

yield. The copper catalyst was removed by filtration, washed twice on the filter with water (50 ml.) and the combined filtrate and washings acidified with sulfur dioxide while kept in an ice-bath. The acidified solution was extracted with ether (500 ml.) in a continuous liquid-liquid extractor for twenty-four hours. The ethereal solution was concentrated on the steam-bath to a small volume (*ca.* 50 ml.), the gentisic acid precipitated by the addition of Skellysolve-C and recovered by filtration. The yield of a light tan colored product was 11.1 g. (72%), m. p. 190°.

Recrystallization from boiling water, after carbon treatment, gave a white crystalline material, m. p. 205°; mixed m. p. with an authentic sample of gentisic acid gave no depression.

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RECEIVED DECEMBER 29, 1949

### Dielectric Constants of Methyl Alcohol-Benzene Mixtures

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In the course of solubility studies with non-aqueous solvents, it was necessary to determine the dielectric constants of methyl alcohol-benzene mixtures over the complete range. Williams, Rosenberg and Rothenberg<sup>1</sup> recently published density data for these same mixtures, and, therefore, it seemed worthwhile to calculate polarization values for methyl alcohol in benzene.

**Materials.**—Reagent grade benzene and methyl alcohol were dried over activated alumina and distilled with a fractionating column. The first and last 20% fractions were discarded and the purified product was stored in Pyrex flasks with sealed stoppers. The index of refraction of the purified methyl alcohol was 1.3277 at 25° compared to the "International Critical Tables" value of 1.32773; for benzene the index of refraction was 1.4977 at 25°, compared to the "International Critical Tables" value of 1.49779 at 25.2°.

**Dielectric Constant Measurement.**—The dielectric constants of a series of methanol-benzene solutions were measured on a wide range frequency bridge<sup>2</sup> using a cell holding 15 ml. and having a cell constant of 1.352  $\mu\text{mf}/\text{unit } \epsilon$ . Measurements were carried out at 500 kc. and 25° and dielectric constant values of the pure benzene and methanol compared very favorably with those reported.<sup>3</sup>

**Results.**— $P_{12}$  values were calculated from the relation

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2} \frac{f_1 m_1 + f_2 m_2}{\rho}$$

and  $P_2$  values were obtained by use of

$$P_{12} = f_1 P_1 + f_2 P_2$$

(1) G. C. Williams, S. Rosenberg and H. A. Rothenberg, *Ind. Eng. Chem.*, **40**, 1273 (1948).

(2) J. L. Oncley and N. R. S. Hollies, "A Wide Range Frequency Bridge, Dielectric Constants and Conductance Studies on Electrolytic Solutions," *Rev. Sci. Instr.*, in preparation.

(3) P. S. Albright and I. J. Gosting, *THIS JOURNAL*, **68**, 1061 (1946).

The data of Williams, Rosenberg and Rothenberg<sup>1</sup> were used to make a plot of density *versus* mole per cent. Since the index of refraction of benzene reported by these authors does not agree with the "International Critical Tables" value, measurements of refractive index for various volume per cent. mixtures were made in this laboratory. A plot of data was used to determine compositions in volume per cent. Then the volume per cent. mole fraction data of Williams, Rosenberg and Rothenberg<sup>1</sup> were plotted to obtain mole fractions for any mixture made up.

Mole frac. MeOH	Dielectric constant	Density	Index of refraction	$P_{12}$	$P_2$
0.0	2.27	0.8724	1.4977	26.6	
.140	3.67	.8684	1.4859	38.9	114
.353	6.41	.8579	1.4643	46.4	82.6
.362	6.70	.8575	1.4637	46.9	82.8
.497	9.20	.8487	1.4459	47.6	68.9
.508	9.54	.8479	1.4439	47.7	68.2
.601	12.24	.8403	1.4281	47.36	61.13
.613	12.83	.8393	1.4264	47.40	60.51
.700	16.33	.8298	1.4092	47.22	54.62
.775	19.69	.8205	1.3924	44.53	49.73
.840	22.95	.8177	1.3762	42.72	45.78
.895	26.30	.8030	1.3595	41.06	42.75
.955	29.51	.7948	1.3420	38.83	39.41
1.000	32.65	.7865	1.3277	37.21	37.21

A plot of  $P_2$  *versus* mole fractions of methyl alcohol is shown in Fig. 1.

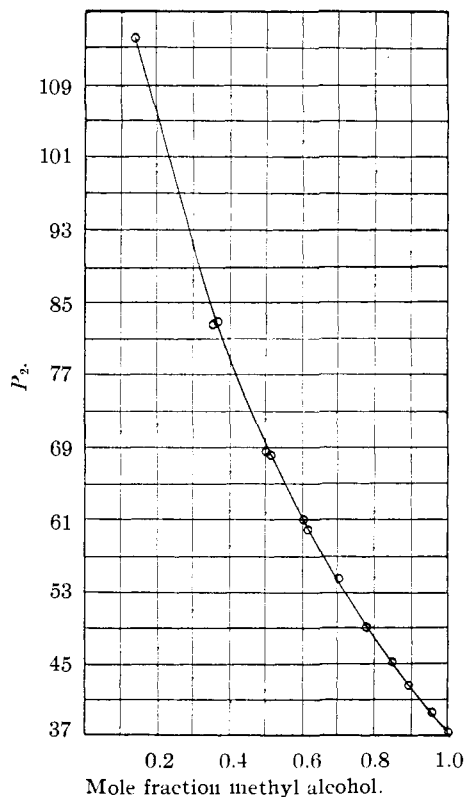


Fig. 1.—Polarization of methyl alcohol in benzene.

### Discussion

The method used for obtaining the dielectric constants is least accurate in the low mole fraction methanol region. Accordingly the results do not justify any conclusions about the polarizability of methanol which has been covered so ably elsewhere.<sup>3,4,5</sup> However, the figures obtained are useful in evaluating the relative contributions of association<sup>6</sup> and field interaction<sup>7</sup> to the anomalous behavior of the dielectric constant as a function of concentration.

The authors wish to express their appreciation to Dr. Norman R. S. Hollies of the Harvard Medical School who measured the dielectric constants and helped with the paper.

(4) J. D. Stranathan, *Phys. Rev.*, **31**, 156 (1928).

(5) J. D. Stranathan, *J. Chem. Phys.*, **6**, 395 (1938).

(6) W. H. Rodebush, D. R. Eddy and L. D. Eubank, *ibid.*, **8**, 899 (1940).

(7) G. Oster and J. G. Kirkwood, *ibid.*, **11**, 175 (1943).

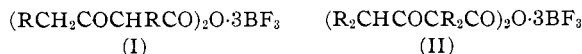
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RECEIVED FEBRUARY 14, 1950

### Formation of Symmetrical Ketones from Self-condensations of Anhydrides by Boron Fluoride<sup>1</sup>

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Meerwein and Vossen<sup>2</sup> reported that, although acetylacetone is formed exclusively in the self-condensation of acetic anhydride by boron fluoride, the corresponding symmetrical mono-ketone is produced mainly with propionic or *n*-butyric anhydride and exclusively with isobutyric anhydride. Intermediate self-acylation products (coördinated with boron fluoride) such as I or II appear to be produced<sup>2</sup> and these, on hydrolysis and decarboxylation, yield the mono-ketone.



procedure for ketones of the type  $(\text{R}_2\text{CH})_2\text{CO}$  for which the convenient method involving the Claisen self-condensation of esters is not generally satisfactory.<sup>3</sup> However, our procedure has not been very satisfactory with 2-ethylhexoic anhydride. Unsuccessful attempts were made to produce mixed ketones from acetic anhydride with caproic, 2-ethylbutyric, and 2-ethylhexoic anhydrides.

### Experimental<sup>4</sup>

Caproic, 2-ethylbutyric, and 2-ethylhexoic anhydrides were prepared by the acetic anhydride-acid exchange method.<sup>5</sup>

In a 1-liter round-bottomed distilling flask fitted with a 25-cm. Vigreux column and downward condenser, were placed 2.5 moles of the acid corresponding to the anhydride desired, 5 moles of acetic anhydride and 0.5% by weight of sulfuric acid. The flask was heated to distil first acetic acid, then the excess acetic anhydride. The residue was distilled twice *in vacuo*. The following anhydrides were prepared by this method: caproic anhydride, b. p. 138–140° at 15 mm; yield, 52%. 2-Ethylbutyric anhydride, b. p. 137–139° at 35 mm; yield, 54%. 2-Ethylhexoic anhydride, b. p. 154–157° at 10 mm; yield, 63%.

**Ketones from Anhydrides (Table I).**—In a 500-ml. three-necked flask was placed 0.25 mole of the anhydride, and an inlet tube for boron fluoride was inserted so that its tip was about two centimeters from the liquid surface. The flask was fitted with a sealed stirrer, low temperature thermometer and a calcium chloride tube serving as a gas outlet, and then immersed in an acetone-Dry Ice-bath until the temperature reached  $-10^\circ$ . Boron fluoride gas was added from a tank as rapidly as possible, with rapid stirring, keeping the temperature around  $0^\circ$ . In ten to twenty minutes excess boron fluoride began to escape from the calcium chloride tube, and the addition was continued fifteen or twenty minutes longer at a slower rate to ensure complete saturation. The addition tube was replaced by a water condenser. To the stirred reaction mixture was added cautiously through the condenser a solution of 102 g. of sodium acetate in 200 ml. of water, and the stirring continued while heating on the steam-bath for an hour. The oil which separated was extracted twice with ether, and the combined ether extracts washed with saturated sodium bicarbonate solution until no further evolution of carbon dioxide occurred. After washing with water, the ether

TABLE I

KETONES FROM SELF-CONDENSATION OF ANHYDRIDES BY BORON FLUORIDE

Anhydride	Ketone	Yield, %	B. p. °C.	Mm.	Analyses, % <sup>a</sup>			
					Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Butyric	Di- <i>n</i> -propyl	60	144–145	atm.	...	...	...	...
Caproic	Di- <i>n</i> -amyl	64	124–125	35	77.58	77.62	13.03	12.72
2-Ethylbutyric	<i>sym</i> -Tetraethylacetone	57	103–104	30	77.58	77.76	13.03*	13.13
2-Ethylhexoic	$\alpha,\alpha'$ -Diethyl-di- <i>n</i> -amyl	32 <sup>b</sup>	157–157.5	35	79.57	79.80	13.36	13.60

<sup>a</sup> Analyses by Clark Microanalytical Laboratories, Urbana, Illinois. <sup>b</sup> Obtained on a 0.1 mole scale by the modified procedure.

We have confirmed this result with *n*-butyric anhydride, avoiding the time-consuming steam distillation employed by the earlier workers, and have extended this convenient method to certain higher ketones (Table I). Various other symmetrical ketones could probably be prepared similarly in satisfactory yields. The method appears to be particularly attractive as a laboratory

(1) This work was carried out under Contract N7onr-455 with the Office of Naval Research.

(2) Meerwein and Vossen, *J. prakt. Chem.*, [2] **141**, 149 (1934).

solution was dried over Drierite and the solvent distilled. The residue was fractionated *in vacuo*.

The above procedure has failed to produce  $\alpha,\alpha'$ -diethyl di-*n*-amyl ketone from 2-ethylhexoic anhydride, 2-ethyl-

(3) See Hauser and Hudson, "Organic Reactions," Vol. I, Chapter 9, John Wiley and Sons, Inc., New York, N. Y., 1942.

(4) Samples of caproic, 2-ethylbutyric and 2-ethylhexoic acids and of *n*-butyric, 2-ethylbutyric and 2-ethylhexoic anhydrides were kindly furnished by the Carbide and Carbon Chemicals Corporation.

(5) This method is based on procedures described in Hickenbottom, "Reactions of Organic Compounds," 2nd ed., Longmans, Green and Company, New York, N. Y., 1948, p. 227; see also Schulz, U. S. Patent 2,163,013, June 20, 1939, C. A., **33**, 7821 (1939).