Tetrahedron, 1965, Vol. 21, pp. 3043 to 3049. Pergamon Press Ltd. Printed in Northern Ireland

THE REACTIONS OF DIALKYL HYDROGEN PHOSPHITES WITH ALKYL VINYL ETHERS

T. NISHIWAKI
The Industrial Research Laboratories, Kao Soap Co., Ltd., Wakayama City, Japan

(*Received* 10 *March* 1965; *in revised form* 26 *May* 1965)

Abstract—The reactions of several dialkyl hydrogen phosphites with isobutyl vinyl ether were undertaken in the presence of ,αα'-azobisisobutyronitrile. The structure of the isolated 1:1 adducts was assumed to be dialkyl β-isobutoxyethylphosphonate on the basis of independent preparations.

IN RECENT years attention has been focussed on the ionic or radical addition reactions of phosphorus compounds with olefinic double bonds.[1] The products of these reactions have a range of applications such as plasticizers,[2] textile finishing agents,[3] and surfactants.[4] Phosphines, phosphorus trichloride, or dialkyl hydrogen phosphites are usually chosen as the phosphorus components in this reaction, while a variety of olefins has been tested, although some of these unsaturated compounds complicate the reaction course, due to polymerization under the reaction conditions.

The radical reaction is preferred for all types of olefinic compounds, the formation of phosphorus-containing heterocycles is a general trend in the aluminium chloride catalysed reaction of olefins with phosphorous trichloride.[5]

In this communication the reaction of several dialkyl hydrogen phosphites (I–a, b, c, d, e) with isobutyl vinyl ether under the radical reaction conditions is described. The use of alkyl vinyl ether minimizes possible telomerization[6] and the absence of allylic hydrogen facilitates the chain addition of dialkyl hydrogen phosphite to the ether.

$$\underset{\underset{\mathrm{O}}{\|}}{\mathrm{HP}}(\mathrm{OR})_2$$

I–a, b, c, d, e

a = Me
b = Et
c = n–Pr
d = n–Bu
e = 2-Ethylhexyl

There is only one instance, although inadequately described, in the literature of a reaction of alkyl vinyl ether with di-n-butyl hydrogen phosphite.[7]

Initially, the reaction between isobutyl vinyl ether (0·2 mole) and di-n-propyl hydrogen phosphite (I–c) in a molar ratio of 1:3 was undertaken with the intermittent additions of benzoyl peroxide (BPO) at 90°. The reaction path was followed by measuring the iodine value. The result indicated that 0·04 mole of BPO and prolonged

---

[1] For reviews of this subject see; P. Crofts, *Quart. Rev.* **12**, 341 (1958); F. Stacey and J. Harris, Jr. *Organic Reactions* **13**, 218 (1963); and M. Grayson, *Chem. and Eng. News* **40**, No. 49, 90 (1962).

[2] D. Swern, W. Palm, B. Ackerman and L. Witnauer, *Chem. and Eng. Data* **3**, 346 (1958).

[3] T. Sakurai, Y. Okamoto and T. Okamoto, *Kogyo Kagaku Zasshi* **65**, 1579 (1962).

[4] M. Kawaka, R. Oda and Y. Ito, *Yukagaku* **10**, 159 (1961).

[5] E. Jungermann, J. McBride, Jr, R. Clutter and A. Mais, *J. Org. Chem.* **27**, 606 (1962) and E. Jungermann's subsequent papers, *Ibid.* **27**, 1833 (1962), *J. Amer. Oil Chem. Soc.* **40**, 41 (1963).

[6] C. Schildknecht, *Vinyl and Related Polymers* p. 598. J. Wiley, New York (1952).

[7] L. Hamilton and R. Williams, U.S. Patent, 2,957,931 (1960).

reaction time were required to reduce the iodine value to nearly zero, as shown in Fig. 1.

However, the distillate, in addition to the original phosphite, was contaminated with appreciable amounts of benzoic acid, as revealed by the IR spectrum and acid value.

Therefore, complete removal of benzoic acid from the reaction mixture by several washings with large amounts of water was attempted, but this caused partial hydrolysis of the anticipated ester of phosphonic acid. This was inferred by the gradual increase in acid value of the organic layer and, further, by the appearance of a broad and weak band near 2500 cm^{-1} in the IR spectrum of the distillate and conceived to be a P—OH stretching vibration and not the starting material.[8] The possibility that decomposition occurred during distillation can be excluded, since authentic di-n-propyl β-isobutoxyethylphosphonate (II–c) can be distilled without decomposition.

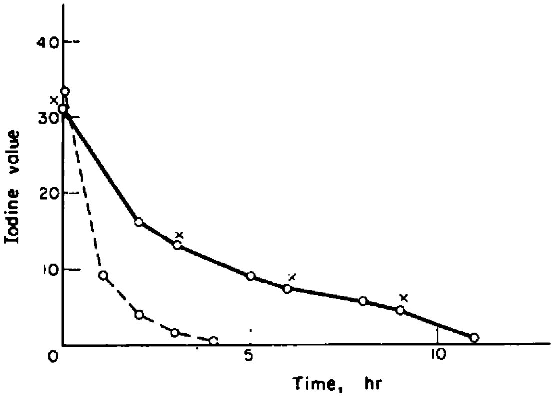
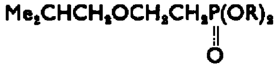
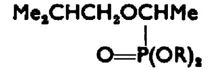


Fig. 1. Effect of radical catalysers on the reaction of isobutyl vinyl ether with di-n-propyl hydrogen phosphite. Molar ratio 1:3, ——— BPO, - - - - AIBN 0·01 mole of BPO was added at the point of X.



$\mathrm{Me_2CHCH_2OCH_2CH_2\underset{\underset{O}{\|}}{P}(OR)_2}$

II–a, b, c, d, e



$\mathrm{Me_2CHCH_2O\underset{\underset{O{=}P(OR)_2}{|}}{C}HMe}$

III–a, b, c, d, e

Other radical initiators, such as di-t-butyl peroxide, which was considered favourable in this respect, was not tried, because of a decomposition temperature higher than the b.p. of isobutyl vinyl ether.

Finally, in all subsequent reactions, α,α'-azobisisobutyronitrile (AIBN) was used. The reaction between isobutyl vinyl ether (0·2 mole) and di-n-propyl hydrogen phosphite (molar ratio 1:3) takes place smoothly in a short period with a small quantity of AIBN (Fig. 1), and an 1:1 adduct is obtained in moderate yield, in which no nitrogeneous compounds can be detected.

Further, an increased yield of the 1:1 adduct was noticed in the presence of a large excess of di-n-propyl hydrogen phosphite (Table 1), since a high concentration of the phosphite results in a long kinetic chain.

---

[8] L. Bellamy, *The Infrared Spectra of Complex Molecules* p. 262. J. Wiley, New York (1954).

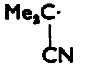
The reactions of isobutyl vinyl ether with dimethyl, di-n-butyl, or di-2-ethylhexyl hydrogen phosphite (I–a, d, e) in the presence of AIBN similarly give the 1:1 adducts, the yields depending on the molar ratio of the reactants (Table 1).

Examination of the residues after fractional distillation presented many problems, and results obtained from IR spectra, revealed that Me_2CH (1370, 1385 cm^{-1}), $P{=}O$ (1260 cm^{-1}) and $P{-}O{-}CH_2CH_2CH_3$ (1000, 1070, 1100, 1150 cm^{-1}) groups (in the case of the reaction product between isobutyl vinyl ether and (I–c))[9] were present. However, it may be assumed from the phosphorous analyses and mol. wt. determinations, coupled with spectroscopic data, that these residues contain the addition products of two or three moles of isobutyl vinyl ether with one mole of dialkyl hydrogen phosphite.

TABLE 1. RELATION BETWEEN THE YIELD OF 1:1 ADDUCT AND THE MOLAR RATIO OF THE STARTING MATERIAL

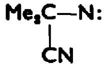
Molar ratio of isobutyl vinyl ether to dialkyl hydrogen phosphite	Dialkyl hydrogen phosphite (I) R	Yield of adduct (%)
1:2·5	Me	35
1:3	n-Pr	16
1:3·3	n-Pr	29
1:5	n-Pr	54
1:6	n-Pr	57
1:2	n-Bu	24
1:2·5	n-Bu	36
1:3	n-Bu	43
1:1·3	2-Ethylhexyl	15
1:2·5	2-Ethylhexyl	22

According to Shostakovskii *et al.*, cleavage of AIBN into such radicals as IV or V and their recombination are the main reason for the sluggish polymerization of vinyl ether in the presence of AIBN and the reaction product for several reasons is considered to be a trimer of vinyl ether.[10] This supports the present assumption.



$Me_2\underset{\underset{CN}{|}}{C}\cdot$

(IV)



$Me_2\underset{\underset{CN}{|}}{C}{-}N{:}$

(V)

Several attempts to obtain a product from the reaction of isobutyl vinyl ether with diethyl hydrogen phosphite (I–b) failed, although a remarkable reduction of iodine value during the reaction was noticed. After the removal of the starting phosphite, tarry material was the main product, in which phosphorus and nitrogen were detected by qualitative tests, and the presence of $P{=}O$ (1265 cm^{-1}), $P{-}OEt$ (1165 cm^{-1}) and Me_2CH (1370, 1385 cm^{-1}) groups could be ascertained.

This is a peculiar situation in this type of reaction, for in all additions of diethyl hydrogen phosphite to the terminal olefins it is reported that the 1:1 adducts are obtained.[11] Moreover, in the reaction of lauryl vinyl ether with diethyl hydrogen

---

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

[10] M. Shostakovskii, V. Gladyshevskaya and A. Khomutov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* 460 (1962), and Refs cited.

[11] For example, R. Sasin, W. Olszewski, J. Russel and D. Swern, *J. Amer. Chem. Soc.* **81**, 6275 (1959).

phosphite in the presence of BPO or AIBN, a 1 : 1 adduct could be isolated by means of molecular distillation.[12]

The 1 : 1 adduct between isobutyl vinyl ether and diethyl hydrogen phosphite can not be considered unstable, because chlorination of the adduct between isobutyl vinyl ether and di-n-propyl hydrogen phosphite, and subsequent treatment with ethanol, affords the corresponding stable ethyl ester, which should be the radical addition product of isobutyl vinyl ether and I–b, if the reaction courses are similar,

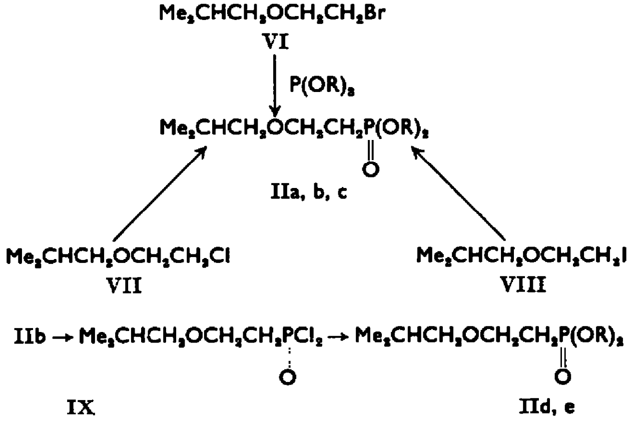
All the 1 : 1 adducts are colourless, mobile and stable liquids,* which show a single peak in vapour–liquid chromatograms. The physical constants and analyses of these adducts are summarized in Table 2.

TABLE 2. PHYSICAL CONSTANTS AND ANALYSES OF THE 1 : 1 ADDUCTS

R	B.p. (o/mm)	n_D^{25}	d_4^{25}	Analyses				
				Formula	Mol. wt.		Phosphorus content	
					Calc.	Found	Calc. (%)	Found (%)
Me	71–75/0·5	1·4198	1·0460	$C_8H_{19}O_4P$	210	213	14·7	15·0
n-Pr	103–107/0.5	1.4283	0.9676	$C_{12}H_{27}O_4P$	266	264	11·6	12·0
n-Bu	121–125/2	1·4310	0·9567	$C_{14}H_{31}O_4P$	294	297	10·5	10·6
2-Ethylhexyl	166–170/0·2	1·4414	0·9205	$C_{22}H_{47}O_4P$	406	405	7·2	7·3

In order to ascertain the exact attachment of the phosphorous group in these adducts, since alternatives II and III are possible, independent preparations of compounds II–a, b, c, d, e were undertaken in accordance with the scheme outlined below.

Although β-isobutoxyethyl chloride (VII) or bromide (VI) may be obtained from β-isobutoxyethanol using thionyl chloride or phosphorous tribromide, the preparation of the corresponding iodide (VIII) is somewhat difficult, but achieved by the application of Landauer's synthetic method[13]—namely the reaction of triphenyl phosphite, β-isobutoxyethanol and ethyl iodide.



---

* No noticeable deterioration was observed after storage in a brown sealed tube for two years.

[12] T. Nishiwaki, to be published.

[13] S. Landauer, and H. Rydon, *J. Chem. Soc.* 2224 (1953).

The Arbuzov type reactions of these halides with trimethyl-, triethyl-, or tri-n-propylphosphite are not straight-forward, and pure dialkyl β-isobutoxyethylphosphonate (II–a, b, c) was obtained in low yield only from β-isobutoxyethyl bromide.

As the synthesis of the corresponding di-n-butyl or di-2-ethylhexyl ester (II–d, e) by means of the Arbuzov reaction necessitates a high reaction temperature, thereby bringing about decomposition, they were prepared by esterification of β-isobutoxyethylphosphonyl dichloride (IX) with an appropriate alcohol.

Refractive indices and IR spectra of the 1:1 adducts are almost identical in every respect with those of the corresponding authentic dialkyl β-isobutoxyethylphosphonates. However, no explanation can be given for the occasional appearance of a broad band of very low intensity near 3300 cm^{-1}, irrespective of the original source of these esters.

From these observations, it is assumed that in isolated 1:1 adducts from the radical catalysed reactions of isobutyl vinyl ether with dialkyl hydrogen phosphites the phosphorous atom is attached to a terminal carbon atom. This assumption is supported by the gas-chromatographical identification in the case of methyl-, n-propyl-, and n-butyl esters prepared from radical reactions. Although several unidentified compounds of low retention volume were also present in the reaction products, alternative compounds III would probably not be formed.

Preliminary evaluation has revealed that 2-ethylhexyl β-isobutoxyethylphosphonate gives plasticized sheets with good low temperature characteristics, but the heat stability at 150° of the milled sheets containing equal amounts of it and dioctyl phthalate are very inferior to sheets with higher proportion of the latter.

EXPERIMENTAL

Mol. wts were determined by the freezing point depression method using benzene as solvent. Iodine values were measured by the method of Teeter *et al.*[14] Fractional distillations were carried out through a 35 cm column filled with McMahon packings. The vapour–liquid chromatography was carried out under the following condition (2-ethylhexyl ester could not be checked because of its high b.p.); the column was 3 m of succinate polyester (30–60 mesh) at 200°: carrier gas was He at 50 ml/min. Dialkyl hydrogen phosphites were synthesized by McCombie's method.[15] β-Isobutoxyethanol was prepared by passing ethylene oxide into isobutanol according to Crecher's procedure.[16] Potassium hydroxide (2% based on isobutanol) was used as catalyst instead of one molecular proportion of sodium.

General procedure for the reaction of isobutyl vinyl ether with dialkyl hydrogen phosphites. A stirred mixture of isobutyl vinyl ether (20 g, 0·2 mole) and an appropriate dialkyl hydrogen phosphite in the molar ratios shown in Table 1 and AIBN (1·6 g, 0·01 mole) was heated at 85° in N_2 atm for 3 hr. After the removal of the starting material, several fractional distillations under red. press. gave 1:1 adducts. The residue after distillation was analysed for P and N content. Typical data for di-n-propyl ester is given in Table 3.

Chlorination of the 1:1 *adduct from isobutyl vinyl ether and di-n-propyl hydrogen phosphite.* The adduct (12·2 g) and PCl_5 (19·2 g) were heated at 110° for 2 hr. After removal of the $POCl_3$ *in vacuo*, the residue was distilled at 86–90°/2 mm to give the chlorinated product (5·8 g), n_D^{25} 1·4562. (Found: P, 14·3; mol. wt. 222. $C_6H_{13}O_2Cl_2P$ requires: P. 14·1%; mol wt. 219.)

Esterification of the chlorinated product. To a stirred and ice-cooled mixture of absolute EtOH (3·2 g) and pyridine (4·6 g), the above-mentioned chlorinated product (4·0 g) was added in portions.

---

[14] H. Teeter, E. Dufek, C. Coleman, C. Glass, E. Melvin and J. Cowan, *J. Amer. Oil. Chem Soc.* **33**, 399 (1956).

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

[16] L. Cretcher and W. Pittenger, *J. Amer. Chem. Soc.* **46**, 1503 (1924).

TABLE 3. MOL. WT. AND PHOSPHORUS AND NITROGEN CONTENT OF THE DISTILLATION RESIDUES FROM THE REACTION OF ISOBUTYL VINYL ETHER AND DI-N-PROPYL HYDROGEN PHOSPHITE

Molar ratio	Mol. wt.	Analyses P (%)	Analyses N (%)
1:3·3	412	7·6	0·2
1:5	425	7·1	0·2
1:6	419	8·0	0·2

The mixture was heated at 100° for 1 hr, and, after cooling, water (10 ml) was added. The separated oil was extracted with ether (20 ml × 2), and the extracts dried (Na_2SO_4) and distilled to give the ester (b.p. 86–89°/0·4 mm), 3·2 g, n_D^{25} 1·4224. (Found: P, 13·4; mol. wt., 235. $C_{10}H_{23}O_4P$ requires: P, 13·0%; mol., wt. 238.)

β-Isobutoxyethyl chloride (VII). To a stirred mixture of β-isobutoxyethanol (58·9 g) and pyridine (39·6 g) thionyl chloride (65·4 g) was added while the temperature was kept below 0°. The mixture was further heated in boiling water for 1·5 hr, acidified with 2 N HCl (90 ml) and extracted with ether (100 ml × 2). The ethereal extracts were washed with 2 N NaOH (90 ml) and after drying (Na_2SO_4) were distilled at 140–142°/760 mm to give β-isobutoxyethyl chloride (51·6 g), yield 70%, n_D^{25} 1·4146. (Found: Cl, 26·1; $C_6H_{13}OCl$ requires: Cl, 26·0%.)

β-Isobutoxyethyl bromide (VI). To phosphorus tribromide (45·9 g) stirred and cooled below −10°, a mixture of β-isobutoxyethanol (55·5 g) and pyridine (3·7 g) was added. Stirring was continued for 30 min at 0°, and then for 2 hr at room temp. The mixture was distilled at atm. press. into a flask containing water until the b.p. was reached at about 190°. The separated oil was collected and dried ($CaCl_2$). Fractional distillation at 49–50°/6 mm gave β-isobutoxyethyl bromide (43·9 g), yield 52%, n_D^{25} 1·4422. (Found: Br, 43·7. $C_6H_{13}OBr$ requires: Br, 44·1%.)

β-Isobutoxyethyl iodide (VIII). Triphenyl phosphite (49·6 g) ethyl iodide (25·0 g) and β-isobutoxyethanol (18·9 g) were heated for 20 hr, during which time the temp rose from 120° to 170°. The distillate, after distillation at 50 mm, was washed with 10% NaOH aq (50 ml × 3), and extracted with ether (50 ml × 3). The extracts were dried (Na_2SO_4) and distilled at 55–60°/7 mm to give β-isobutoxyethyl iodide (10·9 g), yield 30%, n_D^{25} 1·4828. (Found: I, 55·4; $C_6H_{13}OI$ requires: I, 55·6%.)

Dimethyl β-isobutoxyethylphosphonate (II-a). β-Isobutoxyethyl bromide (40·1 g) was heated for 2·5 hr with trimethyl phosphite (27·5 g). Distillation of the reaction mixture gave dimethyl-β-isobutoxyethylphosphonate (7·3 g), yield 16%, b.p. 79–82°/1 mm, n_D^{25} 1·4176. (Found: P, 14·5; $C_8H_{19}O_4P$ requires: P, 14·7%.)

Diethyl β-isobutoxyethylphosphonate (II-b). β-Isobutoxyethyl bromide (23·7 g) and triethyl phosphite (23·4 g) were refluxed for 2 hr with stirring, and the ethyl bromide (6·7 g) collected. Distillation at 87–89°/0·4 mm of the reaction mixture gave diethyl β-isobutoxyethylphosphonate (10·6 g), yield 30%, n_D^{25} 1·4223. (Found: P, 13·1; $C_{10}H_{23}O_4P$ requires: P, 13·0%.)

Di-n-propyl β-isobutoxyethylphosphonate (II–c). β-Isobutoxyethyl bromide (23·7 g) and tri-n propyl phosphite (31·22 g) were heated at 150–200° for 1 hr, and the n-propyl bromide (8·4 g) collected. Distillation at 115–119°/2 mm gave di-n-propyl β-isobutoxyethylphosphonate (10·5 g), yield 30%, n_D^{25} 1·4293. (Found: P, 11·6; $C_{12}H_{27}O_4P$ requires: P, 11·6%.)

β-Isobutoxyethylphosphonyl dichloride (IX). Diethyl β-isobutoxyethylphosphonate (10·0 g) and PCl_5 (17·5 g) were heated for 1 hr at 110°. After removal of $POCl_3$ *in vacuo*, the residue was distilled at 85–89°/2 mm to give β-isobutoxyethylphosphonyl dichloride (6·2 g), yield 67%, n_D^{25} 1·4551. (Found: P, 14·1; Cl, 32·0; $C_6H_{13}O_2Cl_2P$ requires: P, 14·1; Cl, 32·4%.)

Di-n-butyl β-isobutoxyethylphosphonate (II–b). To an ice-cooled mixture of n-butanol (5·0 g) and pyridine (3·6 g) β-isobutoxyethylphosphonyl dichloride (5·0 g) was added portionwise and the mixture heated at 110° for 1 hr. After addition of water (20 ml), extraction with ether (30 ml × 3) and drying of the extracts (Na_2SO_4), di-n-butyl β-isobutoxyethylphosphonate (2·2 g) was isolated by distillation at 126–130°/3 mm, yield 32%, n_D^{25} 1·4309. (Found: P, 10·5; $C_{14}H_{31}O_4P$ requires: P, 10·5%.)

Di-2-ethylhexyl β-isobutoxyethylphosphonate (II–e). To an ice-cooled mixture of 2-ethylhexanol (9·0 g) and pyridine (3·6 g), β-isobutoxyethylphosphonyl dichloride (5·0 g) was added in portions, and the mixture heated for 1 hr at 120°. After adding water (20 ml), extracting with ether (30 ml × 2), drying of the extracts (Na_2SO_4) and distillation, di-2-ethylhexyl-β-isobutoxyethylphosphonate (4·9 g) was obtained, b.p. 170–173°/0·6 mm, yield 53%, n_D^{25} 1·4415. (Found: P, 7·5; $C_{22}H_{47}O_4P$ requires: P, 7·6%.)

Acknowledgement—The author appreciates the technical assistance of Mr. M. Shiga.