A New General Synthesis of Aliphatic and Terminal Alkynes: Flash Vacuum Pyrolysis of β-Oxoalkylidenetriphenylphosphoranes

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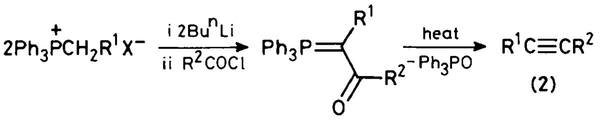
By using flash vacuum conditions the thermal elimination of Ph_3PO from β-oxoalkylidenetriphenylphosphoranes, previously confined to cases with an α-electron withdrawing group, has been extended to provide a general, high yielding synthesis of aliphatic and terminal alkynes.

The sequence of reactions shown in Scheme 1 represents an attractive and potentially versatile method of *de novo* alkyne synthesis, effectively coupling a primary alkyl halide, R^1CH_2X, with an acid chloride, R^2COCl, in three steps to produce the alkyne (**2**). However, although the thermal elimination of Ph_3PO from β-oxoalkylidenetriphenylphosphoranes (**1**) has been known for over 25 years,[1] it has only been successful, using conventional pyrolysis techniques, for cases in which R^1 is an electron-withdrawing group. Thus, while ylides (**1**), where R^1 = Ar,[1—4] COR,[5] CO_2R,[2,3,6] CN,[2,3,7] SR,[8] and SeAr,[9] have all been converted into (**2**), all attempts to obtain purely aliphatic or terminal alkynes from the corresponding ylides where R^1 is an alkyl group or H have failed.[2,3,10] In order to circumvent this problem, Bestmann has recently described two indirect methods to convert (**1**) into (**2**) where R^1 and R^2 are alkyl groups,[11] but these both involve several steps and proceed in overall yields of only 20—40%. We now report that flash vacuum pyrolysis[12] results in the direct conversion of (**1**) into (**2**) where R^1 = H or primary alkyl and R^2 = primary, secondary, tertiary, or cyclo-alkyl, alkenyl, or Ph.

Thus, when ylides (**1a**—**p**), readily obtained by acylation of $Ph_3P{=}CHR^1$ with R^2COCl,[13] were subjected to pyrolysis at 750 °C and 10^{-2} mmHg, Ph_3PO accumulated at the furnace exit and the pure alkynes (**2a**—**p**) were collected in the cold-trap in high yield (Table 1). A particular advantage of this technique is that the products are obtained in pure form,



(1)

Scheme 1

Table 1. Flash vacuum pyrolysis of ylides (**1**) to give alkynes (**2**).

	R^1	R^2	Yield of (**2**)/%		R^1	R^2	Yield of (**2**)/%
a	H	Ph	82	**i**	Me	Me	74
b	H	Et	78	**j**	Bu^n	Bu^n	80
c	H	Pr^n	59	**k**	Bu^n	n-C_5H_{11}	69
d	H	Pr^i	72	**l**	Pr^n	Pr^i	93
e	H	Bu^t	82	**m**	Pr^n	Bu^t	81
f	H	c-C_4H_7[a]	67[b]	**n**	Pr^n	c-C_4H_7	81[b]
g	H	c-C_6H_{11}	64	**o**	Pr^n	c-C_6H_{11}	85
h	H	CH=CHMe	59	**p**	Pr^n	CH=CHMe	82

[a] c = cyclo. [b] Vinyl alkyne, R^2 = $CH=CH_2$, formed at 800—850 °C.

free from solvents, reagents, or by-products. The pyrolyses were generally carried out on a 1 mmol scale (pyrolysis time <1 h) but the utility of this method for the synthesis of multi-gram quantities of alkynes was demonstrated by the preparation of (**2e**) (3.4 g, 82%) and (**2o**) (3.7 g, 85%), each over 95% pure by g.l.c., with pyrolysis times of 3 h.

The failure of conventional pyrolysis for this reaction has been attributed to the competing formation of allenes[2,10] and, in some cases, Ph_3P,[3] but under the present conditions neither of these was detected and the products (**2**) were pure as determined by ^1H and ^{13}C n.m.r. spectroscopy. Only for R^2 = cyclobutyl was an additional fragmentation process observed: extrusion of ethene from the four-membered ring. Thus, pyrolysis of (**1f**) or (**1n**) at 750 °C gave mainly vinyl alkynes with only a small proportion of the desired cyclobutyl alkynes. While lowering the furnace temperature gave an increasing proportion of the latter, the former had not been completely eliminated when, below 600 °C, the ylides began to sublime unchanged. On the other hand pyrolysis of (**1f**) and (**1n**) at 800—850 °C resulted in complete extrusion of ethene to give butenyne and hept-1-en-3-yne in good yield (Table 1).

Melting of the sample in the inlet is often undesirable in flash vacuum pyrolysis as it leads to the unwanted side-reactions characteristic of conventional pyrolysis. Here, however, this was not the case and heating the ylides above their m.p. in the inlet was actually advantageous, giving reduced pyrolysis times. At furnace temperatures below 600 °C the ylides (**1**) sublimed unchanged at 10^{-2} mmHg, but by raising the pressure to 1 mmHg (N_2 leak) alkynes were obtained, even at 450 °C, as the only volatile products, albeit in slightly reduced yield. In line with previous work, conventional pyrolysis of (**1o**) by distillation at 20 mmHg over an open flame gave, in 58% yield, a mixture of hydrocarbons containing only 60% (**2o**) and at least four other components including allenes. Upon repyrolysis under the usual flash vacuum conditions this was unchanged. It therefore appears that the high selectivity observed for alkyne formation results from the very mild conditions associated with the low pressure and short contact time of flash vacuum pyrolysis.

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