[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Physical Constants of Dimethylacetylene

BY G. B. HEISIG AND H. M. DAVIS

Dimethylacetylene was prepared by the action of an equivalent amount of methyl iodide on the sodium salt of methylacetylene.[1] However, the isolation of the product was simplified materially by cooling the solution of dimethylacetylene in ammonia to the temperature of solid carbon dioxide, whereupon the dimethylacetylene crystallized along with the sodium iodide. The mother liquor which was decanted from the solid did not contain an appreciable amount of product. Cold water was added to the residue and the product separated as an oil. Some loss occurred which could have been avoided had a salt–ice mixture been used instead of water.

The methylacetylene was prepared by dropping propylene bromide (2 moles) into a solution of potassium hydroxide in *n*-butyl alcohol (450 g. in 1100 cc.). An 85% yield is obtained if the bromide is added to the potash solution very slowly (four hours) and if the solution is well agitated and maintained at the boiling point. Other workers not taking these precautions have reported yields varying from 67 to 75%.[2]

The alcohol vapor which passed through the reflux condenser serving as the exit tube from the 3-liter, 3-necked flask in which the reaction took place was removed by a trap cooled in ice. The hydrocarbon was collected in a trap immersed in an alcohol–dry-ice bath.

Purification of Dimethylacetylene

Amines and ammonia present in the oil were removed by agitating with dilute hydrochloric acid, and the product was dried with calcium chloride. The sample distilled from 27–31°, indicating some higher boiling impurity. A trace of methyl iodide was removed by allowing it to stand for ten days in a sealed tube over bright sodium ribbon. The sample was then vaporized, and passed through 0.1 *N* sulfuric acid containing methyl orange, 50% sodium hydroxide, and finally through phosphorus pentoxide. Tests on a 0.5-cc. sample proved the absence of a halide. After numerous distillations between cold traps, freezing and pumping off the residual gas, the vapor pressure was 252.8 mm. at the temperature of melting ice and 49.3 at −31.2°. The sample was distilled from a trap at −30°, and then the vapor pressures at the above temperatures were unchanged. About 1.5 cc. of the middle fraction of the sample collected for the work described in this paper was further fractionated. The vapor pressure was the same as that of the large purified sample.

Anal. (Pregl, micro) Calcd. for C_4H_6: C, 88.8; H, 11.2. Found: C, 89.0; H, 11.2.

Vapor pressure measurements with the apparatus and by the procedure previously described[3] were made at approximately 5° intervals over the temperature range between −31.2° and +23.65°. The values can be expressed by the empirical formula

$$\log P = 21.6295 - (2047.473/T) - 4.8153 \log T$$

with an average deviation of 0.6 mm. and with a maximum deviation of 2.4 mm. at 20°. The vapor pressures of the solid at −38.70 and −34.55° are 27.9 mm. and 38.6 mm., respectively. The boiling point obtained by extrapolation from these data is 27.2° as compared with 28.9° given in the "International Critical Tables,"[4] which was apparently computed from Faworsky's[5] value of 27–28° at 734.8 mm. Very little information is given concerning the purity of Faworsky's product. Wislicenus and Schmidt[6] report the boiling point as 27.2–27.6°.

The orthobaric density of the liquid dimethylacetylene at 0 and 25° was found to be 0.715 and 0.688, respectively. The refractive index at 25° determined by means of an Abbe refractometer was 1.3893.

The melting point was determined by lowering the temperature of the automatically controlled low temperature thermostat until the sample solidified. The product was sealed in a thin-walled tube and was under its own vapor pressure. The highest temperature at which the product would solidify was −32.5°. The lowest temperature at which it would remain liquid was −32.8°. In support of the purity of our product the following points may be emphasized: (1) the method of isolating the product excludes the presence of methylacetylene, allene or other substances having a low freezing point, (2) distillation and subsequent fractionation at several temperatures eliminated the possibility of constant boiling mix-

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[1] Heisig, THIS JOURNAL, **53**, 3256 (1931).

[2] Tapley and Giesy, *J. Am. Pharm. Assoc.*, **15**, 115–16 (1926); Hurd, Meinert and Spence, THIS JOURNAL, **52**, 1141 (1930).

[3] Heisig, *ibid.*, **55**, 2311 (1933); Heisig and Hurd, *ibid.*, **55**, 3485 (1933).

[4] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1926, Vol. I, p. 185.

[5] Faworsky, *J. prakt. Chem.*, [2] **42**, 143 (1890).

[6] Wislicenus and Schmidt, *Ann.*, **313**, 221 (1900).

tures, (3) the constancy of the vapor pressure at 0 and −31.2° after severe fractionation, (4) the sharp melting point, (5) the excellent agreement of the analysis with that demanded for dimethylacetylene.

Summary

Pure dimethylacetylene has been synthesized and its isolation has been simplified. The vapor pressure at several temperatures, between the melting and boiling points, has been determined and the data have been fitted to an equation. The refractive index was measured at 25° and the density was determined at 0 and 25°. The boiling point and freezing point lie within 60° of each other.

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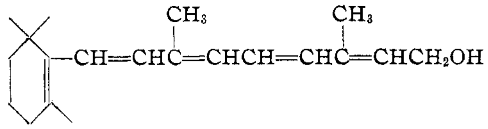
[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Synthesis of Certain Unsaturated Compounds from Beta-Ionone and Tetrahydroionone[1,2,3]

BY R. G. GOULD, JR., AND A. F. THOMPSON, JR.

In 1931 Karrer[4] put forward a structural formula for vitamin A (I) based on a study of highly active fish liver oils.

I



$$\text{—CH=CH}\overset{\text{CH}_3}{\text{C}}\text{=CHCH=CH}\overset{\text{CH}_3}{\text{C}}\text{=CHCH}_2\text{OH}$$

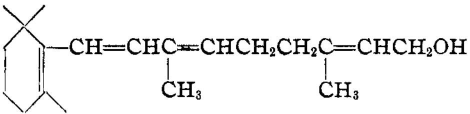
This formula is supported by further work on liver oil concentrates[5] and by the synthesis of perhydrovitamin A.[6] No compounds with vitamin A activity have as yet been synthesized. This would seem to be particularly important inasmuch as the most active concentrates of fish liver oils are admittedly not pure, and no solid derivatives of the vitamin have been obtained.

Ruzicka[7] has synthesized a tetrahydrovitamin A and found it to be biologically inactive.

Karrer[8] has prepared from β-ionone by means of the Reformatsky reaction 2-methyl-4-(2,2,6-trimethylcyclohexenyl-Δ^6)-butadiene-1,3-carboxylic acid, and has also synthesized two highly unsaturated ketones[9] which, however, do not have a carbon skeleton related to that assigned to vitamin A.

Synthesis of the partial reduction products of vitamin A is of interest in connection with the question as to the ability of the animal body to dehydrogenate such compounds to form active vitamin A, and also with the possible vitamin A activity of β-dihydrocarotene. Von Euler[10] has claimed that this compound, prepared by reduction of β-carotene with aluminum amalgam, is somewhat active, but Drummond[11] believes that the activity is entirely due to unchanged β-carotene present as an impurity.

In the work reported in this paper we have achieved the first steps in a projected synthesis of a dihydrovitamin A (II), and also have made progress toward an independent synthesis of perhydrovitamin A. The compounds which we have prepared so far are given in the diagram.



$$\text{—CH=CH}\underset{\text{CH}_3}{\text{C}}\text{=CHCH}_2\text{CH}_2\underset{\text{CH}_3}{\text{C}}\text{=CHCH}_2\text{OH}$$

II

The condensation of acetylene with β-ionone and with tetrahydroionone was carried out by a modification of the reaction developed by Ruzicka[12] and used by Rupe,[13] and F. G. Fischer.[14] These authors used sodamide or metallic sodium as condensing agent; the reaction often goes with great difficulty, and in many cases the yield is

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(1) Part of the material presented here was used in the doctoral theses of both authors.

(2) The authors take great pleasure in acknowledging their indebtedness to Dr. James B. Conant, who suggested the problem and directed the greater part of the work, and to Professor E. P. Kohler for criticisms and suggestions in connection with writing this paper.

(3) The ionone used was kindly furnished us by E. I. du Pont and Company.

(4) Karrer, Morf and Schopp, *Helv. Chim. Acta*, **14**, 1036 (1931); **14**, 1431 (1931).

(5) Heilbronn, Heslop, Morton, Webster, Rea and Drummond, *Biochem. J.*, **26**, 1178 (1932).

(6) Karrer and Morf, *Helv. Chim. Acta*, **16**, 557 (1933); **16**, 625 (1933).

(7) Ruzicka and Fischer, *ibid.*, **17**, 633 (1934).

(8) Karrer, Salomon, Morf and Walker, *ibid.*, **15**, 878 (1932).

(9) Karrer and Morf, *ibid.*, **17**, 3 (1934).

(10) Von Euler, Karrer, Helstrom and Rydbom, *Svensk. Kem. Tidskr.*, **43**, 105 (1931).

(11) Drummond, *J. Soc. Chem. Ind.*, **50**, 183T (1931).

(12) Ruzicka and Fornasir, *Helv. Chim. Acta*, **2**, 182 (1919); Ruzicka, *ibid.*, **6**, 493 (1923).

(13) Rupe and Kambli, *ibid.*, **9**, 672 (1926); Rupe, Messner, and Kambli, *ibid.*, **11**, 449 (1928); Rupe and Giesler, *ibid.*, **11**, 656 (1928); Rupe, Wirz and Lotter, *ibid.*, **11**, 965 (1928); Rupe and Hirschmann, *ibid.*, **14**, 687 (1931).

(14) F. G. Fischer and Lowenberg, *Ann.*, **475**, 183 (1929).