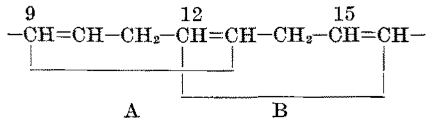
may be considered as the major intermediates:



Linolenate

A gives:

$$-CH_2-\overset{9}{C}H=CH-\overset{11}{C}H=CH-CH_2-CH_2-\overset{15}{C}H=CH- \qquad [1]$$

$$-CH_2-CH_2-\overset{10}{C}H=CH-\overset{12}{C}H=CH-CH_2-\overset{15}{C}H=CH- \qquad [2]$$

B gives:

$$-\overset{9}{C}H=CH-CH_2-\overset{12}{C}H=CH-\overset{14}{C}H=CH-CH_2-CH_2- \qquad [3]$$

$$-\overset{9}{C}H=CH-CH_2-CH_2-\overset{13}{C}H=CH-\overset{15}{C}H=CH-CH_2- \qquad [4]$$

Reduction of either double bond of the conjugated diene system in [1] and [4] would give dienes in which the double bonds are separated by more than one methylene group and would be nonconjugatable with alkali. These unconjugatable dienes would not be reduced further. Their resistance to hydrogenation accounts for their high proportion in the diene fraction of linolenate. Since the conjugated dienes are mostly *trans,trans*, the unreduced double bond from the conjugated system would remain in the *trans* configuration, thus explaining the high isolated *trans* content of the diene fraction. Isomer [2] gives on reduction two dienes, one unconjugatable (10,15-) and the other conjugatable (12,15-) which is reducible to a mixture of 11-,12-,13-,14-,15- and 16-monoenes. Similarly, isomer [3] gives two dienes, 9,14- and 9,12-, the latter giving, like linoleate, a mixture of 8-,9-,10-, 11-,12- and 13-monoenes. By analogy with linoleate, the major isomers would include the 9-,10-,11- and 12-monoenes on one hand and the 12-,13-,14- and 15- on the other.

According to this scheme, a Gaussian distribution of isomeric monoenes is obtained with a max in the middle 12-position; such a distribution conforms to that observed by oxidative cleavage of the *cis* and *trans* monoenes of linolenate. This mechanism assumes that only conjugated systems are reduced and that no selectivity is exhibited for any of the double bonds of these systems. To elucidate further the mechanism of hydrogenation of both linoleate and linolenate, more definitive evidence could be obtained by experiments with radioactive intermediates.

ACKNOWLEDGMENTS

Spectral analyses by Helen M. Peters and 9-,12-,15-monoene standards from C. R. Scholfield.

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Phosphorus Derivatives of Fatty Acids. The Addition of Dialkyl Phosphonates to Unsaturated Acids and the Synthesis of Some 11-Dialkylphosphonoundecanoamides

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Abstract

A series of dialkylphosphonoundecanoic acids and 9(10)-dialkylphosphonostearic acids was prepared by the addition of dialkylphosphonates to 10-undecenoic acid and oleic acid under free radical conditions in 58–66% yield. The phosphonates used were: dimethyl, diethyl, di-*n*-butyl, di-*n*-hexyl and di-2-ethylhexyl. All of the products are colorless, odorless, thermally stable liquids, insoluble in water and soluble in organic solvents. The dialkylphosphonoundecanoic acids were converted into the corresponding acid chlorides by reaction with oxalyl chloride. The acid chlorides were then converted into the corresponding amides by addition of ammonia. All of the amides are white waxy solids except the 2-ethylhexyl derivative which is a high-boiling liquid. Two of the dialkylphosphonoundecanoic acids were converted into the N-decyl substituted amides by heating with *n*-decylamine. The N-*n*-decyl-11-dialkylphosphonoundecanoamides are white waxy solids.

Introduction

THE ADDITION of dialkylphosphonates to unsaturated compounds under free radical conditions has been shown to be a general reaction of wide applicability. Many unsaturated compounds have been used including terminal and non-terminal olefins (1), alkyl undecenoates, alkyl oleates and vinyl esters (2). The P,P-dialkyl 9(10)-phosphonostearates are of particular interest as they are efficient, primary plasticizers imparting good low temperature flexibility to poly(vinyl chloride) compositions containing them (3). In addition, these compounds have low migration losses.

While the literature lists many examples of the addition of dialkylphosphonates to olefins and unsaturated esters, no mention could be found of the reaction with unsaturated acids. The purpose of this investigation was to study the addition of dialkylphosphonates to 10-undecenoic acid and oleic acid and also to prepare certain derivatives of the resulting compounds, namely the amides.

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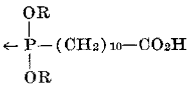
[1] Presented at the AOCS Meeting, New Orleans, 1964.

TABLE I

11-Dialkylphosphono Undecanoic Acids,



$O \leftarrow \overset{OR}{\underset{OR}{P}}-(CH_2)_{10}-CO_2H$

R	Yield %	BP		n_D^{30}	d_4^{30}	Molecular refraction		Phosphorus	
		°C	Mm			Calcd.	Found	Calcd.	Found
CH_3	60	110	0.001	1.4586	1.0693	74.77	75.11	10.5	10.4
C_2H_5	58	125	0.001	1.4555	1.0346	84.06	84.63	9.4	9.5
n-C_4H_9	66	150	0.001	1.4560	1.0012	102.6	102.8	8.2	8.2
2-Ethylhexyl	61	180	0.001	1.4616	0.9589	141.8	140.6	6.5	6.3

All of these compounds were molecularly distilled.

Experimental

All reactions and distillations were conducted in an atmosphere of nitrogen. All melting points are uncorrected and were determined by the capillary tube method.

Starting Materials. All chemicals were commercial products which were fractionally distilled before use: 10-undecenoic acid, bp 136C at 1.5 mm; dimethylphosphonate, bp 72C at 20 mm; diethylphosphonate, bp 73C at 10 mm; di-*n*-butylphosphonate, bp 64C at 0.05 mm; di-*n*-hexylphosphonate, bp 140C at 0.3 mm; di-2-ethylhexylphosphonate, bp 128–130C at 0.1 mm; oleic acid (a low linoleic grade, free of *trans* isomers) bp 203–205C at 4 mm; and *n*-decylamine, bp 218C.

1) *11-Dialkylphosphonoundecanoic Acids.* A mixture of 10-undecenoic acid (0.2 mole), dialkylphosphonate (0.6 mole) and 0.005 mole of *t*-butylperbenzoate or *α,α'*-azodiisobutyronitrile was placed in a 500-ml round-bottomed flask equipped with a thermometer, a magnetic stirrer and a nitrogen inlet tube. The reaction mixture was stirred and heated at 100–110C for four hr. During this period, additional catalyst (0.005 mole) was added after one hr and then after two hr of elapsed reaction time (total catalyst used was 2.5 mole % of dialkylphosphonate). The reaction mixture then was fractionally distilled under diminished pressure to remove unreacted dialkylphosphonate and the residue was then distilled molecularly. Results are summarized in Table I.

2) *11-Diethylphosphonoundecanoic Acid.* A mixture of 26.5 g (0.1 mole) of 11-bromoundecanoic acid and 33.2 g (0.2 mole) of triethylphosphite was heated at 140–160C in an atmosphere of nitrogen for five hr. The ethyl bromide was swept out and collected in a dry ice trap. The reaction mixture then was fractionally distilled under diminished pressure to remove unreacted triethylphosphite and the residue was then distilled molecularly. The yield of product (bp 120–130C at 0.001 mm, n_D^{25} 1.4555) was 4.9 g or 15.2%. Triethyl *ω*-phosphonoundecanoate was also isolated from the reaction mixture. The yield of the ester (bp 90–100C at 0.001 mm, n_D^{25} 1.4390) was 5.2 g or 14.9%.

3) *9(10)-Dialkylphosphonostearic Acids.* A mixture of oleic acid (0.2 mole) and 0.015 mole of *t*-butylperbenzoate or *α,α'*-azodiisobutyronitrile was added dropwise to 0.6 mole of dialkylphosphonate maintained at 100–110C in a 500 ml round-bottomed flask equipped with a thermometer, a magnetic stirrer and a nitrogen inlet tube. After the dropwise addition (ca. five hr), the mixture was heated for an additional three hr. The reaction mixture then was fractionally distilled under diminished pressure to remove unreacted dialkylphosphonate and the residue was then molecularly distilled. Results are summarized in Table II.

4) *11-Dialkylphosphonoundecanoamides.*

A. *Unsubstituted Amides.* The 11-dialkylphosphonoundecanoyl chlorides were prepared by heating 0.1 mole of the 11-dialkylphosphonoundecanoic acid disolved in 100 ml of dry benzene with 12.5 g (0.1 mole) of oxalyl chloride at 60–65C for two hr. The acid chloride then was added dropwise to 100 ml of dry benzene in a 500 ml round-bottomed flask, equipped with an inlet tube for annomia gas, a reflux condenser and a dropping funnel. Both the condenser and funnel were protected by calcium chloride drying tubes. The mixture was heated gently on a steam bath and ammonia was bubbled through as the acid chloride was added. When addition of the acid chloride was complete, the ammonia was added for an additional hr. After several water washes, the benzene solution was dried over anhydrous sodium sulfate and the benzene was removed by distillation. The resulting solid was then crystallized from *n*-hexane. The di-2-ethylhexyl derivative was an oil and was purified by molecular distillation. The properties, yields obtained and analyses of the amides are summarized in Table III.

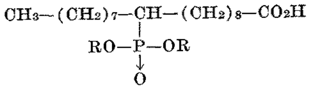
B. *Substituted Amides.* In a 100 ml 3-neck round-bottomed flask equipped with a thermometer and a condenser was added 0.05 mole of 11-dialkylphosphonoundecanoic acid and 7.5 g (0.051 mole) of *n*-decylamine. After the initial slight exothermic reaction had subsided, the mixture was heated to 230C for 15 min. After cooling, the white waxy solid was crystallized from ethanol. Results are summarized in Table III.

Discussion

This paper describes the preparation and properties of a series of 11-dialkylphosphonoundecanoic acids

TABLE II

9(10)-Dialkylphosphono Stearic Acids,



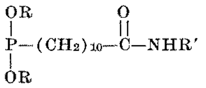
$CH_3-(CH_2)_7-\underset{RO-\underset{\underset{O}{\downarrow}}{P}-OR}{CH}-(CH_2)_8-CO_2H$

R	Yield %	BP		n_D^{25}	d_4^{25}	Molecular refraction		Phosphorus	
		°C	Mm			Calcd.	Found	Calcd.	Found
CH_3	66	140	0.001	1.4638	1.0047	107.3	107.6	7.9	8.2
C_2H_5	61	150	0.001	1.4612	1.0002	116.5	115.3	7.4	7.4
n-C_4H_9	61	160	0.001	1.4645	0.9810	135.1	134.0	6.5	6.6
n-C_6H_{13}	62	210	0.001	1.4625	0.9507	153.7	154.0	5.8	5.6

All of these compounds were molecularly distilled.

TABLE III

11-Dialkylphosphono Undecanoamides,

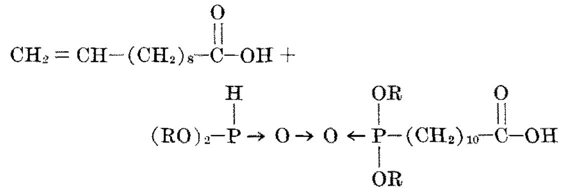


$O \leftarrow \underset{OR}{\overset{OR}{P}}-(CH_2)_{10}-\overset{O}{\overset{\parallel}{C}}-NHR'$

R	R′	MPC	Phosphorus, %		Nitrogen, %	
			Calcd.	Found	Calcd.	Found
CH_3	H	93–94	10.6	10.2	4.8	5.2
C_2H_5	H	79–80	9.7	9.9	4.3	4.4
n-C_4H_9	H	74–75	8.2	8.5	3.7	4.0
2-Ethylhexyl	H	BP 170C at 0.001 mm[a]	6.3	6.1	2.8	2.6
CH_3	n-$C_{10}H_{21}$	144–145	7.2	7.2	3.3	3.2
n-C_4H_9	n-$C_{10}H_{21}$	106–107	6.0	6.1	2.7	2.8

[a] Molecularly distilled.

made by the addition of dialkylphosphonates to 10-undecenoic acid under free radical conditions.



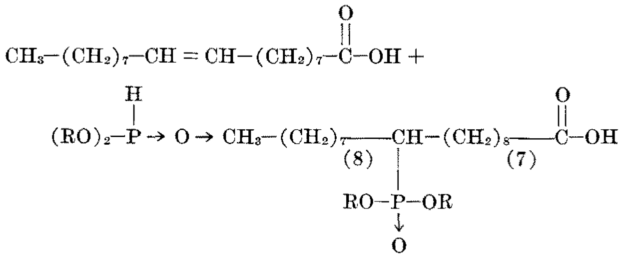
$CH_2=CH-(CH_2)_8-\overset{O}{\overset{\parallel}{C}}-OH + (RO)_2-\overset{H}{\overset{|}{P}} \rightarrow O \rightarrow O \leftarrow \underset{OR}{\overset{OR}{P}}-(CH_2)_{10}-\overset{O}{\overset{\parallel}{C}}-OH$

The reaction is catalyzed by decomposing *t*-butylperbenzoate, *α,α′*-azodiisobutyronitrile or UV radiation (2) and the yields are essentially the same (ca. 60%) regardless which catalyst is employed. The catalyst (2.5 mole percentage based on the dialkyl phosphonate) was mixed with the 10-undecenoic acid and added dropwise to the dialkylphosphonate maintained at 100–110C according to the method of Knight et al. (4). The 11-dialkylphosphonoundecanoic acids prepared include: dimethyl, diethyl, di-*n*-butyl and di-2-ethylhexyl. All of these compounds are thermally stable, colorless liquids at room temp, insoluble in water and soluble in organic solvents. They were purified by molecular distillation. The physical properties, yields obtained and analyses of the 11-dialkylphosphonoundecanoic acids are summarized in Table I.

To further confirm the structure of these compounds, 11-diethylphosphonoundecanoic acid was prepared from 11-bromoundecanoic acid and triethyl phosphite in a Michaelis-Arbuzov reaction.

The boiling point, refractive index and IR spectrum of the compound prepared by addition were identical to that of the compound prepared by the Michaelis-Arbuzov reaction.

A series of 9(10)-dialkylphosphonostearic acids was prepared by the addition of dialkylphosphonates to oleic acid under free radical conditions.



$CH_3-(CH_2)_7-CH=CH-(CH_2)_7-\overset{O}{\overset{\parallel}{C}}-OH + (RO)_2-\overset{H}{\overset{|}{P}} \rightarrow O \rightarrow CH_3-(CH_2)_7\underset{(8)}{—}\underset{\underset{\underset{O}{\downarrow}}{RO-P-OR}}{CH}-(CH_2)_8\underset{(7)}{—}\overset{O}{\overset{\parallel}{C}}-OH$

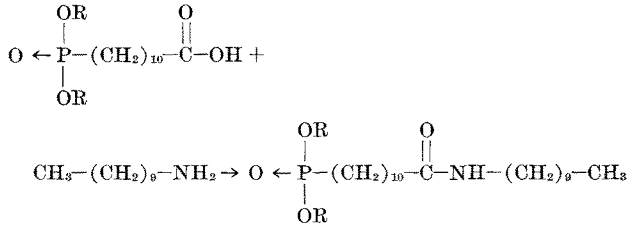
The reaction was catalyzed by decomposing *t*-butylperbenzoate and *α,α′*-azodiisobutyronitrile but not by UV radiation. The 9(10)-dialkylphosphonostearic acids prepared include: dimethyl, diethyl, di-*n*-butyl and di-*n*-hexyl. All of the compounds are thermally stable, colorless liquids at room temp, insoluble in water and soluble in organic solvents. The physical properties, yields obtained and analyses of the 9(10)-dialkylphosphonostearic acids are summarized in Table II.

IR spectra were obtained on all of the phosphono acids with a Perkin-Elmer Infracord model 37. The band assignments are taken largely from Bellamy (5). The IR bands obtained are those expected for compounds with the reported structures. The carboxylic acid carbonyl band is at 1700–1710 cm^{-1}. The P—O (pentavalent phosphorus) vibration is at 960–970 cm^{-1}. The (P)—O—C(aliphatic) in phase stretching vibration is at 1020–1030 cm^{-1} and the (P)—O—C (aliphatic) out of phase stretching vibration is at 1050–1060 cm^{-1} (6). The P → O stretching band is found at 1250–1255 cm^{-1}.

The 11-dialkylphosphonoundecanoic acids were then converted into the corresponding acid chlorides by reaction with oxalyl chloride and then into the corresponding amides by reaction with ammonia (7).

The 11- dialkylphosphonoundecanoamides prepared include: di-methyl, diethyl, di-*n*-butyl and di-2-ethylhexyl. The last compound is a colorless, thermally stable liquid and the others are white waxy solids. The physical properties and analyses of the amides were summarized in Table III.

Two substituted amides were prepared by heating the 11-dialkylphosphonoundecanoic acids with *n*-decylamine (8).



$O \leftarrow \underset{OR}{\overset{OR}{P}}-(CH_2)_{10}-\overset{O}{\overset{\parallel}{C}}-OH + CH_3-(CH_2)_9-NH_2 \rightarrow O \leftarrow \underset{OR}{\overset{OR}{P}}-(CH_2)_{10}-\overset{O}{\overset{\parallel}{C}}-NH-(CH_2)_9-CH_3$

The 11-dialkylphosphonoundecanoic acids used were the dimethyl and the di-*n*-butyl compounds. The N-*n*-decyl-11-dialkylphosphonoundecanoamides are white waxy solids at room temp. The physical properties and analyses of the *n*-decyl substituted amides are summarized in Table III.

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