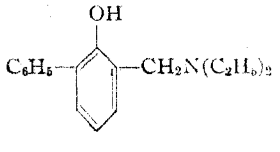
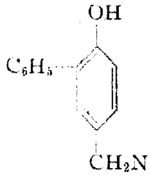
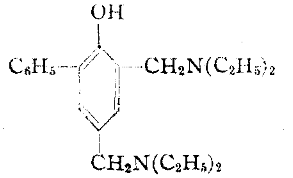


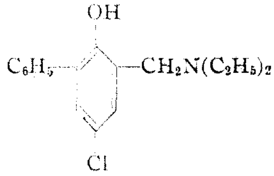
I



II



III



IV

confirmed by synthesizing it from 4-chloro-α-diethylamino-6-phenyl-*o*-cresol (IV).[2] However, attempts to prepare isomer II from 2-chloro-α-diethylamino-6-phenyl-*p*-cresol (V)[2] were unsuccessful.

The Mannich phenols IV and V were prepared from 4-chloro-2-phenylphenol and 2-chloro-6-phenylphenol, respectively.[2] It is important to note that the structures of the starting materials given in the patent literature[4] should be interchanged.[5] These intermediates, the former a liquid and the latter a solid, are properly labeled by the Eastman Kodak Company.

Experimental

Reaction of *o*-Phenylphenol with Formaldehyde and Diethylamine.—A mixture of 6 moles of *o*-phenylphenol, 850 ml. of alcohol, 6 moles of diethylamine and 6 moles of 36% formaldehyde, added in order, was heated for three hours on a steam-bath, during which time the solvent was allowed to distil. After the addition of 500 ml. of water, the mixture was extracted with 1500 ml. of ether, and the ether layer was extracted three times with 500-ml. portions of 2 *N* sodium hydroxide.

The alkaline extract was washed with ether and then treated with 450 ml. of concd. hydrochloric acid, giving a white crystalline solid which was triturated with acetone. The crude product, weighing 278 g., was recrystallized from methanol, giving 228 g. (13% yield) of the pure hydrochloride melting at 223–225°. This compound is soluble in dilute alkali and gives a positive Millon test, indicating that it is the hydrochloride of isomer II.

Anal. Calcd. for $C_{17}H_{21}NO \cdot HCl$: C, 69.97; H, 7.60. Found: C, 69.89; H, 7.48.

The original alkaline-extracted ether solution was washed with water, dried over potassium carbonate, filtered and treated with an excess of alcoholic hydrogen chloride. The precipitated mixture of hydrochlorides melted at 147–170° and weighed 1138 g. The ether filtrate gave another 3.8 g. of hydrochloride melting at 148–149°. Fractional crystallization of the mixture of hydrochlorides from acetone, isopropyl or ethyl alcohol gave 740 g. of a pure hydrochloride melting at 148–149° (42% yield) and 106 g. of a second pure hydrochloride melting at 204–206° (8.5% yield). The 204–206° compound is the dihydrochloride of substance III.[2] The 148–149° compound is insoluble in alkali, fails to give Millon's test and must therefore be the hydrochloride of isomer I.

Anal. Calcd. for $C_{17}H_{21}NO \cdot HCl$: C, 69.97; H, 7.60. Found: C, 70.27; H, 7.32.

Conversion of 4-Chloro-α-diethylamino-6-phenyl-*o*-cresol (IV) to α-Diethylamino-6-phenyl-*o*-cresol (I).—The free base IV was obtained by treating a water solution of 30 g. of the hydrochloride[2] with excess ammonia. The solid product, washed with water and recrystallized from alcohol, gave 23 g. (87%) of IV melting at 69–70°.

Anal. Calcd. for $C_{17}H_{20}ClNO$: N, 4.83. Found: N, 5.01.

Four grams of sodium, in small pieces, was added during the course of one hour to a solution of 5.8 g. of IV in 100 ml. of boiling amyl alcohol. After refluxing for another hour, a little methanol was added to react with the unchanged sodium, concd. hydrochloric acid added in excess, the amyl alcohol steam distilled and the residue extracted with ether. Excess ammonia was added to the acid layer and the liberated base was extracted with ether. The ether solution of the base was washed, dried and treated with excess alcoholic hydrogen chloride. Recrystallization of the precipitated hydrochloride gave 1.4 g. (24%) of white solid melting at 148–149°. A mixed melting point with the 148–149° product obtained directly by the Mannich reaction proved their identity.

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[4] Britton and Bryner, U. S. Patent 1,969,963; *C. A.*, **28**, 6160 (1934).

[5] Weissberger and Salminen, THIS JOURNAL, **67**, 58 (1945).

An Azeotrope between Paraffin Hydrocarbons

BY GEORGE CALINGAERT[1] AND MIECZYSLAW WOJCIECHOWSKI

The occurrence of azeotropism is based on the existence of a deviation from ideality sufficient to overcome the difference in volatility of the two components of the system. Since deviations from ideality are caused by dissimilarity between molecular species,[2] azeotropism is seldom observed between similar materials, and no report is known of a case of azeotropism between isomers.

A publication from this Laboratory[3] gives data on the deviation from ideality for several binary systems of hydrocarbons. In the case of benzene and cyclohexane the observed total pressure exceeded that calculated for ideality by as much as 8% in the middle of the pressure–composition diagram. This fact, coupled with the proximity of the boiling points of the two components, implied the likelihood of existence of an azeotrope, and this was later confirmed experimentally by Scatchard, Wood and Mochel.[3,4] Definite deviations from ideality were observed between chemical homologs, such as paraffin hydrocarbons, and even between isomeric paraffins, though in the latter case the deviations were only of the order of 1% or less. The possibility of existence of azeotropism even then is not excluded, if the vapor pressures of the two components are sufficiently close together. It was thought that such a pair might be found in 2,2,3-trimethylbutane and 2,4-dimethylpentane, which not only boil less than 0.4° apart under atmospheric pres-

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[1] Hobart and William Smith Colleges, Geneva, N. Y.

[2] B. J. Mair, A. R. Glasgow, Jr., and F. D. Rossini, *J. Res. Natl. Bur. Standards*, **27**, 39 (1941).

[3] H. A. Beatty and G. Calingaert, *Ind. Eng. Chem.*, **26**, 504 (1934).

[4] G. Scatchard, S. E. Wood and J. M. Mochel, *J. Phys. Chem.*, **43**, 119 (1939).

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,[6] 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).