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Pyrolysis of β,γ,β′-Trioxo Phosphorus Ylides: Convenient Synthesis of Symmetrical and Unsymmetrical Diacylalkynes

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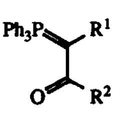
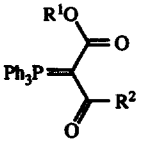
Abstract: Flash vacuum pyrolysis of a series of 1,2,4-trioxo-3-triphenylphosphoranylidene-butane derivatives, formed by acylation of β-oxo-phosphorus ylides with α-oxo-acid chlorides, results in extrusion of Ph_3PO exclusively across the 2,3-position to give diacylalkynes.

Thermal extrusion of triphenylphosphine oxide from α-oxoalkylidenetriphenylphosphoranes **1** is a well established method for the synthesis of alkynes $R^1C{\equiv}CR^2$ which proceeds particularly well using the technique of flash vacuum pyrolysis (f.v.p.). This has been successfully exploited for R^1 = H or alkyl,[1] aryl,[2,3] CN,[2,4] Cl or Br,[5] SR,[6] SeAr,[7] OAr,[8] and $PO(OPh)_2$.[9] Where there are ester and keto carbonyl groups present as in **2** oxygen is eliminated exclusively from the latter to give acetylenic esters $R^2C{\equiv}C{-}CO_2R^1$ in good yield.[2,10,11] The same applies for thioloester groups and this has allowed convenient synthesis of $R^2C{\equiv}C{-}C(O)SMe$.[12] In **3**, where the choice is between two keto carbonyls, selectivity is not surprisingly poor and extrusion gives an almost equal mixture of $R^1COC{\equiv}CR^2$ and $R^1C{\equiv}CCOR^2$.[13] We have now prepared representative examples of the next members of the series **6**, with a keto or ester group on one side of phosphorus and an α-diketo or α-ketoester group on the other, and find that Ph_3PO is lost exclusively across the central position to give diacylalkynes **7**.


(1)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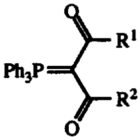
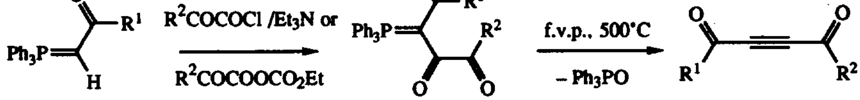

(3)

The ylides **6**, a new class of compound, were obtained in good to excellent yield (*Table*) as stable crystalline solids by reaction of the readily available ylides **4** in THF at room temperature either with acid chlorides in the presence of Et_3N for **6a-i**, or mixed anhydride **5** formed *in situ* from sodium pyruvate and ethyl chloroformate in the case of **6j**.



(4) (5) (6) (7)

When the ylides **6** were subjected to f.v.p. at 500°C and 0.01 torr in a conventional flow system (contact time ≈ 10 ms) extrusion took place across the central positions to give a mixture of Ph_3PO and alkynes **7** in good yield. In most cases the more volatile **7** was collected in the cold trap while Ph_3PO remained at the furnace exit, but where necessary the components were readily separated by column chromatography or distillation. While the mode of reaction for ester-stabilised ylides **6d**-**j** is as expected, it is noteworthy that in cases **a**-**c** none of the alternative products $R^1C{\equiv}CCOCOR^2$ were observed. This therefore provides a convenient two step route from ylides **4** and α-oxoacid derivatives **5** to symmetrical and unsymmetrical diacylalkynes **7**. These are of considerable interest as dienophiles and dipolarophiles for cycloaddition reactions and the present method offers a competitive alternative to existing approaches.[14]

			Formation of **6**		Conversion to **7**				
Entry	R^1	R^2	yield (%)	δ_P	yield (%)	δ_C C≡C		C=O	
a	Ph	Ph	72	+16.5	82	85.8		176.5	
b	Ph	OMe	96	+18.8	23	80.1	80.1	152.7	176.1
c	Ph	OEt	95	+18.1	44	79.7	80.5	152.2	176.1
d	OMe	Ph	61	+15.7	66	(as **b**)			
e	OMe	OMe	68	+16.3	59	74.9		152.6	
f	OMe	OEt	98	+16.5	61	74.3	75.1	151.8	152.3
g	OEt	Ph	67	+15.6	52	(as **c**)			
h	OEt	OMe	81	+16.2	70	(as **f**)			
i	OEt	OEt	91	+16.2	63	74.7		151.8	
j	OEt	Me	62	+15.2	23	77.9	80.8	152.2	182.5

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11. This may be partly due to these compounds existing predominantly in the configuration shown with the ester oxygen *anti* to phosphorus as recently demonstrated in the solid state by X-ray structure determination. See: Abell, A. D.; Trent, J. O.; Morris, K. B. *J. Chem. Soc., Perkin Trans. 2* **1991**, 1077, and previous references therein.
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