

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

The other ester was oxidized slowly by potassium permanganate; spectrum: infrared, 5.82  $\mu$  (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  $\mu$ l. of acetic anhydride and 200  $\mu$ l. of pyridine. The reaction mixtures of both isomers were maintained at 80°. Aliquots of 10  $\mu$ l. 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<sup>1</sup>]

## Phosphorus Derivatives of Fatty Acids. V.<sup>2</sup> Vinyl $\alpha$ -Diethylphosphonates

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RECEIVED JULY 7, 1958

Vinyl  $\alpha$ -bromo esters have been prepared in 30–60% yield from vinyl acetate and the appropriate  $C_2$  to  $C_{18}$  straight chain  $\alpha$ -bromocarboxylic acid (equation 1). By heating the vinyl  $\alpha$ -bromo esters with triethyl phosphite, the corresponding vinyl  $\alpha$ -diethylphosphonates were prepared in 35–75% yield (equation 2). The vinyl  $\alpha$ -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,<sup>4–6</sup> described the preparation and properties of dialkyl acylphosphonates, dialkyl acyloxyethyl phosphonates and trialkyl  $\alpha$ -phosphonates, respectively. The present investigation deals with the synthesis and properties of some new vinyl esters of  $\alpha$ -diethylphosphonocarboxylic acids.

The literature describes numerous examples of unsaturated esters of phosphonic acids.<sup>7–10</sup> These compounds have the general formulas



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.<sup>11–13</sup> In these compounds, the alkenyl group of the ester is attached to carbon and not to phosphorus as in the previous types.

(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.

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

(7) H. W. Coover and J. B. Dickey, U. S. Patent 2,436,027 (1953).

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

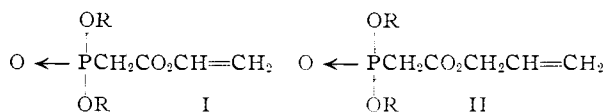
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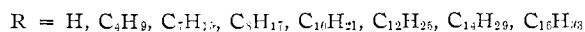
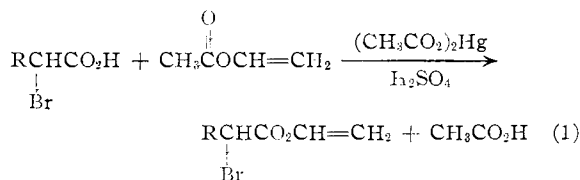
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Apparently there are no reports on the systematic preparation and study of the physical and chemical properties of the vinyl ( $\alpha$ -diethylphosphono)-carboxylate esters, a previously unreported series of polymerizable esters.

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



The properties, yields obtained and analyses of the vinyl  $\alpha$ -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  $\alpha$ -bromo esters with triethyl phosphite in a Michaelis-Arbusov reaction, the corresponding vinyl  $\alpha$ -diethylphosphonates were prepared.

TABLE I

$$\text{VINYL } \alpha\text{-BROMO ESTERS, } \text{RCH} \begin{array}{c} \parallel \\ \text{O} \end{array} \text{COCH}=\text{CH}_2$$

$$\downarrow$$

$$\text{Br}$$

R	Yield, %	B.p.		Bromine, %		$n_{\text{D}}^{20}$	$d_{4}^{20}$	Molecular refraction	
		$^{\circ}\text{C.}$	Mm.	Calcd.	Found			Calcd.	Found
H-	30	50-51	9.0 <sup>a</sup>	48.4	47.9	1.4692	1.5414	29.88	29.89
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> -	43	84-86	2.8 <sup>a</sup>	20.5	20.2	1.4588	1.2360	48.46	48.88
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> -	30	66-67	0.15 <sup>a</sup>	30.3	30.0	1.4608	1.1566	62.39	62.46
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> -	33	92-94	.20 <sup>b</sup>	28.8	28.4	1.4612	1.1298	67.03	67.30
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub> -	46	116-117	.20 <sup>b</sup>	26.2	26.3	1.4617	1.0933	76.32	76.71
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> -	58	137-139	.25 <sup>b</sup>	24.0	23.8	1.4627	1.0699	85.61	85.76
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>13</sub> -	30	165-167	.15 <sup>b</sup>	22.1	22.3	1.4633	1.0554	94.89	94.36
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>15</sub> -	33	190-192	.10 <sup>b</sup>	20.5	20.2	1.4641	1.0304	104.2	104.2

<sup>a</sup> Distilled through a heated, jacketed Vigreux column, 60 cm. long. <sup>b</sup> Distilled through a short Claisen head filled with glass tubing.

TABLE II

$$\text{VINYL } \alpha\text{-(DIETHYLPHOSPHONO) ESTERS, } \text{RCH} \begin{array}{c} \parallel \\ \text{O} \end{array} \text{COCH}=\text{CH}_2$$

$$\downarrow$$

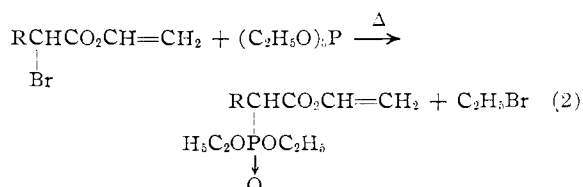
$$\text{H}_5\text{C}_2\text{OPOC}_2\text{H}_5$$

$$\downarrow$$

$$\text{O}$$

R	Yield, %	B.p.		Phosphorus, %		$n_{\text{D}}^{20}$	$d_{4}^{20}$	Molecular refraction	
		$^{\circ}\text{C.}$	Mm.	Calcd.	Found			Calcd.	Found
H- <sup>11,12</sup>	41	98-100	0.25 <sup>a</sup>	13.9	14.2	1.4348	1.1245	51.55	51.54
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> -	38	158-159	7.8 <sup>a</sup>	11.1	11.2	1.4370	1.0436	70.13	69.86
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> -	35	148-149	0.01 <sup>a</sup>	9.6	9.2	1.4422	1.0082	84.06	84.14
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> -	62	146-148	.15 <sup>b</sup>	9.2	8.8	1.4426	0.9990	88.71	88.62
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub> -	47	152-153	.05 <sup>b</sup>	8.6	8.7	1.4443	.9836	97.99	97.94
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> -	39	172-174	.15 <sup>b</sup>	7.9	8.0	1.4459	.9736	107.3	106.9
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>13</sub> -	73	200-202	.10 <sup>b</sup>	7.4	7.6	1.4476	.9659	116.6	115.9
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>15</sub> -	41	165	.002 <sup>c</sup>	6.9	7.3	1.4492	.9596	125.8	124.9

<sup>a</sup> Distilled through a heated, jacketed Vigreux column, 60 cm. long. <sup>b</sup> Distilled through a short Claisen head filled with glass tubing. <sup>c</sup> Molecularly distilled.



The vinyl  $\alpha$ -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  $\alpha$ -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  $\alpha$ -phosphonates are also listed in Table III. The band assignments are taken from Bellamy.<sup>14</sup> The 785-793  $\text{cm.}^{-1}$  bands are also tentatively assigned to P-O-C vibration in accordance with the suggestion of Meyrick and Thompson.<sup>15</sup> As can be seen from Table III, the absorption bands for the trialkyl  $\alpha$ -phosphonates

(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).

are practically identical with those in the vinyl  $\alpha$ -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,  $\text{CM.}^{-1}$ 

	Vinyl $\alpha$ -diethylphosphonates	Trialkyl $\alpha$ -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 $\rightarrow$ O	1257-1267	1256-1265
C=O	1745-1760	1735-1740

On prolonged heating with 0.2% benzoyl peroxide, the vinyl  $\alpha$ -diethylphosphono esters formed very thick viscous oils. In the one case studied, polyvinyl  $\alpha$ -(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  $\alpha$ -bromohexanoic acids were commercial products and were used as received. The  $\alpha$ -bromomyristic,  $\alpha$ -bromopalmitic and  $\alpha$ -bromostearic

