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THE REACTIONS OF DIALKYL HYDROGEN PHOSPHITES WITH ALKYL VINYL ETHERS

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Abstract—The reaction of alkyl vinyl ethers with dialkyl hydrogen phosphites has been examined in the presence of a radical initiator and the efficiency of the catalysers (DBP, AIBN, BPO) for this type of reaction compared and found to decrease in the order given. The spectroscopy as well as the chemical properties of the prepared adducts are described.

FREE radical addition to carbon-carbon multiple linkages to form carbon-phosphorus bonds is an important synthetic method.

The preliminary explanation has been given for the reactions of alkyl vinyl ethers and dialkyl hydrogen phosphites,[1] and the details are reported in this communication. n-Butyl, isobutyl, 2-ethylhexyl, dodecyl and tetradecyl vinyl ethers have been examined in reaction with dimethyl*, diethyl, di-n-propyl, di-i-propyl, di-n-butyl and di-2-ethylhexyl* hydrogen phosphites.

Dialkyl hydrogen phosphites add to isobutyl vinyl ether in the presence of α,α'-azobisisobutyronitrile (AIBN) to give the 1:1-adducts.[1] However, the addition product between this vinyl ether and diethyl hydrogen phosphite could not be isolated, although the formation of a phosphorus-containing liquid was assumed from its phosphorus analysis and IR spectrum. In order to elucidate this anomaly, this reaction was repeated.

In view of the polymerization of alkyl vinyl ether in the presence of acid-type catalysers,[2] the action of hydrochloric acid present in trace quantity could be a possible explanation. Diethyl hydrogen phosphite, prepared in carbon tetrachloride according to the procedure of McCombie *et al.*[3] but fractionally distilled, without passing air after heating the reaction mixture at reflux temperature, is sufficiently pure to add to other unsaturated compounds, such as vinyl acetate or oleic acid, but the 1:1-adduct could not be obtained from n-butyl or isobutyl vinyl ethers. In some cases a mild exothermic reaction, in which the temperature reached 50°, takes place on mixing the vinyl ether and the phosphite at room temperature. However, distillation gave no isolable phosphonate.

The phosphite, fractionally distilled after passing air or nitrogen for a sufficient time, on the other hand, adds successfully to every alkyl vinyl ether examined. But, addition of one or two drops of hydrochloric acid to this *pure* phosphite, or the use of the aged phosphite, in which the main contaminant would be phosphorus acid,

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* Reactions with dimethyl or 2-ethylhexyl hydrogen phosphites were described in a previous paper.

[1] T. Nishiwaki, *Tetrahedron* **21**, 3043 (1965).

[2] C. Schildknecht, A. Zoss and C. McKinley, *Ind. Eng. Chem.* **39**, 180 (1947).

[3] H. McCombie, B. Saunders and G. Stacey, *J. Chem. Soc.* 380 (1945).

appreciably decreases the yield of the 1 : 1-adduct, and the amount of the phosphorus-containing tarry material is increased.

Similar results have been noticed in the addition of silicon compounds to alkyl vinyl ethers.[4]

As it was necessary to know the rate of conversion to the 1 : 1-adduct more accurately, vapour-liquid chromatography was used. The calculated yield in a previous paper was based on the actual quantity of the 1 : 1-adduct isolated after several fractional distillations. The details are described in the Experimental.

Identification of all peaks was difficult, but the detection of the peak of the 1 : 1-adduct is possible by comparison with a pure adduct or an authentic sample prepared in another way. This result, together with relative retention times of the 1 : 1-adducts to diethyl ethylphosphonate are shown in Table 1.

The catalytic activity of benzoyl peroxide (BPO) is relatively inefficient in these

TABLE 1. THE CONVERSION TO, AND THE RELATIVE RETENTION TIMES TO DIETHYL ETHYLPHOSPHONATE OF THE 1 : 1-ADDUCTS

Compound No.	$ROCH_2CH_2P(O)(OR')_2$			Molar ratio	Conversion (%)	Relative retention times (min)
	R	R′	Catalyst[a]			
	Diethyl ethylphosphonate					1·0
I	n-Bu	Et	A	1:1	20	3·4
	n-Bu	Et	A	1:2	41	
	n-Bu	Et	A	1:3	46	
	n-Bu	Et	B	1:1	40	
II	n-Bu	n-Pr	A	1:2	35	4·0
III	n-Bu	i-Pr	A	1:1	12	2·2
	n-Bu	i-Pr	A	1:2	32	
IV	n-Bu	n-Bu	A	1:1	18	6·7
	n-Bu	n-Bu	A	1:2	35	
V	i-Bu	Et	A	1:1	21	2·6
	i-Bu	Et	A	1:2	37	
	i-Bu	Et	A	1:3	41	
VI	2-Ethylhexyl	Et	A	1:1	20	5·3
	2-Ethylhexyl	Et	A	1:2	51	
	2-Ethylhexyl	Et	A	1:3	58	
	2-Ethylhexyl	Et	B	1:1	39	
	2-Ethylhexyl	Et	B	1:2	53	
VII	2-Ethylhexyl	n-Pr	A	1:2	48	6·8
	2-Ethylhexyl	n-Pr	B	1:2	59	
VIII	2-Ethylhexyl	n-Bu	A	1:1	22	9·6
	2-Ethylhexyl	n-Bu	B	1:1	44	
IX	$C_{12}H_{25}$	Et	B	1:1	29	19·0
	$C_{12}H_{25}$	Et	B	1:2	52	
X	$C_{14}H_{29}$	Et	B	1:1	12[b]	—

[a] A; AIBN, B; DBP. 0·01 mole of catalyser was used per 0·2 mole of vinyl ether.

[b] This was the yield of the 1 : 1-adduct actually isolated after several distillations, because its b.p. was too high to trace the reaction by gas chromatography.

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[4] L. Goodman, R. Silverstein and A. Benitez, *J. Amer. Chem. Soc.* **79**, 3073 (1957).

reactions and this activity is even less in the higher alkyl vinyl ethers. For instance, 0·05 mole of BPO is required to reduce the iodine value to nearly zero in a mixture consisting of 0·2 mole dodecyl or tetradecyl vinyl ether and 0·4 mole diethyl hydrogen phosphite, while in this case 0·02 mole of AIBN is sufficient. The reaction is even slow with the addition of a relatively large quantity of BPO at one time. Thus, the rate of abstraction of hydrogen from diethyl hydrogen phosphite by BPO is slow, if the $(RO)_2P(O)\cdot$ radical is the adding species. Similar observations have been made by Shostakovskii *et al.*, who concluded that AIBN is the most effective initiator for the addition of hydrogen sulphide to an alkyl vinyl ether.[5]

This is in contrast to the reaction with the lower alkyl vinyl ethers, where 0·01 mole AIBN is effective for 0·2 mole n-butyl, isobutyl, or 2-ethylhexyl vinyl ethers.

Di-t-butyl peroxide (DBP), on the other hand, is very effective for this type of the addition reaction. An additional advantage is the easy removal of contaminants resulting from decomposition. DBP (0·01 mole) reduces the iodine value to nearly zero in the reaction of 0·2 mole dodecyl or tetradecyl vinyl ether with diethyl hydrogen phosphite in a shorter period than the use of AIBN. Further, the yield of the 1 : 1-adduct is more increased in the presence of DBP than AIBN. This tendency is more marked when the molar ratio of the reactants is 1 : 1 (Table 1).

From these observations it was concluded that the activity of the radical initiators decreases in the order; DBP > AIBN > BPO.

The yield of the 1 : 1-adduct (III) from n-butyl vinyl ether and di-i-propyl hydrogen phosphite is lower than for other straight chain phosphites. Steric factors may not account for this, because the phosphonyl radical formed from this phosphite is not inaccessible to the terminal methylene of the vinyl group, but thermal decomposition, or partial hydrolysis, of the adduct formed may be partly responsible.

It has been reported that prolonged heating of the phosphonic esters at high temperature brings about their transformation to the parent phosphonic acid and olefins.[6] If this is the case in the present branched-chain phosphonate, the distillation residue should be highly acidic, which is disproved, although the IR spectrum of the distillation residue shows several weak absorptions at 2700, 2100 and 1650 cm^{-1}, which may be assigned to P—OH frequencies.[7]

The difficulty encountered during the preparation of an analytical sample is mainly due to the hygroscopic nature of this phosphonate, which certainly causes partial hydrolysis during the addition reaction or subsequent treatments.

The physical constants and analytical data of the 1 : 1-adducts are given in Table 2.

For identification, some anilinium salts of the parent phosphonic acids were prepared. In several reactions between dodecyl vinyl ether and diethyl hydrogen phosphite, evaporative distillation was attempted, and is recorded in the Experimental.

In these additions, the phosphonyl radical should preferably attack the terminal methylene, since the secondary radical thus formed will be more thermodynamically stable than its counterpart.[8] Therefore, the present adducts will be dialkyl β-alkoxyethylphosphonates.

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[5] M. Shostakovskii, E. Prilezhaeva and E. Shapiro, *Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk* 734, (1955). *Chem. Abstr.* **50**, 7080 (1956).

[6] A. Canavan, B. Dowden and C. Eaborn, *J. Chem. Soc.* 331 (1962).

[7] J. Ferraro, *Progress in infrared spectra* Vol. 2; p. 127. Plenum Press, New York (1964)

[8] J. Cadgan and D. Hey, *Quart. Rev.* **8**, 308 (1954).

TABLE 2. PHYSICAL CONSTANTS AND ANALYTICAL DATA OF DIALKYL β-ALKOXYETHYLPHOSPHONATES PREPARED BY THE RADICAL ADDITION REACTIONS OF ALKYL VINYL ETHERS WITH DIALKYL HYDROGEN PHOSPHITES

$ROCH_2CH_2P(O)(OR')_2$

Compound No.	R	R′	b.p. (o/mm)	n_D^{25}	Formula	Analyses Calc. C	(%) H	Found C	(%) H
I	n-Bu	Et	95–97/0·5	1·4259	$C_{10}H_{23}O_4P$	50·41	9·73	50·01	9·36
II	n-Bu	n-Pr	122–125/1·5	1·4302	$C_{12}H_{27}O_4P$	54·12	10·20	54·06	10·24
III	n-Bu	i-Pr	80–84/0·2	1·4250	$C_{12}H_{27}O_4P$	54·12	10·20	53·75	10·18
IV	n-Bu	n-Bu	110–113/0·2	1·4312	$C_{14}H_{31}O_4P$	57·12	10·62	56·88	10·59
V	i-Bu	Et	78–81/0·2	1·4229	$C_{10}H_{23}O_4P$	50·41	9·73	49·96	9·74
VI	2-Ethhexyl	Et	116–118/0·2	1·4357	$C_{14}H_{31}O_4P$	57·12	10·62	56·64	10·63
VII	2-Ethhexyl	n-Pr	119–123/0·2	1·4388	$C_{16}H_{35}O_4P$	59·60	10·94	59·14	10·86
VIII	2-Ethhexyl	n–Bu	128–131/0·2	1·4392	$C_{18}H_{39}O_4P$	61·71	11·22	62·00	11·31
IX	$C_{12}H_{25}$	Et	143–147/0·2	1·4402	$C_{18}H_{41}O_4P$	61·33	11·72	61·00	11·39
X	$C_{14}H_{29}$	Et	168–172/0·2	1·4431	$C_{20}H_{43}O_4P$	63·44	11·45	62·98	11·39

This has been chemically demonstrated, and in this communication the spectroscopic as well as the chemical evidence is presented.

Diethyl β-n-butoxyethylphosphonate (I) was prepared by the Arbuzov reaction of β-n-butoxyethyl bromide and triethyl phosphite, while di-n-butyl β-n-butoxyethylphosphonate (IV) was synthesized by the transesterification of I. These are identical with the respective radical addition products in their physical constants, IR spectra, and the relative retention times to diethyl ethylphosphonate in the vapour–liquid chromatogram.

The NMR spectra support this conclusion. The adducts between alkyl vinyl ether and dialkyl hydrogen phosphite have methylene protons adjacent to phosphorus at ca. $\tau 8{\cdot}0$ as a multiplet, which is due to proton–proton and proton–phosphorus coupling. The methylene protons adjacent to ether oxygen appear at ca. $\tau 6{\cdot}6$ as a triplet.

If the direction of addition is reverse, then an additional split signal of a methyl in a group O—CHMe—P should appear at ca. $\tau 8{\cdot}5$ as expected from the pattern of diethyl α-acetoxyethylphosphonate.[9] Chemical shifts of typical esters are provided in Table 3.

The P—H coupling constant for the methyl ester is 10·5 c/s. With di-i-propyl ester, a multiplet is visible for the methine proton at ca. $\tau 5{\cdot}45$, which may result from overlap of two multiplets, one from proton–proton coupling and the other from proton-phosphorus coupling, assuming the J_{CH_3-CH} and J_{CH-P} constants are close in value, as observed in triethyl phosphite, where a symmetrical five-line pattern is observed due to the close value of J_{CH_2-P} and $J_{CH_2-CH_3}$.[10] With di-n-propyl or di-n-butyl esters, a quartet is visible for the α-hydrogen at ca. $\tau 6{\cdot}05$, which may also be an overlapped signal.

Among the dialkyl β-alkoxyethylphosphonates prepared, the methyl, ethyl or

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[9] R. McConnell and H. Coover, Jr., *J. Amer. Chem. Soc.* **79**, 1961 (1957).

[10] J. Hendrickson, M. Maddox, J. Sims and H. Kaesz, *Tetrahedron* **20**, 449 (1964).

TABLE 3. CHEMICAL SHIFTS FOR DIALKYL β-ALKOXYETHYLPHOSPHONATES

R	R′	$ROCH_2CH_2P(O)(OR')_2$ Chemical shift (τ value) for R′		
		CH_3	CH_2	CH
n-Bu	Et	8·7^t	5·95*	
n-Bu	n-Pr	(α-CH_2)**6·1^q		
n-Bu	i-Pr	8·75^d		5·45^m
n-Bu	n-Bu	(α-CH_2) 6·05^q		
i-Bu	Me	6·4^d		
i-Bu	Et	8·7^t	5·95*	
i-Bu	n-Pr	(α-CH_2) 6·05^q		
i-Bu	n-Bu	(α-CH_2) 6·1^q		
2-Ethyl hexyl	n-Pr	(α-CH_2) 6·1^q		
2-Ethyl hexyl	n-Bu	(α-CH_2) 6·15^q		

d, doublet; *t*, triplet; *q*, quartet; *m*, multiplet

* a five line pattern.

**(α-CH_2) is a methylene adjacent to oxygen atom in a OR′ group.

isopropyl esters of n-butoxyethyl or isobutoxyethyl phosphonic acids are hygroscopic and in the IR spectra of these phosphonates, unless distilled in a dry atmosphere, weak bands appear at ca. 3500, 2100 and 1650 cm^{-1} and a shoulder at ca. 2700 cm^{-1}.

The action of water on the ethyl esters of n-butoxyethyl and isobutoxyethyl phosphonic acids shows that hydrolysis is significant, and only 60–63% of the starting esters could be recovered after distillation. Moreover, in the recovered ester (V), the presence of the carbonyl-containing impurity is assumed from the IR spectrum, and this may be related to an unidentified peak with a relative retention time to diethyl ethylphosphonate of 3·4 min.

The IR absorptions are correlated with the structural units and are shown in Table 4.

The spectra of the ethyl esters of the 1:1-adducts, including those of ethoxyethyl and n-propoxyethyl phosphonic acids (XI and XII) prepared by the Arbuzov reaction (Table 5), show bands of medium intensity at 1488–1466, 1400–1390, 1390–1370 cm^{-1} and a weak band or a shoulder at 1449 cm^{-1} for ethyl esters of the straight-chain alkoxyethylphosphonic acids. The second is absent in diethyl isobutoxyethylphosphonate and the third band is split into a doublet with approximately equal intensity in ethyl esters of isobutoxyethyl- and 2-ethylhexyloxyethylphosphonic acids. The appearance of bands at 1481, 1445, 1395 and 1370 cm^{-1} has been reported by McIvor *et al.*[11] in compounds containing the Et—O—P(O) linkage and these frequencies have been correlated with the C—H deformation modes of an EtO group. However, the compounds examined have been limited to phosphites, phosphates and thiophosphates.

In the present phosphonates the bands at ca. 1470 cm^{-1} are assigned to an asymmetrical mode of CH_3 and/or methylene scissor vibration, and a band or bands in

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[11] R. McIvor, G. Grant and C. Hubley, *Canad. J. Chem.* **34**, 1611 (1956).

TABLE 4. MAJOR IR ABSORPTIONS OF DIALKYL β-ALKOXYETHYLPHOSPHONATES[a]

$ROCH_2CH_2P(O)(OR')_2$

Compound No.	R	R'	PO[e]	C—O—(P)[b,c]	C—O—C	P-O-(C)[b,d]
XI	Et	Et	1258	1164(m)	1111	1031
XII	n-Pr	Et	1253	1163(m)	1099	1028
I	n-Bu	Et	1258	1163(m)	1111	1031
II	n-Bu	n-Pr	1250	1152(m) 1166(sh)	1111	1000
III	n-Bu	i-Pr	1253	1176(m) 1144(m)	1109	983
IV	n-Bu	n-Bu	1258	1152(m) 1170(sh)	1114	985
V	i-Bu	Et	1258	1163(m)	1099	1029
XIII	i-Bu	Me	1255	1188(m)	1111	1031
XIV	i-Bu	n-Pr	1258	1157(m) 1174(sh)	1111	1000
XV	i-Bu	n-Bu	1258	1168(m) 1152(m)	1111	980
XVI	i-Bu	2-Ethyl-hexyl	1256	1149(sh)	1111	1014
VI	2-Ethyl-hexyl	Et	1258	1163(m)	1099	1031
VII	2-Ethyl-hexyl	n-Pr	1255	1155(m)	1106	994
VIII	2-Ethyl-hexyl	n-Bu	1258	1149(m)	1111	980
IX	$C_{12}H_{25}$	Et	1258	1163(m)	1111	1029
X	$C_{14}H_{29}$	Et	1258	1163(m)	1111	1026

[a] Intensities are strong unless otherwise indicated.

[b] These assignments follows L. Thomas and R. Chittenden, *Spectrochim. Acta* **20**, 489 (1964).

[c] The $—CH_2—O—(P)$ and $>CH—O—(P)$ absorptions are reported to be multiple in character by Thomas *et al.*[b] Therefore, frequencies found in the region 1105–1170 cm^{-1} ($—CH_2—O—(P)$) or 1087–1190 cm^{-1} ($>CH—O—(P)$) were cited.

[d] As the $P—O—(CH_2)$ band of n-propyl and higher esters are characteristically broad and complex,[b] only the peak absorption in these esters is cited.

[e] It has been recognized that the phosphoryl absorption of the esters of ethylphosphonic acid appeared as a doublet centered at ca. 1250 cm^{-1}, which has been considered to arise from resonance interaction between the phosphoryl vibration and another vibration of approximately the same frequency. In the present esters of β-alkoxy-substituted ethylphosphonic acid a shoulder is always observed on the lower frequency side of the phosphoryl vibration, ca. 1242–1235 cm^{-1}. It could not, however, be known if this shoulder corresponded to the one half of a doublet of the phosphoryl absorption[f] in esters of ethylphosphonic acid.

[f] L. Thomas and R. Chittenden, *Spectrochim. Acta* **20**, 467 (1964).

1390–1370 cm^{-1} region to a symmetrical bending mode of CH_3 in an alkoxyethyl group, which fall within the established region.

An absorption at 1400–1390 cm^{-1} has been noted in several phosphonate-type esters.[12–15] This absorption is usually observed in the ethyl esters of the straight-chain alkylphosphonic acids as well as phosphorous, phosphoric and thiophosphoric

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[12] C. Overberger and E. Sarlo, *Polymer Letters* **1**, 201 (1963).

[13] B. Ackerman, T. Jordan, R. Eddy and D. Swern, *J. Amer. Chem. Soc.* **78**, 4444 (1965).

[14] B. Ackerman, T. Jordan and D. Swern, *J. Amer. Chem. Soc.* **78**, 6025 (1956).

[15] N. Brace, *J. Org. Chem.* **26**, 3197 (1961).

TABLE 5. IR ABSORPTIONS OF DIALKYL β-ALKOXYETHYLPHOSPHONATES IN THE REGION 1500–1300 cm^{-1}*

$ROCH_2CH_2P(O)(OR')_2$

Compound No.	R	R′	Absorptions
XI	Et	Et	1488(m), 1449(m), 1399(m), 1387(m), 1362(m),
XII	n-Pr	Et	1479(m), 1460(m), 1447(m), 1391(m), 1370(m), 1366(sh)
I	n-Bu	Et	1486(sh), 1474(m), 1471(m), 1449(m), 1399(m), 1346(sh)
II	n-Bu	n-Pr	1488, 1445(sh), 1420(sh), 1397(sh), 1383, 1348(sh), 1309(sh)
III	n-Bu	i-Pr	1471(m), 1416(sh), 1389, 1377, 1305(sh)
IV	n-Bu	n-Bu	1471, 1439(vw), 1420(sh), 1385(m), 1348(vw), 1307(sh)
V	i-Bu	Et	1471(m), 1449(m), 1389(m), 1370(m)
XIII	i-Bu	Me	1468(m), 1414(sh), 1389(m), 1370(m)
XIV	i-Bu	n-Pr	1473, 1449(sh), 1418(sh), 1389(m), 1370(m),
XV	i-Bu	n-Bu	1471, 1439(sh), 1416(sh), 1389(m), 1370(m), 1346(vw)
XVI	i-Bu	2-Ethyl-hexyl	1466, 1414(sh), 1387(m), 1370(m), 1346(vw), 1307(sh)
VI	2-Ethyl-hexyl	Et	1466(m), 1449(sh), 1395(m), 1385(m), 1370(m), 1307(sh)
VII	2-Ethyl-hexyl	n-Pr	1466(m), 1418(sh), 1395(sh), 1383(m), 1307(sh)
VIII	2-Ethyl-hexyl	n-Bu	1466, 1439(m), 1418(sh), 1385(m), 1348(sh), 1305(sh)
IX	$C_{12}H_{25}$	Et	1471(m), 1449(sh), 1393, 1370(m)
X	$C_{14}H_{29}$	Et	1466(m), 1449(sh), 1393, 1370(m)

*Absorption intensities are strong unless otherwise indicated.

TABLE 6. IR ABSORPTIONS OF ETHYL ESTERS OF PHOSPHOROUS, PHOSPHORIC, THIOPHOSPHORIC AND PHOSPHONIC ACIDS IN THE REGION 1500–1300 cm^{-1}

Compounds	Absorptions*
Diethyl hydrogen phosphite	1481(m), 1449(m), 1395, 1370(m)
Triethyl phosphite	1475(m), 1443(m), 1391, 1370(sh)
Diethyl Dithiophosphate	1477(m), 1447, 1395
Triethyl phosphate	1488, 1449, 1397, 1372
Diethyl ethylphosphonate	1481(sh), 1462(m), 1449(m), 1412(sh), 1393, 1370
Diethyl n-butylphosphonate	1468(m), 1449(sh), 1408(sh), 1393(m), 1372
Diethyl n-octylphosphonate	1471, 1449(sh), 1408(sh), 1399, 1370(m)
Diethyl 2-ethylhexylphosphonate	1468, 1412(sh), 1397(m), 1389(sh), 1374(sh)
Diethyl tetradecylphosphonate	1458, 1449(sh), 1408(sh), 1391(m), 1370(m)

*Absorption intensities are strong unless otherwise indicated.

acids listed in Table 6. Brace has attributed this absorption to the C—H deformation mode due to a $H(CF_2)_n$ group in diethyl 2H-perfluoroethyl- or 4H-perfluorobutyl-phosphonates.[15] He assigns absorptions at 1481, 1449 and 1370 cm^{-1} to the CH_3 deformation of an ethyl group.

Katritzky *et al.*, on the other hand, has correlated bands at 1446 ± 1 and 1395 ± 3 cm^{-1} with CH_3·asymmetrical and symmetrical deformations of an ethyl group in several ethyl esters of cyclic phosphites or phosphates.[16] The third band in the present phosphonates shows a reasonably constant frequency which approximately corresponds to the vibrations in the cyclic esters, and it is, therefore, reasonable to associate this absorption with a bending mode of CH_3 of an ethyl group.

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[16] R. Jones and A. Katritzky, *J. Chem. Soc.* 4376 (1960).

Additional evidence for this stems from the absorption at 1400–1390 cm^{-1} which disappears in spectra of such compounds as n-butoxyethyl phosphonic acid (1471, 1387 cm^{-1}) and its dichloride (1481(sh), 1466, 1370, 1344(w) cm^{-1}) or its mono-anilinium salt (1495(w), 1464, 1418(w), 1377 cm^{-1}) as well as dodecyloxyethyl- (1466, 1370 cm^{-1}) or tetradecyloxyethylphosphonic acids (1466, 1370 cm^{-1}).

This absorption (1400–1390 cm^{-1}) is still discernible as a shoulder in n-propyl esters, but disappears in n-butyl esters. The very limited number of these esters examined, however, precludes further discussion.

The mass spectra of the adducts (I, III, IV, V, VI, VII) and the phosphonates (XI, XII) were examined, which confirmed the molecular formula determined on the basis of elemental analysis, but the relative abundance of the molecular ion was very small. In some cases (M + 1) peak was stronger than the parent peak.

Carbon–phosphorus linkage in the phosphonate-type compounds has been reported to be stable under electron bombardment, giving an ion $RP(OH)_3^+$ as a base peak,[17] but an ion $ROCH_2CH_2P(OH)_3^+$ is almost insignificant. Instead, an ion $(ROCH_2CH_2P(OH)_3-2)^+$ was among the prominent peaks in several cases. Other rearranged or related ions in which the carbon–phosphorus bond is intact, such as $(ROCH_2CH_2P(O)(OR')(OH))^+$, $(ROCH_2CH_2P(OR')(OH)_2)^+$, $(ROCH_2CH_2P(O)(OR'))^+$ etc., could not be detected. These are ascribed to the presence of an ether linkage in the alkyl group directly bonded to phosphorus. The cleavage patterns of alkyl ethers themselves have been discussed by McLafferty.[18]

An ion m/e 125 was highly abundant in the spectra of dialkyl alkylphosphonates as well as dialkyl β-alkoxyethylphosphonates.

Other prominent ions, for example, in diethyl β-n-butoxyethylphosphonate are given in Table 7.

TABLE 7. PROMINENT PEAKS IN THE MASS SPECTRUM OF DIETHYL β-n-BUTOXYETHYLPHOSPHONATE

	m/e	R.I.		m/e	R.I.
$P(OH)_2$	65	100	$HP(OH)_2(OEt)$	111	65
$P(O)(OH)_2$	81	54	$P(O)(OEt)_2$	137	50
$HP(O)(OH)_2$	82	34	$HP(O)(OEt)_2$	138	77
$P(O)(OH)(OEt)$	109	96	$HP(OH)(OEt)_2$	139	34
$HP(O)(OH)(OEt)$	110	23			

These may be formed by the scission of the carbon–phosphorus bond, or by a degree of rearrangements of hydrogens from the cleaved alkyl groups, as are noted for dialkyl phosphites,[19] trialkyl phosphites,[17] and trialkyl phosphates.[20]

The detailed discussion of the mass spectra of these adducts and related compounds will be reported elsewhere.

EXPERIMENTAL

n-Butyl and isobutyl vinyl ethers were commercially available and 2-ethylhexyl, dodecyl and tetradecyl vinyl ethers were products from these Laboratories, and were re-distilled before use.

IR spectra were made as films or KBr pellets. The NMR spectra were taken in CCl_4 at 60 MC

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[17] J. Occolowitz and G. White, *Analyt. Chem.* **35**, 1179 (1963).

[18] F. McLafferty, *Analyt. Chem.* **29**, 1782 (1957).

[19] H. Harless, *Analyt. Chem.* **33**, 1387 (1961).

[20] F. McLafferty, *Analyt. Chem.* **28**, 313 (1956).

with TMS as internal reference. The mass spectra were measured on a RMU 6D spectrometer at an ionizing potential of 80 eV. The vapour-liquid chromatography was carried out on a succinate polyester column at 200° in He stream.

General procedure for the addition reactions of alkyl vinyl ethers with dialkyl hydrogen phosphites. Alkyl vinyl ether (0·2 mole) and dialkyl hydrogen phosphite (the molar ratio indicated in Table I), and a radical initiator (0·01 mole) were added in a flask fitted with a mechanical stirrer, a reflux condenser and a thermometer, which was immersed in an oil bath maintained at constant temp. This mixture was heated at the following temps for 3 hr with stirring in N_2 (the reaction time was arbitrarily determined from previous knowledge[1]).

Alkyl vinyl ether	Initiator	Temp
n-Butyl	AIBN	90°
i-Butyl	AIBN	85°
2-Ethylhexyl	AIBN	90°
2-Ethylhexyl	DBP	130°
Dodecyl	DBP	130°
Tetradecyl	DBP	130°

The reaction of n-butyl vinyl ether in the presence of DBP was carried out in an oil bath maintained at 120°. The reaction temp rose gradually from 100° to 118° during 3 hr, but the reaction apparently proceeded much more slowly than the reaction with other vinyl ethers in the presence of DBP. In reactions of 2-ethylhexyl, dodecyl, or tetradecyl vinyl ethers in the presence of DBP, the temp reached 150–160° after the reactions were initiated.

The reaction mixture was distilled at red. press. and separated into the lower and higher boiling fractions at the temp indicated below. After gas chromatography the contents of the 1:1-adducts were determined semiquantitatively.

ROCH$_2$CH$_2$P(O)(OR')$_2$		
R	R'	
n-Bu	Et	75°/1 mm
i-Bu	Et	65°/1 mm
n-Bu	n-Pr	95°/1 mm
n-Bu	i-Pr	80°/1 mm
n-Bu	n-Bu	120°/1 mm
2-Ethylhexyl	Et	120°/1 mm
2-Ethylhexyl	n-Pr	115°/0·5 mm
2-Ethylhexyl	n-Bu	120°/1 mm
$C_{12}H_{25}$	Et	150°/0·5 mm

The lower boiling fractions contained practically no 1:1-adducts. From the higher boiling fractions by fractional distillation in N_2 with a column (35 cm) filled with McMahon packings and preheated with a heating jacket, the pure adducts were obtained. The purity of these adducts were checked by the gas chromatography.

The reaction mixture of tetradecyl vinyl ether and diethyl hydrogen phosphite was fractionally distilled without a column.

As these esters absorbed atmospheric moisture, erratic variations in analytical data were obtained. The liquids, if analysed immediately or after storage in dry N_2, gave satisfactory analyses.

Reaction of dodecyl vinyl ether and diethyl hydrogen phosphite in the presence of BPO. Dodecyl vinyl ether (42·4 g) and diethyl hydrogen phosphite (55·2 g) were heated at 100–110° for 16 hr in N_2, during which time BPO (1·2 g) was added intermittently (total 12·0 g). BPO was added after cooling the reaction mixture to room temp. Ether (50 ml) was added to this mixture, which was washed with water (50 ml × 2) and dried over Na_2SO_4 (during this washing procedure diethyl hydrogen phosphite could be removed). The residue after the removal of dodecyl vinyl ether was molecularly distilled and separated into the following fractions, which were checked by their phosphorus contents.

Fraction No.	b.p./mm	Weight (g)	n_D^{25}	Analysis (P%)
1	63– 80°/10^{-2}	0·9	1·4468	2·1
2	80– 95°/10^{-2}	2·4	1·4469	3·1
3	95–110°/10^{-3}	2·7	1·4468	6·0
4	110–115°/10^{-3}	3·9	1·4450	7·6
5	115–140°/10^{-3}	4·3	1·4468	7·2
6	140–160°/10^{-3}	3·7	1·4489	7·9
7	160–173°/10^{-3}	13·7	1·4488	8·5
8	173–175°/10^{-3}	3·3	1·4490	9·3
9	Residue	10·5	—	8·9

In IR spectra of all of these fractions P=O, P—O—(C), and C—O—(P) frequencies could be discerned, but the absorption of an ether linkage was not detected in fractions 6, 7, 8.

Reaction of dodecyl vinyl ether and diethyl hydrogen phosphite in the presence of AIBN. Dodecyl vinyl ether (42·4 g) and diethyl hydrogen phosphite (55·2 g) were heated at 110° for 6 hr, during which time AIBN (1·6 g) was added with the interval of 3 hr (total 3·2 g). AIBN was added after cooling the reaction mixture to 50°. Any volatile materials were removed under red. press. and the residue evaporatively distilled to give the following fractions.

Fraction No.	b.p./mm	Weight (g)	n_D^{25}	Analysis (P%)
1	138–142°/10^{-2}	7·5	1·4443	5·7
2	139–140°/10^{-2}	7·7	1·4443	6·9
3	140–143°/10^{-3}	5·4	1·4449	6·9
4	138–143°/10^{-3}	5·9	1·4452	6·6
5	143–145°/10^{-3}	6·1	1·4450	6·7
6	147–158°/10^{-3}	2·2	1·4450	6·9
7	Residue	20·6	—	5·0

Fractions 3 4–5 6, showing a fairly constant reflactive index, were recombined and re-distilled to give crude diethyl β-dodecyloxyethylphosphonate, 14·4 g, b.p. 135–138°/0·07 mm, n_D^{25} 1·4442. (Found: P, 7·8%.) Fractions 1–6 showed an IR spectra in accord with the expected structure.

Diethyl β-n-butoxyethylphosphonate. n-Butoxyethyl bromide[21] (36·2 g) and triethyl phosphite (33·2 g) were refluxed for 2 hr, during which time the temp rose from 140° to 160° and 11 ml of ethyl bromide was collected. The distillation of the reaction mixture gave the ester (25·8 g), b.p. 98–101°/0·5 mm, n_D^{25} 1·4258. (Found: C, 54·00; H, 9·77. $C_{12}H_{27}O_4P$ requires: C, 54·12; H, 10·22%.) Relative retention time to diethyl ethylphosphonate was 3·4 min.

Transesterification of diethyl β-n-butoxyethylphosphonate. n-Butanol (44·4 g) and Na (0·3 g) were placed in a reaction flask fitted with a mechanical stirrer, a thermometer and a short fractionating column filled with McMahon packings. The top was connected with a liquid collector and a reflux condenser. To the solution diethyl β-n-butoxyethylphosphonate (23·8 g) was added, and the mixture heated with stirring at 110–120° for 2·5 hr, during which time EtOH (6·6 g) was collected. Gas chromatography of the reaction mixture revealed 4 peaks of retention times (relative to diethyl ethylphosphonate) and percentage areas of (i) 0·6, 70% (n-butanol); (ii) 3·4, 1% (diethyl β-n-butoxyethylphosphonate); (iii) 5·2, 4% (ethyl n-butyl β-n-butoxyethylphosphonate); (iv) 6·7, 25% (di-n-butyl β-n-butoxyethylphosphonate). After removal of n-butanol, several fractional distillations were

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[21] M. Palomaa and A. Kenetti, *Ber. Dtsch. Chem. Ges.* 64, 797 (1931).

carried out, with the column filled with McMahon packings, yielding ethyl n-butyl β-n-butoxyethylphosphonate, b.p. 86–90°/0·5 mm, 2·2 g, n_D^{25} 1·4293. (Found: C, 54·00; H, 9·77. $C_{12}H_{27}O_4P$ requires: C, 54·12; H, 10·22%), and di-n-butyl β-n-butoxyethylphosphonate, b.p. 113–117°/0·5 mm, 2·9 g, n_D^{25} 1·4311.

Hydrolysis of dialkyl β-alkoxyethylphosphonates

n-Butoxyethylphosphonic acid. Diethyl β-n-butoxyethylphosphonate (2·4 g) and conc. HCl (15 ml) were refluxed for 2 hr. Evaporation *in vacuo* gave a light-yellow syrup (1·6 g), which, after keeping over P_2O_5 at 80°/20 mm for 7 hr, was analysed. (Found: C, 38·87; H, 8·12. $C_6H_{15}O_4P$ requires: C, 39·56; H, 8·30%.)

Its *monoanilinium salt* was prepared from the acid (1·4 g) and two equivs of aniline in EtOH and recrystallized from EtOH–ether as colourless slender needles (0·9 g), m.p. 138–139·5°. (Found: C, 51·87; H, 8·02; N, 4·90. $C_{12}H_{22}NO_4P$ requires: C, 52·36; H, 8·05; N, 5·09%.)

Isobutoxyethylphosphonic acid. Diethyl ester (4·0 g) and conc. HCl or 48% HBr (20 ml) were refluxed for 2 hr and treated as before to give a syrupy acid (3·1 g). IR frequencies in the region 1500–1300 cm^{-1} were 1466, 1418(sh), 1385, 1370 cm^{-1}.

The *anilinium salt* was prepared from the acid (1·8 g) and aniline (1·9 g) in EtOH (3 ml) and recrystallized from benzene–EtOH (10:1) as colourless needles, m.p. 139–140°, 1·0 g. (Found: C, 52·21; H, 8·01; N, 4·95. $C_{12}H_{22}NO_4P$ requires: C, 52·36; H, 8·05; N, 5·09%.) IR absorptions in the region 1500–1300 cm^{-1} were 1495(m), 1471(m)m 1462(m), 1425(m), 1385(m), 1370(m), 1340(vw) cm^{-1}.

2-*Ethylhexyloxyethylphosphonic acid.* Diethyl ester (4·0 g), conc. HCl (20 ml) and dioxan (20 ml) were boiled for 2 hr and yielded a syrupy acid, which was dried over P_2O_5 at 100°/20 mm for 5 hr. (Found: C, 50·51; H, 10·06. $C_{10}H_{23}O_4P$ requires: C, 50·41; H, 9·73%). IR absorptions in the region 1500–1300 cm^{-1} were 1466(m), 1418(sh), 1385(m) cm^{-1}.

Dodecyloxyethylphosphonic acid. Diethyl ester (3·5 g), conc. HCl (20 ml), and dioxan (20 ml) were refluxed for 2·5 hr and yielded a syrupy acid (2·9 g), which was dried over P_2O_5 at 100°/20 mm for 5 hr. (Found: C, 56·70; H, 10·68. $C_{14}H_{31}O_4P$ requires: C, 57·12; H, 10·62%.)

Tetradecyloxyethylphosphonic acid. Diethyl ester (2·5 g), conc. HCl (20 ml) and dioxan (20 ml) were refluxed for 2·5 hr and yielded a syrupy acid (1·7 g), which solidified to a waxy-like substance at room temp and was dried over P_2O_5 at 100°/20 mm for 10 hr. (Found: C, 59·55; H, 11·01. $C_{16}H_{35}O_4P$ requires: C, 59·60; H, 10·94%.)

*Action of water on diethyl β-*n*-butoxyethyl or isobutoxyethylphosphonate.* (1) Diethyl β-n-butoxyethylphosphonate (5·4 g) and water (30 ml) were refluxed for 5 hr. The organic layer was extracted with ether, from which the starting ester (3·4 g) was recovered, b.p. 84–88°/0·3 mm, n_D^{25} 1·4263. No impurity was detected in this ester by gas liquid chromatography. The distillation residue weighed 0·5 g. (2) Diethyl β-isobutoxyethylphosphonate (5·7 g) was heated in boiling water (30 ml) for 4 hr. After cooling, the organic layer was extracted with ether and the aqueous layer evaporated to dryness *in vacuo* to a syrup (0·4 g), the IR absorptions were 1724 ($\nu_{O=O}$), 1389, 1366, 1250 ($\nu_{P=O}$), 1183, 1105 (ν_{C-O-C}), 1053, 1020 and 962 cm^{-1}. The ether layer was dried with Na_2SO_4 and distilled to give a liquid (3·4 g), b.p. 94–97°/0·2 mm, n_D^{25} 1·4232. The IR spectrum was identical with the original ester, except for an intense absorption at 1724 cm^{-1}. The gas chromatography showed this to be a mixture of the original ester (94%) and unidentified material (6%) with relative retention time (to diethyl ethylphosphonate) 3·4 min.

n-Butoxyethylphosphonyl dichloride. Diethyl β-n-butoxyethylphosphonate (11·9 g) and PCl_5 (20·9 g) were heated at 90–100° for 45 min. $POCl_3$ was distilled off, leaving the dichloride (4·8 g), b.p. 94–97°/2 mm, n_D^{25} 1·4559. (Found: Cl, 31·7. $C_6H_{13}Cl_2O_2P$ requires: Cl, 32·38%.) IR absorptions were 2933, 2857, 1481(sh), 1466, 1370, 1272, 1235(sh), 1190, 1111, 1026, 995, 966, 909, 855, 820 and 714 cm^{-1}.

The phosphorus compounds required for reference for the IR absorption assignments were known compounds and prepared according to the literature. However, the following two diethyl β-alkoxyethylphosphonates, being unknown compounds, were prepared and also found to be hygroscopic and care was, therefore, necessary in the preparation of analytical sample.

Diethyl β-ethoxyethylphosphonate (XI). β-Ethoxyethyl bromide (36·5 g) and triethyl phosphite (44·4 g) were refluxed for 3 hr with stirring, during which time the temp rose from 130° to 155° and 13 ml EtBr was collected. Distillation gave the ester (31·7 g), b.p. 80–83°/0·8 mm, n_D^{25} 1·4218.

(Found: C, 45·47; H, 9·21. $C_8H_{19}O_4P$ requires: C, 45·71; H, 9·11%.) Relative retention time (to diethyl ethylphosphonate) was 2·2 min.

Diethyl β-n-propoxyethylphosphonate (XII). β-n-propoxyethyl bromide[22] (16·7 g) and triethyl phosphite (16·6 g) were heated for 1 hr, during which time the temp rose from 150° to 190° and EtBr (7·7 g) was collected. Distillation gave the ester (14·1 g), b.p. 89–92°/1·5 mm, n_D^{25} 1·4260. (Found: C, 47·63; H, 9·34. $C_9H_{21}O_4P$ requires: C, 48·21; H, 9·44%.) Relative retention time to diethyl ethylphosphonate) was 2·7 min.

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[22] R. Tallman, *J. Amer. Chem. Soc.* **56**, 126 (1934).