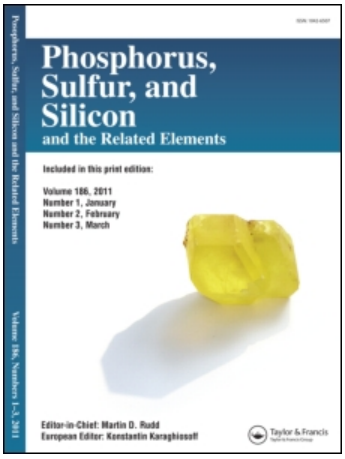

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ON THE REACTIVITY OF PHOSPHOLENE-DICHLOROCARBENE ADDUCTS: RING EXPANSION EFFECTED BY MERCURY ACETATE

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ON THE REACTIVITY OF PHOSPHOLENE-DICHLOROCARBENE ADDUCTS: RING EXPANSION EFFECTED BY MERCURY ACETATE

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The cyclopropane ring in the dichlorocarbene adducts of 1-alkyl-3-methyl-3-phospholene-1-oxides is opened in the reaction with mercury acetate—acetic acid to give the diastereoisomers of 5- and 3-methyl-3-acetoxy-1-alkyl-4-chloro-1,2,3,6-tetrahydrophosphinine-1-oxide. The structure of the isomers has been elucidated by NMR spectroscopy and by synthesis.

Both chlorine atoms of the 3-phospholene-1-oxide-dichlorocarbene adducts can easily be substituted by phenyl groups in a Friedel–Crafts arylation reaction.

INTRODUCTION

Ring expansion of unsaturated cyclic compounds by the addition of dichlorocarbene to the double bond and subsequent transformation of the adduct so formed is a known procedure. Examples for the ring enlargement of unsaturated carbocycles[1] and nitrogen containing heterocycles[2] have been described. Such transformation in the field of heterocycles with phosphorus in the ring have been performed for the first time in our laboratory. 3-Phospholene-1-oxide-dichlorocarbene adducts have been synthesized[3] and their transformations examined. Certain dichlorocarbene adducts gave dihydrophosphinine-1-oxides spontaneously,[3] others gave stable adducts which can be converted to dihydrophosphinines through 1,2,5,6-tetrahydrophosphinine-1-oxides.[4] Ring expansion of dihydrophosphinine-1-oxides to phosphacycloheptatrienes has also been observed.[3] In this paper the mercury acetate–acetic acid induced ring expansion reaction and Friedel–Crafts arylations of several phospholene-1-oxide-dichlorocarbene adducts are discussed.

RESULTS AND DISCUSSION

Reaction of 3-Phospholene-1-oxide-dichlorocarbene Adducts with Mercury Acetate–Acetic Acid

Mercury acetate–acetic acid induced opening for simple[5] and fused cyclopropane rings[6] and for dichlorocyclopropane derivatives[7] has been described in the

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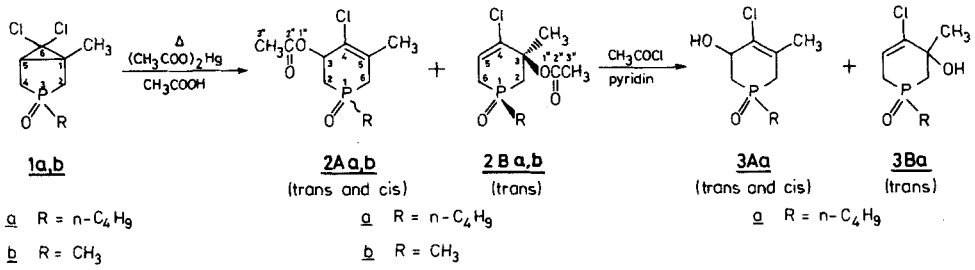


SCHEME I

literature. In the latter case a double bond has also been formed beside the opening of the cyclopropane ring. The use of mercury acetate–acetic acid proved to be suitable also for the opening of the dichlorocyclopropane derivatives of 3-phospholene-1-oxides. On heating the dichlorocarbene adducts of 1-alkyl-3-methyl-3-phospholene-1-oxide (**1a** and **b**) with mercury acetate in acetic acid, a mixture consisting of the three isomers of 3-acetoxy-1-alkyl-4-chloro-methyl-1,2,3,6-tetrahydrophosphinine-1-oxides (**2Aa,b**/trans and cis, **2Ba,b**/trans) has been obtained (Scheme I).

Identification of the Products

Three signals could be found in the ^{31}P NMR spectrum of the crude product obtained from the reaction of adduct **1a** with mercury acetate–acetic acid which were assumed to belong to the isomers of 3-acetoxy-1-*n*-butyl-4-chloro-methyl-1,2,3,6-tetrahydrophosphinine-1-oxide, as mass spectroscopic measurement revealed only one molecular ion ($m/e = 278$). One isomer could be separated by column chromatography, and proved to be **2Ba**, on the basis of the ^1H NMR signal of its olefinic proton, and represents about 20% of the mixture, according to ^{31}P NMR analysis. The other two isomers could be identified by comparison to the products formed in the reaction of the known isomers of 1-*n*-butyl-4-chloro-3-hydroxy-methyl-tetrahydrophosphinine-1-oxide (**3a**) with acetyl chloride. The isomeric mixture of hydroxy derivative **3a** of known composition consisting of the trans and cis form of isomer **3Aa** and the trans form of its isomer **3Ba**, prepared as described earlier,[4] gave the same three isomers on acylation which were formed in the reaction of **1a** with mercury acetate–acetic acid. For this reason it could be concluded, that beside one diastereomer of **2Ba**, which proved to be the trans form, the major (trans) and minor (cis) diastereomers of **2Aa** are formed in the reaction of the dichlorocarbene adduct **1a** with mercury acetate–acetic acid. Three isomers (two diastereoisomers of **2Ab** and one diastereoisomer of **2Bb**) are formed also in the reaction of adduct **1b** with mercury acetate–acetic acid, according to the ^{13}C NMR spectrum. The ratio of the regioisomers (**2Ab** and **2Bb**) was calculated on the basis of the relative ^1H NMR intensity of the olefinic proton of **2Bb**, while the ratio of the diastereoisomers of **2Ab** was determined from the ^1H NMR intensity of the $C_{3''}$—CH_3 signals, assuming the trans form to be predominant. Products **2Ba** and **2Aa**, the latter as a mixture of two stereoisomers, have been characterized by ^{31}P, ^1H, ^{13}C NMR, mass and IR

TABLE I

^{13}C NMR data for 5- and 3-methyl-3-acetyl-1-alkyl-4-chloro-1,2,3,6-tetrahydrophosphinine-1-oxides (2Aa, b and 2Ba, b)

		^{13}C NMR[a] (J_{P-C})											
		C_2	C_3	C_4	C_5	C_6	C—CH_3	$C_{1'}$	$C_{2'}$	$C_{3'}$	$C_{4'}$	$C_{2''}$	$C_{3''}$
4′ 3′ 2′ 1′ $CH_3CH_2CH_2CH$–	A trans, cis[b]	32.8, 33.1 (63.7)(62.3)	70.2, 71.0 (4.4)	125.9, 126.4 (13.2) (8.8)	129.8, 130.7 (5.2)	30.3, 31.0 (60.8)	20.6	27.7, 28.8 (68.9)	23.2 (4.4)	23.8, 23.9 (13.9)(14.7)	13.4	169.7, 169.1	23.8
	B trans	35.5 (57.2)	79.3	136.8 (10.3)	119.5 (7.3)	27.6 (63.0)	21.7	30.2 (70.3)	23.6 (4.4)	24.0 (16.1)	13.5	170.0	26.9
1′ CH_3	A trans, cis[b]	33.9, 34.1 (65.2)(64.5)	69.8, 70.6 (4.4)	125.4, 125.8 (11.0) (9.5)	129.6 130.5 (4.4) (5.2)	31.6, 32.0 (61.5)(62.3)	20.3	13.9, 15.4 (70.3)(69.6)				169.2, 168.7	23.1, 23.5
	B trans	36.4 (63.7)	c	136.1 (10.9)	119.2 (7.3)	28.4 (65.2)	21.1	16.0 (71.8)				169.2	26.2

[a] $CDCl_3$, J given in Hz.
[b] Signals within the appropriate signal pairs could not be assigned to the individual stereoisomers.
[c] Overlapped by the signal of $CDCl_3$.

TABLE II

MS data for 5- and 3-methyl-3-acetyl-1-*n*-butyl-4-chloro-1,2,3,6-tetrahydrophosphinine-1-oxides (**2Aa** and **2Ba**)

Compound		**2A**	**2B**
Fragments	(*m/e*)	Relative intensity (%)	
M^+	278	10	28
$M—Cl]^+$	243	8	7
$M—CH_3CO]^+$	235	70	40
$M—CH_3COO]^+$	219	100	100
$M—CH_3COOH]^+$	218	46	16
$M—CH_3COOH—Cl]^+$	183	7	3
$M—CH_3COOH—C_4H_9]^+ + H$	162	12	5

spectroscopic methods. As the isomers of **2Ab** and **2Bb** could not be separated, the mixture was subjected to spectroscopic examinations. The ^{13}C NMR signals for the regioisomers of **2b** could be assigned on the basis of the ^{13}C NMR data of the separated regioisomers of **2a**. The ^{13}C NMR assignment for the regioisomers was confirmed by Attached Proton Test measurement (APT) in each case. Signals within the appropriate signal pairs for the two diastereoisomers of **2Aa,b** could not be assigned to the individual isomers. ^{13}C NMR data are collected in Table I and some of the MS data can be found in Table II. ^{13}C NMR chemical shifts, P–C couplings and MS fragmentation of the products (**2a,b**) are similar to those reported for the analogous hydroxy- or alkoxy derivatives.[4]

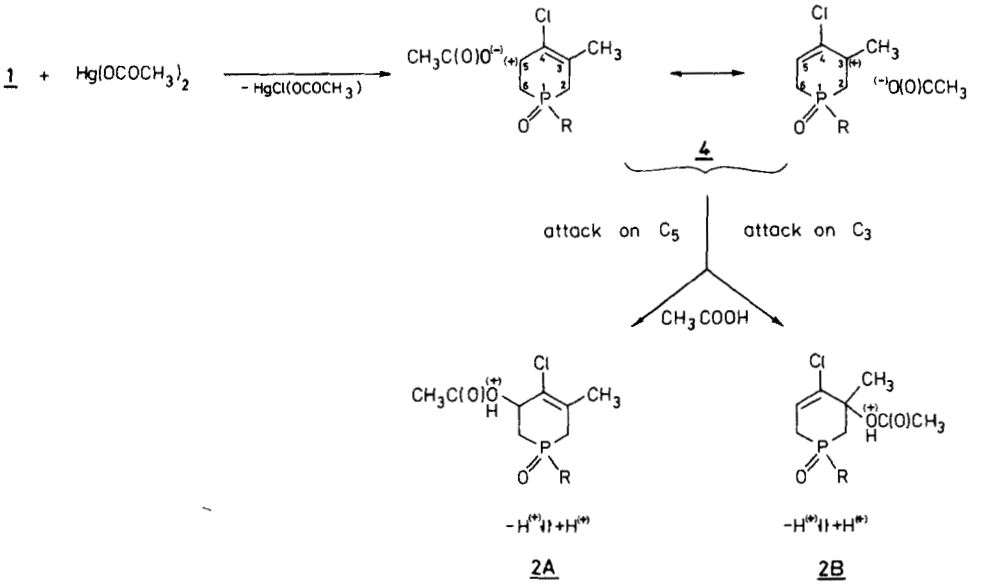
Mechanism of the Reaction

For the opening of the cyclopropane ring two pathways can be considered. One involves the electrophilic attack of mercury acetate on one of the bridged carbon atoms of the cyclopropane ring of adduct **1**, as it was substantiated for other cyclopropane derivatives,[5] to give the isomers of **2** after solvolysis and the elimination of mercury acetate chloride.

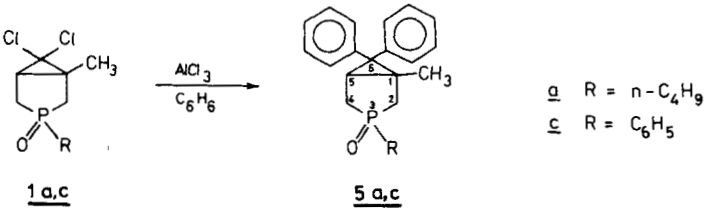
The presence of the chlorine atoms in the cyclopropane ring, however, offers another, more favourable way: mercury acetate can attack one of the halogens of adduct **1**. Cleavage of the C—Cl and C_1—C_5 bond and formation of the double bond are supposed to be synchronous processes[7,8] to give intermediate **4**, which is transformed to the isomers of **2** by the addition of acetic acid (Scheme II).

Arylation of 3-Phospholene-1-oxide-dichlorocarbene Adducts

The effect of another electrophilic reagent, aluminum trichloride, on the dichlorocarbene adducts **1a** and **c** has also been studied in benzene solution. Based on previous work[1b,d,e,4,7] it was expected that the latter reaction would yield the isomers of substituted 4-chloro-methyl-phenyl-1,2,3,6-tetrahydrophosphinine-1-oxides. Instead of opening the cyclopropane ring, however, a smooth Friedel–Crafts reaction of 3-phospholene-1-oxide-dichlorocarbene adducts (**1a**, **c**) with benzene was observed to take place giving the diphenyl derivatives **5a** and **c** (Scheme III). The ^{13}C NMR spectra of the products served the evidence for



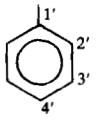
SCHEME II



SCHEME III

TABLE III

^{13}C NMR data for 1-methyl-6,6-diphenyl-3-phosphabicyclo[3.1.0]hexane-3-oxides (**5a** and **c**)

Compound R	^{13}C NMR[a] (J_{P-C})									
	C_1	C_2	C_4	C_5	C_6	C—CH_3	$C_{1'}$	$C_{2'}$	$C_{3'}$	$C_{4'}$
5a	53.2	38.3	32.9	54.5	60.5	24.9	31.6	24.1	24.0	13.5
CH_3—CH_2—CH_2—CH_2	(9.5)	(61.5)	(60.1)	(7.3)	(3.6)	(7.3)	(60.8)	(4.4)	(13.2)	
5c	52.5	43.0	34.0	55.5	61.4	23.5	128.0[b]	128.2[c]	130.0[c]	131.2
	(7.3)	(65.9)	(63.0)	(8.8)	(11.7)		(71.8)	(11.7)	(10.3)	

[a] $CDCl_3$ solution, J given in Hz.
[b] Tentative assignment (one part of the doublet is overlapped).
[c] May be reversed.

TABLE IV

MS data for 1-methyl-6,6-diphenyl-3-phosphabicyclo-[3.1.0]hexane-3-oxides (**5a** and **c**)

Compound	**5a**	**5c**
Fragments	Relative intensity (%)	
M^+	45	26
$M—CH_3]^+$	7	10
$M—R]^+$ (281)	2	100*
$M—CH_3—POR]^+$ (219)	33	21
$M—CH_3—POR]^+—H$ (218)	100	84
$M—R—C_6H_5]^+$ (204)	12	16
$C_7H_7^+$ (91)	16	43
$C_6H_5^+$ (77)	10	11

* And/or $M—C_6H_5]^+$.

structure **6**, as chemical shifts characteristic for the five sp^3 skeleton carbon atoms could be found in the spectra (Table III). ^{13}C NMR signals due to sp^2 skeleton carbon atoms could not be observed. Products **5a** and **c** have been characterized also by ^{31}P, ^1H NMR, mass and IR spectroscopic methods. MS data are listed in Table IV.

The reason for the high tendency for diarylation is yet unclear and examination of this effect is in progress. Another surprising result on the Friedel–Crafts reaction of the dichlorocarbene adduct of cyclopentene has also been described. The isolated products from the reaction of 6,6-dichlorobicyclo[3.1.0]hexane with benzene in the presence of aluminum chloride were saturated cyclohexylbenzene derivatives suggesting a reductive type of Friedel–Crafts reaction.[9]

EXPERIMENTAL

^{31}P, ^1H and ^{13}C NMR spectra were taken on a JEOL FX 100 MHz instrument, operating at 40.26, 100.0 and 25.0 MHz, respectively. Chemical shifts are downfield, relative to 85% phosphoric acid and to tetramethylsilane, respectively, and have a positive sign. All coupling constants are given in Hertz. Infrared spectra were recorded on a SPECORD 75 spectrometer. Mass spectra were obtained on a JEOL-OLSG-2 instrument at 75 eV. 3-Phospholene-1-oxide dichlorocarbene adducts **1a, c** and **b** were prepared as described earlier.[3,10]

5- and 3-Methyl-3-acetyl-1-n-butyl-4-chloro-1,2,3,6-tetrahyrophosphinine-1-oxide, (**2Aa** and **2Ba**). A mixture of 0.5 g (1.96 mmol) of **1a**, 1 g (3.14 mmol) of mercury acetate and 25 ml of glacial acetic acid was heated at 82°C for 62 hours. After cooling, 50 ml of ice-water was added, the mixture was filtered, and the aqueous solution extracted three times with 60 ml of chloroform. The combined organic phases were neutralized with sodium bicarbonate solution, dried over sodium sulfate, and the solvent evaporated to give a crude product in about 70% conversion, containing the three isomers of **2** (52% of **2Aa** trans, 19% of **2Aa** cis and 29% of **2Ba** trans) according to ^{31}P NMR analysis. The components of the mixture were separated by repeated column chromatography on silica gel using chloroform–methanol (97:3), and benzene–acetone (4:6) as eluents, to give 0.02 g (4%) of the trans form of **2Ba** and 0.04 g (7%) of **2Aa** as the mixture of two diastereomers.

2Aa: ^{31}P NMR ($CDCl_3$) δ + 35.7 and +34.5 for the trans and cis diastereoisomers, respectively; ^{13}C NMR, Table I; ^1H NMR ($CDCl_3$) δ0.84–1.03 (m, 3H, C_3,—CH_3), 1.99 (s, 3H, C_5—CH_3), 1.12–1.90 (m, 6H, $(CH_2)_3$), 2.12 (s) and 2.15 (s) total int. 3H, $C_{2''}$—CH_3, 2.20–2.85 (m, 4H, CH_2), MS, Table II; IR (neat) 2930, 1725, 1365, 1220, 820 cm^{-1}.

2Ba: ^{31}P NMR ($CDCl_3$) δ + 37.5; ^{13}C NMR, Table I; ^1H NMR ($CDCl_3$) δ0.84–1.04 (m, 3H, C_3,—CH_3), 1.78 (s, C_3—CH_3) partly overlapped by 1.25–~1.90 (m, $(CH_2)_3$ total int. 9H, 2.08 (s, 3H, $C_{2''}$—CH_3) 2.17–3.03 (m, 4H, CH_2). 5.97 (dt, 1H, CH=, $^3J_{PH}$ = 23, $^3J_{HH}$ = 5); MS, Table II; IR (neat) 2930, 1720, 1360, 1215 cm^{-1}.

5- and 3,1-Dimethyl-3-acetyl-4-chloro-1,2,3,6-tetra-hydrophosphinine-1-oxide, (**2Ab** and **2Bb**) were prepared similarly from **1b**. The crude product was purified as described above to give a mixture, containing 44% of **2Ab**/trans, 34% of **2Ab**/cis and 22% of **2Bb**/trans, according to ^1H NMR analysis; Yield 27%; ^{13}C NMR, Table I; ^1H NMR ($CDCl_3$) δ1.57 (d, $^2J_{PH}$ = 13), 1.62 (d, $^2J_{PH}$ = 13), 1.70 (d, $^2J_{PH}$ = 13) for the P–CH_3 groups of the 3 isomers, 1.77 (s, C—CH_3(B)) total int. 3.66 H, 2.00 (s, 2.34 H, C—CH_3(A)), 2.07 (s, 0.66 H, $C_{2''}$—CH_3(B/trans)), 2.11 (s, 1.02 H, $C_{2''}$—CH_3 (A/cis)), 2.14 (s, 1.32 H, $C_{2''}$—CH_3 (A/trans)), 2.20–3.09 (m, 4H, CH_2). 5.97 (dt, 0.22 H, CH=(B), $^3J_{PH}$ = 19, $^3J_{HH}$ = 5); MS, *m/e* (relative intensity) 236 (M^+, 5), 193 (58), 177 (100), 176 (65); IR (neat) 2900, 1730, 1370, 1220 cm^{-1}.

The Reaction of 5- and 3-Methyl-1-n-butyl-4-chloro-3-hydroxy-1,2,3,6-tetrahydrophosphinine-1-oxide (**3a**) *with Acetyl Chloride.* To a solution of 0.23 g (0.973 mmol) of **3a**[4] (consisting of the **A** trans (47%), **A** cis (35%) and the **B** trans (18%) isomers) in 6 ml of pyridine was added slowly 0.69 g (9.73 mmol) of acetyl chloride at 0°C. The mixture was stirred at room temperature for 8 hours and was then allowed to stand overnight. The mixture was poured on ice, stirred and acidified with conc. hydrochloric acid. After extraction with 30 ml of chloroform, the organic phase was extracted four times with 20 ml of water. The chloroform solution was dried over sodium sulfate, the solvent was evaporated and the crude product was purified by column chromatography (as described above) to give 0.08 g (29%) of **2a** as a mixture of isomers, containing 49% of the **A** trans form, 45% of the **A** cis form and 6% of the **B** trans form.

1-Methyl-3,6,6-triphenyl-3-phosphabicyclo[3.1.0]hexane-3-oxide, (**5c**). A solution of 0.45 g (1.64 mmol) of **1c** and 0.66 g (4.92 mmol) of aluminium trichloride in 15 ml of dry benzene was refluxed for 6.5 hours. After cooling to 8°C 20 ml of benzene and 5 ml of ice water was added with stirring, and the organic phase was then separated and dried over sodium sulfate. The solvent was evaporated and the crude product was purified by column chromatography on silica gel using chloroform–methanol 98.5:1.5 to give 0.2 g (34%) of **5c** after recrystallization from *n*-hexane–ethyl acetate (95:5); m.p. 181–3°C; ^{31}P NMR ($CDCl_3$) δ + 60.6; ^{13}C NMR, Table III; ^1H NMR ($CDCl_3$) δ1.18 (s, 3 H, CH_3), 1.95–2.90 (m, 4 H, CH_2), 3.62–4.04 (m, 1 H, CH), 6.80–7.51 (m, 15 H, Ar); MS, Table IV; IR (KBr disc) 2920, 1580, 1430, 1180, 730 cm^{-1}.

3-n-Butyl-1-methyl-6,6-diphenyl-3-phosphabicyclo-[3.1.0]hexane-3-oxide, (**5a**) was prepared similarly from **1a**. Yield 17%. ^{31}P NMR ($CDCl_3$) δ + 72.4; ^{13}C NMR, Table III; ^1H NMR ($CDCl_3$) δ0.80 (s, 3 H, C_1—CH_3), 0.96 (m, 3 H, C_3,—CH_3), 1.10–3.38 (m, 10 H, CH_2), 3.38–4.30 (m, 1 H, CH), 6.65–7.58 (m, 10 H, Ar); MS, Table IV; IR (film) 2940, 1600, 1450, 1160, 740 cm^{-1}.

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