

Wittig Condensations of a Thietan-2-one with Stabilised Phosphoranes

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(3*R*)-3-Benzyloxycarbonylamino-4,4-dimethylthietan-2-one reacts with ethoxycarbonylmethylenetriphenylphosphorane to give (3*R*)-3-benzyloxycarbonylamino-2-ethoxycarbonylmethylene-4,4-dimethylthietan, as a mixture of (*E*)- and (*Z*)-diastereoisomers; corresponding Wittig condensations occur with cyanomethylene- and acetylidene-triphenylphosphorane.

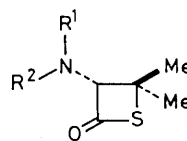
As part of a programme aimed at extending the role of small-ring heterocycles in organic synthesis, we have examined some aspects of the chemistry of thietan-2-ones of type (1). The ability of such heterocycles to participate in C-C bond-forming reactions was unknown until recently, when we showed that they could act as operational equivalents of type (2) towards carbon electrophiles.¹ We now report that the carbonyl group of a thietanone of type (1) undergoes Wittig condensations with stabilised phosphoranes, a finding that considerably enlarges the synthetic capability of these heterocycles.

The thietanone (1a),† m.p. 56–58 °C, $[\alpha]_D^{22} -22^\circ$ (EtOH), was prepared from D-penicillamine (3) in 38% overall yield (after SiO₂ chromatography) by sequential reactions involving benzyloxycarbonyl chloride–sodium hydroxide and dicyclohexylcarbodi-imide. When the thietanone (1a) was heated in boiling benzene for 12 h with the phosphorane (4a), a 3:1 mixture of the thietans (5) and (6) and triphenylphosphine oxide was isolated (after SiO₂ chromatography). Addition of light petroleum to the thietan mixture induced the crystallisation of the (*Z*)-isomer (5) (70%), m.p. 104–106 °C, $[\alpha]_D^{25} +55^\circ$ (CHCl₃); the (*E*)-isomer (6) (20%), m.p. 51–52 °C, $[\alpha]_D^{25} -53^\circ$ (EtOH), slowly crystallised from the mother liquor.

The gross structures of compounds (5) and (6) followed from their analytical and spectroscopic properties. In particular, compounds (5) and (6) showed respective absorptions at 1690 and 1705 cm⁻¹ (carbamate and vinylogous thiocarbonate C:O) in the i.r. region and at 284 (ε 13 100) and 281 nm (ε 17 200) (vinylogous thiocarbonate chromophore) in the u.v. region; in the ¹H n.m.r. spectra (CDCl₃), the olefinic protons of compounds (5) and (6) appeared as doublets at δ 6.00 (*J* 1 Hz) and 5.54 (*J* 2 Hz), respectively. The (*Z*)-geometry of compound (5) was established by X-ray crystallography.‡

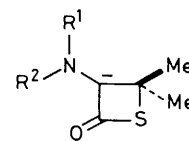
The thietanone (1a) also reacted in boiling benzene with the phosphoranes (4b) and (4c) to give the thietans (7a) (64%), m.p. 171–173 °C, $[\alpha]_D^{25} -40^\circ$ (EtOH), and (7b) (47%), $[\alpha]_D^{25} +10^\circ$ (EtOH); no corresponding reaction occurred when the phosphorane (4d) was employed.

Although intramolecular Wittig condensations of stabilised phosphoranes with thioesters are well documented,² intermolecular examples are rare. In our experience,³ such reactions only occur when the thioesters are unhindered, *i.e.* *S*-esters of thioformic acid, or activated, *e.g.* *S*-esters of trifluorothioacetic acid. Since the five-membered ring thio-lactones (8a) and (8b) failed to undergo Wittig condensations

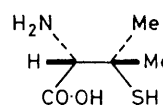


(1)

a; R¹ = H, R² = CO·O·CH₂P h



(2)



(3)

RCH : PPh₃

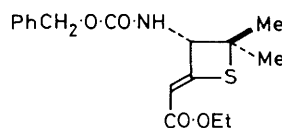
(4)

a; R = CO·OEt

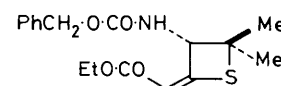
b; R = CN

c; R = COMe

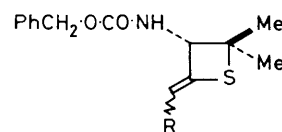
d; R = CHO



(5)



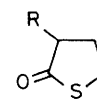
(6)



(7)

a; R = CN

b; R = COMe



(8)

a; R = H

b; R = NHCOMe

with the phosphorane (4a), it is clear that the reactivity of the thio-lactone (1a) must be attributed to an enhancement of the ketonic character of its thioester function, imposed by the geometry of the four-membered ring. In this context, Gilpin *et al.* have noted⁴ that the carbonyl groups of strained bicyclic β-lactams also undergo Wittig condensations with stabilised phosphoranes.

Hitherto, 2-ylidenethietans have been prepared by [2 + 2]-cycloadditions, involving the reactions of thioketenes with alkenes⁵ and of thiones with allenes.⁶ The Wittig condensation of thietan-2-ones with stabilised phosphoranes provides a new route to this relatively unexplored class of compound. Furthermore, the array of reactive functionality, incorporated in the thietans (5)–(7), assures a diverse chemical reactivity of the compounds.

† This compound has been described in racemic form (J. C. Sheehan, *Ann. N.Y. Acad. Sci.*, 1960, **88**, 665; L. Field, W. S. Hanley, P. L. Kelly, W. J. Sanders, J. E. White, I. A. Jaffe, and P. Merryman, *J. Med. Chem.*, 1973, **16**, 1152); Field and his co-workers reported unsuccessful attempts to derive the optically active material.

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