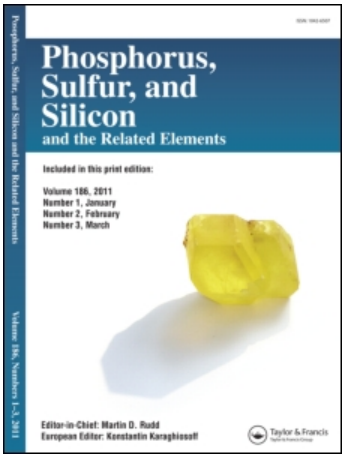

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Petneházy, Imre , Keglevich, György and Tőke, László(1987) 'DIHALOCARBENE ADDITION TO ARYLSUBSTTTUTED VINYL PHOSPHATES UNDER PHASE TRANSFER CATALYTIC CONDITIONS', Phosphorus, Sulfur, and Silicon and the Related Elements, 33: 1, 77 — 82
To link to this Article: DOI: 10.1080/03086648708074285
URL: http://dx.doi.org/10.1080/03086648708074285

Phosphorus and Sulfur, 1987, Vol. 33, pp. 77–82
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DIHALOCARBENE ADDITION TO ARYL-SUBSTITUTED VINYL PHOSPHATES UNDER PHASE TRANSFER CATALYTIC CONDITIONS

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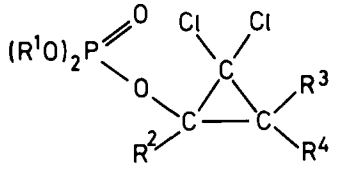
(Received November 20, 1986; in final form December 21, 1986)

Dihalocarbene addition to aryl-substituted vinyl phosphates was carried out both in solid–liquid and in liquid–liquid two phase systems. The dihalocyclopropane adducts of vinyl phosphates could be obtained in better yield using dihalocarbenes generated by the latter method and no hydrolysis of the vinyl phosphate and of the adduct occurred under these circumstances. Eighteen new vinyl phosphate-dihalocarbene adducts were synthetized and characterized.

INTRODUCTION

Dihalocarbene addition to alkenes is a subject of continuing interest, especially regarding addition to special types of alkenes, e.g. to electron poor alkenes in which the formation of a cyclopropyl ring is difficult.[1]

Due to the electron withdrawing effect of the phosphoryl and phenyl groups, vinyl phosphates of type **2** can be regarded as electron-poor alkenes, although the conjugative effect of the lone electron pairs of the oxygen is also important. De Selms and Lin[2] studied the dichlorocarbene addition to alkyl substituted vinyl phosphates. They generated the carbene from sodium trichloroacetate in refluxing dimethoxyethane and obtained the adducts (**1**) in an average yield of 25%. Dibromocarbene addition to vinyl phosphates has not been reported.



1

$R^1 = CH_3, C_2H_5 \qquad R^2, R^3, R^4 = H, CH_3$

SCHEME 1

In the present paper we report on the extension of the reaction to aryl-substituted vinyl phosphates, the use of dibromocarbene and the optimization of the method.

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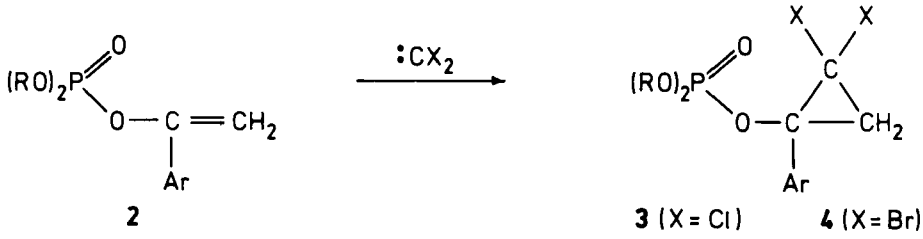
RESULTS AND DISCUSSION

For the generation of dihalocarbene two methods, both using phase transfer catalysis were used: the improved sodium trichloroacetate method[3] and the Makosza method[4] (generation of dihalocarbene from haloform with 50% sodium hydroxide solution). These two methods were compared and also the effect of substituents, temperature and solvent was studied.



2 **3** (X = Cl) **4** (X = Br)

R = CH_3, C_2H_5

Ar = C_6H_5, 2,5-$(H_3C)_2C_6H_3$, 2,4-$(H_3C)_2C_6H_3$, 3,4-$(H_3C)_2C_6H_3$, 4-$C_2H_5C_6H_4$, 4-$CH_3C_6H_4$, 4-ClC_6H_4, 2,4-$Cl_2C_6H_3$, 3,4-$Cl_2C_6H_3$

SCHEME 2

In the first series of experiments dichlorocarbene was generated from sodium trichloroacetate in different solvents in a solid–liquid system using 3% Aliquat (tricaprylmethylammonium chloride) or TEBAC (triethylbenzylammonium chloride) and reacted with the aryl-substituted vinyl phosphates **2c**, **2g**, and **2j**. Results were summarized in Table I. No essential difference could be found between using Aliquat or TEBAC (entries 1 and 2). At lower temperature yields were better and the formation of brown decomposition products could be mostly

TABLE I

The reaction of aryl-substituted vinyl phosphates with dichlorocarbene generated from sodium trichloroacetate (STCA) in solid–liquid two phase system

Entry	Starting material	R	Ar	Solvent	Catalyst	Temperature (°C)	Portion of STCA	Reaction Time (h)	Product	Yield* (%)
1	**2j**	C_2H_5	4-Cl—C_6H_4	$CHCl_3$	Aliquat	63	2	4, 5	**3j**	51
2	**2j**	C_2H_5	4-Cl—C_6H_4	$CHCl_3$	TEBAC	63	2	4	**3j**	48
3	**2j**	C_2H_5	4-Cl—C_6H_4	$CHCl_3$	TEBAC	50	2	14	**3j**	56
4	**2j**	C_2H_5	4-Cl—C_6H_4	$C_6H_5CH_3$	Aliquat	100	4	4	**3j**	30
5	**2c**	CH_3	4-Cl—C_6H_4	$CHCl_3$	Aliquat	63	2	5, 5	**3c**	40
6	**2g**	CH_3	2,5-Cl_2—C_6H_3		Aliquat	63	5	30	**3g**	

0.003 mol of vinyl phosphate, 3 mol % catalyst and 0.006 mol of sodium trichloracetate in 15 ml of solvent was used.

For renewal of the dichlorocarbene source, additional 0.006 mol portions of sodium trichoroacetate were used. Reactions were run until no starting material could be found in the mixtures.

* The yield were calculated after running the reactions on larger scale and fractionating the crude products in vacuo.

TABLE II

The reaction of aryl-substituted vinyl phosphates with dihalocarbene generated in liquid–liquid two phase system

Starting material	R	Ar	X	Reaction time (h)	Product	Yield* (%)
2a	CH_3	C_6H_5	Cl	5	**3a**	69
2b	CH_3	4-$CH_3C_6H_4$	Cl	8	**3b**	51
2c	CH_3	4-ClC_6H_4	Cl	4	**3c**	74
2d	CH_3	2,5-$(CH_3)_2C_6H_3$	Cl	29	**3d**	50
2e	CH_3	3,4-$(CH_3)_2C_6H_3$	Cl	10	**3e**	89
2f	CH_3	2,4-$Cl_2C_6H_3$	Cl	17	**3f**	49
2g	CH_3	2,5-$Cl_2C_6H_3$	Cl	25	**3g**	30
2h	C_2H_5	C_6H_5	Cl	10	**3h**	86
2i	C_2H_5	4-$C_2H_5C_6H_4$	Cl	10	**3i**	68
2j	C_2H_5	4-ClC_6H_4	Cl	7	**3j**	60
2k	C_2H_5	2,4-$(CH_3)_2C_6H_3$	Cl	12	**3k**	67
2l	C_2H_5	2,5-$(CH_3)_2C_6H_3$	Cl	29	**3l**	60
2m	C_2H_5	3,4-$Cl_2C_6H_3$	Cl	10	**3m**	62
2a	CH_3	C_6H_5	Br	10	**4a**	23
2c	CH_3	4-ClC_6H_4	Br	10	**4c**	29
2e	CH_3	3,4-$(CH_3)_2C_6H_3$	Br	13	**4e**	47
2j	C_2H_5	4-ClC_6H_4	Br	8	**4j**	36
2l	C_2H_5	2,5-$(CH_3)_2C_6H_3$	Br	35	**4l**	22

* Yields after distillation in vacuo.

avoided (entries 2 and 3 vs. 4). In acetone or ethanol there was no reaction. Reaction of O,O-dimethyl-4-chlorophenyl-vinyl phosphate (**2c**) was somewhat slower than that of the O,O-diethyl compound (**2j**) (entries 1 and 5). The 2,5-dichlorophenyl compound reacted much slower than the 4-chlorophenyl analogue (entries 5 and 6). O,O-Dimethyl-phenyl-chloro-vinyl phosphate did not add dichlorocarbene.

In the second series of experiments the Makosza method[4] was used to generate dichloro- and dibromo-carbene. A solution of the vinyl phosphate in haloform and 10% TEBAC was stirred with 20 equivalents of 50% aqueous sodium hydroxide at room temperature for several hours resulting in the formation of the dichloro- and dibromocarbene adducts **3** and **4**, respectively. Results were summarized in Table II. It can be seen that in the case of dichlorocarbene addition the liquid–liquid two phase system gave better yields (50–89%) than the liquid–solid system (40–51%, Table I). Yields were the lowest when sodium trichloroacetate was used without catalyst (20–30%).[2] With the Makosza method the completion of the reaction required 4–10 h, in the case of 2,5-disubstituted substrates (**2d–2g**) addition was even slower. The ethyl esters reacted slower than the corresponding methyl esters (cf. **2c** and **2j**). The method was successfully extended to the addition of dibromocarbene, although yields were lower and the reaction more sluggish than with dichlorocarbene.

The main advantage of liquid–liquid phase dihalocarbene generation is that it is carried out under mild conditions. As a consequence yields are good and ester hydrolysis is avoided. We have shown earlier[5] that vinyl phosphates can undergo monodealkylation in the presence of a quaternary ammonium salt. Now it was found that this reaction did not proceed under the present conditions.

TABLE III

Mass spectrum of **3k**

m/e	Rel. Int (%)	Fragment
366	15.9	M^+
351	3.1	$M—CH_3]^+$
330	27.4	$M—HCl]^+$
316	20.4	$351\text{-}Cl]^+$
300	8.5	$316\text{-}O]^+$
295	15.7	$330\text{-}Cl]^+$
213	6.1	$M—(C_2H_5O)_2P(O)O]^+$
212	9.9	213-H
177	93.5	$(CH_3)_2C_6H_3—\underline{C—CCl=CH}]^+$
155	100.0	$(C_2H_5O)_2P(OH)_2]^+$
143	11.9	142 + H
142	27.0	$(CH_3)_2C_6H_3—\underline{C=C=CH}]^+$
141	20.7	142-H
127	25.8	$C_2H_5O—P(OH)_3]^+$
109	20.3	$C_2H_5O—P(O)OH]^+$
105	21.1	$(CH_3)_2C_6H_3]^+$
99	18.8	$P(OH)_4]^+$
81	25.6	$O=P(OH)_2]^+$
79	11.8	$PO_3]^+$
77	15.5	$C_6H_5]^+$
29	44.8	$C_2H_5]^+$

Compounds **3** and **4** are new. They were identified and characterized by IR, ^1H n.m.r. spectroscopy, and in one case by ^{31}P n.m.r. and mass spectrometry. Elemental analysis was performed on all samples.

The alkoxy groups in compounds **3** and **4** are diastereotopic and this is clearly reflected in their ^1H n.m.r. spectra.[6] Thus two doublets can be observed for the two methoxy groups, the methyls of the two ethoxy groups appear as two triplets, while the methylenes of the ethoxy groups appear as more or less resolved multiplets.

As a representative example the mass spectrum of **3k** was examined (Table III). The molecular ion (m/e = 366) was accompanied by the expected isotopic peaks. The base peak (at m/e = 155) was assigned to the fragment $(C_2H_5O)_2P(OH)_2]$ produced by the cleavage of the C—O bond. The other main fragment was $(CH_3)_2C_6H_3\underline{C—C/Cl/=CH}]^+$ (m/e 177) formed by the cleavage of the C—O bond with the loss of one molecule of hydrogen chloride.[7]

EXPERIMENTAL

Instrumentation and analysis

G.l.c. analyses were performed with a Packard chromatograph using a column packed with Chromosorb G, impregnated with QF, silicone oil (2.5 or 5%). A column temperature of 210°C was used with hydrogen as a carrier gas and a thermal conductivity detector. The concentration of vinylphosphates was determined from calibration graphs. Infrared spectroscopy was carried out on a Spektromom 2000 spectrometer. 1H n.m.r. Spectra were recorded on a Perkin-Elmer 60 MHz instrument and, in one case (**3k**) a Jeol FX 100 MHz instrument was used. The same instrument operating at 40.26 MHz was used to obtain the ^{31}P n.m.r. spectrum. Chemical shifts are given relative to TMS and to 85% H_3PO_3, respectively. Positive shifts are downfield, and negative shifts upfield of the reference. The mass spectrum was recorded on a Jeol JMS-01SG-2 instrument at 75 eV.

Starting materials and preparations
Vinyl phosphates were prepared from α-halogenoacetophenones as described earlier.[8,6]

1-(O,O-Diethylphosphoryl)-1-(4-chlorophenyl)-2,2-dichloro-cyclopropane (**3j**) *(Generation of dichlorocarbene from sodium trichloroacetate)*
The mixture of 2.91 g (0.01 mol) of O,O-diethyl-1-(4-chlorophenyl)-vinyl phosphate, 3.71 g (0.02 mol) of sodium trichloroacetate and 0.15 g (0.37 mmol) of Aliquat dissolved in 20 ml of dry chloroform was refluxed till the evolution of carbon dioxide ceased (~3 h). Then the mixture was refluxed further with another 0.02 mol portion of sodium trichloroacetate, during which all of the starting material was consumed (1.5 h, g.l.c. analysis). After washing with water and drying the solvent was evaporated and

TABLE IV

Physical data of compounds **3** and **4**

No.	b.p. °C/Torr (m.p. °C)	^{1}H n.m.r.[a] CH_2 q	CH_3 s	OCH_3 or OCH_2 d	OCH_2 quint[b]	OCH_2-CH_3 tr	Ar m	IR, cm^{-1} P—O—C	P=O
3a[c]	141–3/0.1–0.2	2.40 $^1J_{HH}$ = 10		3.22 3.58	$^3J_{PH}$ = 11		7.10–7.56	1040	1280
3b	155/0.4 (40–1)	d	2.33	3.20 3.60	$^3J_{PH}$ = 12		6.94–7.44	1030	1280
3c	140–2/0.1 (51)	2.36 $^1J_{HH}$ = 10		3.30 3.60	$^3J_{PH}$ = 11		7.15–7.50	1040	1270
3d	142–4/0.4	d	2.34 2.46	3.14 3.66	$^3J_{PH}$ = 12		6.90–7.38	1050	1290
3e	195–8/0.35 (72–3)	d	2.29	3.25 3.62	$^3J_{PH}$ = 12		6.90–7.30	1040	1280
3f	173–7/0.4	2.33 $^1J_{HH}$ = 11		3.38 3.70	$^3J_{PH}$ = 12		7.10–7.61	1030	1270
3g	164–8/0.4 (108–11)	—		—			—	1030	1280
3h	162–4/0.4	2.42 $^1J_{HH}$ = 10		3.63 3.99	^3J = 7	0.96 1.26	$^3J_{HH}$ = 7	1030	1270
3i	148–50/0.25	e	e	3.58 3.95	^3J = 8	e	6.94–7.46	1030	1265
3j	159–60/0.2	2.34 $^1J_{HH}$ = 10		3.66 3.98	^3J = 8	1.01 1.28	$^3J_{HH}$ = 8	1030	1265
3k	143–5/0.075	d	2.29 2.48	3.58 4.00	^3J = 7	0.97 1.28	$^3J_{HH}$ = 7	1030	1260
3l	152.5/0.4 (40–2)	d	2.34 2.44	3.47 3.97	^3J = 7	0.91 1.29	$^3J_{HH}$ = 7	1050	1280
3m	184–6/0.4 (59–60)	2.35 $^1J_{HH}$ = 10		3.71 3.97	^3J = 7	1.08 1.29	$^3J_{HH}$ = 7	1020	1255
4a	158–60/0.2	2.61 $^1J_{HH}$ = 11		3.32 3.77	$^3J_{PH}$ = 11		7.28–7.66	1040	1280
4c	(64–5)	2.47 $^1J_{HH}$ = 10		3.25 3.62	$^3J_{PH}$ = 11		7.26–7.54	1040	1280
4e	(87–9)	d	2.24	3.19 3.59	$^3J_{PH}$ = 11		7.00–7.29	1030	1280
4j	(40–2)	2.57 $^1J_{HH}$ = 10		3.13 4.01	^3J = 7	1.02 1.24	$^3J_{HH}$ = 7	6.87–7.82	1090	1280
4l	(35–40)	d	2.24 2.46	3.55 4.01	^3J = 7	0.91 1.25	$^3J_{HH}$ = 7	6.34–7.75	1040	1270

[a] Shifts are given in ppm and couplings in Hertz. Spectra were recorded in CCl_4, in the case of **3a**, **3k**, **4a**, **4j** and **4l** in $CDCl_3$.
[b] $^3J_{PH} \doteq {}^3J_{HH}$ in Table ^3J.
[c] ^{31}P n.m.r.: δ = 1.93 ppm.
[d] overlapped by the signal of the methyl group(s) in the aromatic ring.
[e] signals are overlapping.

the residue fractionated in vacuo to give 1.9 g (51%) **3j**. Physical, ^{1}H n.m.r. and IR spectroscopic data for **3j** are collected in Table IV.

1-(O,O-Dimethylphosphoryl)-1-(4-chlorophenyl)-2,2-dichlorocyclopropane (**3c**) *(Generation of dichlorocarbene by the Makosza method)*

25 ml dry chloroform solution of 6.57 g (0.025 mol) O,O-dimethyl-1-(4-chlorophenyl)-vinyl phosphate was added dropwise to the mixture of 0.57 g (2.5 mmol) of TEBAC, 50 ml of dry chloroform and 20 g (0.5 mol) of 50% aqueous sodium hydroxide. The temperature was maintained at 26°C and the mixture was stirred until the starting material was consumed (4 h, g.l.c.). The organic layer was washed, dried, evaporated and fractionated in vacuo to give 6.4 g (67%) pure **3c** as an oil, which crystallized with petrolether to give 6 g **3c** as white crystals.

Other dihalocarbonate adducts were prepared similarly. Dibromocarbene adducts were prepared using bromoform instead of chloroform. Physical and spectroscopic data of adducts **3** and **4** are summarized in Table IV. Satisfactory elemental analysis was obtained for all the samples.

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