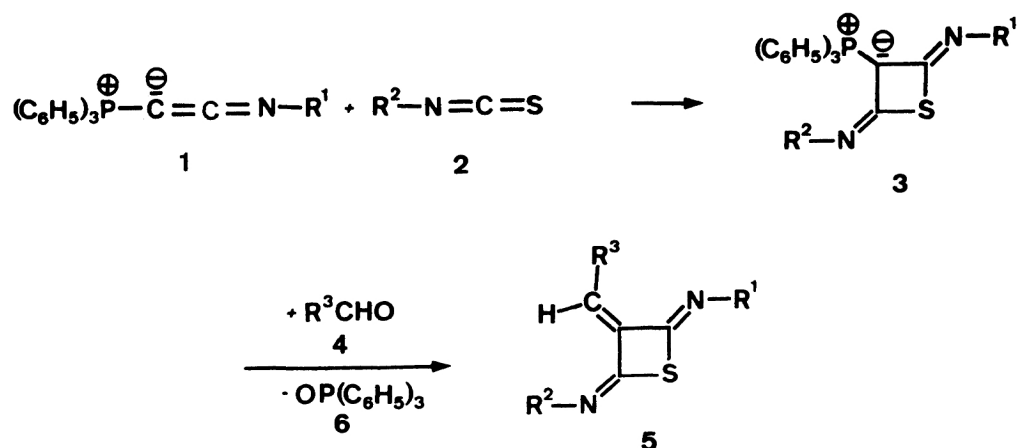


A Simple Route to 2,4-Bisiminothietanes

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N-Substituted keteniminylidetriphenylphosphoranes react with isothiocyanates in a [2+2] cycloaddition to form the four-membered ring phosphonium ylides. These yield the previously unknown arylidene-2,4-bisiminothietanes with aromatic aldehydes.

N-Substituted keteniminylidetriphenylphosphoranes **1**¹⁾ react with isothiocyanates **2** in a regiospecific [2+2] cycloaddition at the C=S double bond to give 3-triphenylphosphoranylidene-2,4-bisiminothietanes **3**.²⁾



The structural assignment of **3** is based principally on NMR data. The ³¹P-signal appears in the range from -4.5 to -6.2 (δ) (H₃PO₄ external standard), which is typical for phosphoranes with four-membered rings. The ¹³C-NMR signals of the C=N groups are found at 147-154 (δ). Signals for C-atoms of a C=S double bond, which should be expected at about 210 (δ), did not appear.

The phosphoranes **3** react with aromatic or heteroaromatic aldehydes **4** to give the yellow to red coloured 2,4-bisiminothietanes **5** with exocyclic C=C double bonds. These have become available for the first time by this route.³⁾ Aliphatic aldehydes **4** failed to react with **3**. Table 2 gives a survey of compounds **5** with R¹=R²=C₆H₅ synthesized.

Table 1. Phosphoranes 3 from 1 and 2

R ¹	R ²	Mp/°C	Yield/%	³¹ P[δ] (H ₃ PO ₄ ext. Standard)
C ₆ H ₅	C ₆ H ₅	198-200	73	-4.37
C ₆ H ₅	p-CH ₃ -C ₆ H ₄	157	86,2	-4.51
C ₆ H ₅	p-(CH ₃) ₂ N-C ₆ H ₄	199-201	94,2	-4.67
C ₆ H ₅	CH ₃	156-157	79	-5.28
C ₆ H ₅	CH ₂ -CH=CH ₂	128	86,8	-5.13
C ₆ H ₅	c-C ₆ H ₁₁	176	91,3	-5.10
C ₆ H ₅	CH ₂ -COOCH ₃	93	30	-4.75
C ₆ H ₅	CH ₂ -C ₆ H ₅	158-160	73,6	-4.93
CH ₃	CH ₃	127	53	-6.14

Table 2. 3-Arylidene- and 3-heteroarylidene-2,4-bis-N-phenyliminothietanes 5 (R¹=R²=C₆H₅) from 3 and aldehydes 4

R ³	Mp/°C	Yield/%	Colour
C ₆ H ₅	115	44,1	yellow
p-CH ₃ -C ₆ H ₄	150	80,5	yellow
p-H ₃ CO-C ₆ H ₄	130	33,8	yellow
p-NO ₂ -C ₆ H ₄	208-210	79	yellow
2,4(NO ₂) ₂ -C ₆ H ₃	176	93	orange
3-F-, 5-NO ₂ -C ₆ H ₃	160	84,4	yellow
3,4(Cl) ₂ -C ₆ H ₃	132	75,8	yellow
p-CN-C ₆ H ₄	152	97,5	orange
	165	83,5	reddish-brown
	158-160	90,7	ruby
	134-135	79,1	yellow
	128	76,2	yellow
	116-117	52,8	yellow

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(Received May 13, 1986)