[CONTRIBUTION FROM THE AIRCRAFT ENGINE RESEARCH LABORATORY OF THE NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS]

The Reduction of Pentaerythrityl Tetrabromide in Ethanol with Zinc. Isolation of Spiropentane

BY VERNON A. SLABEY

There have been conflicting reports as to the formation of spiropentane from the reduction of pentaerythrityl tetrabromide in alcohol by zinc,[1] the latest conclusion being that it is not formed in this way. Murray and Stevenson[1] isolated small amounts of spiropentane by reduction of the tetrabromide with zinc in molten acetamide. It appeared to us from the known ring closure of 1,3-dichloropropane in alcohol with zinc in the presence of sodium carbonate and sodium iodide[2] that a similar closure could be obtained with pentaerythrityl tetrabromide by the same method without the use of acetamide, and such a preparation on a large scale is described below.

Pentaerythrityl tetrabromide was prepared according to the procedure described in "Organic Syntheses."[3] The crude product was extracted with acetone as suggested by Murray and Stevenson.[1]

Five moles (1940 g.) of pentaerythrityl tetrabromide was added in small portions with vigorous stirring to a mixture of 2500 ml. of ethanol, 875 ml. of water, 20 moles (1300 g.) of zinc dust, 5 moles (530 g.) of sodium carbonate, and 0.83 mole (125 g.) of sodium iodide heated to refluxing temperature in a 5-liter flask provided with a mechanical stirrer, a reflux condenser and a device for adding solid tetrabromide. (Time required for addition of tetrabromide was four hours.) Thereafter the mixture was heated for one hour to distil over the last traces of hydrocarbon into two receivers in series chilled with solid carbon dioxide-acetone cooling mixture. The product thus caught was washed with 2 liters of cold water, dried over calcium sulfate and was subjected to three successive fractionations through a 22-mm. glass column, 7 feet in length, packed with $^3/_{32}$-inch single-turn glass helices. The column was rated at 100 theoretical plates at total reflux with methylcyclohexane-*n*-heptane test mixture. In addition to three fractionations, spiropentane was treated with bromine[1] and fractionated over sodium metal.

Three successive preparations such as these and one using double quantities gave total yields after a single fractionation through the column described above varying between 78 and 89% of hydrocarbon products which had the following composition: methylenecyclobutane, 54–58%; spiropentane, 24–28%; 2-methyl-1-butene, 13–18% and 1,1-dimethylcyclopropane, 1–3%.

Two experiments using molten acetamide following the procedure of Murray and Stevenson[1] gave results comparable to those they reported, but the total yields of hydrocarbon after a single fractionation were only 37–38%, which consisted of methylenecyclobutane, 36–10%; spiropentane, 47–60%; and 2-methyl-1-butane, 17–30%. The reaction was objectionable for preparing more than a few grams of hydrocarbon because sublimation of the acetamide into the delivery tubes leading from the reaction flask to the chilled receivers proved troublesome in spite of attempts to heat the delivery tubes and remove the acetamide by bubbling the effluent gases through water.

These results indicate that the product of the reduction of acetamide contained a greater percentage of spiropentane than the product obtained by reduction in ethanol. However, reduction in ethanol yielded more than twice as much hydrocarbon product, and the actual yield of spiropentane was nearly identical in both solvents. Reduction in acetamide produced less methylenecyclobutane than reduction in ethanol; formation of methylenecyclobutane may be suppressed in molten acetamide or thermal decomposition of methylenecyclobutane may occur to yield fragments that are not collected with the other products. The latter is indicated by the low yields of hydrocarbon obtained with molten acetamide. 2-Methyl-1-butene was obtained in comparable amounts from the reduction in either solvent.

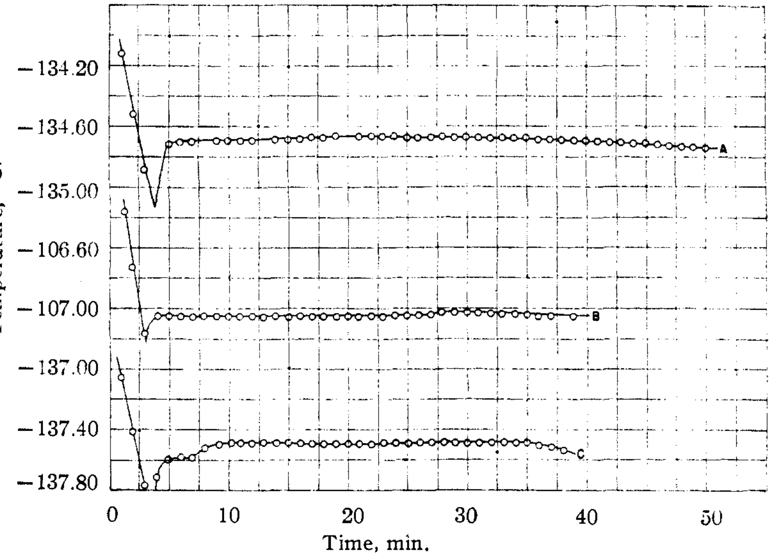

Fig. 1.—Time–temperature freezing curves of (a) methylenecyclobutane, (b) spiropentane, and (c) 2-methyl-1-butene.

Time–temperature freezing curves of methylenecyclobutane, spiropentane and 2-methyl-1-butene, Figs. 1 (a), (b) and (c), respectively, were

---

[1] Murray and Stevenson, THIS JOURNAL, **66**, 812 (1944).

[2] Hass, McBee, Hinds and Gluesenkamp, *Ind. Eng. Chem.*, **28**, 1178 (1936).

[3] Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 476.

TABLE I

PHYSICAL CONSTANTS OF METHYLENECYCLOBUTANE, SPIROPENTANE AND 2-METHYL-1-BUTENE

Compound	F. p., °C.	B. p., °C., 760 mm.	$n^{20}D$	d^{20}_4	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Methylenecyclobutane	−134.68	42.22	1.42087	0.7401	C_5H_8	88.17	87.94	11.83	11.61
Spiropentane	−107.05	39.03	1.41220	.7551	C_5H_8	88.17	87.95	11.83	11.88
2-Methyl-1-butene	−137.50	31.12	1.37781	.6504	C_5H_{10}	85.62	85.72	14.37	14.35

obtained according to the procedure of Rossini and co-workers.[4] Boiling points were determined at 760 mm. in a modified Willard and Crabtree apparatus.[5] All temperature measurements were made with a platinum resistance thermometer calibrated at the National Bureau of Standards. Index of refraction was determined with a precision-type refractometer thermostatically controlled to 20 ± 0.1°. Density was measured at 20° by use of a 5-ml. pycnometer.

Physical constants of the purified methylenecyclobutane, spiropentane and 2-methyl-1-butene are given in Table I.

The time–temperature freezing curves show that all these substances are very pure.

Summary

Reduction of pentaerythrityl tetrabromide in ethanol with zinc in the presence of sodium carbonate and sodium iodide was found to yield a mixture of hydrocarbons consisting of 56% methylenecyclobutane, 26% spiropentane, 15% 2-methyl-1-butene and 1–2% 1,1-dimethylcyclopropane.

The reaction procedure described is less troublesome for preparing large quantities of spiropentane than the molten acetamide reduction method previously reported.

The use of ethanol offers a means of preparing both methylenecyclobutane and spiropentane from the same reaction.

Methylenecyclobutane, spiropentane and 2-methyl-1-butene were obtained in a state of purity and their physical constants were determined.

CLEVELAND, OHIO RECEIVED FEBRUARY 11, 1946

---

[4] Mair, Glasgow and Rossini, National Bureau of Standards Research Paper RP 1397 (1941).

[5] Willard and Crabtree, *Ind. Eng. Chem., Anal. Ed.*, **8**, 79 (1936).

[CONTRIBUTION FROM THE RESEARCH LABORATORY, STANDARD OIL CO. (IND.)]

The Vapor Pressures and Saturated Liquid and Vapor Densities of the Isomeric Hexanes

BY WEBSTER B. KAY

In connection with a study of the physical properties of petroleum hydrocarbons, the vapor pressures and saturated liquid and vapor densities of the five isomeric hexanes were determined over a temperature range from their atmospheric boiling points to their critical points. Previously, similar data have been reported in the literature on *n*-hexane[1] and 2,3-dimethylbutane[1] only.

Experimental

Method and Apparatus.—The static method of measuring vapor pressure was employed. The compressor, pressure gage[2] and method of temperature regulation and measurement[3] have been described. The pressure gage was calibrated with the aid of a pressure balance[4] and checked at 3 atmosphere intervals between 3 and 40 atmospheres, against the vapor pressure of pure water. The vapor pressure–temperature relations for pure water, as given in "International Critical Tables,"[5] were used to determine the true pressure from which the correction for the gage was calculated. For pressures below 3 atmospheres an open mercury column was used.

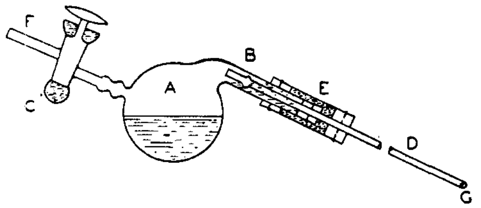

Fig. 1.—The loading apparatus.

Loading the Experimental Tube.—The method of loading the experimental tube with a pure air-free sample of liquid was a modification of that used by Young[6] in his classical vapor pressure studies. A sketch of the apparatus is shown in Fig. 1.

The apparatus was constructed from a 200-cc. Pyrex round-bottom flask A by bending the neck B at a 75° angle to the axis of the flask. A mercury sealed stopcock C was attached to the bottom, as shown. To avoid contamination of the hydrocarbon sample, the stopcock was not lubricated, the closed end of the barrel being filled with enough mercury so that the cock fitted snugly without sticking. Mercury in the cup surrounding the stem of the cock was prevented from spilling out by a rubber cap. The experimental tube D was held in B by a rubber stopper which was made vacuum tight by a mercury seal E. G was a small steel ball used for stirring the sample. The open arm F of the stopcock was connected to a cold trap by rubber tubing so that the apparatus could be manipulated during the filling operation.

The filling operation was carried out as follows: The apparatus was evacuated, C closed and disconnected from the pump and sufficient mercury admitted to A

---

[1] Sidney Young, *Sci. Proc. Roy. Soc.* (Dublin), **12**, 374 (1910).

[2] W. B. Kay, *Ind. Eng. Chem.*, **28**, 1014 (1936).

[3] W. H. Bahlke and W. B. Kay, *ibid.*, **24**, 291 (1932).

[4] A Crosby fluid pressure scale, manufactured by the Crosby Steam Gage & Valve Co., was used.

[5] "International Critical Tables," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1928, p. 233.

[6] Sidney Young, "Stoichimetry," Longmans, Green & Co., New York, N. Y., 1918, p. 124.