of the residual oil gave 4.48 g. (66.6%) of 10-cyanodecyl thiocyanate. A purified product (b.p. 160–162.5° (0.08 mm.), d^{20}_4 0.982, n^{25}_D 1.4806) was obtained by redistillation.

Anal. Calcd. for $C_{12}H_{20}N_2S$: C, 64.25; H, 8.99; N, 12.49; S, 14.29. Found: C, 64.26; H, 9.32; N, 12.58; S, 14.08.

3-Cyanopropyl thiocyanate, b.p. 112.5–115° (0.06 mm.), d^{20}_4 1.100, n^{25}_D 1.4968, was prepared in 76.5% yield from 4-bromobutyronitrile.

Anal. Calcd. for $C_5H_6N_2S$: C, 47.59; H, 4.79; N, 22.21; S, 25.41. Found: C, 47.57; H, 4.86; N, 22.61; S, 25.30.

4-Cyanobutyl thiocyanate, b.p. 131–132° (0.1 mm.), d^{20}_4 1.098, n^{25}_D 1.4921, was prepared from 5-bromovaleronitrile in 72.8% yield.

Anal. Calcd. for $C_6H_8N_2S$: C, 51.40; H, 5.75; N, 19.98; S, 22.87. Found: C, 51.74; H, 5.93; N, 17.51; S, 22.50.

VILLE LA SALLE, QUEBEC

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. VI.[2] ω-Dialkyl Phosphonoundecanoates

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

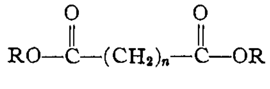
RECEIVED FEBRUARY 16, 1959

A series of ω-bromoundecanoates has been prepared in 55–96% yield from ω-bromoundecanoic acid and alcohols or phenol: $Br(CH_2)_{10}COOH + ROH \rightarrow Br(CH_2)_{10}COOR + H_2O$ where R = CH_3, C_2H_5, n-C_4H_9, n-C_6H_{13}, 2-ethylhexyl, n-$C_{12}H_{25}$, C_6H_5. By heating the ω-bromoundecanoates with trialkyl phosphites, the corresponding ω-dialkyl phosphonoundecanoates were prepared in 53–87% yield: $Br(CH_2)_{10}COOR + (R'O)_3P \rightarrow O \leftarrow P(OR')_2(CH_2)_{10}COOR + R'Br$. Trialkyl ω-phosphonoundecanoates prepared include: R = R' = CH_3, C_2H_5, n-C_4H_9, n-C_6H_{13}, 2-ethylhexyl, n-$C_{12}H_{25}$. Mixed ω-dialkyl phosphonoundecanoates prepared include: R = C_2H_5, R' = n-C_4H_9; R = 2-ethylhexyl, R' = n-C_4H_9; R = $C_{12}H_{25}$, R' = n-C_4H_9; R = C_6H_5, R' = n-C_4H_9; R = n-C_4H_9; R' = 2-ethylhexyl; R = 2-ethylhexyl, R' = C_2H_5; R = C_2H_5, R' = 2-ethylhexyl. The compounds in which R = 2-ethylhexyl and R' = C_2H_5; and R = C_2H_5 and R' = 2-ethylhexyl were prepared by another synthetic method. The ω-dialkyl phosphonoundecanoates are colorless, odorless, thermally stable liquids, insoluble in water and soluble in organic solvents.

In this Laboratory, recent research on the preparation of pure derivatives from fats has been directed mainly toward the correlation of structure with important physical properties desired in plasticizers and also in synthetic lubricants. Groups containing the phosphorus atom, for example, are known to impart useful properties to plasticizers, and a number of phosphorus-containing plasticizers are commercially available.

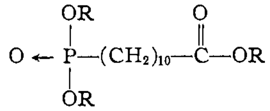
For the past four years we have been systematically preparing long-chain phosphorus compounds of various types. These are trialkyl phosphates,[4] dialkyl acyloxyalkyl phosphates,[4] dialkyl acyloxyalkylphosphonates[5] and alkyl (α-dialkylphosphono)-alkanoates.[6]

Since most low temperature plasticizers are dialkyl esters (I) of dicarboxylic acids, such as adipates, azelates and sebacates, it was decided to prepare a series of compounds similar to these dibasic esters but containing a dialkylphosphono group in place of one carboxylic ester group. The ω-dialkyl phosphonoundecanoates (II) are such a series of compounds; their preparation is described here. No reports on the preparation and study of the physical and chemical properties of the ω-dialkyl phosphonoundecanoates could be found in the literature.



$$RO-\overset{\overset{O}{\|}}{C}-(CH_2)_n-\overset{\overset{O}{\|}}{C}-OR$$

I



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

II

n = 4, 7, 8

This paper also describes the preparation and properties of a series of ω-bromoundecanoates, used as intermediates in the preparation of II. They were prepared from ω-bromoundecanoic acid and alcohols or from the acid chloride and phenol. The esters prepared include: methyl, ethyl, n-butyl, n-hexyl, 2-ethylhexyl, n-dodecyl and phenyl. All of these compounds are colorless liquids at room temperature, insoluble in water and soluble in organic solvents. The physical properties, yields obtained and analyses of the ω-bromoundecanoates are summarized in Table I.

By heating the ω-bromoundecanoates with a 100% molar excess of trialkyl phosphite at elevated temperature for several hours, the ω-dialkyl phosphonoundecanoates were prepared in 53–87% yield. After the unused trialkyl phosphite was removed, the residue was distilled under diminished pressure.

The trialkyl ω-phosphonoundecanoates prepared include: trimethyl, triethyl, tri-n-butyl, tri-n-hexyl, tri-2-ethylhexyl and trilauryl. The mixed ω-phosphonoundecanoates synthesized include: ethyl ω-di-n-butyl, 2-ethylhexyl ω-di-n-butyl, lauryl ω-di-n-butyl, phenyl ω-di-n-butyl, n-butyl ω-di-2-ethylhexyl, 2-ethylhexyl ω-diethyl and ethyl ω-di-2-ethylhexyl. The last two compounds were prepared from 2-ethylhexyl undecenoate and diethyl phosphonate, and ethyl undecenoate and di-2-ethylhexyl phosphonate under free radical

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

[2] Paper V is in THIS JOURNAL, **80**, 6336 (1958).

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

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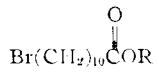
TABLE I

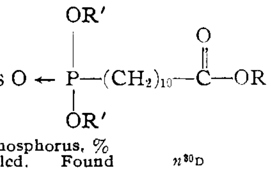
ω-BROMOUNDECANOATES, 

$Br(CH_2)_{10}\overset{\overset{O}{\|}}{C}OR$

R	Yield, %	B.p. °C.	Mm.	Bromine, % Calcd.	Found	n^{20}_D	d^{30}_4	Molecular refraction Calcd.	Found
CH_3[c]	78	118–119	0.1[a]	..	..	1.4604	....	....	....
C_2H_5[d]	89	142–143	.8[a]	..	..	1.4574	....	....	....
n-C_4H_9	96	120–121	.03[a]	24.8	24.4	1.4581	1.0809	81.23	81.13
n-C_6H_{13}	77	152–153	.15[a]	22.8	22.5	1.4594	1.0577	90.52	90.36
2-Ethylhexyl	81	159–160	.05[a]	21.2	20.9	1.4610	1.0417	99.81	99.45
n-$C_{12}H_{25}$	81	140	.002[b]	18.4	18.0	1.4618	1.0081	118.4	118.2
C_6H_5	55	110	.002[b]	23.4	23.3	1.5030	1.1622	86.98	86.81

[a] Distilled through a short Claisen head filled with glass tubing. [b] Molecular distillation. [c] Reported b.p. 175–176° at 14 mm.; ref. 10. [d] Reported b.p. 144–145° at 5 mm.; ref. 11.

TABLE II

ω-DIALKYL PHOSPHONOUNDECANOATES 

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

R	R	Yield, %	B.p. °C.	Mm.	Phosphorus, % Calcd.	Found	n^{30}_D	d^{30}_4	Molecular refraction Calcd.	Found
CH_3	CH_3	60	153–154	0.08[a]	10.0	9.8	1.4456	1.0385	79.40	79.12
C_2H_5	C_2H_5	78	163–164	.15[a]	8.8	8.8	1.4410	0.9910	93.44	93.67
n-C_4H_9	n-C_4H_9	78	193–194	.01[a]	7.1	7.3	1.4458	.9573	121.3	121.0
n-C_6H_{13}	n-C_6H_{13}	53	170	.002[b]	6.0	6.1	1.4492	.9364	149.1	148.7
2-Ethylhexyl	2-Ethylhexyl	57	200	.004[b]	5.2	5.3	1.4530	.9257	176.9	176.1
n-$C_{12}H_{25}$	n-$C_{12}H_{25}$	60	255 M.p. 30–31	.001[b]	4.0	4.1	1.4559	.9040	232.7	231.9
C_2H_5	n-C_4H_9	87	184–186	.10[a]	7.6	7.4	1.4443	0.9664	112.0	111.8
2-Ethylhexyl	n-C_4H_9	75	160	.001[b]	6.3	6.2	1.4490	.9426	139.9	139.6
n-$C_{12}H_{25}$	n-C_4H_9	75	180	.004[b]	5.7	5.5	1.4500	.9298	158.4	158.1
C_6H_5	n-C_4H_9	71	160	.003[b]	6.8	6.5	1.4734	1.0080	127.0	126.6
n-C_4H_9	2-Ethylhexyl	81	170	.003[b]	5.7	5.5	1.4503	0.9316	158.3	157.7
2-Ethylhexyl	C_2H_5	54	140	.001[a]	7.1	7.1	1.4472	.9611	121.2	120.9
C_2H_5	2-Ethylhexyl	53	160	.001[a]	6.0	6.0	1.4500	.9401	149.0	148.3

[a] Distilled through a short Claisen head filled with glass tubing. [b] Molecular distillation.

conditions, to be described in a forthcoming publication. All of the ω-dialkyl phosphonoundecanoates are colorless high-boiling liquids, except the trilauryl derivative which is a white solid melting at 30–31°. The physical properties, yields obtained and analyses of the ω-dialkyl phosphonoundecanoates are summarized in Table II.

Preliminary results indicate that the ω-dialkyl phosphonoundecanoates show promise as plasticizers for poly-(vinyl chloride). Most of the compounds yield well plasticized sheets with good mechanical properties and low stiffness temperatures. The results of plasticizer evaluation will be reported elsewhere.

Infrared spectra were obtained on the ω-dialkyl phosphonoundecanoates. Table III lists the carbonyl absorptions and the absorption bands which may be associated with the phosphorus-containing portion of the molecule. The band assignments are taken largely from Bellamy.[7] The infrared bands obtained are those expected for compounds with the reported structures. The ester carbonyl band is at 1733–1737 cm.$^{-1}$ for all compounds, except the phenyl ester which shows the expected shift to higher frequency, 1760 cm.$^{-1}$ The P → O stretching band is found at 1250–1253 cm.$^{-1}$.

On the basis of some diethyl alkylphosphonates, Gillis, *et al.*,[8] have assigned the 1026–1030 cm.$^{-1}$ bands to the (P)–O–C (aliphatic) in-phase stretching vibration. In the ω-dialkyl phosphonoundecanoates, this band varies from 1034 cm.$^{-1}$ for the methyl and ethyl derivatives down to 1007 cm.$^{-1}$ for the hexyl derivative. Gillis and co-workers also assigned the 1049–1055 cm.$^{-1}$ bands to the (P)–O–C (aliphatic) out-of-phase stretching vibration. In the ω-dialkyl phosphonoundecanoates, this band varies from 1049–1073 cm.$^{-1}$, depending on the alkyl group.

For most of the ω-dialkyl phosphonoundecanoates, the 961–982 cm.$^{-1}$ bands have been assigned to P–O (pentavalent phosphorus) vibration. This band is found at 915 cm.$^{-1}$ for the methyl derivative and at 935 cm.$^{-1}$ for the *n*-dodecyl derivative.

The 794 cm.$^{-1}$ band has been assigned by Meyrick and Thompson[9] to P–O–(C) vibration. Gillis, *et al.*, assigned the 777–785 cm.$^{-1}$ bands to the same vibration. In the ω-dialkyl phosphonoundecanoates this band is found at 785 cm.$^{-1}$ for the ethyl derivatives and at 812 cm.$^{-1}$ for the methyl derivative. All of the other derivatives have a broad band at 800–840 cm.$^{-1}$. The reason for the broad band is not understood.

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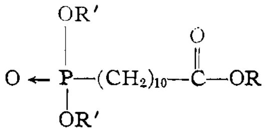
[8] R. G. Gillis, J. F. Horwood and G. L. White, THIS JOURNAL, **80**, 2999 (1958).

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

TABLE III

INFRARED FREQUENCIES (CM.$^{-1}$) AND BAND ASSIGNMENTS FOR ω-DIALKYL PHOSPHONOUNDECANOATES



$$O \leftarrow P(OR')_2-(CH_2)_{10}-C(=O)-OR$$

R	R′	C=O	P → O stretching	(P)-O-C stretching in phase	(P)-O-C stretching out of phase	P^v-O	P-O-(C) stretching, assym.
CH_3	CH_3	1735	1253	1034	1060	915	812
C_2H_5	C_2H_5	1735	1252	1034	1061	961	785
2-Ethylhexyl	C_2H_5	1735	1251	1035	1063	963	785
n-C_4H_9	n-C_4H_9	1734	1252	1028	1072	978	800–840
C_2H_5	n-C_4H_9	1733	1250	1025	1068	977	800–840
2-Ethylhexyl	n-C_4H_9	1735	1252	1025	1072	978	810–840
n-$C_{12}H_{25}$	n-C_4H_9	1737	1255	1025	1072	980	815–840
C_6H_5	n-C_4H_9	1760	1250	1026	1073	980	815
n-C_6H_{13}	n-C_6H_{13}	1737	1252	1007	1062	962	805–818
n-$C_{12}H_{25}$	n-$C_{12}H_{25}$	1737	1252	1010	1065	935	830–845
2-Ethylhexyl	2-Ethylhexyl	1735	1252	1015	1049	982	815–830
n-C_4H_9	2-Ethylhexyl	1735	1252	1017	1050	980	820–830
C_2H_5	2-Ethylhexyl	1735	1252	1017	1050	982	815–825

Experimental

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

Starting Materials.—Methyl alcohol, ethyl alcohol, n-butyl alcohol, ω-bromoundecanoic acid, phenol and trilauryl phosphite were the best available commercial products and were used as received. The remaining trialkyl phosphites and alcohols were commercial products which were fractionally distilled before use: trimethyl phosphite, b.p. 107–109°; triethyl phosphite, b.p. 151–155°; tri-n-butyl phosphite, b.p. 120–124° at 9 mm.; tri-n-hexyl phosphite, b.p. 123–126° at 0.15 mm.; tri-2-ethylhexyl phosphite, b.p. 148–150° at 0.25 mm.; n-hexyl alcohol, b.p. 157–158°; 2-ethylhexyl alcohol, b.p. 183–184°; and lauryl alcohol, b.p. 94–96° at 0.3 mm.

Alkyl ω-bromoundecanoates.—Methyl ω-bromoundecanoate[10] and ethyl ω-bromoundecanoate[11] were prepared by refluxing ω-bromoundecanoic acid with a 5-molar excess of absolute methanol and ethanol, respectively, 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 ω-bromoundecanoates were prepared in the conventional way with azeotropic removal of water[12]; they were also fractionally distilled.

Phenyl ω-Bromoundecanoate.—ω-Bromoundecanoyl chloride was prepared by heating 53 g. (0.2 mole) of ω-bromoundecanoic acid dissolved in 75 ml. of dry benzene with 25 g. (0.2 mole) of oxalyl chloride at 60–65° for two hours. To the acid chloride was added a mixture of phenol (18.8 g., 0.2 mole) and pyridine (17.4 g., 0.22 mole) dissolved in 50 ml. of dry benzene. After one wash with dilute hydrochloric acid solution, followed by several water washes, the ester was dried over anhydrous sodium sulfate and fractionally distilled under diminished pressure. The properties, yields obtained and analyses of the ω-bromo esters are summarized in Table I.

ω-Dialkyl phosphonoundecanoates were prepared by heating the ω-bromoundecanoates with a 100% molar excess of trialkyl phosphite at 160–190° in an atmosphere of nitrogen. The alkyl bromide was swept out and collected in a Dry Ice trap. The reaction was stopped when the weight of alkyl bromide became constant. In most reactions 90 to 95% of the calculated amount of alkyl bromide was obtained in 4 to 5 hr. With tri-2-ethylhexyl phosphite and trilauryl phosphite, the heating time was extended to 20 hr. and the reaction mixture was heated at 50 mm. to facilitate removal of the alkyl bromide. The entire reaction mixture was then fractionally distilled to obtain the pure ω-dialkyl phosphonoundecanoate. Results are summarized in Table II.

Triethyl γ-Phosphonobutyrate.—A mixture of 50 g. (0.256 mole) of ethyl γ-bromobutyrate and 85 g. (0.512 mole) of triethyl phosphite was heated at 160–170° in an atmosphere of nitrogen for 4 hr. The ethyl bromide was swept out and collected in a Dry Ice trap. The entire reaction mixture was then fractionally distilled. Triethyl γ-phosphonobutyrate (boiling point 126–128° at 0.5 mm., n^{30}_D 1.4334, d^{30}_D 1.0772) was obtained in 60% yield as a colorless, odorless liquid.

Anal. Calcd. for $C_{10}H_{21}O_5P$: P, 12.3. Found: P, 12.2.

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. Results are summarized in Table III.

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 L. Ogg, Mrs. Ruth B. Kelly and Miss Laverne H. Scroggins for elemental analyses.

PHILADELPHIA 18, PENNA.

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