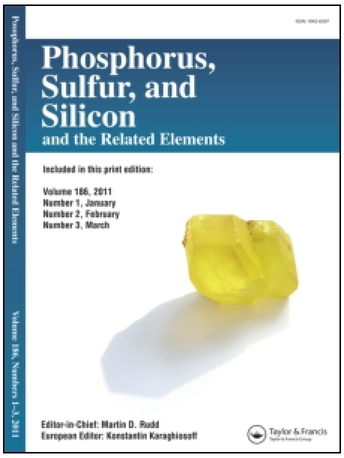

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Reactivity of Diphosphene towards Oxygen and Diazo Derivatives: New Method of Obtaining Stable Diphosphiranes

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To cite this Article Koenig, Max , Etemad-moghadam, Guita , Tachon, Christine and Bellan, Jacques(1987) 'Reactivity of Diphosphene towards Oxygen and Diazo Derivatives: New Method of Obtaining Stable Diphosphiranes', Phosphorus, Sulfur, and Silicon and the Related Elements, 30: 1, 425 — 428

To link to this Article: DOI: 10.1080/03086648708080611

URL: http://dx.doi.org/10.1080/03086648708080611

Phosphorus and Sulfur, 1987, Vol. 30, pp. 425–428
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REACTIVITY OF DIPHOSPHENE TOWARDS OXYGEN AND DIAZO DERIVATIVES : NEW METHOD OF OBTAINING STABLE DIPHOSPHIRANES.

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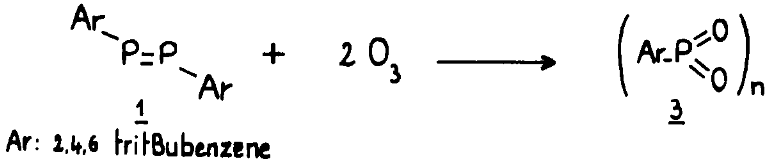
Abstract Different aspects of the reactivity of the diphosphene are presented : reactivity of the lone pair and/or reactivity of the double bond.

In the reactivity of diphosphenes, competition exists between the three possible reaction sites, the two phosphorus lone pairs and the double bond. In order to show these different possibilities, we have on the one hand oxidised the diphosphene by ozone and singlet oxygen and on the other hand reacted it with diazo derivatives.

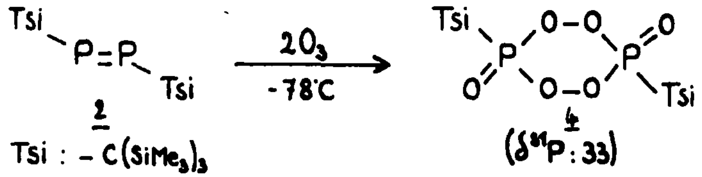
1 - OZONOLYSIS

Ozone reacts on diphosphene at low temperature with a 2:1 (ozone : diphosphene) stoichiometry. In all cases the reaction is fast, leading to the breaking of Phosphorus-Phosphorus double bond as well as the oxidation of the phosphorus lone pairs (1) (reactions A) :

(A_1)



(A_2)



2 - ACTION OF SINGLET OXYGEN ($^1O_2$)

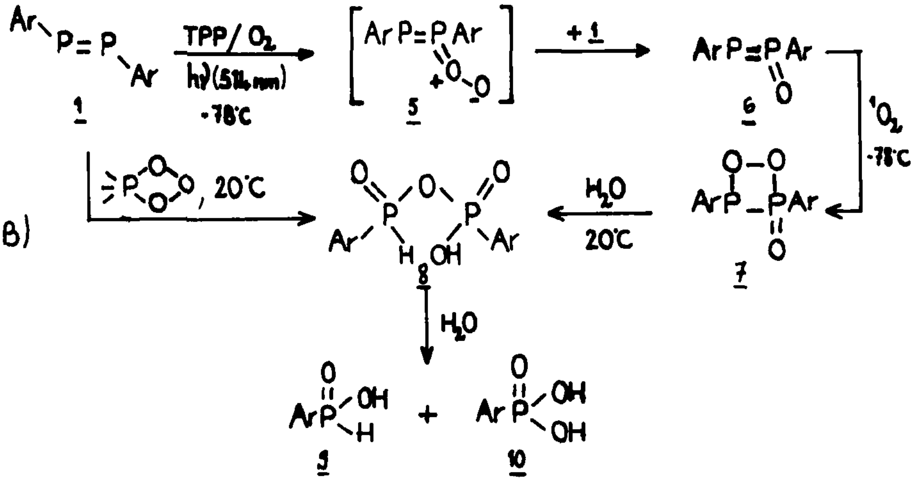
Singlet oxygen produced chemically from different phosphorus ozonides or produced photochemically (sentitizer : tetraphenylporphine (TPP) or sensitox II) reacts on the diphosphene 1 (2) (reaction B).

At room temperature, the action of singlet oxygen leads after breaking of the P-P double bond, to the formation of the anhydride 8 which slowly hydrolyses to give the corresponding phosphinic acid 9 and phosphonic acid 10.

The photo oxidation of 1 (TPP, λ = 514 nm) at -78 °C leads to diphosphene oxide 6 (3) and dioxodiphosphetane 7.

The compound 7 (δ_1 = 5.9 δ_2 = 55.8 J_{PP} = 159 Hz) is stable for several days at -78 °C. At room temperature, it decomposes and hydrolyses to give the corresponding acids 9 and 10.

(B)



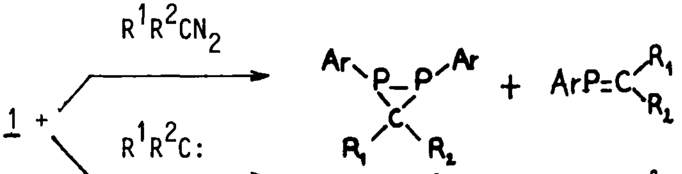
Compounds	3	4	6	7	8	9	10
$\delta^{31}P$ δ_1	13 30 18	+33	70	6,9	15.8	24,7	26,9
δ_2			206	55,8	18,3		
J_{PP} Hz			684	159	21		
J_{PH} Hz					627	580	

Table 1 : ^{31}P NMR parameters of compounds 3-10

3 - REACTIONS WITH DIAZO DERIVATIVES AND CARBENES

In the light of results obtained on the phosphaalkenes (4), we have reacted the diazo derivatives and the halocarbenes with the trans diphosphene 1 in the following reaction (C) (5, 6) :

(C)



11a-f

12 a-f

a : $R^1 = R^2 = H$

b : $R^1 = R^2 = Ph$

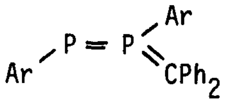
c : $R^1 = R^2 =$ 9-fluorenyl

d : $R^1 = R^2 = Cl$

e : $R^1 = R^2 = Br$

f : $R^1 = Ph$; $R^2 = Br$

The reaction in all cases produces diphosphirane (80%) and phosphaalkene (20%). During the reaction of the diphenyldiazomethane, the presence of the intermediate 13 was detected by NMR ^{31}P.



13

$\delta_A = 208{,}4$

$\delta_B = 66{,}7$

$^1J_{PP} = 676$ Hz

The values of $\delta^{31}P$ and $\delta^{13}C$ for the phosphorus atoms and for the intracyclic carbon are strongly shifted towards high field as in the case of the cyclopropanes and their analogues (7, 8) :

$$-141 < \delta^{31}P < -49$$
$$29.8 < \delta^{13}C < 30.8 \text{ and } {}^{1}J_{CP} \approx 20 \text{ Hz}$$

The trans configuration of the Ar substituents in the diphosphiranes imply that the cycloaddition reaction is stereoselective.

The absence of the cycloaddition adduct [2+3](4) and the fact that the cyclopropanation reactions only take place under conditions in which carbenes are formed (heating and/or irradiation of the diazo derivatives), lead us to consider the diphosphiranes as the result of the attack of the carbenes on the diphosphene.

Compounds	a	b	c	d	e	f
$\delta^{31}P$ 11	-141.0 $^{2}J_{PCH}$= 14Hz	-74	-59.2	-68.8	-70.35	δ_A=-49.2 δ_B=-77.9 $^{1}J_{PP}$=168Hz
$\delta^{31}P$ 12	289	241	253.5	232	269	

Table 2 : $\delta^{31}P$ NMR parameters of diphosphiranes 11 and phosphaalkenes 12

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