Phenylethyl Ether.**—Ethyl α-chloroethyl ether was prepared according to the directions of Swallen and Boord.[3] The material boiling from 44–51° (170 mm.) was used in the reaction described below. The chloro ether hydrolyzes rapidly and fumes in moist air, but can be stored with no apparent decomposition in a glass-stoppered flask at 0°.

Phenylmagnesium bromide (50% excess) was prepared from magnesium (3.6 g.) and bromobenzene (23.2 g.) in dry ether (75 ml.). Ethyl α-chloroethyl ether (12 g.) was dissolved in dry ether (60 ml.) and the mixture placed in a three-necked flask equipped with a mercury-sealed Hershberg stirrer, a reflux condenser protected with a calcium chloride tube, and a dropping funnel similarly protected. The solution was cooled in ice and the Grignard reagent added dropwise with stirring over the course of thirty minutes. A grayish precipitate formed immediately, and the reaction proceeded with a hissing sound. The mixture was stirred under reflux for an additional hour, cooled and poured into ice water. The residue remaining in the reaction flask was dissolved with dilute sulfuric acid and the solution added to the ice water. The ether layer was separated, washed twice with water, with sodium bicarbonate solution until neutral, again

TABLE I

ATTEMPTED ASYMMETRIC SYNTHESES

| Run | α-Chloro ether, moles | Optically active agent | Active agent, moles | α-Phenyl ether Yield, % | |
|---|---|---|---|---|---|
| | | | | Yield, % | $[\alpha]^{23}D$ |
| 1 | 0.074 | Methyl tetramethyl-α-D-glucoside | 0.074 | 69 | 0.00° |
| 2 | .074 | Brucine | .038 | ..[a] | − .08 |
| 3 | .068 | Tetraacetylglucosyl chloride | .034 | 88[b] | .00 |
| 4 | .055 | *d*-Bromocamphor | .055 | 80 | 2.85[c] |
| 5 | .074 | Methyl tetramethyl-α-D-glucoside and activated alumina | .074 | 56 | 0.00 |

[a] The product obtained from Run 2 was not ethyl α-phenylethyl ether as indicated by b. p. (91–97° (17 mm.)) and refractive index ($n^{21}D$ 1.5308). The product rapidly decolorized bromine in carbon tetrachloride and slowly decolorized permanganate in acetone. *Anal.* C, 78.07, 78.20; H, 7.93, 7.85. Its identity is being established. [b] Tetraacetylglucosylbenzene was isolated by acetylation of the residue on evaporation of the water layer; yield, 43%. [c] The rotation here was due to contamination by camphor derivatives. When the crude product was redistilled into two fractions the first (b. p. 72–74° (17 mm.)) had $[\alpha]^{23}D$ 0.43°, and the second (b. p. 74–76° (17 mm.)) had $[\alpha]^{23}D$ 2.23°. The undistilled residue had a strong camphor-like odor.

---

(1) Betti and Lucchi, *Boll. sci. facolta chim. ind., Bologna*, No. 1–2, 2 (1940); *C. A.*, **34**, 2354 (1940).

(2) Tarbell and Paulson, THIS JOURNAL, **64**, 2842 (1942).

(3) Swallen and Boord, *ibid.*, **52**, 654 (1930).