phenylpropiophenone reported in the literature is 65–66°.[8]

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.61; H, 6.23. Found: C, 79.67; H, 6.12.

The 2,4-dinitrophenylosazone, recrystallized from ethyl acetate, melted at 233–234°.

Anal. Calcd. for $C_{27}H_{20}N_8O_8$: N, 19.17. Found: N, 19.39.

Further reduction of the acyloin in ethanol solution, using platinum oxide as catalyst, gave the diol of m.p. 84° described below in 85% yield.

Platinum Oxide–Ethanol.—Two moles of hydrogen was taken up. The residual sirup solidified on stirring with petroleum ether and chilling, weight 3.1 g. Evaporation of the petroleum ether gave 1.8 g. of an oil from which 217 mg. of the osazone of α-hydroxy-β-phenylpropiophenone was obtained on treatment with dinitrophenylhydrazone. The solid gave 2.1 g. of needles, m.p. 79.5–81°, after one recrystallization from benzene–ligroin; further crystallizations raised the m.p. to 84° but resulted in considerable losses. Periodic acid titration[9] indicated that all fractions, including those from the mother liquors, consisted exclusively of 1,2-diol.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.91; H, 7.07. Found: C, 79.15; H, 6.82.

Benzoyl chloride in pyridine gave the dibenzoate in 75% yield, m.p. 157° from much ethanol.

Anal. Calcd. for $C_{29}H_{24}O_4$: C, 79.79; H, 5.54. Found: C, 80.27; H, 5.39.

The diacetate was prepared with acetic anhydride in pyridine and melted at 71–72°.

Anal. Calcd. for $C_{19}H_{20}O_4$: C, 73.04; H, 6.46. Found: C, 73.59; H, 6.46.

Saponification of 1.1 g. of the dibenzoate regenerated 0.52 g. (90%) of the 1,2-diol, m.p. 84–84.5°. Periodic acid oxidation of the diol in methanol solution gave an oil which was converted to a mixture of dinitrophenylhydrazones. Chromatography over alumina (solvent benzene, eluent benzene–ether) led to the separation of the dinitrophenylhydrazones of benzaldehyde and phenylacetaldehyde in 85 and 82% yield, respectively.

Repetition of the work of Trevoy and Brown[10] who recently reported that a diol identical with that of Levy and Dvoleitzka-Gombinska[8] was obtained by lithium aluminum hydride reduction of benzalacetophenone oxide led to the isolation in 77% yield of an unsharply melting product, m.p. 72–80°, whose 1,2-diol content was only 80%. From this material we obtained the dibenzoate of m.p. 157° in 50% yield; and on saponification the diol of m.p. 84°.

Other Solvent–Catalyst Combinations.—Platinum oxide in ethyl acetate and acetic acid, palladium–charcoal in ethanol, ether, ethyl acetate and acetic acid, Raney nickel in ethanol, ether and ethyl acetate gave oily or solid diol mixtures which usually could be converted to 50–80% of crystalline material melting in the range 65–73°. Frequently a small amount of pure diol of m.p. 84° separated from the mother liquors of the first recrystallization on standing. Each time a solution of 1 g. of the mixture in 25 ml. of benzene was chromatographed through a column of 30 g. of alumina and developed with benzene, benzene–ether (4:1), benzene–ether (1:1) and ether. Ordinarily several eluate fractions yielded material melting sharply at 84° after recrystallization from petroleum ether, together with much lower melting material.

The diastereoisomer of m.p. 128° was isolated only from the oil obtained by reduction of benzalacetophenone oxide in ethanol with Raney nickel. Several fractions obtained after chromatography over alumina (solvent benzene, eluate benzene–ether) and crystallization from petroleum ether melted above 110°; these were combined and fractionally crystallized until the melting point remained constant at 128°. Periodic acid oxidation of this material, weight 73 mg., resulted in the characteristic odor of benzaldehyde.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.91; H, 7.07. Found: C, 78.77; H, 7.00.

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[8] A. McKenzie, G. Martin and H. G. Rule, *J. Chem. Soc.*, **105**, 1583 (1915); E. P. Kohler and R. H. Kimball, THIS JOURNAL, **56**, 729 (1934); C. Prévost and A. Sommière, *Bull. soc. chim.*, [5] **2**, 1151 (1935); P. Julian, E. W. Meyer, A. Magnani and W. Cole, THIS JOURNAL, **67**, 1203 (1945).

[9] E. Jackson, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 361.

[10] L. W. Trevoy and W. G. Brown, THIS JOURNAL, **71**, 1675 (1949).

Complex of Polysilicic Acid with N-Diethylaniline Hydrochloride

BY RALPH K. ILER

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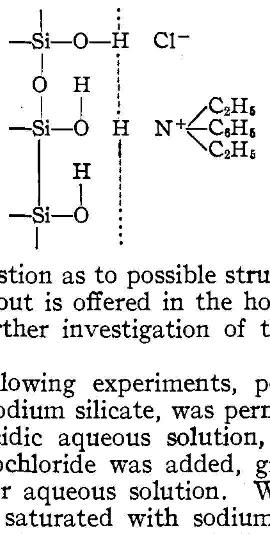
Kirk[1] first reported that complexes of polysilicic acid with electron donor compounds such as ethers and amides can be isolated from aqueous solution by a salting-out technique. It might therefore be expected that polysilicic acid might similarly combine with an amine to form an addition compound corresponding to a substituted ammonium salt of polysilicic acid. However, it has now been found that the complex salted out of a solution containing polysilicic acid and diethylaniline hydrochloride, contains silica combined with the amine hydrochloride rather than with the amine. Since the nitrogen atom in the amine salt does not possess a free pair of electrons, it is evident that the association of this salt cannot involve the formation of a hydrogen bond between the nitrogen atom and the hydrogen of polysilicic acid. In this complex, the relationship of the components might be represented by the following scheme, in which the electronegative chlorine, oxygen and nitrogen atoms are associated through hydrogen bonds.



This suggestion as to possible structure is purely speculative, but is offered in the hope that it will stimulate further investigation of this interesting system.

In the following experiments, polysilicic acid, made from sodium silicate, was permitted to polymerize in acidic aqueous solution, then diethylaniline hydrochloride was added, giving a homogeneous, clear aqueous solution. When the solution is then saturated with sodium chloride, the complex of polysilicic acid and diethylaniline hydrochloride separates either as a viscous second liquid phase or as a white precipitate, depending upon the degree of polymerization of the polysilicic acid. Neither polysilicic acid nor diethylaniline hydrochloride alone can be salted out of solution by this procedure.

Experimental

Preparation of Polysilicic Acid.—A solution of sodium silicate, 1.715 molar with respect to SiO_2, was first prepared

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[1] J. S. Kirk, U. S. Patents 2,408,654 and 2,408,656 (1946).

by diluting commercial sodium silicate (Grasselli 20WW Grade, containing 28.4% SiO_2 and 8.72% Na_2O).

Five hundred and eighty-five milliliters of this solution was then run into 415 ml. of 1.52 normal hydrochloric acid at 20° with violent agitation. The solution of sodium silicate was added in a stream about 0.1 inch in diameter directed into the vortex of the stirred acid, addition being complete in about 5 minutes. The resulting solution of polysilicic acid had a *p*H of 1.65, and was 1 molar with respect to SiO_2. Sol A: Half of the above solution of polysilicic acid was aged for 1 hour at 25°. Sol B: The other half of the above solution was aged for 2 hours at *p*H 1.65, 25°; then the *p*H was raised to 2.25 by the addition of 2 *N* NaOH and the sol aged further for 4.5 hours at 25°.

Sols A and B were mixed with a 2.0 molar solution of aniline hydrochloride in the proportions shown in Table I, stirred for 5 minutes, saturated with sodium chloride by adding solid salt and stirring for five minutes, and then centrifuged in order to isolate the complex.

TABLE I

Expt.	Volume of sol, ml.	Volume of 2 molar DEAH,[a] ml.	Solid NaCl added	Separated complex
1	500 A	250	200	80 ml. heavy viscous fluid
2	500 A	125	166	50 ml. heavy fluid, more viscous than 1
3	500 B	250	200	198 ml. white soft paste containing emulsified brine
4	500 B	125	166	156 ml. white soft paste containing emulsified brine
5	None	250 plus 250 H_2O	133	Clear solution—no phase separation

[a] DEAH, diethylaniline hydrochloride.

The compositions of the recovered complexes, based on analyses for silica, nitrogen, chlorine and sodium are shown in Table II. It is evident that as the age of the sol increases, the ratio of silica to diethylaniline hydrochloride in the complex also seems to increase; this is probably due to the diminishing combining power of the silicic acid as it polymerizes. In experiment 2 there was not enough excess amine hydrochloride to combine with all the silica, but after the sol had been aged, as in 4, this quantity of the amine salt was more nearly adequate. The ratio of hydrogen chloride to diethylaniline in the complex approximates unity.

TABLE II

Experiment	1	2	3	4
Recovered complex, ml.	80	50	198	156
grams (approx.)	100	62	250	195
SiO_2, %	24.99	33.90	11.48	12.67
Diethylaniline (nitrogen analysis), %	35.2	31.4	13.7	10.0
NaCl (sodium analysis), %	1.91	1.63	15.95	27.4
HCl (Total chloride minus chloride equivalent to sodium), %	9.77	8.47	4.10	2.19
Mol ratio in complex: $\left(\frac{HCl}{\text{diethylaniline}}\right)$	1.14	1.10	1.2	0.9
Mol ratio in complex: $\left(\frac{SiO_2}{\text{diethylaniline}}\right)$	1.77	2.69	2.09	3.15
Mol ratio in original solution: $\left(\frac{SiO_2}{\text{diethylaniline}}\right)$	1.0	2.0	1.0	2.0
SiO_2 recovered in complex, %	83	56	96	82
Diethylaniline recovered, %	48	52	46	52

In the cases of the liquid complexes obtained in experiments 1 and 2, the total water in the complex can be estimated by difference, assuming that the sodium chloride is present as emulsified, saturated brine and subtracting this water from the total. This calculation gives 14.3% water in complex 1, and 21.5% in complex 2. However, no attempt was made to dehydrate the complex, and probably only a portion of this water was in chemical combination with the silica.

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The Ultraviolet Absorption Spectra of Two Arylalkylphosphinic Acids and Related Compounds

BY H. H. JAFFÉ AND LEON D. FREEDMAN

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The ultraviolet absorption spectra of a number of arylphosphonic and diarylphosphinic acids were reported in a recent paper from this Laboratory.[1] We have now determined the absorption spectra of (*o*-bromophenyl)-ethylphosphinic and (*p*-nitrophenyl)-ethylphosphinic acids. Table I lists the wave lengths of the absorption maxima and the corresponding molar extinction coefficients for these compounds and several related arylphosphonic and diarylphosphinic acids.

TABLE I

Compound	λ_{max}	ϵ_{max}
BrC_6H_5	264.5[a]	163
o-$BrC_6H_4PO_3H_2$	270.5[a]	847
(*o*-$BrC_6H_4)_2PO_2H$	275[a]	1780
(*o*-$BrC_6H_4)C_6H_5PO_2H$	273.5[a]	1430
(*o*-$BrC_6H_4)C_2H_5PO_2H$	271[a]	1010
(*p*-$O_2NC_6H_4)C_2H_5PO_2H$	266[b]	8100

[a] Secondary band. [b] Primary band.

Our previous data showed that the absorption spectra of unsymmetrical diarylphosphinic acids ($ArAr'PO_2H$) may be calculated by averaging the extinction coefficients of the corresponding symmetrical diarylphosphinic acids (Ar_2PO_2H and Ar'_2PO_2H).[1] A similar relationship holds approximately for the arylalkylphosphinic acids, if it is assumed that the absorption of diethylphosphinic acid is negligible compared to the absorption of diarylphosphinic acids in the region 240 to 300 mμ. This assumption is reasonable in view of the facts that phosphoric acid does not absorb appreciably in this region, and that the ethyl radical is not a chromophore. The primary band [observed in (*p*-nitrophenyl)-ethylphosphinic acid] and the secondary band [observed in (*o*-bromophenyl)-ethylphosphinic acid] occur at shorter wave lengths than would have been predicted; the molar extinction coefficients, however, can be calculated with an error of less than 20% by means of the above relationship.

o-Bromobenzenephosphonic acid has an ultraviolet absorption approximately 5 times as intense as that of bromobenzene. This intensification is outside the limits 1.5 to 4 reported previously.[1] Otherwise, the data reported in the present paper on the absorption spectra of *o*-bromobenzenephosphonic, bis-(*o*-bromophenyl)-phosphinic and (*o*-bromophenyl)-phenylphosphinic acids are in agreement with the generalizations made in the previous paper.

The ultraviolet absorption spectra were determined by the procedure previously used.[1] All measurements were made with 1.0-cm. silica cells in a temperature controlled room (21 ± 2°). The molar extinction coefficient, ε, was calculated from the equation: $\epsilon = D/lc$, where D = optical density, l = absorption cell thickness in cm., and c = the concentration of the sample in moles per liter.

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(1) H. H. Jaffé and L. D. Freedman, THIS JOURNAL, **74**, 1069 (1952).