hexene from the laws of ideal solutions, an azeotrope in the system cyclohexene–1,4-dioxane was observed. To ascertain more fully the nature of this azeotropic system at atmospheric pressure, a further study on this pair of liquids has been made. A description of the vapor–liquid equilibrium has been obtained.

To ascertain the composition of vapor in equilibrium with the liquid solution, approximately 75 cc. of cyclohexene was placed in a 250-cc. round-bottom flask to which a distilling head was attached by a ground glass standard taper joint. A Liebig condenser was attached to the distilling head. The flask was almost totally immersed in a bath of paraffin oil. A boiling tube was kept in the flask to prevent bumping. The boiling point of the cyclohexene was measured with the bulb of the thermometer immersed in the liquid. A small amount of 1,4-dioxane was added and approximately 10 cc. was distilled from the solution. This distillate was removed and the next 2 cc. of the distillate was collected for analysis. The temperature of the boiling solution was observed during the collection of this latter portion of the distillate. A small sample of residue was removed immediately from the flask for analysis. The original 10 cc. of distillate was returned to the flask and a second small portion of the 1,4-dioxane added. The procedure was repeated until the composition remaining in the flask was approximately 50 mole per cent. of 1,4-dioxane. For compositions containing a greater proportion of 1,4-dioxane, a similar procedure was followed starting with pure 1,4-dioxane and adding small amounts of cyclohexene.

The analyses of the several solutions were made by means of an Abbe refractometer thermostated at 25°. In preliminary work, standard samples of these cyclohexene–1,4-dioxane solutions had been weighed out and the index of refraction of the several solutions measured. The data obtained in making up the reference solutions are given in Table I.

TABLE I

REFRACTIVE INDICES OF STANDARD SAMPLES OF CYCLOHEXENE–1,4-DIOXANE

Cyclohexene, mole %	$n^{25}D$	Cyclohexene, mole %	$n^{25}D$
100.0	1.4437	65.1	1.4339
95.2	1.4420	45.3	1.4290
89.8	1.4407	31.1	1.4260
86.8	1.4398	20.6	1.4235
80.3	1.4378	10.6	1.4216
69.9	1.4350	0.0	1.4198

In Table II are given the boiling temperatures of 21 solutions of 1,4-dioxane in cyclohexene and the composition of vapor in equilibrium with each of these solutions. A minimum-boiling azeotrope containing 84.3 mole per cent. of cyclohexene and boiling at 83.9° at 749.7 mm. pressure will be noted.

TABLE II

CYCLOHEXENE–1,4-DIOXANE SYSTEM (749.7 MM.)

Temp.,[a] °C.	Cyclohexene, mole %		Temp.,[a] °C.	Cyclohexene mole %	
	Liquid	Vapor		Liquid	Vapor
84.35	100.0	100.0	87.6	41.9	61.5
84.00	91.3	89.9	89.5	34.0	53.0
83.95	88.0	97.9	90.6	30.0	49.9
83.90	86.8	86.5	93.0	23.1	42.0
83.90	84.3	84.3	94.5	18.0	36.9
84.3	73.9	77.0	96.2	13.0	32.0
84.6	69.0	73.8	97.0	10.3	28.2
84.5	69.9	73.8	97.9	8.9	27.0
85.3	61.0	69.1	99.9	5.0	13.9
85.9	55.7	68.2	101.0	3.0	9.0
86.4	51.1	65.0	102.0	0.0	0.0
86.9	47.5	62.8			

[a] The boiling temperatures of the pure liquids with the thermometer bulb in the condensing vapor phase were 82.7° at 755.3 mm. for the cyclohexene and 101.5° at 751.2 mm. for the 1,4-dioxane.

The simple distilling assembly used is always more than one theoretical plate and the composition data on both sides of the azeotrope are only approximate. However, the azeotropic composition at 84.3 mole per cent. of cyclohexene should still be valid. The temperatures reported are approximately 1 to 1.5° higher than the actual values since the thermometer was totally immersed in the boiling liquid.

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Polarization of Ethylene Dichloride in Benzene

BY ARTHUR A. VERNON AND ELBERT V. KRING

Vernon, Wyman and Avery[1] reported the dielectric constants of ethylene dichloride–benzene mixtures over the complete range. It seemed worthwhile to determine the densities of these solutions and calculate the polarization of ethylene dichloride since the only reported measurements were made in very dilute solutions.[2,3,4]

The only P_2 data are those reported by Gross.[3]

Ethylene dichloride and benzene were purified as previously reported[1] and the densities of the solutions were determined by the specific gravity bottle method.

An equation was established for the density–concentration curve

$$d = d_A x_A + d_B x_B - a x_A x_B$$

where d = density, x = mole fraction, a = 0.07345 and subscripts A and B refer to benzene and ethylene dichloride, respectively. Table I gives the observed densities, the densities calculated according to the equation, P_{12} and P_2 values for

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[1] Vernon, Wyman and Avery, THIS JOURNAL, **67**, 1922 (1945).

[2] Williams, *Z. physik. Chem.*, **A138**, 75 (1928).

[3] Gross, *Physik. Z.*, **32**, 567 (1931).

[4] Muller, *ibid.*, **34**, 689 (1933).

TABLE I

POLARIZATION AND DENSITIES OF BENZENE–ETHYLENE DICHLORIDE MIXTURES

Mole frac. $C_2H_4Cl_2$	Dielectric constant	$P_{1,2}$	P_2	d^{25}_4 obs.	d^{25} calcd.	Deviation
0.000				0.8739		
.113	2.791	33.096	83.698	.9086	0.9085	−0.0001
.211	3.318	38.077	80.805	.9397	.9400	+ .0003
.342	3.879	41.980	71.468	.9863	.9844	− .0019
.446	4.707	46.912	72.081	1.0192	1.0214	+ .0022
.605	5.914	51.406	67.568	1.0802	1.0810	+ .0008
.719	6.940	54.137	64.878	1.1247	1.1261	+ .0014
.857	8.455	56.734	61.753	1.1846	1.1832	− .0014
1.000	10.365	58.959	58.959	1.2453		

ethylene dichloride calculated from the measured densities. Figure 1 is a plot of P_2 *versus* mole fraction including the values of Gross.[3]

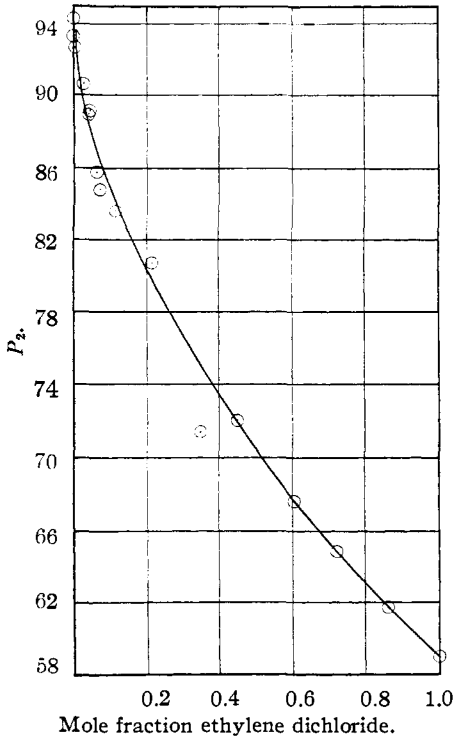

Fig. 1.—Polarization of ethylene dichloride in benzene solutions.

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The Preparation of 6,7-Diethoxy-1-(3′,4′-diethoxybenzyl)-isoquinoline

BY JOHN WEIJLARD, EDWARD F. SWANEZY AND ELEANOR TASHJIAN

Perparin, 6,7-diethoxy-1-(3′,4′-diethoxybenzyl)-isoquinoline, the tetraethyl analog of papaverine, is reported to be more active than papaverine as an antispasmodic.[1] Although its preparation from N-(3,4-diethoxyphenylacetyl)-β-hydroxy-β-(3,4-diethoxyphenyl)-ethylamine has been reported,[2] the details are meager, and the preparation and characterization of the requisite intermediates are not recorded.

We have prepared perparin from N-(3,4-diethoxyphenylacetyl)-β-(3,4-diethoxyphenyl)-ethylamine by ring closure to the dihydroisoquinoline, and dehydrogenation of the latter, the same series of steps that were employed by Kindler and Peschke for the preparation of papaverine.[3]

β-(3,4-Diethoxyphenyl)-ethylamine, required for the preparation of the amide, was prepared by catalytic hydrogenation of 3,4-diethoxymandelonitrile.

Experimental

3,4-Diethoxybenzaldehyde.[4]—Six hundred and sixty-four grams of ethyl vanillin (4 moles) was mixed with 400 cc. of diethyl sulfate (472 g., 3 moles), the pasty mixture was stirred in a stainless steel container while 680 cc. of 30% sodium hydroxide solution was added in 30–40-cc. portions over a period of one hour. The temperature was about 40°. The mixture was warmed to 80° when complete solution was obtained. The solution was held at 80–82° and rapidly stirred while 440 cc. of additional diethyl sulfate (520 g., 3.4 moles) was added in 20–30-cc. portions over a period of one hour. The solution was stirred for another half-hour at 80°, then 120 cc. of 30% sodium hydroxide was added and stirred an additional ten minutes. The solution was cooled to room temperature and extracted with ether, the ether extract was washed with 5% sodium hydroxide solution, then with water until free from alkali. The ether was distilled and the residue was dried *in vacuo;* yield 736 g. (95%) of a nearly water white sirup which was used without further purification in the experiments. A sample for analysis was distilled and practically all distilled at 128–130° and 2 mm. pressure.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.03; H, 7.26. Found: C, 67.83; H, 7.46.

3,4-Diethoxymandelonitrile.—This compound was made from 3,4-diethoxybenzaldehyde in nearly quantitative yields according to directions for 3,4-dimethoxymandelonitrile.[5] The melting point is 42–43°.[6]

β-(3,4-Diethoxyphenyl)-ethylamine.[7]—Sixty-six grams of the crude 3,4-diethoxymandelonitrile (0.3 mole) was dissolved in 400 cc. of alcohol, 30 cc. of concd. aqueous hydrochloric acid was added followed by 1.5 g. of platinum oxide, then hydrogenated at 10 to 20 lb. of pressure. About 75% of the theoretically required hydrogen was absorbed in six hours, then the reduction stopped. The catalyst was filtered and the solution concentrated to dryness *in vacuo*. The residue was dissolved in water and extracted with ether to remove substances that had not been reduced. To the solution was added 75 cc. of 30% sodium hydroxide, the precipitated amine was extracted with ether and the ether extract was dried over anhydrous sodium sulfate. The ether was removed *in vacuo*, and the residue distilled at about 125° and 1 mm. pressure; yield 26.6 g. (42.4%).

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(1) Issekutz, Leinzinger and Dirner, *Arch. exp. Path. Pharmakol.*, **164**, 158 (1932).

(2) Wolf, U. S. Patent 1,962,224; *C. A.*, **28**, 4841 (1934).

(3) Kindler and Peschke, *Arch. d. Pharm.*, **272**, 236–241 (1934).

(4) Prepared by Ide and Buck, THIS JOURNAL, **54**, 3305 (1932), but since no experimental details were given, the preparation is included here.

(5) Pictet and Gams, *Ber.*, **42**, 2949 (1909).

(6) Incidentally, the compound was found to be a convenient starting material for the preparation of 3,4-diethoxymandelic acid ester by cold esterification of the nitrile in alcohol with hydrochloric acid, and for the preparation of 3,4-diethoxymandelic acid by mild hydrolysis of the ester.

(7) Prepared previously by electrolytic reduction of 3,4-diethoxy-ω-nitrostyrene by Slotta and Haberland, *Angew. Chem.*, **46**, 769 (1933).