Tetrahedron Letters,Vol.30,No.52,pp 7411-7414,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

CATIONIC RING OPENING OF FUNCTIONALIZED DIPHOSPHIRANES :

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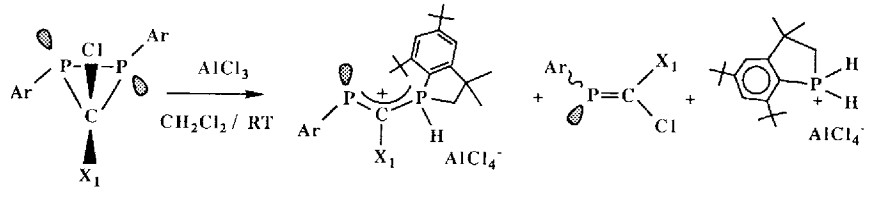
Abstract : *The functionalized diphosphiranes **1a-c**, in presence of Lewis acid, undergo two kinds of reaction:the ring opening leading to the phosphenium-phosphonium ion **2a-c** obtained according to an electrocyclic reaction and the fragmentation giving phosphaalkene **3a-c** and phosphonium ion **4**. The deprotonation reaction of **2a-c** in hexane leads to phosphino-phosphaalkenes **6a-c**.*

Owing to the leaving groups on the intracyclic carbon, and the presence of bulky substituents on the phosphorus atoms, the functionalized diphosphiranes are convenient models for the study of P-P bond rupture (1,2). Recently, we have demonstrated that the anionic ring opening leads to the 1,3-diphosphapropenes *via* the detectable 1,3-diphosphaallyl anion intermediate (3), whereas the photochemical ring opening is the main reaction leading to the functionalized 1,3-diphosphapropenes via the diphosphiranyl and 1,3-diphosphaallyl radical intermediates (4).

Today we report the action of Lewis acid on the functionalized diphosphiranes **1a-c** giving rise to the cationic ring opening reactions.

When one equivalent of aluminium trichloride is added to **1a-c** in anhydrous solution of dichloromethane, no reaction occurs at low temperature (-78° C), but two competitive reactions (reaction A) are observed when the temperature rises 0° C :

- the ring opening reaction leading to **2a-c** as main products,
- the fragmentation reaction giving the phosphaalkenes **3a-c** and the phosphonium **4**.



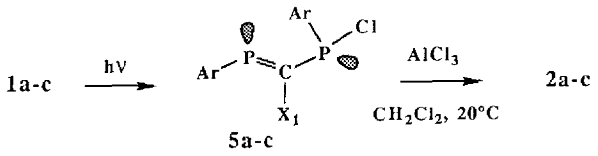
1a-c **2a-c** **3a-c** **4**

Reaction A

	a	b	c
X_1	Cl	Ph	CH_3

Ar : 2,4,6 -Tri -*tert* - butylbenzene

In order to determine the nature of the intermediate involving in this reaction, we have studied the action of $AlCl_3$ on 1,3-diphosphapropenes **5a-c** obtained by photochemical ring opening (4) of the corresponding diphosphirane **1a-c** (reaction B).



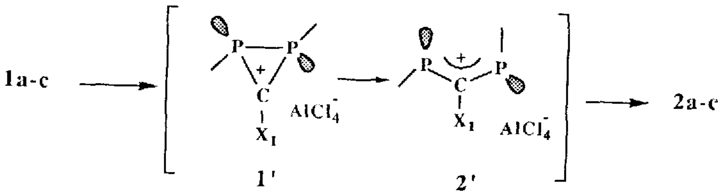
Reaction B

This reaction, already observed by Karsch and coll. (5), leads to the same compounds **2a-c** without the by-products **3** and **4**.The structures of **2** and by-products are confirmed by ^{31}P (Table I, and ref.6) and ^{27}Al NMR. The presence of $AlCl_4^-$ is detected in each case (δ ^{27}Al : 103 ppm).

^{31}P / compounds	a				b				c			
	$\delta_{P(A)}$	$\delta_{P(X)}$	J_{PP}	J_{PH}	$\delta_{P(A)}$	$\delta_{P(X)}$	J_{PP}	J_{PH}	$\delta_{P(A)}$	$\delta_{P(X)}$	J_{PP}	J_{PH}
5	276	75	106		272	84	161		273	84	143	
2	342	25,4	133	532	333	25,4	207	508	348	24	166	532
6	284	20	266		268	17	248		278	6	305	

Table I : ^{31}P NMR parameters of compounds **5a-c**, **2a-c** and **6a-c**.

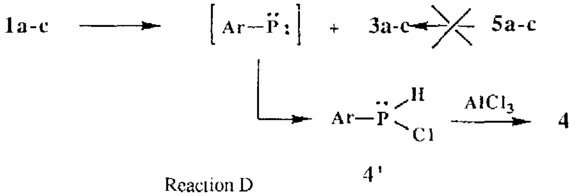
Compound **2** is formed *via* the presumed diphosphiranium ion **1'** and diphosphaallyl **2'** cations after the cationic rupture of extracyclic C-Cl bond inducing the preferential P-P bond rupture (reaction C). Contrarely to the photochemical (4) or anionic (3,7) ring opening reactions, the cationic intermediates are not detected.



Reaction C

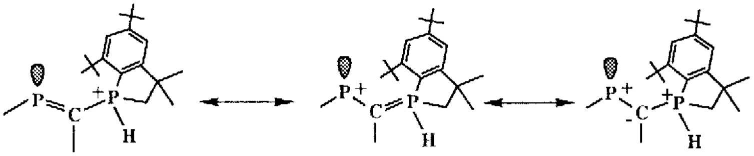
This result confirms the instability of the phosphenium ion with two carbon atoms as substituents. Thus the oxidative addition of tert-butyl group to a proximal electropositive center leading to phosphonium ion (thermodynamically more favourable) occurs after the ring opening.

The presence of phosphaalkene **3a-c** and phosphonium ion **4** as by-products only arise from a fragmentation reaction of the starting diphosphirane **1a-c** without any C-Cl bond rupture and allylic intermediate. The unstable phosphinidene generated (in the triplet state) by this reaction, was stabilized by an oxidative addition and leads to the chlorophosphane intermediate **4'**, which in presence of unreacted $AlCl_3$ gives the phosphonium ion **4** (reaction D).



Reaction D

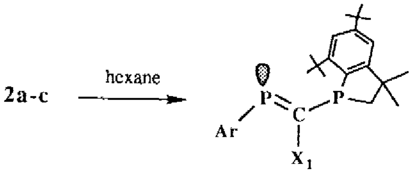
According to the ${}^{2}J_{PP}$ values, the products **2** have a trans configuration around the double bond and their structure in solution in dichloromethane, benzene or toluene can be described as a resonance structure between phosphaalkene-phosphonium ion (I), phosphenium ion-phosphorane (II) and phosphenium-phosphonium ions (III).



(I) (II) (III)

The dicoordinated phosphorus atoms of **2a-c** are more deshielded than the chemical shift of λ^3,σ^2 phosphorus compounds (phosphaalkenes **3** and 1,3-diphosphapropenes **5** and **6**). This important shift ($\Delta\delta$ = 60 ppm) indicates a phosphenium character for the P_A (8). Moreover, the chemical shift of tetracoordinated phosphorus atom (P_B) and the magnitude of the ${}^{1}J_{PH}$ coupling constants around 520 Hz, are characteristic of phosphonium compounds (9). Consequently, the mesomeric form (III) should be the most important of the resonance structures. Similar situation is observed for the mesomeric triphosphonium dications (10).

The compounds **2a-c** are soluble in dichloromethane and more surprisingly in benzene and toluene in which they are stable during few months at room temperature. On the other hand, **2a-c** in hexane undergo instantaneously a deprotonation reaction leading to 1,3-diphosphapropenes **6** (reaction E).

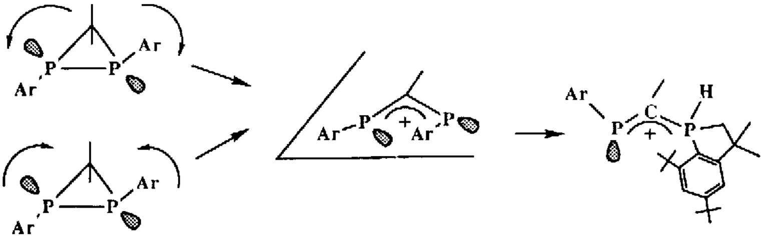


6a-c

Reaction E

This reaction related to equilibrated reactions between phosphonium $\rightleftharpoons$ phosphine, has yet been observed by Fluck (11) in acidic media.

The ring opening of diphosphiranes belongs to the class of electrocyclic reactions. As predicted on theoretical grounds, the cationic ring opening occurs by a disrotatory process. The two possible disrotatory processes give the same allyl intermediate (with exo-endo Ar substituents) leading to either trans or cis isomer. We obtained only the trans isomer. This observation is consistent with a selective oxidative addition on the phosphorus atom bearing the tert-butyl group in the endo position.



Disrotatory pathways leading to the trans phosphenium-phosphonium **2**

Acknowledgements

We thank Dr I. Tkatchenko (Laboratoire de Chimie de Coordination) for his hospitality in his laboratory and the CNRS (GRECO Basses Coordinences) for their financial support.

References

1) G. Etemad-Moghadam, J. Bellan, C. Tachon and M. Koenig, Tetrahedron (1987), 43, 1793.
2)M. Gouygou, J. Bellan, J. Escudié, C. Couret, A. Dubourg, J.P. Declercq and M. Koenig, J. Chem. Soc. Chem. Commun. (1989), 593
3) M. Gouygou, C. Tachon, M. Koenig and G. Etemad-Moghadam, New J. Chem (1989), 13, 315.
4)M. Gouygou, C. Tachon, A. Dubourg, J.P. Declercq, J. Jaud, G. Etemad-Moghadam and M. Koenig (submitted to publication).
5) a- H.H. Karsch, H.U. Reisacher and G. Müller, Angew. Chem. Int. Ed. Engl. (1986), 25, 454.
b- H.H. Karsch, F.H. Köhler and H.U. Reisacher, Tetrahedron Letters (1984), 25, 3687.
6) ^{31}P NMR parameters in C_6D_6, δ : **3a** (232.3); **3b** (228.1, Z isomer) and (238.8, E isomer); **3c** (224.8, E isomer) and (225.3, Z isomer); **4** (-17.6, J_{PH} = 521 Hz); **4'** (23.8, J_{PH} = 214 Hz).
7) M.Gouygou, C.Tachon, R.El Ouatib, O. Ramarijaona, G. Etemad-Moghadam and M. Koenig, Tetrahedron Letters (1989), 30, 177.
8) a- M.G. Thomas, C.W. Schultz and R.W. Parry, Inorg. Chem. (1977), 16, 994.
b- K. Dimroth and P. Hoffmann, Chem. Ber. (1966), 1325.
c- A.H. Cowley, Chem. Rev. (1985), 367.
9) G.A. Olah and C.W. Mc Farland, J. Org. Chem. (1969), 34, 1832.
10) G.H. Birum and C.N. Matthews, J. Amer. Chem. Soc.(1966), 88, 4198.
11) G. Heckmann, B. Neumüller and E. Fluck, Z. Anorg.Allg.Chem. (1987), 554, 146.

(Received in France 29 September 1989)