The first ester reacted immediately with a dilute solution of potassium permanganate; spectrum: infrared, 5.80 μ (ester).

The other ester was oxidized slowly by potassium permanganate; spectrum: infrared, 5.82 μ (ester). It was concluded that this ester was the acetate of *trans*-sabinene hydrate.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.48; H, 10.21. Found: C, 73.29; H, 10.49.

Acetylation of *cis*-Sabinene Hydrate with Acetic Anhydride and Pyridine.—The acetylation of *cis*-sabinene hydrate was carried out as described above for *trans*-sabinene hydrate. *cis*-Sabinene hydrate (40%) and its acetate (44%) and a mixture of hydrocarbons (16%) were isolated as the products of this reaction by vapor phase chromatography.

Comparative Reaction Rates of the Sabinene Hydrates with Pyridine and Acetic Anhydride.—A sample of 50 mg. of sabinene hydrate was dissolved in 200 μl. of acetic anhydride and 200 μl. of pyridine. The reaction mixtures of both isomers were maintained at 80°. Aliquots of 10 μl. were removed at 0, 2, 4, 8 and 20 hours. These aliquots were analyzed on a 12-foot Carbowax-coated vapor phase chromatography column maintained at 130°. The area of the peak resulting from the alcohol was divided by the total area of all the chromatogram peaks to give the approximate percentage of the alcohol. The results are given in Table I.

STANFORD, CALIF.

[CONTRIBUTION FROM THE FATTY ACID PRODUCERS' COUNCIL OF THE ASSOCIATION OF AMERICAN SOAP AND GLYCERINE PRODUCERS, INC., AND THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Phosphorus Derivatives of Fatty Acids. V.[2] Vinyl α-Diethylphosphonates

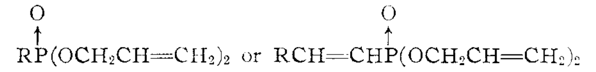
BY RICHARD SASIN,[3] ROSE MARIE NAUMAN[3] AND DANIEL SWERN

RECEIVED JULY 7, 1958

Vinyl α-bromo esters have been prepared in 30–60% yield from vinyl acetate and the appropriate C_2 to C_{18} straight chain α-bromocarboxylic acid (equation 1). By heating the vinyl α-bromo esters with triethyl phosphite, the corresponding vinyl α-diethylphosphonates were prepared in 35–75% yield (equation 2). The vinyl α-phosphonates are colorless, odorless liquids which are insoluble in water and soluble in organic solvents. Under prolonged heating with benzoyl peroxide, they form polymers with a low degree of polymerization.

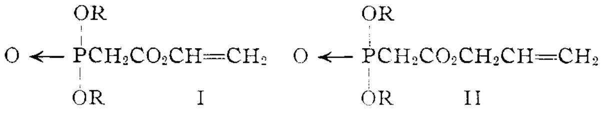
The first three papers in this series,[4–6] described the preparation and properties of dialkyl acylphosphonates, dialkyl acyloxyethyl phosphonates and trialkyl α-phosphonates, respectively. The present investigation deals with the synthesis and properties of some new vinyl esters of α-diethylphosphonocarboxylic acids.

The literature describes numerous examples of unsaturated esters of phosphonic acids.[7–10] These compounds have the general formulas



$$R\overset{O}{\overset{\uparrow}{P}}(OCH_2CH{=}CH_2)_2 \text{ or } RCH{=}CH\overset{O}{\overset{\uparrow}{P}}(OCH_2CH{=}CH_2)_2$$

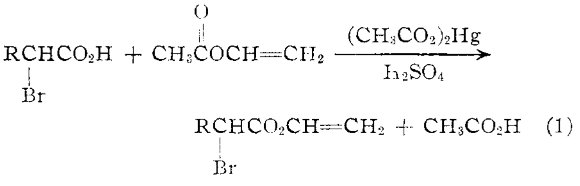
In contrast to alkenyl phosphonates, the literature reports relatively few examples of alkenyl phosphonocarboxylates. The examples appear to be limited to the vinyl (I) and allyl (II) phosphonoacetates.[11–13] In these compounds, the alkenyl group of the ester is attached to carbon and not to phosphorus as in the previous types.



$$O \leftarrow \overset{OR}{\underset{OR}{P}}CH_2CO_2CH{=}CH_2 \quad \text{I} \qquad O \leftarrow \overset{OR}{\underset{OR}{P}}CH_2CO_2CH_2CH{=}CH_2 \quad \text{II}$$

Apparently there are no reports on the systematic preparation and study of the physical and chemical properties of the vinyl (α-diethylphosphono)-carboxylate esters, a previously unreported series of polymerizable esters.

This paper describes the preparation and properties of the vinyl esters of bromoacetic, α-bromocaproic, -pelargonic, -capric, lauric, -myristic, -palmitic and -stearic acids. These compounds, most of which have not been described previously, were prepared from the appropriate α-bromocarboxylic acid and vinyl acetate by acidolysis in the presence of mercuric sulfate.



$$\underset{\substack{|\\Br}}{RCH}CO_2H + CH_3\overset{O}{\overset{\|}{C}}OCH{=}CH_2 \xrightarrow[H_2SO_4]{(CH_3CO_2)_2Hg} \underset{\substack{|\\Br}}{RCH}CO_2CH{=}CH_2 + CH_3CO_2H \quad (1)$$

$R = H, C_4H_9, C_7H_{15}, C_8H_{17}, C_{10}H_{21}, C_{12}H_{25}, C_{14}H_{29}, C_{16}H_{33}$

The properties, yields obtained and analyses of the vinyl α-bromo esters are summarized in Table I. These esters are colorless, odorless (except for the acetate which is strongly lachrymatory), high-boiling liquids insoluble in water and soluble in organic solvents.

By heating the vinyl α-bromo esters with triethyl phosphite in a Michaelis–Arbuzov reaction, the corresponding vinyl α-diethylphosphonates were prepared.

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[1] Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

[2] Presented at the Fall Meeting of the American Chemical Society, Chicago, Ill., September 7–12, 1958. Paper IV in this series, *Ind. Eng. Chem.*, data series (1958).

[3] Fellow of the Fatty Acid Producers' Council of the Association of American Soap and Glycerine Producers, Inc.

[4] B. Ackerman, T. A. Jordan, C. R. Eddy and D. Swern, THIS JOURNAL, **78**, 4444 (1956).

[5] B. Ackerman, T. A. Jordan and D. Swern, *ibid.*, **78**, 6025 (1956).

[6] B. Ackerman, R. M. Chladek and D. Swern, *ibid.*, **79**, 6524 (1957).

[7] H. W. Coover and J. B. Dickey, U. S. Patent 2,636,027 (1953).

[8] R. V. Lindsey, Jr., U. S. Patent 2,439,214 (1948).

[9] C. S. Marvel and J. C. Wright, *J. Polymer Sci.*, **8**, 255 (1952).

[10] A. D. F. Toy, THIS JOURNAL, **70**, 186 (1948).

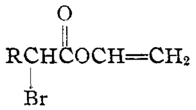
[11] R. H. Wiley, U. S. Patent 2,478,441 (1949).

[12] G. Kamai and V. A. Kukhtin, *J. Gen. Chem. U.S.S.R.*, **24**, 1819 (1954); *C. A.*, **50**, 7720h (1956).

[13] G. Kamai and V. A. Kukhtin, *Zhur. Obshchei Khim.*, **24**, 1855 (1954); *C. A.*, **49**, 13072g (1955).

TABLE I

VINYL α-BROMO ESTERS,



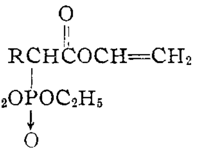
$$\underset{\mathrm{Br}}{\mathrm{RCH}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OCH{=}CH_2}$$

R	Yield, %	B.p. °C.	B.p. Mm.	Bromine, % Calcd.	Bromine, % Found	n^{30}_D	d^{30}_4	Molecular refraction Calcd.	Molecular refraction Found
H-	30	50-51	9.0[a]	48.4	47.9	1.4692	1.5414	29.88	29.89
$CH_3(CH_2)_3$-	43	84-86	2.8[a]	20.5	20.2	1.4588	1.2360	48.46	48.88
$CH_3(CH_2)_6$-	30	66-67	0.15[a]	30.3	30.0	1.4608	1.1566	62.39	62.46
$CH_3(CH_2)_7$-	33	92-94	.20[b]	28.8	28.4	1.4612	1.1298	67.03	67.30
$CH_3(CH_2)_9$-	46	116-117	.20[b]	26.2	26.3	1.4617	1.0933	76.32	76.71
$CH_3(CH_2)_{11}$-	58	137-139	.25[b]	24.0	23.8	1.4627	1.0699	85.61	85.76
$CH_3(CH_2)_{13}$-	30	165-167	.15[b]	22.1	22.3	1.4633	1.0554	94.89	94.36
$CH_3(CH_2)_{15}$-	33	190-192	.10[b]	20.5	20.2	1.4641	1.0304	104.2	104.2

[a] Distilled through a heated, jacketed Vigreux column, 60 cm. long. [b] Distilled through a short Claisen head filled with glass tubing.

TABLE II

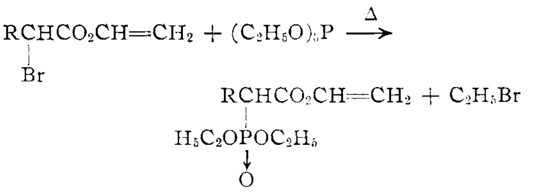
VINYL α-(DIETHYLPHOSPHONO) ESTERS,



$$\underset{\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{H_5C_2OPOC_2H_5}}}{\mathrm{RCH}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OCH{=}CH_2}$$

R	Yield, %	B.p. °C.	B.p. Mm.	Phosphorus, % Calcd.	Phosphorus, % Found	n^{30}_D	d^{30}_4	Molecular refraction Calcd.	Molecular refraction Found
H-[11,12]	41	98-100	0.25[a]	13.9	14.2	1.4348	1.1245	51.55	51.54
$CH_3(CH_2)_3$-	38	158-159	7.8[a]	11.1	11.2	1.4370	1.0436	70.13	69.86
$CH_3(CH_2)_6$-	35	148-149	0.01[a]	9.6	9.2	1.4422	1.0082	84.06	84.14
$CH_3(CH_2)_7$-	62	146-148	.15[b]	9.2	8.8	1.4426	0.9990	88.71	88.62
$CH_3(CH_2)_9$-	47	152-153	.05[b]	8.6	8.7	1.4443	.9836	97.99	97.94
$CH_3(CH_2)_{11}$-	39	172-174	.15[b]	7.9	8.0	1.4459	.9736	107.3	106.9
$CH_3(CH_2)_{13}$-	73	200-202	.10[b]	7.4	7.6	1.4476	.9659	116.6	115.9
$CH_3(CH_2)_{15}$-	41	165	.002[c]	6.9	7.3	1.4492	.9596	125.8	124.9

[a] Distilled through a heated, jacketed Vigreux column, 60 cm. long. [b] Distilled through a short Claisen head filled with glass tubing. [c] Molecularly distilled.



$$\underset{\mathrm{Br}}{\mathrm{RCH}}\mathrm{CO_2CH{=}CH_2} + (C_2H_5O)_3P \xrightarrow{\Delta} \underset{\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{H_5C_2OPOC_2H_5}}}{\mathrm{RCH}}\mathrm{CO_2CH{=}CH_2} + C_2H_5Br \quad (2)$$

The vinyl α-diethylphosphonates are colorless, odorless, high-boiling liquids insoluble in water and soluble in organic solvents. The properties, yields obtained and analyses of these esters are summarized in Table II.

Infrared spectra were obtained on the vinyl α-diethylphosphonates. Within the series differences among the spectra were only those minor variations which would be expected from the differences in chain length. Table III lists the carbonyl absorption and the absorption bands which may be associated with the phosphorus-containing portion of the molecule. For comparison, the absorption bands of the trialkyl α-phosphonates are also listed in Table III. The band assignments are taken from Bellamy.[14] The 785–793 cm.$^{-1}$ bands are also tentatively assigned to P–O–C vibration in accordance with the suggestion of Meyrick and Thompson.[15] As can be seen from Table III, the absorption bands for the trialkyl α-phosphonates are practically identical with those in the vinyl α-diethylphosphonates except for the carbonyl absorption. This is not surprising inasmuch as vinyl esters are known to show a marked enhancement of the carbonyl frequency. Furthermore, the corresponding band intensities in the two series are essentially identical.

TABLE III

ASSIGNMENT OF ABSORPTION BANDS, CM.$^{-1}$

	Vinyl α-diethylphosphonates	Trialkyl α-phosphonates
P–O–C	785–793	785–793
P–O (pentavalent phosphorus)	960–970	964–967
P–O–C (aliphatic)	1030–1035	1027–1032
P–O–Ethyl	1150–1165	1156–1168
P→O	1257–1267	1256–1265
C=O	1745–1760	1735–1740

On prolonged heating with 0.2% benzoyl peroxide, the vinyl α-diethylphosphono esters formed very thick viscous oils. In the one case studied, polyvinyl α-(diethylphosphono)-myristate, the weight average molecular weight was found to be only 83,000.

Experimental

All the reactions and distillations described were conducted in an atmosphere of nitrogen.

Starting Materials.—Bromoacetic and α-bromohexanoic acids were commercial products and were used as received. The α-bromomyristic, α-bromopalmitic and α-bromostearic

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[14] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954.

[15] C. I. Meyrick and H. W. Thompson, *J. Chem. Soc.*, 225 (1950).

acids were prepared from the appropriate pure fatty acid and bromine in the conventional manner.[16] The melting points of the α-bromo acids were 41–42°, 49–50° and 56–57°, respectively. The remaining α-bromo acids were commercial products which were fractionally distilled before use: α-bromopelargonic acid, b.p. 138° at 0.8 mm.; α-bromocapric acid, b.p. 153–154 at 0.3 mm.; and α-bromolauric acid, b.p. 160–162° at 0.8 mm. Vinyl acetate, b.p. 72–74°, and triethyl phosphite, b.p. 151–155°, were obtained from the commercial grades by fractional distillation.

Vinyl α-Bromoesters.—The procedure of Toussaint and MacDowell[17] was modified slightly. After the vinyl acetate (1.25 moles), α-bromo acid (0.25 mole), mercuric acetate (1.6 g.) and sulfuric acid (0.15 ml.) were heated, the reaction mixture was cooled, dissolved in 150 ml. of ether and washed with water until the washings were neutral to litmus. The ether solution was dried over anhydrous sodium sulfate, the ether was removed by distillation and the product was distilled under diminished pressure. The results are summarized in Table I.

Vinyl α-diethylphosphonates were prepared by heating the vinyl α-bromo esters with a 100% molar excess of triethyl phosphite at 160–190° in an atmosphere of nitrogen. The ethyl bromide was swept out and collected in a Dry Ice trap. The reaction was stopped when the weight of ethyl bromide became constant (usually 4–5 hr.). Generally, 90 to 95% of the calculated amount of ethyl bromide was obtained. The entire reaction mixture was then fractionally distilled to obtain the pure vinyl α-diethylphosphonate. The results are summarized in Table II.

Infrared Studies.—Infrared absorption spectra were obtained with a Beckman IR-3 spectrophotometer, using sodium chloride prisms. A spacer approximately 0.02 mm. thick was used between two sodium chloride windows for the samples.

Polymerization.—A typical long chain vinyl phosphonate, namely, vinyl α-(diethylphosphono)-myristate (5 g.), was heated at 80° with 0.2% benzoyl peroxide for 48 hours. The mixture then was dissolved in 30 ml. of benzene and the polymer was precipitated with 800 ml. of methanol. The methanol solution was decanted and the polymer again was dissolved and precipitated. After the methanol was decanted, the polymer was dried in a vacuum desiccator. It was a thick, very viscous oil. The polymer had a weight average molecular weight of 83,000 by the light scattering method.

Acknowledgment.—The authors wish to thank Mr. Winfred E. Parker for the infrared studies, Dr. L. P. Witnauer and Mrs. Jeanne G. Fee for molecular weight determinations, and Mrs. Ruth B. Kelly, Miss Laverne H. Scroggins, Mrs. Dolores Bowe and Dr. Clyde L. Ogg for analyses.

PHILADELPHIA 18, PENNA.

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(16) R. S. Sweet and F. L. Estes, *J. Org. Chem.*, **21**, 1426 (1956).

(17) W. J. Toussaint and L. G. MacDowell, Jr., U. S. Patent 2,299,862 (1942).

[CONTRIBUTION FROM THE SOUTHERN REGIONAL RESEARCH LABORATORY[1]]

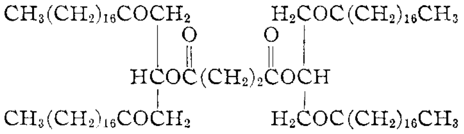
1,3-Diolein and 1,3-Distearin Esters of Fumaric, Succinic and Adipic Acids[2]

BY R. O. FEUGE AND T. L. WARD

RECEIVED JUNE 2, 1958

The 1,3-diolein and 1,3-distearin esters of fumaric, succinic and adipic acids were prepared by reaction between the 1,3-diglycerides and the acid chlorides of the dibasic acids in the presence of pyridine or quinoline, special precautions being taken in most instances to reduce the amount of side reaction. The reaction products were purified and a number of their physical properties were determined. The melting points of the highest melting polymorph of the products derived from distearin ranged from 82.1 to 89.8°. The compounds derived from diolein either could not be obtained in a crystalline form or crystallization was incomplete; hence no melting points were determined for these compounds. From X-ray diffraction patterns it was concluded that the quick-chilled and the highest melting forms of the distearin-containing compounds crystallized in a structure equal in length to about that of two stearic acid chains. The compounds crystallized as long thin needles. All of the diglyceride esters of the dibasic acids were quite viscous when compared with cottonseed oil at the same temperature. The viscosity of the diolein-containing compounds ranged between 77.00 and 116.70 centistokes at 38.8°. The viscosity of the distearin-containing compounds ranged between 11.42 and 20.64 centistokes at 98.8°.

The acylation of the diglycerides of edible, fat-forming acids with certain dibasic acids like fumaric, succinic and adipic should produce compounds having a number of practical uses. Such compounds, as exemplified by bis-(glycerol 1,3-distearate) succinate might be expected to possess some of the properties of the synthetic ester lubricants. In addition they might be expected to be edible and digestible since fumaric and succinic acids occur in the Krebs cycle. However, at the present time there is no proof that the compounds which will be described are edible.



$$\begin{array}{ccc} CH_3(CH_2)_{16}COCH_2 & & H_2COC(CH_2)_{16}CH_3 \\ | & & | \\ HCOC(=O)(CH_2)_2C(=O)OCH & & \\ | & & | \\ CH_3(CH_2)_{16}COCH_2 & & H_2COC(CH_2)_{16}CH_3 \end{array}$$

A search of the literature has failed to reveal any previous reports on the properties of the compounds which will be described in the present report. Indeed, there appears to be little information available on any of the compounds which can be formed from diglycerides and dibasic acids. Among the few references to be found is that in a patent by Blake[3] claiming the preparation of bis-(glycerol dioleate) malate. The patent was concerned primarily with the use of bis-(glycol monolaurate) malate and bis-(glycol monostearate) malate as minor surface-active components of cutting oils.

To some degree the diglyceride esters of dibasic acids would be expected to resemble the synthetic ester lubricants investigated at the Naval Research Laboratory by Zisman and his co-workers.[4–7] These lubricants, which include di-(2-ethylhexyl)

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(1) One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

(2) Presented in part at the 128th National Meeting of the American Chemical Society, Minneapolis, Minn., Sept. 11–16, 1955.

(3) E. S. Blake, U. S. Patent 2,531,801 (1950).

(4) R. W. Miller, P. N. Craig and J. K. Wolfe, Naval Research Laboratory Report P-2573, June, 1945.

(5) E. M. Bried, H. F. Kidder, C. M. Murphy and W. A. Zisman, *Ind. Eng. Chem.*, **39**, 484 (1947).

(6) D. C. Atkins, Jr., H. R. Baker, C. M. Murphy and W. A. Zisman, *ibid.*, **39**, 491 (1947).

(7) C. M. Hain, D. T. Jones, R. L. Merker and W. A. Zisman, *ibid.*, **39**, 500 (1947).