the temperature being kept below 30° and the addition lasting 8 hr. The mixture was then stirred overnight. The solvent was removed in the same manner as above. the reaction product was a black (bright yellow in thin layers), viscous oil.

Anal. Calcd. for $C_{12}H_{24}Cl_3FeO_4$: Cl, 26.9 (ionic chlorine, 9.0); Fe, 14.2; mol. wt., 395. Found: Cl, 27.1 (ionic chlorine, 8.9); Fe, 14.5; mol. wt., 390.

Hydrolysis of the ferric chloride–propylene oxide reaction product. The procedure was the same as in the former case except that the iron-containing residue after being heated with water and filtered out was extracted with two 50-ml. portions of acetone. The acetone extract was then combined with the other filtrates. The amount of the ferric chloride–propylene oxide product was 197 g. (0.5 mole), and 130 g. (85% yield) of the chlorohydrins was isolated. The results of the fractional distillation of the mixture are summarized in Table II.

TABLE II

IRON-FREE COMPONENTS OF THE HYDROLYZED FERRIC CHLORIDE–PROPYLENE OXIDE REACTION PRODUCT

	No. of C_3H_6O Units in the Chlorohydrin			
	1	2	3	4
B.b., °C.	46–50	97–103	85–94	Residue
p, mm.	25	20	2	...
n_D^{25}	1.4370	1.4412	1.4440	1.4501
Mol. wt. calcd.	94.5	152.6	210.7	258.8
% OH calcd.	18.0	11.1	8.1	6.3
% Cl calcd.	37.5	23.3	16.8	13.2
Mol. wt. found	95	163	212	280
% OH found	17.5	10.7	8.2	5.9
% Cl found	37.8	22.8	17.0	13.1

FREEPORT, TEX.

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

Reaction of Ketene with Dialkyl Hydrogen Phosphites and Acylphosphonates

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Diethyl 1-acetoxyvinylphosphonate was obtained when a crude β-propiolactone—diethyl hydrogen phosphite reaction mixture containing excess diethyl hydrogen phosphite was treated with ketene. The structure of the diethyl 1-acetoxyvinylphosphonate was proved by reducing this compound to the known diethyl 1-acetoxyethylphosphonate. The enol form of diethyl acetylphosphonate is a probable intermediate in the reaction of diethyl hydrogen phosphite with ketene to form diethyl 1-acetoxyvinylphosphonate. The infrared spectra of the products obtained when diethyl acetylphosphonate is treated with ketene indicate that a lactone, probably the β-lactone of 3-diethylphosphono-3-hydroxybutyric acid, is formed in addition to diethyl 1-acetoxyvinylphosphonate.

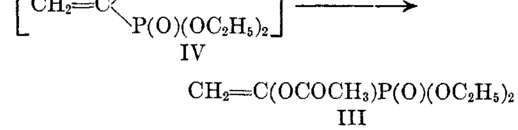
In recent papers, the reaction of phosphites with lactones was described.[1,2] The phosphonates derived from the interaction of trialkyl phosphites with lactones were stable, distillable materials; however, those derived from the interaction of dialkyl hydrogen phosphites with lactones were rather sensitive to distillation, even at low pressures. For example, the reaction products from diethyl hydrogen phosphite and β-propiolactone included diethyl 3-hydroxypropionylphosphonate (I) and tetraethyl 1,3-dihydroxypropylidenediphosphonate (II).

$HOCH_2CH_2C(O)P(O)(OC_2H_5)_2$
I

$HOCH_2CH_2C(OH)[P(O)(OC_2H_5)_2]_2$
II

In an attempt to stabilize these products by acetylation, the crude diethyl hydrogen phosphite-β-propiolactone reaction mixture was treated with ketene. Although the product obtained was distillable, it did not prove to be the acetyl derivative of either I or II. Again, the higher boiling fractions were rather unstable to distillation at low pressures.

The distillable material was found to be diethyl 1-acetoxyvinylphosphonate (III). This product apparently was formed by reaction of ketene with excess diethyl hydrogen phosphite present in the reaction mixture, since good yields of III were obtained by reaction of pure diethyl hydrogen phosphite with ketene. This reaction was observed independently by Kennedy and Meaburn.[3] The formation of III could be explained by the following equation:



$$(C_2H_5O)_2P(O)H + CH_2{=}C{=}O \xrightarrow{BF_3} \left[CH_2{=}C\begin{matrix}OH\\P(O)(OC_2H_5)_2\end{matrix}\right] \xrightarrow{CH_2=C=O} CH_2{=}C(OCOCH_3)P(O)(OC_2H_5)_2$$

IV

III

The postulated intermediate, IV, is the enol form of diethyl acetylphosphonate. This is a probable intermediate since carbonyl compounds are known to react readily with dialkyl hydrogen phos-

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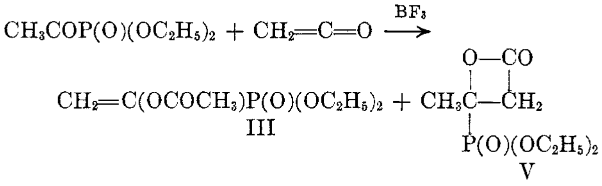
(1) R. L. McConnell and H. W. Coover, Jr., *J. Am. Chem. Soc.*, **78**, 4450 (1956).

(2) R. L. McConnell and H. W. Coover, Jr., *J. Am. Chem. Soc.*, **78**, 4453 (1956).

(3) J. Kennedy and G. M. Meaburn, *Chem. & Ind. (London)*, 930 (1956).

phites.[1,4-6] The enol, IV, formed *in situ* would be rapidly converted to the acetoxy derivative (III). To determine if IV is the intermediate, diethyl acetylphosphonate was treated with ketene under the same conditions used for the diethyl hydrogen phosphite-ketene reaction. The result was the formation of some III as well as the isomeric lactone (V). The presence of V was strongly suggested since


III
V

the infrared spectra of the distillation fractions contained a carbonyl band at 5.45 μ, which is characteristic of a lactone structure. Also, the analyses were correct for $C_8H_{15}O_5P$ which is the molecular formula for both III and V. The reaction of ketene with carbonyl compounds to form lactones is well known.[7,8] It is likely, then, that the acetylphosphonate, in addition to enolizing to IV and then reacting with ketene to produce III, also reacted directly with ketene to form V.

Isomers III and V codistilled and were therefore difficult to separate by distillation. Also, much of the lactone probably decomposed during the initial distillation of the reaction mixture.

In the preparation of diethyl 1-acetoxyvinylphosphonate from diethyl hydrogen phosphite and ketene, the use of a solvent, such as toluene, was found advantageous. The reaction mixtures were easier to process and the yields of III were higher when a solvent was used. The attempted use of acetic anhydride instead of ketene was not successful.

The structure of III was proved by a catalytic reduction using Raney nickel to produce diethyl 1-acetoxyethylphosphonate (VI).

$$CH_2{=}C(OCOCH_3)P(O)(OC_2H_5)_2 + H_2 \xrightarrow{\text{Raney Ni}} \underset{\text{VI}}{CH_3CH(OCOCH_3)P(O)(OC_2H_5)_2}$$

The physical properties and infrared spectrum of VI obtained by reduction of III were identical with those of diethyl 1-acetoxyethylphosphonate prepared earlier by other methods.[9]

In addition, we prepared VI by treating diethyl 1-hydroxyethylphosphonate with acetic anhydride in pyridine.

$$CH_3CHOHP(O)(OC_2H_5)_2 + (CH_3CO)_2O \xrightarrow{\text{pyridine}} CH_3CH(OCOCH_3)P(O)(OC_2H_5)_2$$

EXPERIMENTAL

Diethyl 1-acetoxyvinylphosphonate (III). (*a*) *By reaction of ketene with crude diethyl hydrogen phosphite–β-propiolactone reaction mixture.* Diethyl hydrogen phosphite (110.4 g., 0.8 mole) and β-propiolactone (28.8 g., 0.4 mole) were mixed and heated at 150–173° with stirring for 17 hr. After 5 drops of boron fluoride etherate was added to the crude reaction mixture, ketene was bubbled in through a fritted glass disk while the flask was cooled externally with an ice-water bath. The temperature rose to a maximum of 80°. After 45 min., 49.4 g. of ketene had been absorbed by the reaction mixture. The crude mixture (a light yellow oil) was allowed to stand overnight, and was then distilled *in vacuo* through a 6-in. Vigreux column to obtain the following fractions: (*1*) 6.0 g., b.p. 25–95° (2.5 mm.), n_D^{20} 1.3978; (*2*) 13.6 g., b.p. 95–112° (2.6 mm.), n_D^{20} 1.4298; (*3*) 63.0 g., b.p. 112–125° (2.7–3.2 mm.), n_D^{20} 1.4344; (*4*) 23.4 g., b.p. 120–126° (1.9–3.5 mm.), n_D^{20} 1.4290. At this point, decomposition became excessive and the distillation was stopped. The residue was a dark, resinous material.

Redistillation of 50 ml. of fraction (*3*) through a 12-in. Vigreux column gave a forerun of 11 ml., b.p. 64–80° (0.9–0.3 mm.), n_D^{20} 1.4261, and 30 ml. of diethyl 1-acetoxyvinylphosphonate, b.p. 79–80° (0.3–0.4 mm.), n_D^{20} 1.4378.

Anal. Calcd. for $C_8H_{15}O_5P$: C, 43.24; H, 6.80; P, 13.94. Found: C, 43.21; H, 6.94; P, 13.95.

The infrared spectrum of this compound is compatible with III since it contains a terminal methylene band at 11.55 μ, a conjugated unsaturation band at 6.15 μ, a carbonyl band at 5.65 μ, and the usual phosphoryl and C—O—P bands. These bands are in complete agreement with those reported by Kennedy and Meaburn.[3]

(*b*) *By reaction of ketene with diethyl hydrogen phosphite.* Diethyl hydrogen phosphite (110.4 g., 0.8 mole) and 20 drops of boron fluoride etherate were dissolved in 110 ml. of toluene. Ketene was bubbled into the solution through a fritted glass disk. The temperature of the solution rose to 80°. At this point the temperature was moderated by external cooling, and the temperature was maintained in the 30–80° range by occasional cooling. Escaping ketene was returned to the reaction flask by means of a Dry Ice-cooled condenser. After 1 hr., 72.5 g. of ketene had been condensed in the reaction mixture (67.2 g. of ketene required). About 2 g. of anhydrous sodium carbonate was added to the solution and the material was distilled *in vacuo* through a 6-in. Vigreux column. A forerun boiling up to 97° (2.1 mm.) was removed, and then 71.7 g. (40.4%) of product distilling at 97–99° (2.0 mm.) was collected, n_D^{20} 1.4370. The infrared spectrum of this sample was identical with that obtained on the diethyl 1-acetoxyvinylphosphonate obtained in the previous experiment.

Diethyl 1-acetoxyvinylphosphonate (III) *and 3-diethylphosphono-3-hydroxybutyric acid, β-lactone* (V). Diethyl acetylphosphonate (18.0 g., 0.1 mole) and 10 drops of boron fluoride etherate were placed in 50 ml. of toluene, and ketene was introduced through a fritted glass disk, with stirring. After 30 min., 12 g. of ketene had condensed in the reaction mixture. The solution was then stirred for 2 hr. at 25° and finally heated on a steam bath for 15 min. The solvent was removed and the residue was distilled *in vacuo* through a 6-in. Vigreux column to obtain the following fractions: (*1*) 2.6 g., b.p. 60–79° (0.5–0.8 mm.), n_D^{20} 1.4262; (*2*) 4.2 g., b.p. 80–97° (0.8–1.4 mm.), n_D^{20} 1.4320; (*3*) 4.9

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(4) W. E. Craig and W. F. Hester (to Rohm and Haas Co.), U. S. Patent **2,485,573** (1949).

(5) E. K. Fields (to Research Corp.), U. S. Patent **2,579,810** (1951).

(6) A. R. Stiles (to Shell Development Co.), U. S. Patent **2,593,213** (1952).

(7) F. E. Küng (to The B. F. Goodrich Co.), U. S. Patent **2,356,459** (1944).

(8) T. L. Gresham, J. E. Jansen, F. W. Shaver, and W. L. Beears, *J. Am. Chem. Soc.*, **76**, 486 (1954).

(9) R. L. McConnell and H. W. Coover, Jr., *J. Am. Chem. Soc.*, **79**, 1961 (1957).

g., b.p. 96–120° (1.2–1.8 mm.), n_{D}^{20} 1.4402. The distillation was stopped at this point because of decomposition. The residue was tarry. Fractions (1), (2), and (3) were combined and redistilled through a 6-in. Vigreux column to give the following fractions: (*1*) 4.6 g., b.p. 57–75° (0.7 mm.), n_{D}^{20} 1.4250 (diethyl acetylphosphonate); (*2*) 0.1 g., b.p. 75–84° (0.7 mm.), n_{D}^{20} 1.4322; (*3*) 1.2 g., b.p. 86–106° (0.7 mm.), n_{D}^{20} 1.4420; (*4*) 2.2 g., b.p. 109–112° (0.7–0.8 mm.), n_{D}^{20} 1.4430.

Anal. Calcd. for $C_8H_{15}O_5P$: C, 43.24; H, 6.80; P, 13.94. Found on fraction (3): C, 43.78; H, 7.13; P, 14.33.

The infrared spectra of fractions (*3*) and (*4*) indicated the presence of both diethyl 1-acetoxyvinylphosphonate and the β-lactone of 3-diethylphosphono-3-hydroxybutyric acid in addition to traces of diethyl acetylphosphonate.

Diethyl 1-acetoxyethylphosphonate (VI). (*a*) *From diethyl 1-acetoxyvinylphosphonate.* Diethyl 1-acetoxyvinylphosphonate (11.1 g., 0.05 mole) dissolved in 50 ml. of absolute ethyl alcohol was placed in a pressure bottle, and 5 g. of a suspension of Raney nickel in ethyl alcohol was added. Hydrogen was added until the pressure reached 45 p.s.i., and the temperature was raised to 57°. The reaction was continued at this temperature until 0.05 mole of hydrogen had been absorbed (2.5 hr.). The Raney nickel was removed by filtration and 0.2 g. of anhydrous sodium carbonate was added to the filtrate. The solution was then distilled *in vacuo* through a 6-in. Vigreux column. After the forerun had been removed up to a head temperature of 101° (3.0 mm.), 4.0 g. (35.7%) of diethyl 1-acetoxyethylphosphonate was collected at 101–102° (3.0 mm.), n_{D}^{20} 1.4265.

Anal. Calcd. for $C_8H_{17}O_5P$: C, 42.85; H, 7.64. Found: C, 42.47; H, 7.90.

The infrared spectrum of this sample of diethyl 1-acetoxyethylphosphonate was identical with that of this ester prepared by other methods.[9]

(*b*) *From diethyl 1-hydroxyethylphosphonate.* Acetic anhydride (40.8 g., 0.4 mole) and diethyl 1-hydroxyethylphosphonate[9] (36.4 g., 0.2 mole) were dissolved in 100 ml. of pyridine, and the solution was stirred for 24 hr. The reaction mixture was distilled *in vacuo* through a 6-in. column packed with glass helices. After the pyridine and forerun up to a temperature of 94° (1.8 mm.) had been removed, 26 g. (58%) of diethyl 1-acetoxyethylphosphonate was collected at 94–96° (1.8 mm.), n_{D}^{20} 1.4265.

Anal. Calcd. for $C_8H_{17}O_5P$: C, 42.85; H, 7.64; P, 13.82. Found: C, 43.09; H, 7.68; P, 14.04.

The infrared spectrum of this product was identical with that of this ester prepared by other methods.[9]

KINGSPORT, TENN.

[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE, THE WEIZMANN INSTITUTE OF SCIENCE]

Steroids and Triterpenoids of Citrus Fruit. II. Isolation of Citrostadienol[1]

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Received November 4, 1957

Grapefruit peel oil was found to contain citrostadienol, a new doubly unsaturated steroidal alcohol. The isolation of this compound as well as of β-sitosterol and friedelin from orange peel oil is also reported.

In the first paper of this series we described the isolation of β-sitosterol and friedelin from grapefruit peel oil. Further investigation of the content of the nonvolatile unsaponifiable fraction of this oil has now revealed the presence of an additional compound called by us citrostadienol, $C_{30}H_{50}O \pm CH_2$,[2] m.p. 162–164°, $[\alpha]_D$ +24°.

This compound was first found in the β-sitosterol mother liquors. Later, it could be isolated directly by careful chromatography on alumina of the total crystalline material obtained from the unsaponifiable fraction of the peel oil. The quantity of the isolated citrostadienol amounted to only *ca.* 0.01% of the total. In order to obtain more of this compound large quantities of grapefruit peel oil were needed. Due to the difficulty in obtaining such quantities of this peel oil the more readily accessible orange peel oil was examined for its content of citrostadienol.

The isolation of a steroid from sweet orange (*Citrus Aurentium sinesis*) peel oil was reported already in 1900. Stephan[3] obtained from the peel of Italian sweet oranges a compound with m.p. 138° giving a Liebermann-Burchardt color.[4] A phytosterol with similar constants was isolated by Naves from Guinea oranges.[5] Matlack in an extensive study of the constituents of California orange peel oil succeeded in isolating two phytosterols melting at 139° and 150°, respectively (the acetates melted at 128° and 113.5–114°, respectively), and a "phytosterylin".[6] The compound with m.p. 139° later referred to as "sitosterol" possesses the physical constants of β-sitosterol, as is the case with the compounds isolated by Naves[5] and by Stephan.[3] The "phytosterylin" is most probably β-sitosterol glycoside.[7] This glycoside was found recently to be a constituent of orange juice.[8]

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(1) Presented in part at the 18th Meeting of the Chemical Society of Israel, 1955 (*cf. Bull. Res. Coun. Israel,* **5A**, 105 (1955). For Part I, see "Steroids and Triterpenoids of Grapefruit," Weizmann, Meisels, and Mazur, *J. Org. Chem.*, **20**, 1173 (1955).

(2) The distinction between the C_{29}, C_{30}, and C_{31} formulations cannot be made on the basis of the molecular weight determination by the *Rast* method or by C, H analyses.

(3) Stephan, *J. prakt. Chem.*, **62**, 523 (1900).

(4) The molecular formula given for this compound, $C_{28}H_{48}O_2$, undoubtedly included water of crystallization. It is known that the plant 3β-hydroxy steroids may contain water of crystallization, which is removed only with difficulty.

(5) Naves, *Parfums France*, **10**, 181 (1932).

(6) Matlack, *J. Am. Pharm. Assoc.*, **18**, 24 (1928).

(7) Matlack, *J. Org. Chem.*, **5**, 104 (1940).

(8) Swift, *J. Am. Chem. Soc.*, **74**, 1099 (1952).