the ratio of 5 to 5 to 2 (called E. P. A.),[10] or methylcyclohexane. These solvents do not crystallize on cooling, but freeze to clear glasses.

Icing.—Considerable difficulty was experienced in the early experiments because of ice or carbon dioxide particles crystallizing out on the optical faces of the absorption cells or the inside of the Dewar. A very thin coat of silicone oil 703 rubbed on the optical faces proved effective in preventing this difficulty (suggested by Professor D. Lipkin). Careful evacuation of the Dewar prevented frosting on the outside wall.

Spectral Curves.—All the spectral curves shown represent smooth curves drawn through points taken at 50 Å. intervals by even fifties.

Concentration Effect.—All sets of spectral data at room and liquid air temperature were taken on the same solution. The data at liquid air temperature, however, had to be corrected due to the fact that the solvents contract on freezing, and thus change the concentration. The correction factor for E. P. A. is 0.76.

Part 2. Fluorescence Spectra

Apparatus.—The apparatus centered about a Steinheil (München, Germany) three prism glass spectrograph. For spectra such as that shown in Figs. 2 and 5, the sample was placed in an unsilvered Dewar flask, and illuminated with a G. E. AH-6 mercury arc (midget sun) filtered by a 2″ water filter to cut down the heat and by a Corning 5543 filter to remove any red light. The fluorescence light was filtered by a Corning filter 3480 to remove the exciting light, and focused on the slit of the spectrograph by a suitable lens arrangement. The spectrograph was equipped with entrance slits (fishtail type) which permitted both the room and liquid nitrogen pictures to be taken without moving the plate settings. This made possible comparative pictures which were independent of any small errors in wave length calibration. The plates were calibrated for wave length from a mercury spectrum using Hartmann's formula.[11] The spectra in Fig. 2 were photographed with an extra long arm on the exit side of the spectrograph, accounting for the excellent dispersion obtained for these curves.

For the curves shown in Fig. 7, the exciting light from the midget sun was first passed through a monochromater of the Littrow type.[12] The limiting wave lengths (spectral band width) of the resultant monochromatic light were determined by photographing the light on a calibrated plate in the Steinheil spectrophotometer. Fluorescence was excited with this light in the usual way. The fluorescence was focused on the entrance slits of the Steinheil, any exciting light being removed by a Corning filter 2408. Due to the drastically lower intensity of the exciting light in these experiments, a short arm was employed on the exit side of the Steinheil, thus making the dispersion considerably less than that obtained with the longer arm. Exposure times for these experiments with monochromatic light and the short exit arm on the spectrophotometer were about 8 hours; for the experiments with direct midget sun excitation and the long exit arm on the spectrophotometer about 10 minutes.

Solvents.—The same solvents were used as those employed for absorption work (E. P. A. and methylcyclohexane).

Icing.—Icing in the interior of the Dewar flask was prevented with silicone 703 as in the absorption work. Outside frosting on the unsilvered Dewar was prevented by an air stream directed against the portions of the flask where the light passed.

Plates.—All photographs were made on Kodak spectroscopic plates I-M, hypersensitized by treating with a 4% solution of 28% ammonia just before use.

Tracings of Spectral Plates.—The spectral plates were traced on a photoelectric densitometer. The curves shown in Figs. 2, 5 and 7 are direct reproductions of these tracings.

Summary

1. Evidence has been obtained from an examination of absorption and fluorescence spectra taken at room and liquid air–liquid nitrogen temperatures which supports the proposition that porphin free bases exist as equilibrium mixtures of compounds resulting from the tautomerism of the imino hydrogens.

2. Absorption spectra at room and liquid air temperatures of a chlorin free base and a deuterium porphin free base are interpreted as indicating that the same tautomerism is present in these porphyrin free bases.

3. Resonance in the porphin free base is discussed, and a reasonable structure for the resonance hybrid is presented.

ST. LOUIS, MISSOURI RECEIVED NOVEMBER 30, 1949

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[10] Lewis, Magel and Lipkin, THIS JOURNAL, 62, 2973 (1940).

[11] Sawyer, "Experimental Spectroscopy," Prentice-Hall, New York, N. Y., 1944, p. 230.

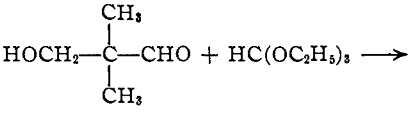
[12] We wish to express our appreciation to Professor S. Velick of the Washington University Medical School for the loan of this instrument.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Reaction of Hydroxyaldehydes with Ethyl Orthoformate. II. β-Hydroxyaldehydes

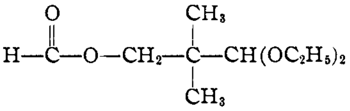
BY ELLIOT R. ALEXANDER AND ELLIOT N. MARVELL[1]

In an earlier communication,[2] it was shown that the reaction of hydroxypivaldehyde (I) with ethyl orthoformate led to 3,3-diethoxy-2,2-dimethylpropyl formate (II) as the only product which could be isolated. Furthermore, this product appeared to arise from the direct interaction of the hydroxyaldehyde with ethyl orthoformate and not as a secondary reaction product of hydroxypivaldehyde diethylacetal. In this paper is described a study of the reaction with several other β-hydroxyaldehydes.



$$HOCH_2-C(CH_3)_2-CHO + HC(OC_2H_5)_3 \longrightarrow$$

I



$$H-C(=O)-O-CH_2-C(CH_3)_2-CH(OC_2H_5)_2$$

II

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[1] Oregon State College, Corvallis, Oregon.

[2] Alexander and Marvell, THIS JOURNAL, 71, 15 (1949).

Experimental[3]

Reaction of Acetaldol with Ethyl Orthoformate.—A mixture of freshly distilled acetaldol (44.1 g., 0.5 mole), ethyl orthoformate (75.0 g., 0.52 mole), 75 ml. of dry ethanol and 1.0 g. of dry ammonium chloride was boiled under reflux for one-half hour. The volatile products were removed by distilling the reaction mixture until the temperature of the vapor reached 80°. The product was washed with water, taken up in ether, and dried over anhydrous magnesium sulfate. After evaporation of the ether, this material was distilled through an eight-inch, electrically heated column packed with glass helices. The product (26.5 g., 31%) (calculated as pure formate ester) was obtained as a colorless refractive liquid, b. p. 86–87° (13 mm.); n^{20}_{D} 1.4160; d^{20}_{20} 1.9674. Calculated on the basis of the formate ester of acetaldol diethylacetal, the following analytical results were obtained.

Anal. Calcd. for $C_9H_{18}O_4$: C, 56.82; H, 9.54; ethoxyl, 47.37; M^{20}_{D}, 48.72; mol. wt., 190. Found: C, 57.11; H, 9.73; ethoxyl, 38.95; M^{20}_{D}, 49.15; mol. wt., 183, 178.

Infrared analysis showed that the major portion of this material was an ester but that there was present a small amount (probably about 5%) of a hydroxylated impurity. From the next experiment it can be seen that this impurity was probably acetaldol diethylacetal.

Acetaldol Diethylacetal.—A portion (10.0 g.) of the mixture of products obtained above was saponified with 1.3 molar potassium hydroxide in dry ethanol.[2] When ether was added to the residual liquid, a solid precipitated which melted at 152–180°. The solid was very soluble in water and reduced potassium permanganate solution instantaneously. A *p*-bromophenacyl ester[4] melted at 138.5–140°. The corresponding derivative of formic acid melts at 140°.

The ether solution of the reaction mixture was dried, filtered, and the ether was removed *in vacuo*. One pellet of potassium hydroxide was then added and the residue was distilled through an electrically heated, eight inch column packed with glass helices. Acetaldol diethylacetal (6.8 g., 81–84%) was obtained as a colorless liquid, b. p. 89–89.5° (14 mm.) or 53–54° (1.5 mm.)[5]; n^{20}_{D} 1.4210; d^{20}_{20} 0.9362.

Anal. Calcd. for $C_8H_{18}O_3$: C, 59.23; H, 11.18; M^{20}_{D}, 43.96; mol. wt., 162. Found: C, 59.39; H, 11.30; M^{20}_{D}, 43.93; mol. wt., 160.

Reaction of Propionaldol with Ethyl Orthoformate.—Freshly distilled propionaldol[6] (58.1 g., 0.5 mole) was treated with ethyl orthoformate in the manner which has already been described.[2] Distillation of the product through an electrically heated, eight inch column packed with glass helices gave two distinct products and a large distillation residue which was discarded. The lower boiling material, b. p. 86° (14 mm.); n^{20}_{D} 1.4253; d^{20}_{20} 0.9320 weighed 12.0 g. Its infrared analysis showed only ether linkages to be present. We believe this material to be 2,4-diethyl-5-methyl-6-ethoxy-1,3-dioxane.

Anal. Calcd. for $C_{11}H_{22}O_3$: C, 65.30; H, 10.97; ethoxyl, 22.25; M^{20}_{D}, 55.74; mol. wt., 202. Found: C, 64.96; H, 10.96; ethoxyl, 22.61; M^{20}_{D}, 55.59; mol. wt., 197.

The second fraction, 30.0 g., n^{20}_{D} 1.4250, d^{20}_{20} 0.9442, distilled at 96° (14 mm.). This substance gave a positive ceric nitrate test and slowly reduced aqueous potassium permanganate. It gave a color with fuchsin reagent after standing several minutes, but showed no reaction with Fehling or Tollens reagents. An iodoform test was negative and there was no reaction with a solution of bromine in carbon tetrachloride. In contact with metallic sodium, however, hydrogen was evolved. These properties suggested that the product was a mixture of propionaldol diethylacetal and its formate ester.

Anal. Calcd. for 50% $C_{11}H_{22}O_4$ and 50% $C_{10}H_{22}O_3$: C, 61.82; H, 10.90; M^{20}_{D}, 55.48; ethoxyl, 44.11; mol. wt., 204. Found: C, 61.97; H, 10.88; M^{20}_{D}, 55.28; ethoxyl, 39.27; mol. wt., 266, 231.

Infrared analysis showed the presence of ester and hydroxyl groups.

Propionaldol Diethylacetal.—A sample (22.0 g.) of the mixture obtained above was saponified in the manner already described. The solid product, obtained by the addition of ether to the reaction mixture, was extremely hygroscopic, highly basic, and melted only partially between 150 and 160°. An aqueous solution of this solid reduced potassium permanganate but a *p*-bromophenacyl ester could not be prepared. The ethereal solution of the ester was evaporated *in vacuo* and the residue fractionally distilled through an electrically heated six-inch column packed with glass helices. Propionaldol diethylacetal (14.5 g., 75%) was obtained as a homogeneous colorless liquid, b. p. 62–63° (1.0 mm.); n^{20}_{D} 1.4280; d^{20}_{20} 0.9262.

Anal. Calcd. for $C_{10}H_{22}O_3$: C, 63.12; H, 11.66; M^{20}_{D}, 53.02. Found: C, 63.40; H, 11.68; M^{20}_{D}, 52.85.

Isobutyraldol.—Considerable difficulty was experienced in obtaining isobutyraldol free from the trimer of isobutyraldehyde. In our hands the procedure of Saunders, Murray and Cleveland[7] led almost exclusively to the trimer. It was found, however, that detrimerization could be carried out by distilling the trimer *in vacuo* (13 mm.) through an electrically-heated eight-inch column packed with glass helices. The bath temperature and the jacket were adjusted so that distillation proceeded slowly at 106°. Redistillation of this material gave isobutyraldol, b. p. 109–110° (13 mm.); n^{20}_{D} 1.4443.

Reaction of Isobutyraldol with Ethyl Orthoformate.—Isobutyraldol (21.5 g., 0.149 mole) was treated with 33.0 g. (0.224 mole) of ethyl orthoformate in the manner already described. Distillation through the eight inch column packed with glass helices gave 15.4 g. of a nonhomogeneous, water-white liquid, b. p. 64–72° (0.3 mm.); n^{20}_{D} 1.4336–1.4349. Infrared analysis showed the presence of ester linkages and hydroxyl groups. In view of the next experiment we believe that this material was a mixture of isobutyraldol diethylacetal and its formate ester.

Isobutyraldol Diethylacetal.—A sample of the mixture described above (9.0 g.) was saponified in the usual way. The solid product obtained by the addition of ether to the evaporated reaction mixture was converted to its *p*-bromophenacyl ester, m. p. 138–139°. It showed no depression in melting point when admixed with an authentic sample of *p*-bromophenacyl formate. The ether soluble portion was evaporated and the residue was distilled through an electrically heated column packed with glass helices. Two fractions of isobutyraldol diethyl acetal amounting to 6.1 g. were collected; b. p. 79–81° (1.0 mm.); n^{20}_{D} 1.4354; d^{20}_{20} 0.9205.

Anal. Calcd. for $C_{12}H_{26}O_3$: C, 66.10; H, 12.00; M^{20}_{D}, 62.44. Found: C, 66.11; H, 12.21; M^{20}_{D}, 61.98.

Results and Discussion

In Table I are summarized the products which are formed from the reaction of ethyl orthoformate with β-hydroxyaldehydes. The most striking feature of the table is that hydroxypivaldehyde was the only starting material which led to a pure product. With each of the other hydroxy aldehydes, mixtures of the hydroxy acetals and the formate esters of these acetals were obtained. In addition to this mixture, propionaldol gave rise to still another product

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[3] All melting points and boiling points are uncorrected.

[4] Shriner and Fuson, "Systematic Identification of Organic Compounds," John Wiley and Sons, New York, N. Y., 1948, p. 157.

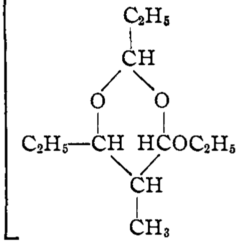
[5] A boiling point of 79–81° (12 mm.) was reported for this compound by Wohl and Frank, *Ber.*, **35**, 1904 (1902).

[6] Grignard and Abelmann, *Bull. soc. chim.*, [4] **7**, 639 (1910).

[7] Saunders, Murray and Cleveland, THIS JOURNAL, **65**, 1715 (1943).

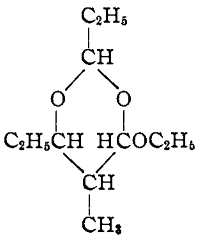
TABLE I

PRODUCTS FORMED IN THE REACTION OF β-HYDROXYALDEHYDES WITH ETHYL ORTHOFORMATE

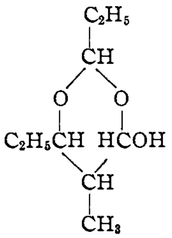
Starting material	Products	Yield, %
$HOCH_2C(CH_3)_2CHO$	$HCOOCH_2C(CH_3)_2CH(OC_2H_5)_2$	32[2]
$CH_3\overset{OH}{C}HCH_2CHO$	$CH_3\overset{HCOO}{C}HCH_2CH(OC_2H_5)_2$[d]	30[a]
	$CH_3\overset{OH}{C}HCH_2CH(OC_2H_5)_2$	1[a]
$CH_3CH_2\overset{OH}{C}HCH(CH_3)CHO$	$CH_3CH_2\overset{HCOO}{C}HCH(CH_3)CH(OC_2H_5)_2$[d]	14[b]
	$CH_3CH_2\overset{OH}{C}HCH(CH_3)CH(OC_2H_5)_2$	16[b]
		20
$(CH_3)_2CH\overset{OH}{C}HC(CH_3)_2CHO$	$(CH_3)_2CH\overset{HCOO}{C}HC(CH_3)_2CH(OC_2H_5)_2$[d]	31[c]
	$(CH_3)_2CH\overset{OH}{C}HC(CH_3)_2CH(OC_2H_5)_2$	12[c]

[a] Calculated on the basis of 95% formate ester and 5% hydroxy acetal. [b] Calculated on the basis of 50% formate ester and 50% hydroxy acetal. [c] Calculated on the basis of 75% formate ester and 25% hydroxy acetal. [d] Not isolated.

which we believe to be 2,4-diethyl-5-methyl-6-ethoxy-1,3-dioxane (III). Infrared analysis showed that all of the oxygen atoms were present as ether linkages and it had the correct analysis for carbon, hydrogen, molecular weight, ethoxyl groups, and molecular refractivity. It seems likely that this material arises through the presence of a trimer of propionaldehyde (IV) which could not be separated from propionaldol by distillation. Such a trimer predominates in the attempted preparation of isobutyraldol[7] and a product similar to IV can be obtained from the reaction of ethyl orthoformate with the pure trimer of isobutyraldehyde.[8]



III



IV

Acknowledgment.—We are indebted to Dr. Foil A. Miller and Mrs. J. L. Johnson for the determination and interpretation of the infrared data mentioned in this paper. The microanalyses were performed by Miss Theta Spoor and the Howard Clark Microanalytical Laboratories.

Summary

In continuation of the study of the reaction of ethyl orthoformate with hydroxyaldehydes, it has been found that acetaldol, propionaldol and isobutyraldol lead to mixtures which are apparently the hydroxyaldehyde diethylacetal and its formate ester. From propionaldol, there was also isolated 2,4-diethyl-5-methyl-6-ethoxy-1,3-dioxane. It seems probable that this material arises through the presence of a trimer of propionaldehyde which could not be separated by distillation from propionaldol.

URBANA, ILLINOIS RECEIVED FEBRUARY 1, 1950

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(8) Alexander and Marvell, THIS JOURNAL, 71, 15 (1949).