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FORMATION OF AMMONIOPHOSPHORANES BY TRANSANNULAR INTERACTION IN DIBENZ[c,f][1,5]AZAPHOSPHOCINE SYSTEM

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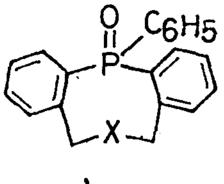
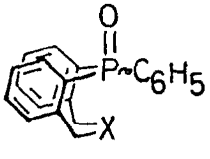
Abstract Dibenz[c,f][1,5]azaphosphocine 12-oxide derivatives (1a, 3) and their related compounds were prepared and NMR spectral change of these samples by the addition of SOCl$_2$ or t-BuMe$_2$SiOTf are reported. The NMR parameters (^{1}H and ^{31}P) are consistent with bicyclic phosphoranes for at least 1a' and 3', each contains a transannular hypervalent Cl-P-NMe bond.

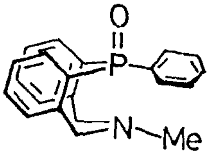
The concept of hypervalent bond[1] and the syntheses of various hypervalent organic compounds of typical elements[2] have elicitted high interest among physical-organic chemists recently. In this connection, we showed the formation of several 10-S-4 sulfuranes which visualized stepwise the transition state of the attack of a nucleophile at the sulfonium group by means of transannular interaction between the sulfur and the nitrogen atoms in dibenzo[b,g][1,5]thiazocine derivatives.[3] Recently, formation of 10-P-5 phosphatranes by transannular interaction between the phosphorus and the nitrogen atoms of bicyclic amine phosphate was verified by means of ^{31}P NMR spectral analysis by Verkade et al.[4]

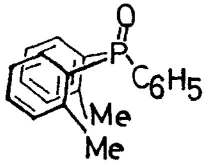
In order to examine the problem using our own model, we prepared the requisite 5,6,7,12-tetrahydro-12-phenyl-6-methyldibenz[c,f][1,5]azaphosphocine 12-oxide (1a) and related phosphine oxides (1b,c),[5,6] which have the corresponding skeleton to sulfuranes.[3] The spectral features of the phosphine oxide (1) indicate that only a single conformer of eight-membered ring is present in these heterocycles[3,7] and the preferred conformer of 1 is confirmed to exist as TB or BB form.[8] They do not show any temperature dependence in ^{1}H NMR spectrum from -50 °C to 35 °C. Petrov and his coworkers suggested that the most symmetrical conformation (BB form) is the most stable one on the basis of an examination of Stuart-Briegleb models and chemical behaviors of 1.[5] The relative stereochemistry at the phosphorus


1a-c

	X
1a	N-Me
1b	S
1c	O


1 TB or BB

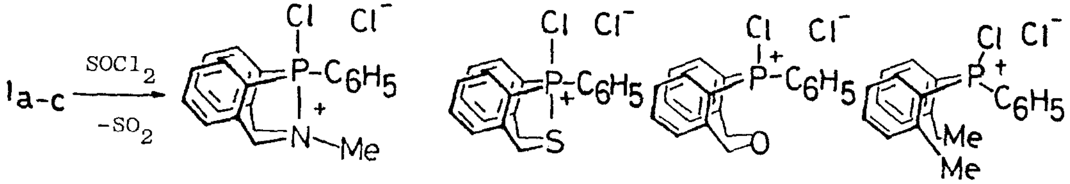

1a


2

atom of 1a was determined by ^1H NMR spectral considerations. The proton of N-methyl group appears at very high field (δ 1.29) which is readily ascribed to the ring current effect of the benzene ring substituted at the phosphorus atom. Therefore, the phenyl group must occupy the quasi-axial position of TB form of 1a.

When a molar equivalent of $SOCl_2$ was added to 1a in CD_3CN solution, there were observed a strong upfield shift of the ^{31}P NMR peak from δ 26.0 to δ -8.3 and distinct downfield shift of the N-CH_2 and N-Me signals in the ^1H NMR spectrum. On the other hand, the reference compound (2) showed a strong downfield shift of ^{31}P NMR peak from δ 34.5 to δ 50.7 by the same treatments (Table I). The spectral features of 1a are consistent with the formation of the ammoniophosphorane (10-P-5 species) as illustrated by 1a'[4] and they did not change even in the presence of excess $SOCl_2$.

When a molar equivalent of $SOCl_2$ was introduced into a CD_3CN solution of 1c, both the ^{31}P ($\Delta\delta$ = 14 ppm) and CH_2-peaks in the NMR spectra appeared at more downfield position. This behavior is analogous to that of conversion of 2 into a phosphonium salt (2': $\Delta\delta$ = 16 ppm). On the other hand, addition of $SOCl_2$ into a CD_3CN solution of 1b showed almost no apparent change of the ^{31}P NMR peak but a distinct downfield shift of CH_2 peak in the ^1H NMR spectrum, which shows that 1b' is intermediate between phosphonium and phosphorane character. According to the ^{31}P chemical shift along with the ^1H NMR spectra, the effectiveness of the donor for making hypervalent phosphorus species is in the following order in this system, i.e., N-Me $>$ S $\gg$ O.



1a' , 1b' , 1c' 2'

In the next step, P-Me derivative (3)[9] was prepared from methylphosphonous dichloride by the same methodology as that of 1a. The P-Me proton appears as a doublet (J = 14.3 Hz) at δ 1.91 and N-Me proton does as a singlet at δ 2.34 in $CDCl_3$ solution, respectively. The N-Me proton is located at ca. 1 ppm downfield relative to its counterpart (1a) due to the absence of extra anisotropic effect by P-phenyl group. This fact certifies the assigned relative configuration at the phosphorus of 1 and 3.

Addition of a molar equivalent of $SOCl_2$ to 3 in CD_3CN solution shows the following NMR spectral changes similarly to 1a; a ^{31}P peak is shifted from δ 26.8 for 3 to δ -12.1 for 3' and both N-Me and N-CH_2 signals for 3' are moved to downfield relative to that for 3 (Table II). Addition of 1 equiv of t-$BuMe_2SiOTf$ to 3 in CD_3CN solution gave rise to a new upfield peak in the ^{31}P NMR spectrum at δ 17.6 (3''). The ^{31}P NMR spectrum of the

Table I. Selected ^{31}P and ^{1}H NMR Spectral Data of **1a**-**c** and Their Change with $SOCl_2$

compd	^{31}P NMR (δ[a], CD_3CN) with[b]			^{1}H NMR of CH_3 or CH_2 (δ, CD_3CN) with[b]		
	nothing	$SOCl_2$	effect[c]	nothing[d]	$SOCl_2$	effect[c]
1a	26.0	-8.3	upfield	1.29 3.28 3.69 (ABq)	1.90 4.17 4.31 (ABq)	downfield
1b	24.8	24.7	unchanged	3.63 3.81 (ABq)	4.31(s)	downfield
1c	28.2	42.2	downfield	4.45	4.91	downfield
2	34.5	50.7	downfield	2.51	2.43	

[a], ext. ref.: H_3PO_4. [b], addition of 1 molar equiv. [c], shift of the corresponding peak relative to that in the absence of $SOCl_2$. [d], measured in $CDCl_3$ solution.

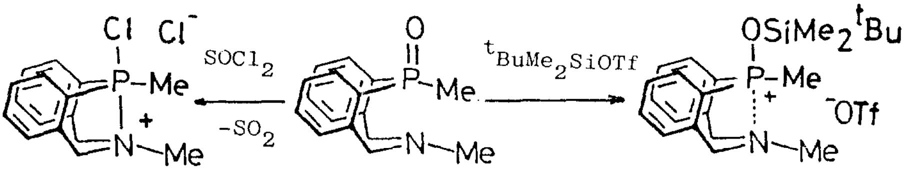
Table II. Selected ^{31}P and ^{1}H NMR Spectral Data of **3** and **4** and Their Change with t-$BuMe_2SiOTf$ and $SOCl_2$

compd	^{31}P NMR (δ[a], CD_3CN) with[b]			
	nothing	t-$BuMe_2SiOTf$	$SOCl_2$	effect[c]
3	26.8	17.6	-12.1	upfield
4	32.2	61.5	71.1	downfield

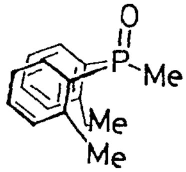
compd	^{1}H NMR (δ, CD_3CN) N-CH_3 with[b]			P-CH_3 with[b]			
	nothing[d]	t-$BuMe_2SiOTf$	$SOCl_2$	nothing[d]	t-$BuMe_2SiOTf$	$SOCl_2$	effect[c]
3	2.34	2.43	3.06	1.91	2.26	2.93	downfield
4	—	—	—	2.01	2.63	3.09	downfield

[a], ext. ref.: H_3PO_4. [b], addition of 1 molar equiv. [c], shift of the corresponding peak relative to that in the absence of additive. [d], measured in $CDCl_3$.

reference compound (**4**: δ 32.2) was shifted into downfield from δ 61.5 to δ 71.1 by the change of additive from t-BuMe$_2$SiOTf to SOCl$_2$. These facts are probably caused mainly by the change of hybridization of phosphorus atom which is assisted by absorption of electron from participating bonds. The present conclusion is consistent with the formation and character of hypervalent bond.[1-4]



3' **3** **3''**



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6) **1a**: mp 205-207 °C; ^{1}H NMR (δ, CDCl$_3$) 1.29 (s, 3H), 3.28 and 3.69 (ABq, J=14.8 Hz, 4H), 7.0-7.6 (m, 11H), and 8.6-8.9 (m, 2H); Mass (m/e) 333 (M$^+$, 100%), 318 (M$^+$-15, 51%), 291 (M$^+$-42, 42%). **1b**: mp 190-193 °C (lit^5 193-195°C); ^{1}H NMR (δ, CDCl$_3$) 3.63 and 3.81 (ABq, J=14.0 Hz, 4H), and 7.0-7.9 (m, 13H); Mass (m/e) 336 (M$^+$, 100%). **1c**: mp 204-208 °C (lit^5 217-219 °C); ^{1}H NMR (δ, CD$_3$CN) 4.45 (s, 4H), 7.1-7.7 (m, 11H), and 8.5-8.8 (m, 2H); Mass (m/e) 320 (M$^+$, 100%), 291 (M$^+$-29, 50%), 226 (M$^+$-94, 76%). **2**: mp 124-127 °C (lit^5 135-137 °C); ^{1}H NMR (δ,CDCl$_3$) 2.51 (s, 6H) and 6.9-7.8 (m, 13H). **1a'**: ^{1}H NMR (δ, CD$_3$CN) 1.90 (s, 3H), 4.17 and 4.31 (ABq, J=15.8 Hz, 4H), 7.2-8.0 (m, 11H), and 8.6-8.9 (m, 2H). **1b'**: ^{1}H NMR (δ, CD$_3$CN) 4.31 (s, 4H), 7.0-7.9 (m, 11H), and 8.4-8.7 (m, 2H). **1c'**: ^{1}H NMR (δ, CD$_3$CN) 4.91 (s, 4H), 7.2-8.1 (m, 11H), and 8.4-8.8 (m, 2H).

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8) The description of "TB" and "BB" refers to "twist boat" and "boat boat" conformations in eight-membered ring.[3,7]

9) **3**: mp 69.0-70.5 °C; ^{1}H NMR (δ, CDCl$_3$) 1.91 (d, ^{2}J(PCH)=14.3 Hz, 3H), 2.34 (s, 3H), 3.58 and 3.84 (ABq, J=15.1 Hz, 4H), 7.1-7.7 (m, 6H), and 8.4-8.7 (m, 2H); Mass (m/e) 271 (M$^+$, 60%), 256 (M$^+$-15, 80%), 242 (M$^+$-29, 48%), 229 (M$^+$-42, 100%). **4**: ^{1}H NMR (δ, CDCl$_3$) 2.06 (d, ^{2}J(PCH)=13.0 Hz, 3H), 2.33 (s, 6H), and 7.1-7.8 (m, 8H); Mass (m/e) 244 (M$^+$, 23%), 228 (M$^+$-16, 100%). **3'**: ^{1}H NMR (δ, CD$_3$CN) 2.93 (d, ^{2}J(PCH)=13.4 Hz, 3H), 3.06 (s, 3H), 4.49 and 4.85 (ABq, J=15.7 Hz, 4H), and aromatic signals. **3''**: ^{1}H NMR (δ, CD$_3$CN) 2.26 (d, ^{2}J(PCH)=13.9 Hz, 3H), 2.43 (s, 3H), 3.92 (brs, 4H), and aromatic signals.

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