Tetrahedron Letters, Vol 32, No 42, pp 5965-5968, 1991
Printed in Great Britain

0040-4039/91 $3 00 + 00
Pergamon Press plc

Sonochemistry in the Diphosphirane Series

G. Etemad-Moghadam[a], M. Rifqui[a], P. Layrolle[a], J. Berlan[b], and M. Koenig[a]

a) Laboratoire de Molécules Phosphorées, URA 454 - Université Paul Sabatier, 31062 Toulouse - France

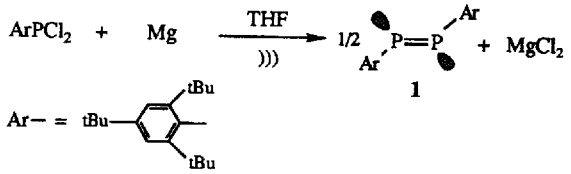
b) Laboratoire de synthèse organique en milieux polyphasiques, Institut de Génie Chimique, Chemin de la Loge, Toulouse - France

Key Words Ultrasound - Diphosphene - Diphosphirane - Cyclopropanation - Substitution

Abstract Sonication improves substantially the rate of formation of diphosphene 1 with respect to standard procedures The cyclopropanation of 1 using sonochemical generation of methylene or halogeno-carbenes constitutes an interesting alternative in the diphosphirane synthesis Furthermore, ultrasonic effects in a chlorinated solvent allow the first substitution of a diphosphirane without ring-opening

Significant progress has been made recently both in the understanding [1] and on the practical uses of high intensity ultrasonic waves in organic synthesis [2,3] However, there have been only few reports in phosphorus chemistry [4] In this paper, we report our preliminary study concerning the effects of ultrasound on the formation of multiple bonds (diphosphene synthesis), and the cyclopropanation and substitution reactions

The diphosphene **1**, a phosphorus analogue of alkenes, has been synthesized in 1981 by Yoshifuji [5] This heterogeneous reaction involving magnesium metal and dichloro-2,4,6-tritertiobutyl-phenyl phosphine constitutes a good example for the study of the influence of sonic parameters governing the sonochemical effects We have examined the influence of temperature and concentration upon the rate of formation of diphosphene **1**.



In the range - 40 °C to 20 °C, we have compared the amount of **1** at different temperature after 30 minutes irradiation of the reacting mixture (argon saturated 0 25 M solution of the dichlorophosphine and magnesium turnings), using a microtip-horn (3 mm) [6] The amount of **1** was determined by ^{31}P NMR spectroscopy, and is compared with that obtained under magnetic stirring (Figure 1) It can be seen that sonication improves substantially the yield of formation of the diphosphene (65 % at 5 °C) with respect to standard procedures (22 % at 20 °C) While, under stirring, the yield decreases with the reaction temperature, under sonication an optimum is observed at 5 °C This complex effect of the temperature on sonochemical reactions is now well understood [7]

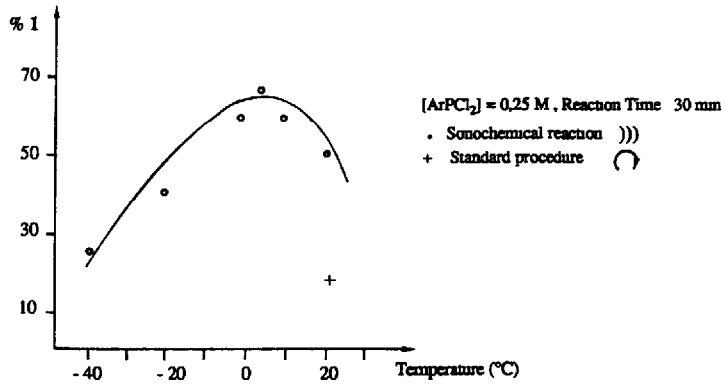


Figure 1 Percentages of diphosphene **1** vs temperature

Whereas no noticeable effect of the concentration of dichlorophosphine on the rate of formation of **1** was observed under stirring, with ultrasounds the amount of **1** increases from 38 to 65 % when the concentration decreases from 0 66 to 0 25 M Depending on the nature of the ultrasound generator, microtip or cup horn,[6] the amount of **1** is about 2 or 4 times higher than under standard conditions, respectively (Table 1)

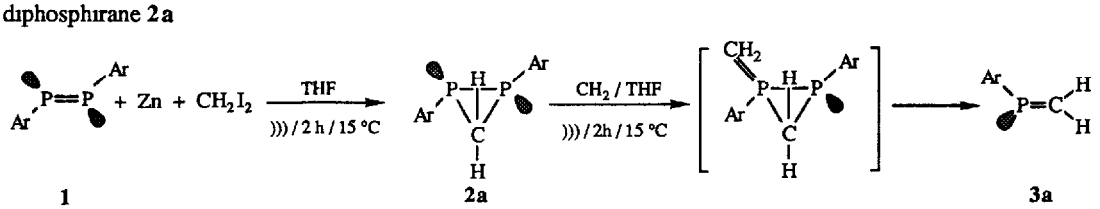
Conditions	Reaction Time (mn)	Temperature (°C)	[$ArPCl_2$] (M)	% $ArPCl_2$	% 1
◠	30	20	0 25	78	22
))) microtip	30	20	0 25	51	49
))) Cup Horn	30	15	0 25	6	94

Table 1 Influence of the ultrasound generator

In this text, we use the now admitted symbol))) for sonication, and◠ for "silent" or non-sonochemical stirred reactions

Thus, ultrasound irradiation increases the rate of formation of diphosphene **1** but no noticeable effect on the maximum overall yield of the reaction is observed.

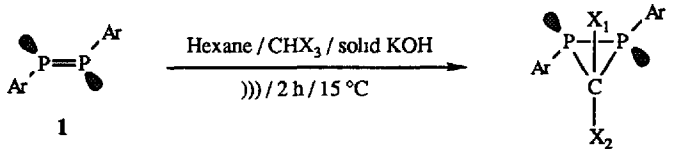
Starting from **1**, we have attempted some cyclopropanation under sonication The Simmons-Smith cyclopropanation does not proceed readily unless the zinc is previously activated [8] The advantage of ultrasonic irradiation in the activation of zinc has been shown in the cyclopropanation of olefins [9] In the same way, under sonication, **1**, when treated at 15 °C for 2 h in THF in the presence of zinc powder and diiodomethane, leads to diphosphirane **2a**



Under these conditions, the diphosphirane **2a** reacts with the excess of methylene, leading to phosphaalkene **3a** The latter becomes the sole product after a prolonged sonication As in the case of the oxidation

reaction of diphosphiranes by ozone, the addition of methylene on phosphorus lone pairs destabilizes the cyclic form and promotes the cheletropic reaction [10] It must be noted that diphosphirane **2a** is stable i) without methylene under sonication, and ii) in the presence of a large excess of diazomethane [11]

In this field, we have already reported the synthesis of diphosphiranes by cyclopropanation of diphosphenes with halogenocarbenes [12] However, the generation of carbenoids requires either n-butyllithium or freshly sublimed potassium terbutoxide In order to simplify this reaction, we have tested this reaction under sonochemical conditions in the presence of an excess of potassium hydroxide pellets and a haloform in hexane



1

2b $X_1 = X_2 = Cl$

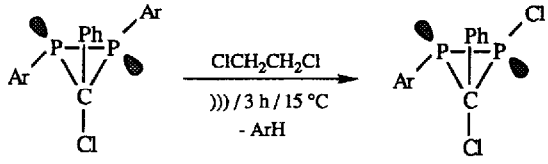
2c $X_1 = X_2 = Br$

The diphosphiranes **2b** and **2c** are quantitatively obtained when hexane is used as solvent The yield of the reaction dramatically decreases when chloroform alone is used as solvent and reagent (7-10%) This phenomenon could be attributed to the loss of the "efficiency" of the cavitation, since chloroform is probably much too dense with respect to the acoustic energy emitted by the ultrasonic generator [13,14] The same reaction in a biphasic liquid-liquid system (50 % aqueous KOH / $CHCl_3$) was not found to work Under the same conditions (heterogeneous liquid-solid or liquid-liquid reactions), the non-sonicated reaction does not occur (Table 2) Moreover, in sharp contrast to what occurs in the Simmons-Smith reaction, it must be noted that no trace of phosphaalkene resulting from a cheletropic reaction was detected.

Conditions	Reaction Time (h)	Solvent	Base	Haloform	2b (%)	2c (%)
◯	2	Hexane	solid KOH	$CHCl_3$	0	-
				$CHBr_3$	-	0
))) microtip	3	Chloroform	solid KOH	$CHCl_3$	7	-
	1	Hexane	solid KOH	$CHBr_3$	-	10
))) Cup horn	2	Chloroform	aqueous KOH (50 %)	$CHCl_3$	0	-
	2	Hexane	solid KOH	$CHCl_3$	100	-
				$CHBr_3$	-	100

Table 2 Sonicated synthesis of the gem-dihalogenodiphosphiranes **2b-c**

Under ultrasound irradiation, in 1,2-dichloroethane at 15 °C for 3 h, the diphosphirane **2d** (X_1 = Ph, X_2 = Cl) undergoes a substitution without ring-opening, leading to chloro-diphosphirane **4** (30 %) [15] This quite unexpected substitution of the aryl group by a chlorine atom has never been previously observed. In this case, sonication constitutes an efficient and original procedure of activation in a homogeneous medium It can be anticipated that a single electron transfer is involved in a key step of this "true" sonochemical reaction, as already described by Luche [1]



2d **4**

In conclusion, we have shown that sonication can be considered as an interesting alternative for the formation of P=P double bonds within a short reaction time, and increases the rate of their cyclopropanation. These heterogeneous sonochemical reactions can be considered as "false" sonochemical reactions sonication produces highly active depassivated surfaces, leading to the acceleration of the reaction The easy formation of gem-dihalogenodiphosphiranes by using inexpensive KOH pellets instead of tBuOK or n-BuLi can be also attributed to the dispersing effect of ultrasounds The sonochemical Simmons-Smith reaction of diphosphene involves the conversion of P=P into P=C bond *via* the cheletropic fragmentation of the diphosphirane intermediate

Finally, sonochemical unexpected substitution of diphosphirane in chlorinated solvents (homogeneous system) can be considered as one of the few examples of "true" sonochemical reactions [1] This clearly shows that ultrasounds are not only efficient through their physical effects (disruption of solids, micro-mixing,) but can also have "specific" chemical effects The use of sterically bulky moieties as protective groups is extremely effective to accomplish kinetic stabilization of unstable and unusual organophosphorus compounds in a low coordination state This in turn involves a decrease of their chemical reactivity The unexpected sonochemically promoted substitution of the bulky phenyl substituent by halogen is of great potential synthetic interest, since the resulting functionnalized compound was expected to lead to an enhanced overall reactivity

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(6) Apparatus Ultrasound generator, Bioblock Vibracell 600 W (20 kHz), microtip (ϕ = 3 mm), cup horn (ϕ = 60 mm) The temperature was measured with a thermocouple placed outside the ultrasonic beam, to avoid sound absorption leading to erroneous readings Control experiments have shown that dichlorophosphine without magnesium is stable under sonochemical conditions
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(15) ^{31}P NMR data of **4** (C_6D_6) δ 7, - 52 , $^1J_{P\text{-}P}$ = 171 Hz MS (DCI / NH_3) m/e 467 (M^+, ^{35}Cl)

(Received in France 19 July 1991)