New Syntheses of 1- and 2-Phenylthiobutadienes

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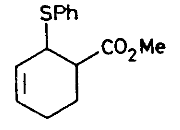
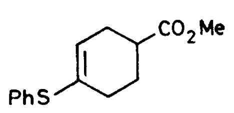
Summary The Horner–Wittig reaction with sulphenylated allylphosphine oxides and the rearrangement and oxidation of α-hydroxy-bis(phenylthio) acetals are used to make 1- and 2-phenylthiobutadienes respectively.

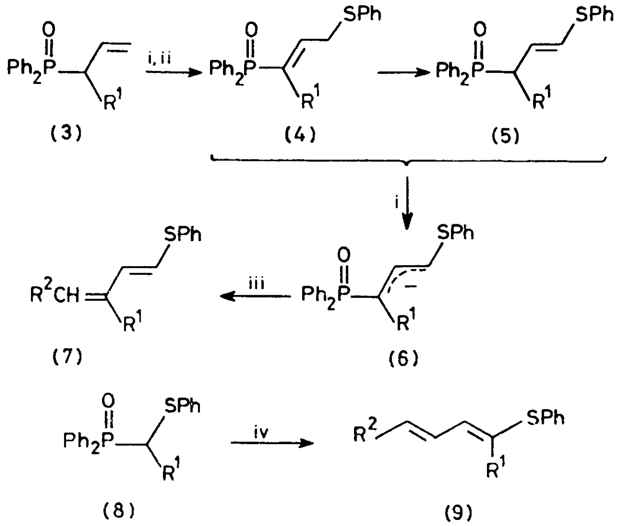
Diels–Alder reactions with 1-phenylthio (1-PhS) butadiene give cyclic allyl sulphides (*e.g.*, **1**) from which allylic alcohols, cyclic dienes, or aromatic compounds can be made.[1] 2-PhS butadiene on the other hand gives cyclic vinyl sulphides (*e.g.*, **2**) which are potential ketones.[2] Both these reactions are regiospecific; PhS is more powerful even than RO in determining the orientation of Diels–Alder reactions.[2,3] Most syntheses of PhS-butadienes are suitable only for the parent compounds,[1,2,4] but we now report convergent syntheses of substituted compounds of both types.



(1)

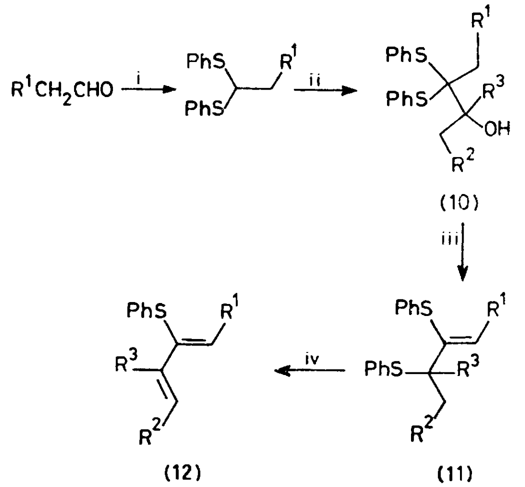


(2)



Scheme 1. i, BuLi; ii, Ph_2S_2; iii, R^2CHO; iv, (1) i, (2) $R^2CH{=}CHCHO$.

1-Alkylallylphosphine oxides (**3**), readily available by the rearrangement of phosphinite esters,[5] form anions with BuLi which give mixtures of α- and γ-adducts with most electrophiles. However, with diphenyl disulphide (Scheme 1) only the γ-adduct (**4**) is formed (*e.g.*, $R^1=Me$, 71%) as the α-adduct gives (**4**) by a [1,3] PhS shift.[6] The vinyl sulphide (**5**) is formed from (**4**) under the reaction conditions but this does not matter as (**4**) and (**5**) both give the same anion (**6**) which reacts with aldehydes to give the 3,4-disubstituted dienes (**7**; *e.g.*, $R^1=Me$, $R^2=Ph$, 68%) by the Horner–Wittig reaction.[7] For 1,4-dialkyl derivatives (**9**) it is better to use reagents (**8**)[8] on enals (*e.g.*, $R^1=Pr^i$, $R^2=Ph$, 92%;[8] $R^1=H$, $R^2=Me$, 96%).



Scheme 2. i, PhSH, HCl; ii, BuLi, $R^2CH_2COR^3$; iii, $SOCl_2$, Et_3N; iv, (1) $NaIO_4$, (2) heat.

The route to substituted 2-PhS butadienes (**12**) (Scheme 2) starts with the alcohols (**10**) made in good yield from bis(phenylthio) acetals and aldehydes or ketones.[9] On treatment of these alcohols with thionyl chloride and triethylamine, one PhS group migrates, assisted no doubt by the other, to give compounds (**11**) containing vinylic and allylic PhS groups (*e.g.*, $R^1=Me$, $R^2=R^3=H$, 90%; $R^1=Bu^t$, $R^2=H$, $R^3=Me$, 76%). The vinylic PhS group is conjugated enough for the allylic PhS group to be selectively oxidised to the sulphoxide; thermal elimination of this sulphoxide then gives the 2-PhS diene (**12**), *e.g.*, $R^1=Ph$, $R^2=Me$, $R^3=H$, 62% overall from (**11**).

We have carried out Diels–Alder reactions of both types of diene with acrylate esters and they give substituted derivatives of (**1**) and (**2**), *e.g.*, from (**9**; $R^1=H$, $R^2=Me$), 90%, from (**12**; $R^1=Bu^t$, $R^2=H$, $R^3=Me$), 78%.

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