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Flash Vacuum Pyrolysis of Dialkyl Diazobenzylphosphonates forming Styrenes via a Wittig Type Intermediate

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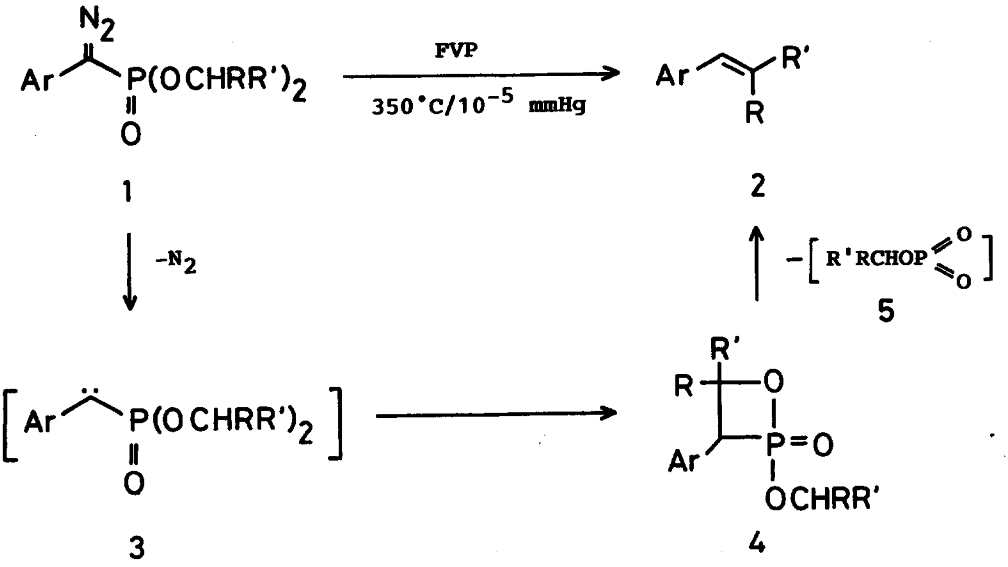
Abstract: Phenylphosphonylcarbene generated in gas phase at high temperature produced 1,2-oxaphosphetane 1-oxides as a result of intramolecular C-H insertion into ester alkyl group, which underwent fragmentaion leading to styrene derivatives and metaphosphate at higher temperature.

Carbenes and nitrenes generated in solution may be trapped so efficiently by reagents or solvents that a range of potential intramolecular reactions will not occur.[1] By contrast, carbenes and nitrenes generated by gas-phase pyrolysis at low pressures are less likely to undergo intermolecular reactions, whereas intramolecular rearrangements are commonplace.[1,2] This has permitted the straightforward synthesis of many useful organic compounds which are not readily obtained from the reaction in solution. During the course of our study on the reaction of phosphoryl carbenes,[3] we found that phosphonylcarbene generated under flash vacuum pyrolytic conditions (FVP) produced styrenes in moderate to reasonable yields and that the fragmentation reaction proceeded via 1,2-oxaphosphetane 1-oxide intermediates.

Flash vacuum pyrolysis (350°C/10^{-5}Torr) of dimethyl α-diazobenzylphosphonate (**1a**)[4] provided styrene (**2a**) as a sole isolable volatile product in 60 % yield. Similar reactions were soon found to occur in FVP of other dimethyl α-diazobenzylphosphonates (**1d** ∿ **g**) having a series of m- and p-substituents as well as α-diazonaphthylmethylphosphonate (**1h** ∿ **i**). Similarly, β-methylstyrene (**2b**) or dimethylstyrene (**2c**) was obtained in FVP of diethyl (**1b**) or diisopropyl diazophosphonates (**1c**), respectively.

The formation of these styrenes in FVP of **1** is reasonably understood in terms of the initial formation of phosphonylcarbene (**3**), followed by intramolecular C-H insertion forming 1,2-oxaphosphetane 1-oxide (**4**) and its subsequent fragmentation. Actually trimethyl phosphate was detected when the unvolatile pyrolysate of **1a** was treated with methanol and CH_2N_2, suggesting the presence of metaphosphate (**5**)[5], a fragment of the oxaphosphetane (**4**), presumably as polymers. More convincingly, the oxaphosphetane[5] was isolated when the pyrolysis was carried out at lower temperature. Thus, FVP of **1c** at 275°C resulted in a significant decrease in the yield of styrene to leave less volatile pyrolysate in the pyrolysis tube. Short path distillation (143 °C /0.6mmHg) of the pyrolysates provided 3,3-dimethyl-4-phenyloxaphosphetane 1-

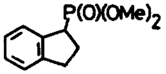
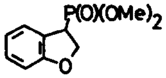


oxide (**4c**) which was characterized by NMR and MS. FVP of the oxaphosphetane (**4c**) at 350 °C afforded the dimethylstyrene. These results support the idea proposed above.

In order to know the limit and scope of the present fragmentation reaction, we attempted the FVP of **1** having a series of ortho substituents. The results indicated that the phosphonylcarbenes (**3k** ∿ **n**) having readily accessible hydrogens at ortho or α position gave benzocyclic compounds (**6** ∿ **8**) or H migration product (**9**) as a result of the intramolecular C-H insertion reaction into the proximate C-H bonds at the complete expense of styrenes. Thus, although FVP of α -diazo-2-bromobenzylphosphonate (**1j**) provided the expected styrene (**2j**), 2-alkyl or 2-alkoxy derivatives (**1k** ∿ **m**) gave benzocyclic compounds (**6** ∿ **8**) upon FVP, while **1n** produced β - phosphonylstyrenes (**9**). These results, especially that even benzocyclobutene (**6**) formation gains over styrene formation, suggest that insertion of **3** into the C-H bonds of ester alkyl groups leading to **4** is not energetically favorable process although these C-H bonds must be activated toward carbene by resonance electron donation of oxygen atom.[6] This is in accordance with the observation that no trace of **4** and/or **2** were detected in the reaction of **3** generated photolytically at much lower temperature.[7]

A priori, other feasible intramolecular pathways for phenylphosphonylcarbenes (**3**) generated in the gas phase are phenylcarbene rearrangement[2,8,9] and Wolff type rearrangement[5,10] of substituents on phosphorus. However, the pyrolysates of **1f** or **1g** included no trace of benzocyclic compounds expected to be formed as a result of carbene-carbene rearrangement. This is reasonably understood in terms of high activation energy[9] accompanied by this rearrangement. Careful examination of the

Table FVP of Arymethyldiazophosphonate (1)

				Products (%)	
1	Ar	R	R'	2	others
a	C_6H_5	H	H	59.9	
b	C_6H_5	H	CH_3	30.0(E/Z=1.3)	
c	C_6H_5	CH_3	CH_3	26.1	
d	$4\text{-}ClC_6H_4$	H	H	39.4	
e	$3\text{-}ClC_6H_4$	H	H	35.2	
f	$4\text{-}MeOC_6H_4$	H	H	51.2	
g	$3\text{-}MeC_6H_4$	H	H	53.5	
h	$1\text{-}C_{10}H_7$	H	H	87.4	
i	$2\text{-}C_{10}H_7$	H	H	64.5	
j	$2\text{-}BrC_6H_4$	H	H	22.4	
k	$2\text{-}MeC_6H_4$	H	H	0	 6 (67.7)
l	$2\text{-}EtC_6H_4$	H	H	0	 7 (71.4)
m	$2\text{-}MeOC_6H_4$	H	H	0	 8 (63.9)
n	$C_6H_5CH_2$	H	H	0	$PhCH{=}CHP(O)(OMe)_2$ 9 (71.1, E/Z=5.4)

pyrolysates eliminated, on the other hand, the presence of any products expected from the latter rearrangement. Wolff type rearrangements have been observed usually for phosphonylcarbenes bearing more mobile substituents such as Ph or H and the rearrangement including alkoxy groups has not been reported[9,10] at least in liquid phase at room temperature. The present results indicate that alkoxy migration in 3 is much less favorable even at this high temperature than the C-H insertion process which is usually classified as the least efficient reaction channels for most carbenes. Taking those facts into account, the reaction of 3 under FVP conditions forming **4** and then 2 is considered to be fairly selective. This can be compared with the FVP of methyl phenyldiazoacetate, which provided more than 10 products including a small amount of styrene (2%).[11]

In conclusion, the present reaction can be used as a convenient one-step preparation of 1,2-oxaphosphetanes which are important analogues of the Wittig intermediate when carried out at lower temperature, while, at much higher temperature, it will be employed not only as a new synthetic route for preparing alkenes but also for generating metaphosphates, another important short-lived phosphorus (V) compounds having coordination number 3.

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