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Reaction of Dichlorocarbene with 1,2-Dihydro 1,2 λ^3-Azaphosphinine-Boranes : Dichlorocyclopropanation and Insertion into Boron-Hydrogen Bond.

Christian Bedel and André Foucaud*

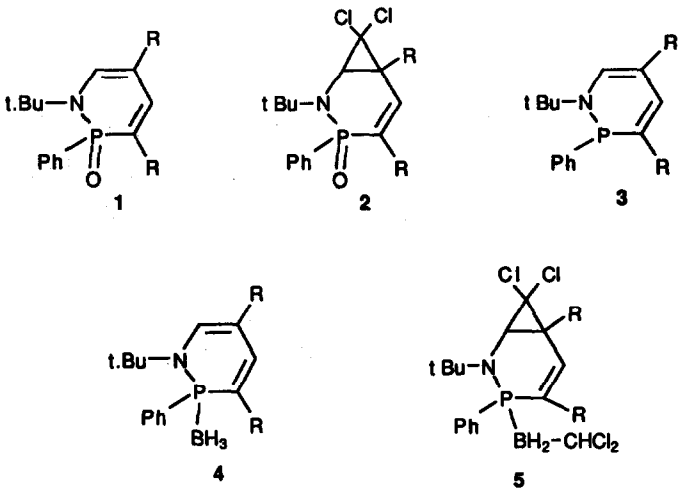
Laboratoire de Physicochimie Structurale, associé au CNRS, Université de Rennes, Campus de Beaulieu, 35042 Rennes, France.

Key words : Phosphine-boranes, cyclopropanation, carbene insertion into B-H bond.

Abstract - The reaction of dichlorocarbene with 1,2-dihydro 1,2 λ^3-azaphosphinine-boranes gave regioselective dichlorocyclopropanation and also insertion of dichlorocarbene into B-H bond. This insertion reaction is general and can be a useful synthetic method for the preparation of functionalized phosphine-boranes.

Recently, we have shown that the regioselective dichlorocyclopropanation of 1,2-dihydro 1,2-azaphosphinine 2-oxides **1** with dichlorocarbene afforded **2** [1]. However, the reaction of dichlorocarbene with 1,2-dihydro 1,2 λ^3-azaphosphinines **3** failed. We report here the synthetic approach to dichlorocarbene-azaphosphine adducts using azaphosphinine-boranes as P- protected starting products.

The phosphine-borane complexes can be obtained by reaction of phosphines with H_3B-SMe_2 [3,4]. The azaphosphinine-boranes **4** have been prepared in almost quantitative yield by the reaction of 1,2-dihydro 1,2 λ^3-azaphosphinines **3** [2] with H_3B-SMe_2 in dichloromethane [5]. The reaction of dichlorocarbene with **4** under phase transfer conditions gave the adducts **5** [6]. The regioselective cyclopropanation (addition of dichlorocarbene on C_5-C_6 double bond of **4**) was accompanied by insertion of dichlorocarbene into B-H bond to yield a dichloromethylsubstituted borane. When a shorter time of reaction of dichlorocarbene with **4a** was used (30 min.), **4a**, **5a** and **6** were obtained as major products. Compound **6**, which arises only from the cyclopropanation, was purified by chromatography on silica gel. Then, the formation of **6** shows that the cyclopropanation of **4a** is a faster reaction than the insertion reaction of dichlorocarbene into B-H bond.

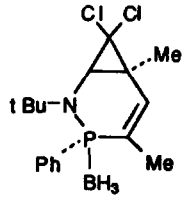


a : R = Me ; b : R = Et ; c : R = Pr

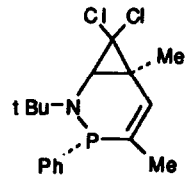
Table. Selected spectral data for **4**, **5**, **6** and **7** in $CDCl_3$

	^1H NMR δ (J_{PH}) (300 MHz)			^{13}C NMR δ (J_{PC}) (75 MHz)					^{31}P NMR	^{11}B NMR
Compd	H-4	H-6	$CHCl_2$	C-3	C-4	C-5	C-6	C-7	δ (121MHz)	δ (J_{BP}) (96 MHz)
4a	6.39	6.27		116.2	128.2	110.2	135.7		46.9	-34.8
	(23.5)	(11)		(60.7)	(7.5)	(8)				(63)
4b	6.49	6.25		121.1	127.8	118.6	133.9		45.6	-34.7
	(27)	(9)		(58.7)	(7.1)	(10.2)				(66)
4c	6.47	6.23		120.0	128.8	117.4	135.4		45.2	-34.6
	(25)	(11)		(58.0)	(7.3)	(8)				(69)
5aA[a]	6.35	2.91	5.74	129.9	136.2	33.5	49.6	70.1	23.2	-20.9
	(22)	(2.4)	(9)	(59.9)		(12.3)	(5.7)	(3.6)		(59)
5aB[a]	6.28	2.89	5.66						37.9	-22.9
	(21)	(3)	(12)							
5bA[a]	6.45	2.95	5.74	136.3	132.5	37.5	49.4	70.0	23.6	-20.7
	(24)	(4)	(8.5)	(56.8)		(12)	(4.9)	(4.7)		(60)
5cA[a]	6.44	2.93	5.75	134.4	131.8	36.9	49.4	70.1	23.5	-21.4
	(24)	(3)	(8)	(56.6)		(12)	(4.8)			(76)
6	6.14	3.02		128.5	130.9	34.5	51.4	69.7	39.2	-35.9
	(21.7)	(2.2)		(46)	(6)	(11)	(5.5)			(57)
7	5.79	2.88		138.0	127.1	35.7	49.6	70.8	8.2	
	(10)			(4.8)						

[a] The ^{13}C NMR signals of $CHCl_2$ of **5** (δ = 72 ppm) were broad.



6



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As dichlorocarbene may attack the double bond of **4** from the two sides of the diastereotopic face of the six membered ring, adducts **5** may be formed in two diastereoisomeric forms **A** and **B**, separated by chromatography (silica gel, 1 : 12 diethyl ether/petroleum ether). The **A** : **B** ratio determined on the crude reaction mixture by ^{1}H NMR was 10 : 1 for **5a** and 3 : 1 for **5b** and **5c**. Treatment of **6** with dichlorocarbene gave **5aA**. Structures of **4**, **5** and **6** were determined by IR, ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, ^{11}B NMR and MS spectral analyses (table). Mass spectra indicate M^+ and $[M\text{-}BH_3]^+$ for **4** and $[M\text{-}BH_2CHCl_2]^+$ for **5**. Furthermore, the borane group of the major isomer **5a A** should be readily removed by treatment with diethylamine to give **7** with retention of configuration at phosphorus atom [7]. Oxidation of **7** with H_2O_2 yielded **2aA**, identical with major isomer obtained by the cyclopropanation of **1a** [1]. It has been shown by single crystal X-ray crystallography that the cyclopropane ring and the phenyl group of **2aA** are on the opposite side of the six membered ring [1]. The higher preference for the formation of the isomer **A** can be explained by the prefered addition of the dichlorocarbene on the less sterically hindered face of the ring of **4**. When the steric requirement of the R group increases, the repulsive interaction between C_5-R group and phenyl group in the transition state increases and the **A**:**B** ratio decreases.

This unprecedented insertion reaction of dichlorocarbene into B-H bond of phosphine-boranes is general. Thus, the phosphine-borane complexes **8a-c** were prepared according to the procedure reported for complexes **4**. The reaction of dichlorocarbene with **8** was accomplished using the procedure reported for the preparation of **5**. At room temperature for 30 min., **8a** gave **9a** (60 %). In the same conditions, **8b** was converted to **9b** in 62 % yield. When the reaction of dichlorocarbene with **8b** was performed at 40°C for 30 min, a mixture of **9b** (30 %) and **10b** (40 %) was obtained. The triisopropylphosphite-borane **8c**, treated with dichlorocarbene at 40°C for 1 h gave a mixture of **9c** (40 %) and **10c** (60 %). **9** and **10** were separated by flash chromatography on silica gel (ether - petroleum ether) [8].

$R_3P—BH_3$ **8** a-c

$R_3P—BH_2—CHCl_2$ **9** a-c

$R_3P—BH(CHCl_2)_2$ **10** b-c

a : R = Ph ; b : R = 4.Me-C_6H_4 ; c : R = iPrO

In conclusion, the regioselective dichlorocyclopropanation of 1,2-dihydro 1,2 λ^3-azaphosphinine has been achieved. We have also found that the insertion reaction obtained from treatment of phosphine-boranes with dichlorocarbene can be a new and general method for the preparation of functionalized boranes.

References and notes :

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Schmidbauer, H. ; Wimmer, T. ; Lachmann, J. ; Müller, G. *Chem. Ber.* **1991**, *124*, 275.

5 The typical procedure is as follows : a solution of azaphosphinine **3** (2 mmol) in dry CH_2Cl_2 (15 ml) was added to a 1M solution of H_3B-SMe_2 (2 ml), the mixture was heated to reflux for 1 h, then the solvant was evaporated to provide **4**.

6 A solution of **4** (1 mmol) and triethylbenzylammonium chloride (50 mg) in alcohol free chloroforme (10 ml) was added to 50 % aqueous sodium hydroxide (3.2 g). The mixture was stirred at 40°C for 2 h. The organic layer was separeted, washed with water and dried. The solvent was evaporated off and **5** was purified by chromatography on silica gel.

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8 Selected data for **9** and **10**. **9a**, F = 134°C. ^1H NMR δ 5.53 (1H, dt, J = 6, 5.8 Hz, C<u>H</u>Cl_2). ^{31}P NMR δ 20.2 ; ^{11}B NMR δ -22.3. **9b** oil, ^1H NMR δ 5.49 (1H, dt, J = 5.6, 5.6 Hz, C<u>H</u>Cl_2). ^{31}P NMR δ 9.2 ; ^{11}B NMR - 22.4. **9c** oil. ^1H NMR δ 5.56 (1H, dt, J = 4.4 Hz, C<u>H</u>Cl_2) ; ^{31}P NMR δ 88.6 ; ^{11}B NMR - 12.02. **10b** F = 157°C. ^1H NMR δ 5.56 (1H, dd, J = 10.4 Hz, C<u>H</u>Cl_2). ^{31}P NMR δ 8.46 ; ^{11}B NMR δ -12.02. **10c** oil. ^1H NMR δ 5.67 (1H, dd, J = 16,4 Hz, C<u>H</u>Cl_2). ^{31}P NMR δ 74.7 ; ^{11}B NMR δ = -23.5. These compounds have satisfactory analytical data.

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