sure, but also differ sufficiently in structure so that their heats of vaporization also differ by enough to cause their vapor pressure curves actually to cross.[5]

2,4-Dimethylpentane was prepared by dehydration and hydrogenation of commercial 2,4-dimethyl-3-pentanol, and a sample of 2,2,3-trimethylbutane was kindly supplied by Dr. F. D. Rossini of the National Bureau of Standards. These two materials were characterized ebulliometrically by differences between boiling point and condensation temperature[6] of 0.029° for the trimethylbutane, and 0.042° for the dimethylpentane.

Using the ebulliometric method of Swietoslawski,[6] it was determined that at 67.58° the two materials had the same vapor pressure, 505.2 mm.[7] A 50% mixture of the two hydrocarbons was then prepared and its boiling point under the same pressure was found to be 67.71°, or 0.13° above that calculated for an ideal mixture. This constitutes conclusive evidence of the existence of negative azeotropy in this system. Additional exploration indicated that this was about the center of the region of existence of the azeotrope, which fades out below 55, and above 75°.

This is a vivid illustration of the fact that the disparity between the two species of molecules need not be very large for azeotropy to exist, provided the vapor pressures are sufficiently close together. This fact should probably be kept in mind when analyzing the results of close fractionations of complex mixtures of similar compounds, such as petroleum, for instance.

[5] A. F. Forziati, W. R. Norris and F. D. Rossini, *J. Res. Natl. Bur. Standards*, **43**, 555 (1949).

[6] W. Swietoslawski, "Ebulliometry," 2nd English Ed., Chemical Publishing Co., New York, N. Y., 1937; M. Wojciechowski, *J. Res. Natl. Bur. Standards*, **17**, 453 (1936).

[7] This compares with 64.66° and 459.75 mm. calculated from the vapor pressure curves of the pure components.[5] This crossing point is inherently extremely sensitive to sample purity and operating conditions, and its actual position is not a controlling factor in the existence or absence of azeotropy.

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The Dehydration of Phenylmethylcarbinol with Iodine

BY A. J. CASTRO[1]

Iodine has been used in a number of instances[2] for the dehydration of tertiary alcohols. Although considerably less common, there have been several reports[3] describing the successful use of this substance[4] for the conversion of secondary alcohols to olefins. While an attempt to obtain 3,4-dimethoxystyrene from 3,4-dimethoxyphenylmethylcarbinol with iodine apparently gave poor results,[5] it has been found in this Laboratory that styrene could be prepared in a yield of 52.1–60.5% from phenylmethylcarbinol by such means. This was accomplished by heating a solution of iodine in phenylmethylcarbinol ($7.8\text{-}13.4 \times 10^{-3}$ *M*) so that a steady distillation occurred and the temperature of the distillate was not allowed to rise above 162°.

The styrene prepared by this procedure had a purity of 93.6%.[7] Although a product of higher purity was obtained when the dehydration was conducted at reduced temperature and pressure, the reaction proceeded more slowly and the yield of styrene dropped to 20%, while α,α'-diphenyldiethyl ether[8] was formed in a yield of 30.3%.

Experimental

Phenylmethylcarbinol.—This compound was prepared by the aluminum isopropoxide reduction of acetophenone using a procedure similar to one that has been described.[11] Another source was the Eastman Kodak Co. product.

Dehydration at Elevated Temperature and Ordinary Pressure.—Thirty-two and eight-tenths grams of phenylmethylcarbinol and 68.5 mg. of iodine were placed in a modified Claisen flask and heated in a bath, 212–249° (av. 229°), so that a steady distillation occurred while the major portion of the distillate was collected in the range 147–162°. After 71 minutes iodine vapors were apparent in the reaction flask and the distillation ceased. Although the bath temperature was raised to 287° nothing more distilled. The distillate was shaken with ether, the ether layer separated from the water fraction, washed successively with a solution of sodium thiosulfate and water, and dried with sodium sulfate while the mixture was stored in an ice-chest. The dried and filtered solution was distilled and 16.9 g. (60.5%)[12] of styrene was collected at 48.6–53° (27.5–28.6 mm.). When redistilled this liquid boiled at 60–60.5° (40 mm.); $n^{21.6}_{D}$ 1.5439 (lit.[13] 1.5462); m. p. of dibromide 72.6–73.6° (mixed m. p. with authentic dibromide showed no depression); bromine addition number[14] 143.3, 143.4 and 144.2 (average value corresponds to 93.6% styrene). This styrene polymerized to a clear solid in the presence of sunlight or benzoyl peroxide.

The addition of hydroquinone or 2,5-dihydroxy-1,4-benzoquinone[15] to the reaction flask did not alter the yield appreciably. In all the experiments a small amount of 1,3,5-trinitrobenzene was placed in the receiver prior

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[2] For example: (a) Hibbert, THIS JOURNAL, **37**, 1748 (1915); (b) Whitmore and co-workers, *ibid.*, **55**, 406 (1933); **56**, 176 (1934).

[3] In addition to ref. 2 (a), other examples include: (a) Grignard and Vesterman, *Bull. soc. chim. France*, **37**, 427 (1925); (b) Sabetay and Bleger, *ibid.*, **47**, 468 (1930).

[4] Hibbert[2a] has proposed that iodine functions as a catalyst for the dehydration process. However, it has also been suggested[5] that the dehydration is brought about by hydriodic acid which is formed.

[5] Houben, "Die Methoden der organischen Chemie," Vol. II, 3rd ed., Georg Thieme, Leipzig, 1925, p. 561.

[6] Frank, Adams, Allen, Gander and Smith, THIS JOURNAL, **68**, 1365 (1946).

[7] It is considered that ethylbenzene may be the impurity.

[8] This compound has been reported[9,10] as the main product, along with styrene, from the acid catalyzed dehydration of phenylmethylcarbinol at lower temperatures.

[9] Wuyts, *Bull. soc. chim. Belg.*, **30**, 30 (1921).

[10] Descamps, *ibid.*, **33**, 139 (1924).

[11] Wilds in Adams, *et al.*, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 203.

[12] Yields are calculated on the basis of the quantity of alcohol charged.

[13] Patnode and Scheiber, THIS JOURNAL, **61**, 3449 (1939).

[14] Uhrig and Levin, *Ind. Eng. Chem., Anal. Ed.*, **13**, 90 (1941).

[15] Prepared by George B. Rice using the method of Jones and Shonle, THIS JOURNAL, **67**, 1034 (1945).

to the dehydration and added from time to time during isolation of the product.

Dehydration at Reduced Temperature and Pressure.—A mixture of 40 g. of the alcohol, 81 mg. of iodine and 0.4 g. of 2,5-dihydroxy-1,4-benzoquinone was heated for 125 minutes at a bath temperature of 168–186° and aside from occasional fluctuations the product was collected in the range 79–95.5°. The system was maintained at 454–494 mm. during this period, except for about 20 minutes when it was lowered to 401–408 mm. The distillate and the undistilled residue were treated separately and yielded 6.6 g. of styrene, b. p. 49.5–50.8° (28 mm.); $n^{22}\text{D}$ 1.5449 (lit.[13] 1.5460). Fractionation of the remaining material gave an additional 0.2 g. of styrene, b. p. 53–63° (32 mm.) (total yield 20%), 3.2 g. of reddish-golden colored (impure) phenylmethylcarbinol, b. p. 106–113° (29.5–31 mm.); m. p. of α-naphthylurethan[16] 105.8° (mixed m. p. with an authentic sample not depressed), and 11.2 g. (30.3%) of α,α′-diphenyldiethyl ether, b. p. 165–170° (28–28.5 mm.). The purified ether was a colorless oil with a very faint pleasant odor, b. p. 169.7–170.7° (31 mm.) (lit.[17] 175–177 (31 mm.)); $n^{25.5}\text{D}$ 1.5391; $d^{25.5}_4$ 1.000 (lit.[9] d^{15}_4 1.0058).

Anal.[18] Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.76, 84.91; H, 7.99, 8.06.

Acknowledgment.—The author is grateful to the Research Corporation for a Frederick Gardner Cottrell grant in support of this investigation.

[16] Shriner and Fuson, "The Systematic Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 136.

[17] Ward, *J. Chem. Soc.*, 455 (1927).

[18] Microanalyses by Huffman Microanalytical Laboratory, Denver, Colorado.

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The Magnetic Susceptibility of Vitamin B_{12}

BY HARVEY DIEHL, ROY W. VANDER HAAR AND ROBERT R. SEALOCK

It is naturally of interest to determine the valence of the cobalt atom present in the vitamin B_{12} molecule. The behavior of the material in a magnetic field offers one way to do this. Although the simple salts of bivalent and trivalent cobalt are paramagnetic (three and four unpaired electrons, respectively), the situation is quite different among the coördination compounds. With the exceptions to be noted, the cobaltous ammines are paramagnetic, the cobaltic diamagnetic. The magnetic moments of the cobaltous ammines (these are taken to include the chelate ring compounds) fall between 1.73 and 5.50[1,2] Bohr magnetons, depending on whether the bonds are essentially covalent or ionic. The exception to this is a limited number of cobaltous compounds which have the property of reversibly absorbing and releasing molecular oxygen; the deoxygenated forms of such materials are paramagnetic, the oxygenated forms diamagnetic. The first of these materials, bi-(disalicylalethylenediimine)-μ-aquo-dicobalt, was discovered by Pfeiffer and Tsumaki[3,4] and investigated later in detail by Diehl[5] and others. Michaelis[6] later showed that a solution of cobaltous chloride, ammonia and ammonium chloride possessed these same properties. The cobalt histidine compound investigated by Burk and his co-workers[7] was shown by Michaelis[8] to become diamagnetic on oxygenation.

Although practically all of the numerous hexacovalent cobaltic compounds are diamagnetic[9] there are a few exceptions. Potassium hexafluocobaltate, $K_3[CoF_6]$, is paramagnetic from which it is inferred that the cobalt–fluoride bonds are essentially ionic. The few binuclear cobaltic ammines containing peroxo-, bridging groups which have been examined have been reported contradictorily as being diamagnetic[10,6] and paramagnetic[11,12]; it has been assumed that these compounds contain both tri- and quadrivalent cobalt. This is a subject which needs re-examination.

In view of the sharp difference in the magnetic moment between the coördination compounds of the two valence states, it seems likely that the magnetic behavior of vitamin B_{12} should afford some clue to the valence of the cobalt in the molecule.

Experimental Work

Apparatus.—The measurements were made by the Gouy method using a magnet built by the Consolidated Engineering Company of Pasadena, Calif., their Model 23-104A. This magnet developed a field of 11,000 gauss at 10 amp. Power was supplied to the magnet by a dry plate rectifier preceded by a voltage regulator of large capacity. The power supply was provided with a reversing switch so that following a series of measurements at progressively increasing field strengths, a reverse current could be passed of sufficient size to remove the residual field. A semi-micro balance, Ainsworth Type TCX, was used. Two tubes of the usual type with a glass septum at the center were used, tube A having an internal diameter of 0.24 cm. and B an internal diameter of 0.46 cm. The material was placed in the upper part of the tube, the column of material extending well out of the field. No particular provision was made for temperature control other than to maintain the room temperature about 25°; at 10 amp. the magnet did not heat sufficiently to raise the temperature appreciably during a measurement.

Material.—Crystalline vitamin B_{12}, 1.2 g., was supplied by E. R. Squibb and Sons of New Brunswick, N. J. This material was used without further purification.

Procedure.—Solid materials were well packed into the tubes by tapping the tube one hundred times after each small addition of material. Sufficient time, upwards of

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[1] Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943, p. 174.

[2] Mellor and Goldacre, *J. Proc. Roy. Soc. N. S. Wales*, **73**, 233 (1939); Mellor and Craig, *ibid.*, **74**, 495 (1940).

[3] Pfeiffer, Breith, Lübbe and Tsumaki, *Ann.*, **503**, 84 (1933).

[4] Tsumaki, *Bull. Jap. Chem. Soc.*, **13**, 352 (1938).

[5] Diehl, *et al.*, *Iowa State Coll. J. Sci.*, **21**, 271, 278, 287, 311, 316, 326, 335 (1947); **22**, 91, 110, 126, 129, 141, 150, 165 (1948); **23**, 273 (1949).

[6] Michaelis, *Arch. Biochem.*, **17**, 201 (1948).

[7] Burk, Hearon, *et al.*, *J. Biol. Chem.*, **165**, 723 (1946); *Fed. Proc.*, **6**, 242, 259, 260 (1947); **7**, 148 (1948); *J. Nat. Cancer Inst.*, **9**, (1948).

[8] Michaelis, *Arch. Biochem.*, **14**, 17 (1947).

[9] Rosenbohm, *Z. physik. Chem.*, **93**, 693 (1919).

[10] Feytis and Haller, *Compt. rend.*, **152**, 708 (1911).

[11] Mathieu, *ibid.*, **218**, 907 (1944).

[12] Malatesta, *Gazz. chim. ital.*, **72**, 287 (1942).