Distillation of the filtrate gave 1.6 ml. of VII, a clear, colorless, viscous liquid which boiled at 96–98° (0.2 mm.), $n^{25}D$ 1.5522. The product crystallized to white needles when cooled slightly below room temperature.

Anal. Calcd. for $C_{14}H_{38}P_2Si_4$: P, 16.3; Si, 29.5; mol. wt., 380.6. Found: P, 16.4; Si, 28.5; mol. wt., 377.

WILMINGTON 98, DEL.

[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. VII.[2] Addition of Dialkyl Phosphonates to Unsaturated Compounds

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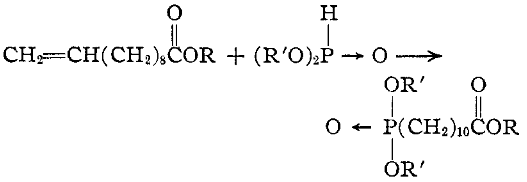
The addition of dialkyl phosphonates to unsaturated compounds under free radical conditions has been shown to be a general reaction of wide applicability. Addition proceeds smoothly with unsaturated compounds containing a terminal or an isolated double bond and also with a series of vinyl esters. Trialkyl ω-phosphonoundecanoates were prepared in 53–66% yield by the addition of dialkyl phosphonates to alkyl undecenoates (eq. 1), R = R' = CH_3, C_2H_5, n-C_4H_9, 2-ethylhexyl; R = 2-ethylhexyl, R' = C_2H_5; R = C_2H_5, R' = 2-ethylhexyl. These reactions were catalyzed by decomposing peroxides and also by ultraviolet radiation. Addition of dialkyl phosphonates to alkyl oleates in the presence of peroxides yielded trialkyl 9(10)phosphonostearates in 66–77% yield (eq. 2), R = R' = CH_3, C_2H_5, n-C_4H_9, 2-ethylhexyl; R = C_2H_5, R' = n-C_4H_9; R = n-C_4H_9, R' = C_2H_5; R = 2-ethylhexyl, R' = C_2H_5. Similarly, addition of dialkyl phosphonates to vinyl esters gave dialkyl 2-acyloxyethylphosphonates in 45–61% yield (eq. 3), R = C_2H_5, $CH_3(CH_2)_2$, $CH_3(CH_2)_7$, $CH_3(CH_2)_{10}$, $CH_3(CH_2)_{16}$; R' = CH_3, C_2H_5, n-C_4H_9, 2-ethylhexyl. All the phosphonates are colorless, thermally stable, high-boiling liquids, except dimethyl and diethyl 2-stearoxyethylphosphonates, which are white solids melting at 45 and 47°, respectively.

Study of the radical-catalyzed addition of dialkyl phosphonates to unsaturated compounds has been confined largely to compounds containing relatively reactive double bonds. The patent literature, for example, describes the radical-catalyzed addition of dialkyl phosphonates to 1-octene, 1-dodecene, allyl dodecyl ether, allyl acetate and methyl undecenoate.[4] The peroxide-catalyzed addition of diethyl phosphonate to vinyl acetate also was reported recently.[5] These authors unequivocally proved that the reaction product is diethyl 2-acetoxyethylphosphonate.

Little has been published on the radical-catalyzed addition of dialkyl phosphonates to non-terminal or relatively unreactive double bonds. While the present work was in progress, Stiles, Vaughan and Rust[6] reported the preparation of dialkyl alkylphosphonates by the addition of dialkyl phosphonates to some non-terminal olefins, as well as to terminal ones, in the presence of decomposing peroxides or ultraviolet radiation. The non-terminal olefins used were 2-butene, cyclohexene and diisobutylene; yields of addition products were generally low.

In this paper we show that the radical-catalyzed addition of dialkyl phosphonates to unsaturated compounds is a general reaction and that fair to good yields (45–77%) of products readily are obtained. The phosphonates employed are dimethyl, diethyl, di-*n*-butyl and di-2-ethylhexyl phosphonates, and the unsaturated compounds are a series of alkyl undecenoates (terminal double bond), alkyl oleates (non-terminal, isolated double bond) and vinyl esters (terminal, activated double bond). The physical properties of the phosphonates obtained also are described.

ω-Dialkyl phosphonoundecanoates were prepared in 53–66% yield by adding dialkyl phosphonates to alkyl undecenoates in the presence of decomposing *t*-butyl perbenzoate or ultraviolet radiation. Yields were essentially the same with decomposing peroxide or ultraviolet catalysis.



$$CH_2{=}CH(CH_2)_8\overset{\overset{O}{\|}}{C}OR + (R'O)_2\overset{\overset{H}{|}}{P} \rightarrow O \longrightarrow O \leftarrow \underset{\underset{OR'}{|}}{\overset{\overset{OR'}{|}}{P}}(CH_2)_{10}\overset{\overset{O}{\|}}{C}OR \tag{1}$$

Symmetrical trialkyl ω-phosphonoundecanoates prepared include: trimethyl, triethyl, tri-*n*-butyl and tri-2-ethylhexyl. The indices of refraction and infrared spectra of these compounds were identical to those prepared from the ω-bromoundecanoate and trialkyl phosphite in a Michaelis–Arbuzov reaction,[2] thus proving that the phosphorus was attached to the terminal carbon. The mixed ω-phosphonoundecanoates synthesized include: 2-ethylhexyl-ω-diethyl and ethyl-ω-di-2-ethylhexyl. All of these compounds are thermally stable, colorless liquids at room temperature, insoluble in water and soluble in organic solvents. The physical properties, yields obtained and analyses of the ω-dialkyl phosphonoundecanoates are summarized in Table I.

Trialkyl 9(10)-phosphonostearates were prepared in 66–77% yield by adding dialkyl phosphonates to alkyl oleates in the presence of *t*-butyl perbenzoate.

The symmetrical trialkyl 9,(10)-phosphonostearates prepared include: trimethyl, triethyl, tri-*n*-butyl and tri-2-ethylhexyl. The mixed 9(10)-phosphonostearates synthesized include: ethyl 9(10)-di-*n*-butylphosphono, *n*-butyl 9(10)-diethylphosphono

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[1] Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[2] Presented at the Fall Meeting of the American Chemical Society, Atlantic City, N. J., September 13–18, 1959. Paper VI in this series is THIS JOURNAL, **81**, 4335 (1959).

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

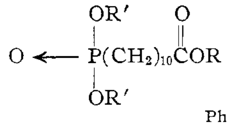
[4] United States Rubber Co., British Patent 694,772 (1953).

[5] R. L. McConnell and H. W. Coover, Jr., THIS JOURNAL, **79**, 1961 (1957).

[6] A. R. Stiles, W. E. Vaughan and F. F. Rust, *ibid.*, **80**, 714 (1958).

TABLE I

TRIALKYL ω-PHOSPHONOUNDECANOATES,



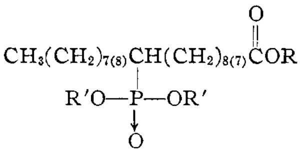
$O \leftarrow \overset{OR'}{\underset{OR'}{P}}(CH_2)_{10}\overset{O}{\overset{\|}{C}}OR$

R	R′	Yield, %	B.p. °C.	B.p. Mm.	$n^{30}D$	d^{30}_4	Phosphorus, % Calcd.	Phosphorus, % Found	Molecular refraction Calcd.	Molecular refraction Found
CH_3	CH_3[c]	60	154–155	0.06[a]	1.4456	....	..	..	...	...
C_2H_5	C_2H_5[c]	58	161–162	.10[a]	1.4410	....	..	..	...	...
n-C_4H_9	n-C_4H_9[c]	66	150	.001[b]	1.4458	....	..	..	...	...
2-Ethylhexyl	2-Ethylhexyl[c]	61	200	.002[b]	1.4534	....	..	..	...	...
2-Ethylhexyl	C_2H_5	53	140	.001[b]	1.4472	0.9611	7.1	7.1	121.2	120.9
C_2H_5	2-Ethylhexyl	53	160	.001[b]	1.4500	0.9401	6.0	6.0	149.0	148.3

[a] Distilled through a short Claisen head filled with glass tubing. [b] Molecularly distilled. [c] Previously prepared by another method; see ref. 2.

TABLE II

TRIALKYL 9(10)-PHOSPHONOSTEARATES,[a]

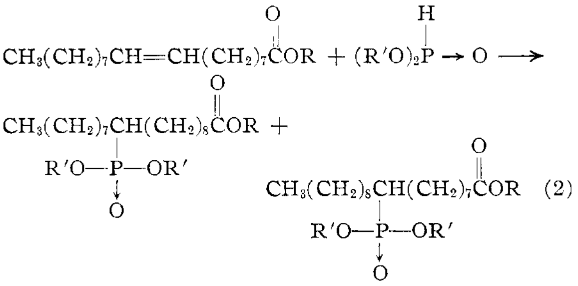


$CH_3(CH_2)_{7(8)}\underset{R'O-\underset{\downarrow O}{P}-OR'}{CH}(CH_2)_{8(7)}\overset{O}{\overset{\|}{C}}OR$

R	R′	Yield, %	B.p. °C.	B.p. Mm.	$n^{30}D$	d^{30}_4	Phosphorus, % Calcd.	Phosphorus, % Found	Molecular refraction Calcd.	Molecular refraction Found
CH_3	CH_3	68	130	0.001	1.4531	0.9889	7.6	7.3	111.9	111.2
C_2H_5	C_2H_5	75	140	.001	1.4492	.9596	6.9	7.0	125.8	125.4
n-C_4H_9	n-C_4H_9	66	170	.001	1.4502	.9372	5.8	5.9	153.7	152.8
2-Ethylhexyl	2-Ethylhexyl	67	200	.002	1.4555	.9148	4.4	4.4	209.4	208.2
C_2H_5	n-C_4H_9	77	155	.001	1.4504	.9435	6.1	6.2	144.4	143.9
n-C_4H_9	C_2H_5	67	150	.001	1.4489	.9473	6.5	6.3	135.1	134.9
2-Ethylhexyl	C_2H_5	68	170	.001	1.4512	.9362	5.8	5.5	153.7	153.3

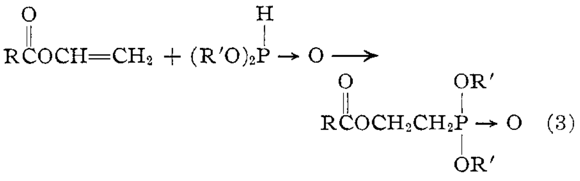
[a] All of these compounds were molecularly distilled.

and 2-ethylhexyl 9(10)-diethylphosphonostearate. Attempts to catalyze the reaction with ultraviolet radiation yielded only unchanged reactants. Attempts to prepare these compounds from an alkyl 9(10)-bromostearate and trialkyl phosphite in a Michaelis–Arbuzov reaction also yielded unchanged reactants. All of the 9(10)-phosphonostearates are colorless, high-boiling, thermally stable liquids, insoluble in water and soluble in organic solvents. The physical properties, yields obtained and analyses of these compounds are summarized in Table II.



$$CH_3(CH_2)_7CH{=}CH(CH_2)_7\overset{O}{\overset{\|}{C}}OR + (R'O)_2\overset{H}{\overset{|}{P}}\rightarrow O \longrightarrow CH_3(CH_2)_7\underset{R'O-\underset{\downarrow O}{P}-OR'}{CH}(CH_2)_8\overset{O}{\overset{\|}{C}}OR + CH_3(CH_2)_8\underset{R'O-\underset{\downarrow O}{P}-OR'}{CH}(CH_2)_7\overset{O}{\overset{\|}{C}}OR \quad (2)$$

Dialkyl 2-acyloxyethylphosphonates were prepared in 45–65% yield by the dropwise addition of vinyl esters to dialkyl phosphonates in the presence of t-butyl perbenzoate.



$$R\overset{O}{\overset{\|}{C}}OCH{=}CH_2 + (R'O)_2\overset{H}{\overset{|}{P}}\rightarrow O \longrightarrow R\overset{O}{\overset{\|}{C}}OCH_2CH_2\overset{OR'}{\underset{OR'}{P}}\rightarrow O \quad (3)$$

The yields obtained were considerably better than that reported for the addition of diethyl phosphonate to vinyl acetate.[5] The dialkyl 2-acyloxyethylphosphonates include those prepared by the addition of dimethyl, diethyl, di-n-butyl and di-2-ethylhexyl phosphonates to the vinyl esters of prepionic, butyric, pelargonic, myristic and stearic acids.

The index of refraction and infrared spectra of diethyl 2-myristoxyethylphosphonate and diethyl 2-stearoxyethylphosphonate prepared by addition were identical to those prepared from the 2-bromoethyl esters of myristic and stearic acids and triethyl phosphite in a Michaelis–Arbuzov reaction.[7] The dialkyl 2-acyloxyethylphosphonates are colorless, high-boiling, thermally stable liquids at room temperature, except dimethyl and diethyl 2-stearoxyethylphosphonates, which are white solids melting at 45 and 47°, respectively. The physical properties, yields obtained and analyses of the dialkyl 2-acyloxyethylphosphonates are summarized in Table III.

Infrared spectra were obtained on all of the phosphonates prepared. The absorption bands which may be associated with the phosphorus-containing portion of the molecule were essentially the same as those reported for the ω-dialkylphosphonoundecanoates.[2]

Experimental

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

Starting Materials.—Methyl alcohol, ethyl alcohol, n-butyl alcohol, undecylenic acid and oleic acid (a low linoleic-grade, free of *trans* isomers) were the best available commercial products and were used as received. Vinyl stearate was a commercial product which was crystallized from acetone.

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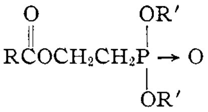
[7] B. Ackerman, T. A. Jordan and D. Swern, THIS JOURNAL, **78**, 6025 (1956).

TABLE III

DIALKYL 2-ACYLOXYETHYLPHOSPHONATES,



$R\overset{\overset{O}{\|}}{C}OCH_2CH_2\overset{OR'}{\underset{OR'}{P}} \rightarrow O$

R	R′	Yield, %	B.p. °C.	B.p. Mm.	n^{30}_D	d^{30}_4	Phosphorus, % Calcd.	Phosphorus, % Found	Molecular refraction Calcd.	Molecular refraction Found
CH_3CH_2	CH_3	61	96–97	0.15[a]	1.4316	1.1621	14.7	14.4	46.87	46.87
CH_3CH_2	C_2H_5	55	103–104	.06[a]	1.4291	1.0936	13.0	12.7	56.16	56.17
CH_3CH_2	n-C_4H_9	45	126–128	.01[a]	1.4340	1.0232	10.5	10.3	74.75	74.91
CH_3CH_2	2-Ethylhexyl	45	110	.001[b]	1.4437	0.9692	7.6	7.5	111.8	111.4
$CH_3(CH_2)_2$	CH_3	65	93–94	.01[a]	1.4328	1.1345	13.8	13.4	51.52	51.30
$CH_3(CH_2)_2$	C_2H_5	45	98–99	.01[a]	1.4300	1.0745	12.3	12.0	60.81	60.64
$CH_3(CH_2)_2$	n-C_4H_9	58	142–143	.13[a]	1.4346	1.0118	10.1	10.1	79.40	79.46
$CH_3(CH_2)_2$	2-Ethylhexyl	52	120	.001[b]	1.4440	0.9580	7.4	7.4	116.5	116.6
$CH_3(CH_2)_7$	CH_3	55	125–126	.02[a]	1.4407	1.0448	10.5	10.6	74.75	74.35
$CH_3(CH_2)_7$	C_2H_5	50	80	.001[b]	1.4373	1.0102	9.6	9.9	84.04	83.65
$CH_3(CH_2)_7$	n-C_4H_9	45	95	.001[b]	1.4400	0.9738	8.2	8.1	102.6	102.4
$CH_3(CH_2)_7$	2-Ethylhexyl	49	150	.001[b]	1.4472	0.9429	6.3	6.3	139.7	139.1
$CH_3(CH_2)_{12}$	CH_3	49	120	.002[b]	1.4477	1.0020	8.5	8.4	97.98	97.31
$CH_3(CH_2)_{12}$	C_2H_5[c]	57	130	.001[b]	1.4450	0.9773	..	..	107.2	106.9
$CH_3(CH_2)_{12}$	n-C_4H_9	60	145	.001[b]	1.4462	.9603	6.9	7.2	125.8	124.7
$CH_3(CH_2)_{12}$	2-Ethylhexyl	49	170	.001[b]	1.4517	.9331	5.5	5.6	163.0	162.1
$CH_3(CH_2)_{16}$	CH_3	45	150	.002[b]	1.4434[e]	.9585[e]	7.4	7.3	116.7	116.4
$CH_3(CH_2)_{16}$	C_2H_5[d]	49	M.p. 45 160	.001[b]	1.4410[e]	.9405[e]	..	..	125.8	125.9
$CH_3(CH_2)_{16}$	n-C_4H_9	47	M.p. 47 175	.002[b]	1.4487	.9392	6.1	6.1	144.4	144.1
$CH_3(CH_2)_{16}$	2-Ethylhexyl	46	205	.003[b]	1.4530	.9219	5.0	5.0	181.6	180.9

[a] Distilled through a short Claisen head filled with glass tubing. [b] Molecularly distilled. [c] Previously reported b.p. 157–159° at 0.1 mm., n^{30}_D 1.4440; see ref. 7. [d] Previously reported b.p. 185–191° at 0.1 mm., n^{50}_D 1.4411; see ref. 7. [e] Taken at 50°.

The remaining vinyl esters, 2-ethylhexyl alcohol and the dialkyl phosphonates were commercial products which were fractionally distilled before use: vinyl propionate, b.p. 94–95°; vinyl butyrate, b.p. 115–116°; vinyl pelargonate, b.p. 133–134° at 50 mm.; vinyl myristate, b.p. 148–150° at 5 mm.; 2-ethylhexyl alcohol, b.p. 183–184°; dimethyl phosphonate, b.p. 72° at 20 mm.; diethyl phosphonate, b.p. 73° at 10 mm.; di-*n*-butyl phosphonate, b.p. 64° at 0.05 mm.; and di-2-ethylhexyl phosphonate, b.p. 128–130° at 0.1 mm.

Alkyl Undecenoates and Alkyl Oleates.—Methyl and ethyl undecenoate and methyl and ethyl oleate were prepared by refluxing the appropriate acid with a 5-molar excess of absolute methanol or ethanol, using naphthalene-2-sulfonic acid as catalyst. After several water washes, followed by drying over anhydrous sodium sulfate, the esters were fractionally distilled under diminished pressure. The other alkyl undecenoates and alkyl oleates were prepared in the conventional way with azeotropic removal of water[8]; they were also fractionally distilled.

ω-Dialkyl Phosphonoundecanoates. Method A.—A mixture of alkyl undecenoate (0.2 mole) and dialkyl phosphonate (0.6 mole) was placed in a quartz flask. The solution, blanketed with nitrogen, then was irradiated at a distance of 1 inch by a 140 watt ultraviolet lamp (high pressure quartz mercury arc) for 6 hr. at a temperature of 100–110°. The entire reaction mixture then was fractionally distilled under diminished pressure to obtain the pure ω-dialkyl phosphonoundecanoates (Table I).

Method B.—A mixture of alkyl undecenoate (0.2 mole), dialkyl phosphonate (0.6 mole) and 0.005 mole of *t*-butyl perbenzoate was placed in a 500-ml. round-bottom flask equipped with a magnetic stirrer and a nitrogen inlet tube. The reaction mixture was stirred and heated at 100–110° for 4 hours. During this period, additional peroxide (0.005 mole) was added after 1 hour and after 2 hours of elapsed reaction time (total peroxide used was 2.5 mole % of dialkyl phosphonate). The reaction mixture then was fractionally distilled under diminished pressure to obtain the pure ω-dialkyl phosphonoundecanoates. Results are summarized in Table I.

Trialkyl 9(10)-phosphonostearates were prepared from alkyl oleates and dialkyl phosphonates by method B above, except that a six-hour reaction time was used. Results are summarized in Table II.

Dialkyl 2-Acyloxyethylphosphonates.—Dialkyl phosphonate (0.3 mole) and 0.0025 mole of *t*-butyl perbenzoate were placed in a 500-ml. round-bottom 3-neck flask, equipped with a magnetic stirrer, a nitrogen inlet tube and a dropping funnel and heated to 100°. Vinyl ester (0.1 mole) was added dropwise, while the temperature was maintained at 100–110°. Additional peroxide (0.0025 mole) was added after 1 and 2 hours. The addition of vinyl esters was complete after about 2.5 hours and the solution was stirred for one additional hour. The reaction mixture then was fractionally distilled under diminished pressure to obtain the pure dialkyl 2-acyloxyethylphosphonates. Results are summarized in Table III.

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.

Acknowledgment.—The authors wish to thank Dr. C. Roland Eddy, Mr. Carl Leander and Mr. Winfred E. Parker for the infrared studies, and Dr. Clyde E. Ogg, Mrs. Ruth B. Kelly and Miss Laverne H. Scroggins for analyses.

PHILADELPHIA 18, PENNA.

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[8] D. Swern and E. F. Jordan, Jr., THIS JOURNAL, **67**, 902 (1945).