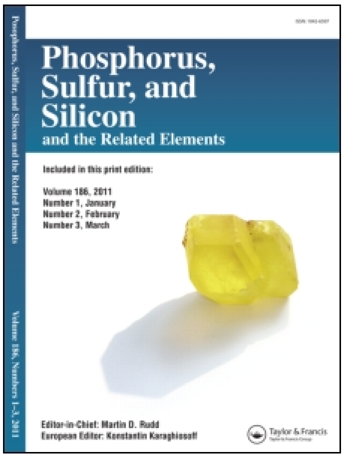

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UNUSUAL DIRECTION OF THE ARBUZOV REACTION OF DIALKOXYMETHYLPHOSPHONITES AND THEIR ANALOGUES

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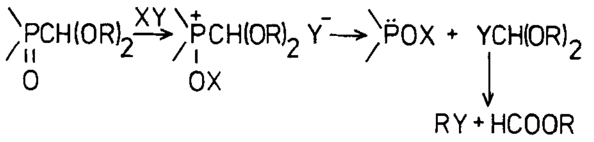
The alkylation and acylation reactions of dialkoxymethylphosphonites and their analogues have been studied. The Arbuzov rearrangement of these compounds was accompanied by the P—C bond cleavage with retention of three-coordinate phosphorus atom.

It is known[1] that the Arbuzov reaction intermediates (for example phosphonium salts) are changed into phosphoryl species, according to the usual scheme. Recently, we have described the facile P—C bond rupture in the dialkoxymethylphosphonium salts which were obtained from the compounds containing the phosphoryl group.[2]



$$\underset{O}{\underset{\parallel}{>P}}CH(OR)_2 \xrightarrow{XY} \underset{OX}{\underset{|}{>\overset{+}{P}}}CH(OR)_2\,Y^- \longrightarrow >\ddot{P}OX + \underset{RY + HCOOR}{\underset{\downarrow}{YCH(OR)_2}} \qquad (1)$$

The present paper deals with the Arbuzov reaction of 0,0-dialkyl(dialkoxymethyl)phosphonites and their analogues; many of these reactions have led to rather striking results.

For example, the interaction of these phosphonites with methyl, allyl and methoxymethyl iodides proceeds under mild conditions to give a mixture of three types of phosphinates, **1**–**3**. The major products are the phosphinates, **1** obtained via the usual Arbuzov rearrangement; the amount of phosphinates, **2**, **3** in the reaction mixtures, according to the ^{31}P nmr spectra, is about 10–20%.

The phosphinates **2**, **3** are formed via a complex reaction sequence, including P—C bond cleavage in the phosphonium salts (A) and subsequent interaction of the intermediates with the primary reagents. The P—C bond cleavage may be caused by the attack of iodide ion on the electrophilic central carbon atom of the dialkoxymethyl group in the intermediate (A). Methoxymethyl chloride reacts with diethoxymethylphosphonite at 100°C, increasing the amount of the P—C bond cleavage products, **2a**, **3c** to about 60%.

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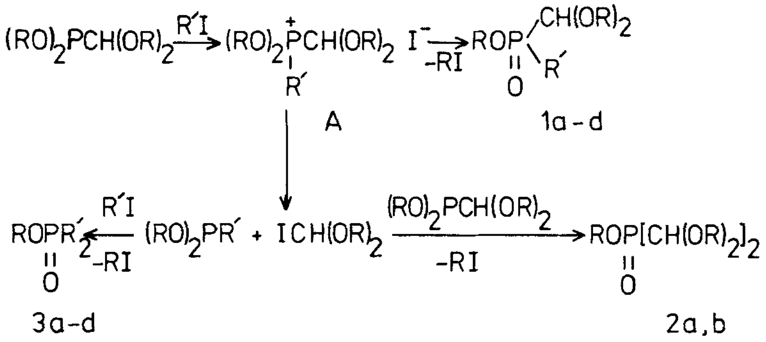
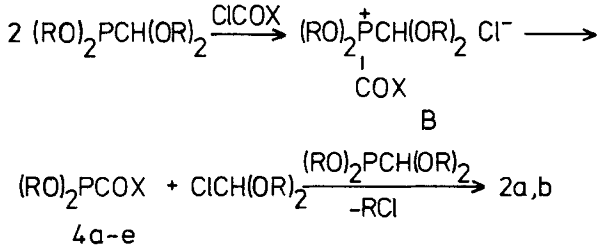


(2)

R = Et: **2a** and R' = Me: **1a**, Allyl: **1c**, $MeOCH_2$: **1d**;
R = Bu: **2b** and R' = Me: **1b**; for **3a–d** the radicals (R, R') are the same.

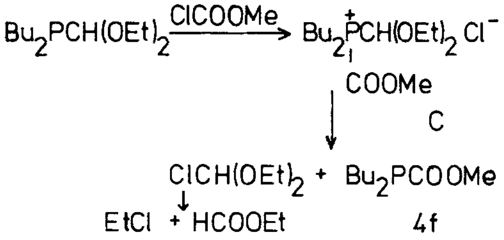
The only P—C bond cleavage takes place by the interaction of dialkoxymethylphosphonites with acyl chlorides, with formation of α-carbonylphosphonites, **4** and phosphinates, **2**.



(3)

R = Et: **2a** and X = MeO; **4a**, BuO: **4b**, *t*-Bu: **4d**, *i*-Pr: **4e**;
R = Bu: **2b** and X = MeO: **4c**.

This interaction proceeds smoothly upon refluxing the mixture in ether; it is necessary to use a second equivalent of dialkoxymethylphosphonite to react with the dialkoxymethyl chloride formed by the decomposition of the phosphonium salt (B). This scheme may be confirmed by interaction of dibutyl(diethoxymethyl)phosphine with methoxycarbonyl chloride forming dibutyl(methoxycarbonyl)phosphine, **4f**.



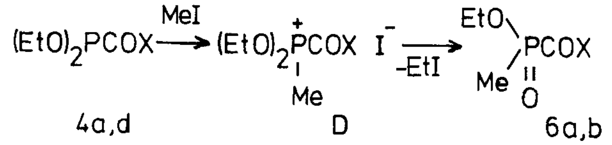
(4)

In this case unstable diethoxymethyl chloride can not compete with methoxycarbonyl chloride and readily decomposes into ethyl chloride and ethyl formate.

The analogous cleavage of the P—C bond takes place also by the reaction of 0,0-diethyl(diethoxymethyl)phosphonite with carbon tetrachloride to give trichloromethylphosphonite, **5** and phosphinate, **2a**.

$$2\,(EtO)_2PCH(OEt)_2 \xrightarrow[-EtCl]{CCl_4} \underset{5}{(EtO)_2PCCl_3} + 2a \qquad (5)$$

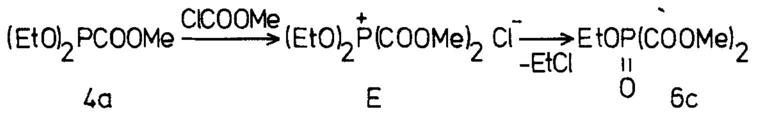
It should be emphasized that the phosphonites **4**, **5**, containing electronegative groups in their molecules do not react with initial acyl chlorides or carbon tetrachloride under mild conditions, due to the decreasing phosphorus nucleophilicity. In fact, the α-carbonylphosphonites, **4a,d** react with methyl iodide only upon reflux in acetonitrile to give products of the Arbuzov rearrangement, **6a,b**.



(6)

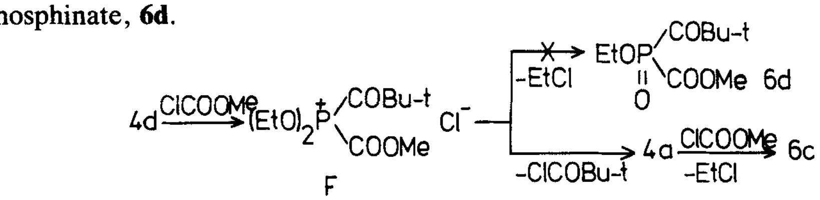
X = MeO : 6a ; t-Bu : 6b.

Under the same conditions (heating up to about 90°C) the interaction between phosphonite, **4a** and methoxycarbonyl chloride also produces the expected phosphinate, **6c**.



$$\underset{4a}{(EtO)_2PCOOMe} \xrightarrow{ClCOOMe} \underset{E}{(EtO)_2\overset{+}{P}(COOMe)_2\ \overset{-}{Cl}} \xrightarrow{-EtCl} \underset{6c}{EtO\underset{\underset{O}{\|}}{P}(COOMe)_2} \qquad (7)$$

By contrast, the reaction of α-carbonylphosphonite, **4d** with excess methoxycarbonyl chloride has unexpectedly led to the phosphinate, **6c**, but not the phosphinate, **6d**.

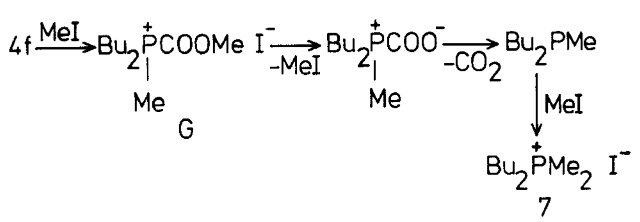


(8)

This case also illustrates the unusual direction of the Arbuzov reaction which is connected with the P—C bond cleavage in the intermediate (F), and the following rearrangement of phosphonite, **4a**. Such difference in the decomposition of the phosphonium salts, D, E and F may be explained by the smaller volume of chloride anion and higher electrophilicity of the carbon atom in the tert-butylcarbonyl group. Thus, the attack of the chloride anion on the carbonyl group in the phosphonium salt, F is preferred.

The P—C bond lability is also observed in the unsuccessful attempt to synthesize the phosphonium salt, G from the phosphine, **4f** and methyl iodide. The mixing of the reagents is accompanied by rapid formation of carbon dioxide to give the stable phosphonium salt, **7**.

The decay of salt, G proceeds, evidently via attack of iodide anion on the methyl group to give carbon dioxide and methyldibutylphosphine which readily reacts with methyl iodide with formation of compound, **7**.



(9)

We have observed a certain analogy between the reactivity of dialkoxymethylphosphonites and of α-carbonylphosphonites. Their common significant property is the P—C bond lability in the intermediate phosphonium salts. Therefore, these substances are rather valuable for the synthesis of new types of organophosphorus compounds.

EXPERIMENTAL

All operations were conducted in a dry argon atmosphere in vigorously dried solvents.

PMR spectra were recorded on a Tesla BS-467 spectrometer (60 MHz) with Me_4Si as an internal standard, in C_6D_6 or $CDCl_3$ solvents.

^{13}C and ^{31}P nmr spectra were recorded on a JEOL FX-100 spectrometer in the same solvents, with Me_4Si as internal standard (^{13}C, 25.14 MHz) and an 85% solution of H_3PO_4 in D_2O as external standard (^{31}P, 42.26 MHz). The positive chemical shifts are given in the downfield from standard.

Some physical data of compounds **1–7** are given in Table I.

Phosphinates, **1–3**. Alkyl iodide (0.02 mole) was added dropwise with stirring to the 0,0-dialkyl(dialkoxymethyl)phosphonite (0.02 mole) in 15 ml of ether. The mixture was refluxed for 2 hr. The solvent was removed. According to ^{31}P nmr data the residue consisted of the phosphinates **1–3** mixture; it was fractionated to give the phosphinates, **1**. The ^{31}P nmr chemical shifts of the phosphinates, **2, 3** were identical to those of authentic samples.

Carbonylphosphonites, **4a–e** *and O-alkylbis(dialkoxymethyl)phosphinates,* **2a,b**. Acyl chloride (0.03 mole) was added dropwise with stirring to the 0,0-dialkyl(dialkoxymethyl)phosphonite (0.06 mole) in 50 ml of ether. The mixture was refluxed for 4 hr, the solvent was removed, and the residue was fractionated to give the title phosphonites, **4a–e** and the phosphinates, **2a,b**. Dibutyl(methoxycarbonyl)phosphine **4f**, (4.9 g; 85%) was obtained in a similar way from dibutyl(diethoxymethyl)phosphine (7 g; 0.028 mole) and methoxycarbonyl chloride (2.7 g; 0.028 mole).

0,0-Diethyl(trichloromethyl)phosphonite, **5** *and 0-ethylbis(diethoxymethyl)phosphinate,* **2a**. The solution of 0,0-diethyl(diethoxymethyl)phosphonite (11.2 g; 0.05 mole) in 30 ml of carbon tetrachloride was refluxed for 4 hr. The solvent was removed, and the residue was fractionated to give the phosphonite, **5** (3.1 g; 52%) and the phosphinate, **2a** (5.2 g; 69%).

α-Carbonylphosphinates, **6a,b**. The solution of α-carbonylphosphonite, **4a** or **4d** (0.02 mole) and methyl iodide (0.022 mole) in 20 ml of acetonitrile was refluxed for 3 hr. The solvent was removed, and the residue was fractionated to give the phosphinates, **6a,b**.

0-Ethylbis(methoxycarbonyl)phosphinate, **6c**. The mixture of 0,0-diethyl(methoxycarbonyl)phosphonite, **4a** (2.9 g; 0.016 mole) and methoxycarbonyl chloride (1.6 g; 0.016 mole) was heated at 80°C to 90°C for 1 hr, then it was distilled to give the phosphinate, **6c**, (2.6 g; 70%). The phosphinate, **6c**, (4.9 g; 85%) was also obtained in a similar way after refluxing the mixture of the phosphonite, **4d**, (5.7 g; 0.028 mole) and methoxycarbonyl chloride (5.3 g; 0.056 mole) in 5 ml of benzene.

Dimethyldibutylphosphonium iodide, **7**. Methyl iodide (7.1 g; 0.05 mole) was added dropwise with stirring to the solution of dibutyl(methoxycarbonyl)phosphine, **4f**, (5 g; 0.024 mole) in 10 ml of acetonitrile at 10°C to 20°C. Spontaneous heating of the mixture and formation of carbon dioxide were observed. The solvent was removed, the residue was crystallized from a mixture of chloroform and diethyl ether to give compound, **7**.

TABLE I

Some physical data of compounds, **1**–**7**; δ, ppm; J, Hz

Compound no.	Yield (%)	b.p. (1 mm)	n_D^{20}	*Found* Calcd. (%)			Empirical formula	Fragment PCH or PC=O				
				C	H	P		δ_H (d)	$^2J_{PH}$	δ_P[a] (s)	δ_C (d)	$^1J_{PC}$
1a	87	75	1.4345	*45.49* 45.71	*9.02* 9.11	*14.61* 14.73	$C_8H_{19}O_4P$	4.45	7	42.5	101.1	153.5
1b	81	125	1.4396	*56.96* 57.12	*10.73* 10.62	*10.26* 10.52	$C_{14}H_{31}O_4P$	4.47	7	42.2	—	—
1c	77	87	1.4475	*51.05* 50.84	*8.79* 8.96	*13.35* 13.11	$C_{10}H_{21}O_4P$	4.53	8	39.1	—	—
1d	55	79	1.4375	*45.31* 45.00	*8.75* 8.81	*12.62* 12.89	$C_9H_{21}O_5P$	4.63	9	35.0	99.7	141.0
2a[b]	87	103	1.4351	—	—	—	—	4.65	9	28.9	99.6	138.0
2b	90	155	1.4427	*60.04* 60.25	*10.71* 10.80	*7.14* 7.06	$C_{22}H_{47}O_6P$	4.57	10	28.2	—	—
4a	96	40	[c]	*39.86* 40.01	*7.10* 7.27	*17.05* 17.19	$C_6H_{13}O_4P$	—	—	132.4	177.3	35.0
4b	90	62	[c]	*48.45* 48.64	*8.51* 8.62	*14.07* 13.94	$C_9H_{19}O_4P$	—	—	134.7	—	—
4c	89	68	[c]	*50.59* 50.84	*8.90* 8.96	*12.94* 13.11	$C_{10}H_{21}O_4P$	—	—	135.1	—	—
4d	95	42	[c]	*52.27* 52.42	*9.18* 9.29	*15.34* 15.02	$C_9H_{19}O_3P$	—	—	148.4	227.5	57.4
4e	94	39	[c]	*49.75* 49.99	*8.78* 8.92	*15.97* 16.12	$C_8H_{17}O_3P$	—	—	143.9	228.5	44.4
4f	85	57	[c]	*58.65* 58.80	*10.19* 10.36	*15.25* 15.17	$C_{10}H_{21}O_2P$	—	—	−17.4	—	—
5[b]	52	54	[c]	—	—	—	—	—	—	138.3	—	—
6a	54	68	1.4361	*35.90* 36.15	*6.84* 6.67	*18.40* 18.65	$C_5H_{11}O_4P$	1.58	16	27.2	170.7	175.8
6b	72	59	1.4368	*49.95* 50.00	*8.96* 8.92	*16.00* 16.12	$C_8H_{17}O_3P$	1.48	14	33.0	219.4	91.6
6c	70	104	1.4455	*34.03* 34.30	*5.10* 5.28	*14.61* 14.74	$C_6H_{11}O_6P$	—	—	−6.0	167.3	197.8
7[b]	93	m.p. 168–169°C	—	—	—	—	—	2.20	14	30.1	—	—

[a] δ_P, **3a** 49.5; δ_P, **3b** 49.2; δ_P, **3c** 44.7; δ_P, **3d** 41.0; s—singlet, d—doublet.

[b] The constants of compounds, **2a**, **5** and **7** are in agreement with the reported values.[3,4,5]

[c] Because of the ease of oxidation the refractive index of this compound was not measured.

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