Anal. Calcd. for $C_6H_9FO_3$: C, 48.65; H, 6.08. Found: C, 48.64; H, 6.26.

2,4-Dinitrophenylhydrazone, yellow crystals from methanol, m.p. 91–91.5°. *Anal.* Calcd. for $C_{12}H_{13}FN_4O_6$: C, 43.90; H, 3.99; N, 17.07. Found: C, 43.71; H, 4.16; N, 17.19.

Ethyl 8-fluoro-3-oxoöctanoate was prepared from 6-fluorohexanoyl chloride[4] (7.6 g., 0.05 mole) in the same way. Distillation of the residue after solvent removal gave the ester, b.p. 106–114° (2–3 mm.). This was purified by being dissolved in petroleum ether and washed once with 10% sodium bicarbonate (10 ml.). This volume of sodium bicarbonate should not be exceeded, since the water-soluble sodium salt of the enol form of the ketoester is readily formed and remains in the aqueous phase. After washing with water, ethylene chloride was added to the organic layer, and the solvents were removed under reduced pressure. The residue on fractionation yielded ethyl 8-fluoro-3-oxoöctanoate (5 g., 49%) of b.p. 107° (3 mm.) and $n^{25}\mathrm{D}$ 1.4223.

Anal. Calcd. for $C_{10}H_{17}FO_3$: C, 58.83; H, 8.33. Found: C, 58.75; H, 8.32.

When the esterification method of purification was carried out (see above), **ethyl 6-fluorohexanoate** (9.2 g., 57%) was obtained, b.p. 80–83° (10 mm.), $n^{25}\mathrm{D}$ 1.4072 [Buckle, *et al.*,[2] report b.p. 82–84° (14 mm.)].

Anal. Calcd. for $C_8H_{15}FO_2$: C, 59.27; H, 9.26. Found: C, 59.11; H, 9.16.

Ethyl 9-fluoro-3-oxononanoate was prepared from 7-fluoroheptanoyl chloride[4] (8.3 g., 0.05 mole) in the same way. Distillation of the residue after solvent removal gave the ester, b.p. 115–118° (1.3 mm.). This was purified by being dissolved in petroleum ether and washed with 10% sodium bicarbonate (10 ml.) and with water. Ethylene chloride was added to the petroleum ether solution, and the solvents were removed under reduced pressure. The residue on fractionation yielded ethyl 9-fluoro-3-oxononanoate (4.7 g., 43%) of b.p. 122° (1.7 mm.) and $n^{25}\mathrm{D}$ 1.4247.

Anal. Calcd. for $C_{11}H_{19}FO_3$: C, 60.54; H, 8.72. Found: C, 60.45; H, 8.70.

Ethyl 12-fluoro-3-oxododecanoate was prepared from 10-fluorodecanoyl chloride[4] (10.4 g., 0.05 mole) in the same way. Distillation of the residue after solvent removal gave the ester, b.p. 141–144° (2 mm.). This was recrystallized several times from petroleum ether, yielding pure ethyl 12-fluoro-3-oxododecanoate (5.9 g., 42%), m.p. 47–47.5°.

Anal. Calcd. for $C_{14}H_{25}FO_3$: C, 64.59; H, 9.68. Found: C, 64.32; H, 9.91.

The phenyl pyrazolone derivative, colorless crystals from methanol, m.p. 96–96.5°. *Anal.* Calcd. for $C_{18}H_{25}FN_2O$: N, 9.21. Found: N, 9.31.

1-Fluoro-2-heptanone.—Hexanoyl chloride (8.0 g., 0.06 mole) was added to a well-stirred ethereal solution of diazomethane (12.6 g., 0.3 mole), cooled in an ice-bath. Stirring was continued for two hours, and the ether was then removed. The residue (12 g.) in ether (40 ml.) was slowly added to liquid anhydrous hydrogen fluoride (5 g.) in a polyethylene flask immersed in a Dry Ice–acetone-bath. The mixture was allowed to warm slowly to room temperature overnight, and then was poured over anhydrous potassium fluoride (20 g.). The liquid was decanted, the solid cake was washed with dry ether, and the combined ethereal solutions were dried over anhydrous potassium fluoride. After removal of the ether, the residue on fractionation gave 1-fluoro-2-heptanone (3.0 g., 38%) of b.p. 54° (13 mm.) and $n^{25}\mathrm{D}$ 1.4048.

Anal. Calcd. for $C_7H_{13}FO$: C, 63.60; H, 9.91. Found: C, 63.83; H, 9.81.

1-Fluoro-2-octanone was prepared similarly from heptanoyl chloride in 23% yield, b.p. 70° (11 mm.) and $n^{25}\mathrm{D}$ 1.4112. *Anal.* Calcd. for $C_8H_{15}FO$: C, 65.71; H, 10.34. Found: C, 65.82; H, 10.48.

1-Fluoro-2-decanone was prepared similarly from nonanoyl chloride in 40% yield, b.p. 99° (11.5 mm.) and $n^{25}\mathrm{D}$ 1.4205. *Anal.* Calcd. for $C_{10}H_{19}FO$: C, 68.91; H, 11.00. Found: C, 68.83; H, 11.02.

1,7-Difluoro-2-heptanone was prepared similarly from 6-fluorohexanoyl chloride[4] in 60% yield, b.p. 102–104° (42 mm.) and $n^{25}\mathrm{D}$ 1.4115. *Anal.* Calcd. for $C_7H_{12}F_2O$: C, 55.98; H, 8.06. Found: C, 55.88; H, 7.87.

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LONDON, ONTARIO, CANADA

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, TENNESSEE EASTMAN COMPANY, DIVISION OF EASTMAN KODAK COMPANY]

Preparation and Properties of Diethyl Acetoxyalkylphosphonates

BY RICHARD L. MCCONNELL AND HARRY W. COOVER, JR.

RECEIVED JUNE 29, 1956

Diethyl 1-acetoxyalkylphosphonates were prepared from diethyl 1-hydroxyalkylphosphonates and ketene in good yields. The infrared spectrum of diethyl 1-acetoxyethylphosphonate was compared with that of the product of the reaction of vinyl acetate and diethyl hydrogen phosphite in the presence of sodium ethoxide. It was thus shown that the reaction product is diethyl 1-acetoxyethylphosphonate rather than diethyl 2-acetoxyethylphosphonate. For comparison, diethyl 2-acetoxyethylphosphonate was prepared by the Arbuzov reaction of 2-bromoethyl acetate and triethyl phosphite. The addition of diethyl hydrogen phosphite to vinyl acetate in the presence of benzoyl peroxide also gave diethyl 2-acetoxyethylphosphonate. The infrared spectra of the two products were identical.

In 1952, Pudovik reported that dialkyl hydrogen phosphites react with vinyl acetate to produce dialkyl 2-acetoxyethylphosphonates according to the equation[1]

$$CH_3COOCH{=}CH_2 + HP(O)(OR)_2 \xrightarrow{NaOR} CH_3COOCH_2CH_2P(O)(OR)_2 \quad (1)$$

Pudovik gave no real proof of structure, stating only that saponification of the reaction product from diethyl hydrogen phosphite and vinyl acetate

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[1] A. N. Pudovik, *J. Gen. Chem.* (*U.S.S.R.*), Consultants Bureau English Translation, **22**, 537 (1952).

gave a viscous oil which did not crystallize. He assumed this product to be 2-hydroxyethylphosphonic acid.

We were studying the base-catalyzed addition of dialkyl hydrogen phosphites to unsaturated systems at the time, and it appeared to us that the dialkyl hydrogen phosphites should have added according to Markownikoff's rule as shown in equation 2

$$\mathrm{CH_3COOCH{=}CH_2 + HP(O)(OR)_2 \xrightarrow{NaOR} CH_3COOCH(CH_3)P(O)(OR)_2} \quad (2)$$

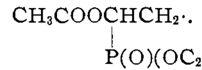
This addition is comparable to the reaction of acetic acid with vinyl acetate to produce ethylidene diacetate.[2]

In repeating Pudovik's reaction using vinyl acetate and diethyl hydrogen phosphite, we obtained a product having physical properties similar to those described in his paper.

In order to prove the structure of this vinyl acetate–diethyl hydrogen phosphite reaction product, we prepared diethyl 1-acetoxyethylphosphonate and diethyl 2-acetoxyethylphosphonate by unequivocal methods. Diethyl 1-acetoxyethylphosphonate was prepared from diethyl 1-hydroxyethylphosphonate and ketene (equation 3). The isomeric diethyl 2-acetoxyethylphosphonate was prepared from 2-bromoethyl acetate and triethyl phosphite (equation 4).

$$\mathrm{CH_3CH(OH)P(O)(OC_2H_5)_2 + CH_2{=}C{=}O \xrightarrow{BF_3} CH_3COOCH(CH_3)P(O)(OC_2H_5)_2} \quad (3)$$

$$\mathrm{CH_3COOCH_2CH_2Br + (C_2H_5O)_3P \longrightarrow CH_3COOCH_2CH_2P(O)(OC_2H_5)_2 + C_2H_5Br} \quad (4)$$

We also treated vinyl acetate with diethyl hydrogen phosphite in the presence of benzoyl peroxide. Diethyl 2-acetoxyethylphosphonate is the product to be expected from a peroxide-catalyzed reaction of this type since the intermediate free radical, $\mathrm{CH_3COO\dot{C}HCH_2P(O)(OC_2H_5)_2}$, would be more stable than  $\mathrm{CH_3COO\underset{\displaystyle P(O)(OC_2H_5)_2}{\underset{|}{C}}HCH_2\cdot}$. Therefore, this reaction can be illustrated by equations

$$\mathrm{Catalyst \longrightarrow R\cdot} \quad (5)$$

$$\mathrm{R\cdot + HP(O)(OC_2H_5)_2 \longrightarrow RH + \cdot P(O)(OC_2H_5)_2} \quad (6)$$

$$\mathrm{CH_3COOCH{=}CH_2 + \cdot P(O)(OC_2H_5)_2 \longrightarrow CH_3COO\underset{\cdot}{C}HCH_2P(O)(OC_2H_5)_2} \quad (7)$$

$$\mathrm{CH_3COO\underset{\cdot}{C}HCH_2P(O)(OC_2H_5)_2 + HP(O)(OC_2H_5)_2 \longrightarrow CH_3COOCH_2CH_2P(O)(OC_2H_5)_2 + \cdot P(O)(OC_2H_5)_2} \quad (8)$$

There is a characteristic difference in the stability of diethyl 1- and 2-acetoxyethylphosphonates on distillation. Diethyl 2-acetoxyethylphosphonate is somewhat sensitive to heat and undergoes cleavage on distillation causing contamination of the product with diethyl hydrogen phosphite. We found that diethyl 2-acetoxyethylphosphonate could be stabilized by distilling it in the presence of a small amount of anhydrous sodium carbonate. It was shown by the absence of characteristic P–H bands from both the infrared and the nuclear magnetic resonance spectra that samples of diethyl 2-acetoxyethylphosphonate which were distilled over anhydrous sodium carbonate did not contain diethyl hydrogen phosphite. Diethyl 1-acetoxyalkylphosphonates did not decompose on distillation.

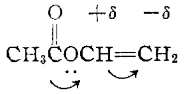
The infrared spectrum of diethyl 1-acetoxyethylphosphonate prepared according to equation 3 is identical to that of the product obtained by the base-catalyzed addition of diethyl hydrogen phosphite to vinyl acetate. Also, the infrared spectrum of diethyl 2-acetoxyethylphosphonate prepared according to equation 4 is identical to that of the product obtained by the peroxide-catalyzed addition of diethyl hydrogen phosphite to vinyl acetate.

The main difference in the infrared spectra of diethyl 1- and 2-acetoxyethylphosphonates occurs in the 10- to 14-μ region. In the spectrum of diethyl 1-acetoxyethylphosphonate a band appears at 11.7 μ which is not present in the spectrum of diethyl 2-acetoxyethylphosphonate. The spectrum of the 1-acetoxy compound also has a doublet at 9.55–9.8 μ, whereas that of the 2-acetoxy compound has a single peak at 9.7 μ. The spectrum of diethyl 1-acetoxyethylphosphonate has a peak at 12.5 μ; in the spectrum of diethyl 2-acetoxyethylphosphonate, this peak is shifted to 12.6 μ and has a different shape. Of course, the spectra of both compounds contain peaks which are characteristic of C–H stretching, C–H bending and ester carbonyl, P=O, P–O–$\mathrm{C_2H_5}$, and POC groups.[3]

These infrared spectra[4] indicate, therefore, that the base-catalyzed addition product of diethyl hydrogen phosphite and vinyl acetate is diethyl 1-acetoxyethylphosphonate rather than diethyl 2-acetoxyethylphosphonate.

The nuclear magnetic resonance spectra[5] of diethyl 1- and 2-acetoxyethylphosphonates are also different. In particular, the triplet expected from the methylene group adjacent to the acetoxy group of diethyl 2-acetoxyethylphosphonate is indicated. A set of two triplets due to the methylene group adjacent to the phosphonyl group is also observed. Because of overlapping peaks, it was not possible to account for all of the protons in the 1-acetoxy compound. However, the spectrum observed is consistent with the proposed structure.

The mechanism of the base-catalyzed reaction of vinyl acetate probably involves the nucleophilic attack of the diethyl hydrogen phosphite on the carbon atom in the 1-position of the vinyl group. This carbon atom is probably more electropositive than the one in the 2-position if the adjacent oxygen atom donates electrons to the double bond as



$$\mathrm{CH_3\overset{\displaystyle O}{\overset{\|}{C}}\ddot{O}\overset{+\delta}{C}H{=}\overset{-\delta}{C}H_2}$$

The inductive effect of the oxygen atom would also tend to make the carbon atom in the 1-position more electropositive.

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[2] R. C. Fuson, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 74.

[3] L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

[4] The infrared spectra were obtained on an infrared recording spectrophotometer made by Baird Associates, Incorporated. The spectra have been submitted to the National Research Council Committee on spectral absorption data.

[5] The nuclear magnetic resonance spectra were obtained on a high resolution nuclear magnetic resonance spectrometer made by Varian Associates. It was operated at 40 megacycles, and the spectra were run for the proton resonance.

Of all the methods which we used in preparing dialkyl acetoxyalkylphosphonates, the acetylation of dialkyl hydroxyalkylphosphonates with ketene gave the highest yields (62% for diethyl 1-acetoxyethylphosphonate). We also prepared diethyl 1-acetoxybutylphosphonate in good yield (86.5%) from diethyl 1-hydroxybutylphosphonate and ketene.

Experimental

Diethyl 1-Hydroxyethylphosphonate.[6,7]—A mixture of acetaldehyde (44.0 g., 1.0 mole), diethyl hydrogen phosphite (138.1 g., 1.0 mole) and triethylamine (5 ml.) was heated with stirring at 90° for 2 hours. Fractionation of the reaction mixture under reduced pressure through a short Vigreux column gave 47.0 g. (26.0%) of a colorless liquid, b.p. 111–112° (2.2 mm.), $n^{20}D$ 1.4340. This compound was soluble in water and the common organic solvents.

Anal. Calcd. for $C_6H_{15}O_4P$: C, 39.56; H, 8.30. Found: C, 39.49; H, 8.02.

Diethyl 1-Acetoxyethylphosphonate.—Diethyl 1-hydroxyethylphosphonate (7.0 g., 0.0385 mole) and 1 drop of boron trifluoride etherate were placed in a round-bottomed flask which was cooled in an ice-bath. The contents of the flask were stirred while ketene was bubbled in through a fritted glass disc. After 2.6 g. (0.062 mole) of ketene had condensed in the reaction mixture, the ketene source was removed and the mixture was stirred at 25° for 3 hours to allow the excess ketene to evaporate. The crude product was distilled under reduced pressure through a short Vigreux column. Diethyl 1-acetoxyethylphosphonate (5.3 g., 62%) was obtained as a colorless liquid, b.p. 88–91° (1.1 mm.), $n^{20}D$ 1.4265. This compound is soluble in water and the common organic solvents.

Anal. Calcd. for $C_8H_{17}O_5P$: C, 42.85; H, 7.64. Found: C, 42.73; H, 7.57. The residue consisted of about 3 g. of an amber oil.

Reaction Product of Vinyl Acetate and Diethyl Hydrogen Phosphite Using a Sodium Alkoxide Catalyst (Diethyl 1-Acetoxyethylphosphonate).—Vinyl acetate (17.2 g., 0.2 mole) and diethyl hydrogen phosphite (40.0 g., 0.29 mole) were mixed, and 3.5 ml. of a concentrated solution of sodium ethoxide in ethyl alcohol was added dropwise with stirring. The reaction was mildly exothermic, and the temperature gradually rose to 40°. The reaction mixture was stirred for 2 hours and then dissolved in ethyl ether. The ether solution was washed twice with water and then dried over sodium sulfate. The ether was removed on a steam-bath, and the residual oil was distilled under reduced pressure through a short Vigreux column. After the excess diethyl hydrogen phosphite was removed, a colorless liquid (7.5 g., 16.7%) was obtained, b.p. 102–103° (1.3 mm.), $n^{20}D$ 1.4268.

Anal. Calcd. for $C_8H_{17}O_5P$: C, 42.85; H, 7.64. Found: C, 42.21; H, 7.91.

Diethyl 1-Hydroxybutylphosphonate.[6,7]—A mixture of butyraldehyde (36.0 g., 0.5 mole), diethyl hydrogen phosphite (69.0 g., 0.5 mole) and triethylamine (5 ml.) was heated with stirring at 90° for 1.5 hours. Fractionation of the reaction mixture under reduced pressure through a short Vigreux column gave 53 g. (50%) of a colorless liquid, b.p. 125–129° (1.3–1.5 mm.), $n^{20}D$ 1.4358. This compound is soluble in water and the common organic solvents.

Anal. Calcd. for $C_8H_{19}O_4P$: C, 45.71; H, 9.11. Found: C, 45.94; H, 9.15.

Diethyl 1-Acetoxybutylphosphonate.—The reaction of diethyl 1-hydroxybutylphosphonate (10.5 g., 0.05 mole), ketene (3.0 g., 0.0715 mole) and boron trifluoride etherate (2 drops) was carried out according to the procedure described for diethyl 1-acetoxyethylphosphonate. Distillation of the reaction product under reduced pressure through a short Vigreux column gave 10.9 g. (86.5%) of diethyl 1-acetoxybutylphosphonate, b.p. 101–102° (1.0 mm.), $n^{20}D$ 1.4308.

Anal. Calcd. for $C_{10}H_{21}O_5P$: C, 47.61; H, 8.39. Found: C, 47.56; H, 8.38.

Diethyl 2-Acetoxyethylphosphonate.—A mixture of 2-bromoethyl acetate (83.5 g., 0.5 mole) and triethyl phosphite (124.4 g., 0.75 mole) was refluxed with stirring for 13 hours when the evolution of ethyl bromide was complete. The reaction mixture was distilled under reduced pressure through a short Vigreux column to obtain 31.5 g. (28%) of a colorless liquid, b.p. 94–99° (1.2 mm.), $n^{20}D$ 1.4359. This material was distilled over 1 g. of anhydrous sodium carbonate to obtain an analytical sample, b.p. 105–107° (1.0 mm.), $n^{20}D$ 1.4350.

Anal. Calcd. for $C_8H_{17}O_5P$: P, 13.82. Found: P, 13.82.

Reaction Product of Vinyl Acetate and Diethyl Hydrogen Phosphite Using a Benzoyl Peroxide Catalyst (Diethyl 2-Acetoxyethylphosphonate).—A mixture of vinyl acetate (17.2 g., 0.2 mole), diethyl hydrogen phosphite (110 g., 0.8 mole) and benzoyl peroxide (0.1 g.) was heated with stirring on the steam-bath for 9 hours. During the initial stages of the reaction, the vinyl acetate refluxed gently. The reaction mixture was allowed to stand overnight at 25°, and then 0.2 g. of hydroquinone was added. The mixture was then fractionated under reduced pressure through a short Vigreux column. After the excess diethyl hydrogen phosphite was removed, a colorless oil (6.2 g., 14%) was obtained, b.p. 96–97° (0.7 mm.). This material was distilled over 0.3 g. of anhydrous sodium carbonate to obtain an analytical sample, b.p. 101–103° (1.0 mm.), $n^{20}D$ 1.4322. This compound is soluble in water and the common organic solvents.

Anal. Calcd. for $C_8H_{17}O_5P$: C, 42.85; H, 7.64. Found: C, 42.73; H, 7.65.

The residue consisted of 20.2 g. of a dark, viscous oil containing 5.73% phosphorus.

Acknowledgment.—The authors wish to thank Dr. H. W. Patton and Mr. M. V. Otis for their help in interpreting the nuclear magnetic resonance spectra and the infrared spectra, respectively.

KINGSPORT, TENNESSEE

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(6) E. K. Fields (to Research Corporation), U. S. Patent 2,579,810 (1951). In this patent only the boiling points of the products are listed.

(7) V. S. Abramov, *J. Gen. Chem.* (*U.S.S.R.*), Consultants Bureau English Translation, **22**, 709 (1952).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, TENNESSEE EASTMAN COMPANY, DIVISION OF EASTMAN KODAK COMPANY]

Reaction of Triethyl Phosphite with 2-Haloacrylates

BY H. W. COOVER, JR., MARVIN A. MCCALL AND J. B. DICKEY

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The reaction of triethyl phosphite with methyl 2-haloacrylates was investigated. The product of the reaction was catalytically reduced, and the resulting compound was compared with authentic samples of methyl 2- and 3-diethylphosphonopropionates. On the basis of infrared absorption spectra and physical properties it was shown that the reduced product was methyl 3-diethylphosphonopropionate. It is therefore concluded that the product formed by the reaction of triethyl phosphite with methyl 2-haloacrylates is methyl 3-diethylphosphonoacrylate. A possible mechanism to explain the formation of the 3- rather than the 2-diethylphosphonoacrylate is discussed.