TABLE I

REACTIONS WITH PERBENZOIC ACID

Ketone RCOR' R	R'	Moles of per acid consumed[a] by 0.10 mole of ketone	Product ROCOR' B. p., °C.	Mm.	$n^{25}D$	Yield,[b] %	M. p. α-naphthyl-urethan
Cyclohexyl	CH_3	0.100	74.5–76.5	23	1.4401	67	127–128
Phenyl	CH_3	.065	93–93.5	22	1.5200	63	133
Cyclopropyl	CH_3	.010					
β-Naphthyl	CH_3	.095	M. p. 67–68			67	123[c]
Mesityl	CH_3	.107	111–120	12[d]			
Phenyl	C_2H_5	.073	98–99	18	1.5003	73	132–133

[a] Corrected for approximate degree of spontaneous decomposition of per acid. [b] Based on ketone and corrected for recovered ketone. [c] M. p. of the β-naphthol itself; not converted to urethan. [d] No mesitol could be detected upon attempted saponification with base.

determine the extent of spontaneous decomposition of the per acid during this time interval.

The chloroform solution was then shaken with dilute sodium carbonate solution to remove the benzoic and residual perbenzoic acids, and this treatment followed by a water wash. The chloroform was then distilled off, and the residual product separated into ketonic and non-ketonic fractions by the use, where possible, of Girard Reagent T. The ketonic fraction, when liquid, was converted to its semicarbazone for purification and identification, while the non-ketonic ester fraction was generally distilled directly under reduced pressure.

A portion of each ester fraction was saponified with base, and the resulting alcohol or phenol converted into its α-naphthylurethan for final identification purposes. In all cases, only a single α-naphthylurethan was obtained from each ester product.

The data obtained from the reactions studied are shown in Table I.

Summary

The reaction of perbenzoic acid in moist chloroform solution with cyclohexyl methyl ketone, acetophenone and β-acetonaphthone for ten day periods at room temperature furnishes cyclohexyl acetate, phenyl acetate and β-naphthyl acetate, respectively, in yields approximating 65%.

The reaction of perbenzoic acid with cyclopropylmethyl ketone under these conditions does not occur.

Propiophenone reacts smoothly under these conditions to furnish the single product phenyl propionate in 73% yield.

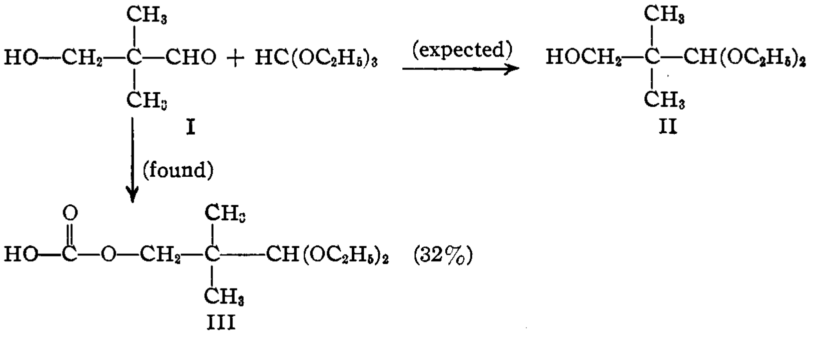
LOS ANGELES, CALIFORNIA RECEIVED JULY 26, 1948

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

Reaction of Hydroxyaldehydes with Ethyl Orthoformate. I. Hydroxypivaldehyde

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

During another investigation the preparation of hydroxypivaldehyde diethyl acetal (II) was attempted by allowing hydroxypivaldehyde (I) to react with ethyl orthoformate.[2] Instead of the expected hydroxy acetal (II), the only product which could be isolated from the reaction mixture was 3,3-diethoxy-2,2-dimethylpropyl formate (III).



$$HO-CH_2-C(CH_3)_2-CHO + HC(OC_2H_5)_3 \xrightarrow{\text{(expected)}} HOCH_2-C(CH_3)_2-CH(OC_2H_5)_2$$

$$\text{I} \xrightarrow{\text{(found)}} HO-\overset{O}{\overset{\|}{C}}-O-CH_2-C(CH_3)_2-CH(OC_2H_5)_2 \quad (32\%)$$

The structure of III was established by saponification of the ester with potassium hydroxide in dry ethanol. Potassium formate was isolated and a new compound was formed which had the correct molar refractivity and analysis for the hydroxy acetal (II). In addition, the structure for the formate ester (III) is supported by an infrared analysis (which showed the presence of an ester group but no hydroxyl group), by the correct molecular refractivity and by a molecular weight determination.

The formation of the ester (III) during the reaction was surprising. An examination of the literature has revealed that apparently the simultaneous formation of acetal and ester is novel in type. One explanation might be that an ester interchange occurred between the hydroxy acetal and ethyl formate or ethyl orthoformate. Experiment, however, has ruled out either of these possi-

---

[1] Present address: Oregon State College, Corvallis, Oregon.

[2] Claisen, *Ber.*, **29**, 1007 (1896).

bilities. When the hydroxy acetal (II) was treated with ethyl formate or ethyl orthoformate under conditions identical to those used for the preparation of 3,3-diethoxy-2,2-dimethylpropyl formate (III), a very complex mixture of products was formed but no ester could be isolated.

We, therefore, believe that the ester is formed not by a secondary process from the hydroxy acetal but as a result of the direct interaction of ethyl orthoformate with the hydroxy aldehyde. The scope and implications of the reaction are being investigated.

Experimental[3]

Reaction of Hydroxypivaldehyde with Ethyl Orthoformate.—A mixture of 51.0 g. (0.5 mole) of hydroxypivaldehyde,[4] 75.0 g. (0.52 mole) of ethyl orthoformate, 75 ml. of dry ethanol and 1.0 g. of dry ammonium chloride was boiled under reflux for thirty minutes. The volatile products were removed by distilling the reaction mixture until the temperature of the vapors reached 80°. The residual material was washed with two 50-ml. portions of distilled water and the washings were extracted twice with 50-ml. portions of ether. The water washed product and the ether extracts were then combined and dried over anhydrous magnesium sulfate. After evaporation of the ether, the product was distilled through an eight-inch electrically-heated column packed with glass helices. Distillation yielded 31.0 g. (32%) of 3,3-diethoxy-2,2-dimethylpropyl formate, b. p. 93–94° (13 mm.), n^{20}_{D} 1.4200, d^{20}_{20} 0.9633. An infrared absorption spectrum indicated the presence of a carbonyl group, ether linkages, and the absence of a hydroxyl group.[5]

Anal.[6] Calcd. for $C_{10}H_{20}O_4$: C, 58.80; H, 9.94; MR 53.60; mol. wt., 204. Found: C, 58.90; H, 10.05; MR, 53.33; mol. wt., 203.

Preparation of Hydroxypivaldehyde Diethyl Acetal.—To a solution prepared from 7.0 g. (0.1 mole) of potassium hydroxide in 75 ml. of dry ethanol was added 20.0 g. (0.1 mole) of 3,3-diethoxy-2,2-dimethylpropyl formate. The mixture became warm, turned light yellow, and a flocculent white solid precipitated. Distilled water (1.5 ml.) was added and the mixture was boiled under reflux for three hours. After removing as much alcohol as possible on the steam-bath, the mixture was cooled, and 100 ml. of ether was added. Potassium formate precipitated and was removed by suction filtration. After drying on a clay plate the salt melted at 162–165°. A mixed melting point with an authentic sample melted at 164–165°.[7] After removing the ether from the filtrate, distillation yielded 14.5 g. (84%) of hydroxypivaldehyde diethylacetal, b. p. 55° (1.0 mm.), n^{20}_{D} 1.4259, d^{20}_{20} 0.9335.

Anal. Calcd. for $C_9H_{20}O_3$: C, 61.33; H, 11.44; MR, 48.58. Found: C, 61.43; H, 11.48; MR, 48.36.

Reaction of Hydroxypivaldehyde Diethyl Acetal with Ethyl Orthoformate.—Hydroxypivaldehyde diethylacetal (10.0 g., 0.057 mole) was treated with ethyl orthoformate under conditions identical with those described for the reaction of hydroxypivaldehyde with ethyl orthoformate. After drying and removing the ether it was attempted to distill the reaction mixture as before. A small amount of ethyl orthoformate and some material boiling at 85–185° (1.0 mm.) was obtained but the major part of the reaction mixture remained in the distilling flask. No pure components could be separated from the volatile portion on redistillation. The high boiling point of this material showed that no hydroxypivaldehyde diethylacetal nor 3,3-diethoxy-2,2-dimethylpropyl formate could have been present.

Reaction of Hydroxypivaldehyde Diethyl Acetal with Ethyl Formate.—Freshly prepared hydroxypivaldehyde diethyl acetal (10.0 g., 0.057 mole) was treated with ethyl formate (4.2 g., 0.057 mole) under conditions identical with those described for the reaction of hydroxypivaldehyde with ethyl orthoformate. After removal of the ether, 4.4 g. of ethyl formate (b. p. 52–54°) was recovered which must have contained a small amount of alcohol. On attempted distillation only a clear tough resin was obtained.

Summary

When ethyl orthoformate is allowed to react with hydroxypivaldehyde the only product which can be isolated is 3,3-diethoxy-2,2-dimethylpropyl formate. This product arises from the direct interaction of the hydroxyaldehyde with ethyl orthoformate and not as a secondary reaction product of hydroxypivaldehyde diethylacetal.

---

(3) All melting and boiling points are uncorrected.

(4) Stiller, Harris, Finkelstein, Keresztesy and Folkers, THIS JOURNAL, **62**, 1787 (1942).

(5) We are indebted to Dr. Foil A. Miller and Mrs. J. L. Johnson for the determination and the interpretation of the spectrum of this sample.

(6) We are indebted to Miss Theta Spoor for the carbon–hydrogen microanalyses reported in this paper.

(7) The melting point of pure potassium formate is 165–167°.

URBANA, ILLINOIS RECEIVED AUGUST 26, 1948

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE CORN PRODUCTS REFINING COMPANY]

Osmotic Pressure Studies on Corn Amylose

BY F. C. CLEVELAND AND R. W. KERR

The average molecular magnitude of the two fractions of starch still is a matter of some uncertainty. Even for the amylose fraction of corn starch, which has probably received more attention than any other starch component, estimations of size have been made which vary by 100%, or more. On the basis of sedimentation and diffusion studies, Fox[1] set a minimum value of 540 glucose units by the use of the acetate of a subfraction of corn amylose in methyl acetate solutions. Dumbrow[2] used a similar product and obtained a value of 375 by similar methods. Foster and Hixon[3] calculated that the DP_n for corn amylose was 260 from osmotic pressure measurements of the acetate in chloroform. Principally from viscosity measurements by Foster and Hixon,[4] Foster[5] has estimated that corn amylose, extracted

---

(1) T. J. Fox, Dissertation, Columbia University, New York. N. Y., 1943.

(2) B. A. Dumbrow, Dissertation, Columbia University, New York, N. Y., 1944.

(3) J. Foster and R. Hixon, THIS JOURNAL, **66**, 557 (1944).

(4) J. Foster and R. Hixon, *ibid.*, **65**, 618 (1943).

(5) J. E. Foster, Dissertation, Iowa State College, Ames, Iowa, 1943.