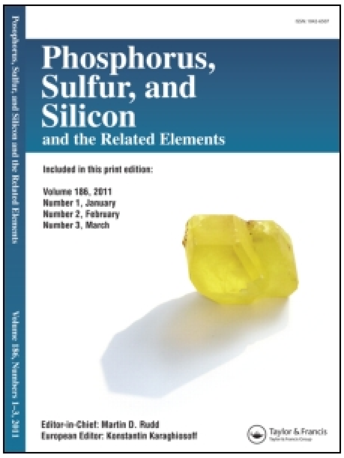

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STRUCTURAL STUDIES OF A NOVEL HETEROCYCLIC PHOSPHORANE

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STRUCTURAL STUDIES OF A NOVEL HETEROCYCLIC PHOSPHORANE

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Reaction of 2,2,6-trimethylthiochroman-3,4-dione with an excess of methylenetriphenylphosphorane yields the stabilised ylide (4) by way of an α-ketol rearrangement. X-Ray crystallography indicates that (4) exists as the (*Z*)-isomer and provides supporting evidence for an enolate structure.

Keywords: Thiochroman-3,4-dione; α-ketol rearrangement; methylenetriphenylphosphorane; X-ray crystallography

INTRODUCTION

The regiospecific formation of C=C bonds by reaction of phosphorus-stabilised carbanions with carbonyl compounds is a widely used organic transformation which has been extensively reviewed[1]. The application of the Wittig reaction[2] to *o*-quinones and α-diketones has received relatively scant attention. Reaction of one equivalent of a P-stabilised carbanion with an α-diketone affords an α,β-unsaturated ketone resulting from preferential attack of the carbanion at the more electrophilic C=O group[3]. The generation of 1,3-dienes from α-diketones and two equivalents of a

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P-stabilised carbanion is variable[4] and frequently the α,β-unsaturated ketone is the major product.

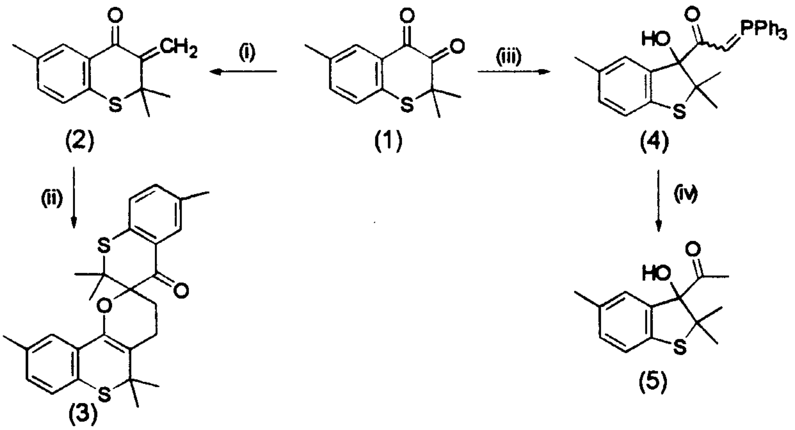
We have previously reported[5] the reaction of thiochroman-3,4-diones (1) with one equivalent of methylenetriphenylphosphorane to afford 3-methylenethiochroman-4-one (2), which underwent a facile hetero Diels-Alder cycloaddition to give the pentacycle (3). Reaction of the dione with an excess of methylenetriphenylphosphorane gave a crystalline solid which was tentatively assigned as the stabilised ylide (4) on the basis of spectroscopic evidence, though no evidence for the geometry or position of the ylide double bonds was available (Scheme 1).

We now report the absolute structure of this novel ylide as determined by X-ray crystallography.

DISCUSSION

Bond lengths and angles obtained from X-ray crystallographic studies on 'reactive' alkylidene triphenylphosphoranes ($Ph_3P{=}CR'R''$) have been collated[6] and indicate that the P-C ylide bond length in these compounds is *ca* 1.67 Å, very close to the theoretical P-C double bond distance of 1.667 Å, but appreciably different from the P-C single bond length of 1.872 Å[7]. Replacement of the phenyl groups with bulky alkyl groups results in a lengthening of the P-C ylide bond[8]. There are relatively few reports of X-ray crystallographic data for stabilised β-oxophosphoranes ($Ph_3P{=}CHC(O)R$)[9a–g], but the P-C ylide bond length in these examples is slightly longer, *ca* 1.74 Å, than that in the reactive ylides.

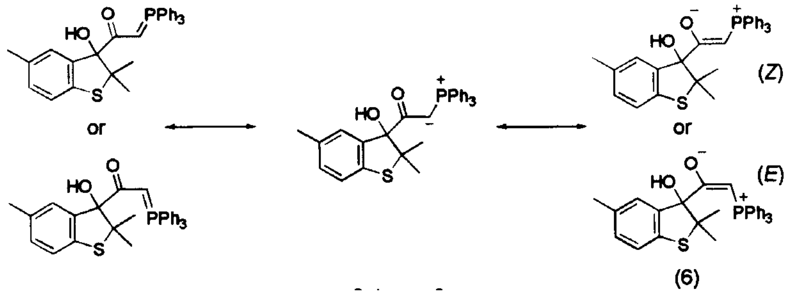
Data for the present ylide (4) indicate a P-C(13) bond length of 1.723(2) Å which is comparable with those values reported for stabilised ylides. The C(13)-C(12) bond distance of 1.383(3) Å in (4) is shorter than the theoretical C-C single bond length of 1.54 Å but compares favourably with the C=C bond length of 1.34 Å, indicating significant double bond character. The O(2)-C(12) bond distance of 1.252(3) Å is marginally longer than the typical C=O bond length of 1.21 Å but is shorter than the C-O single bond length of 1.43 Å[10]. This shortening of the C-CO and lengthening of the C=O bonds is attributed to significant delocalisation of the carbanion lone pair of electrons through the carbonyl group, thus providing an enolate type structure (6) (Scheme 2). Evidence for such enolisa-



Reagents and conditions: (i) 1 eq. $CH_2=PPh_3$, THF, 0 °C, N_2; (ii) room temperature; (iii) 2eq. $CH_2=PPh_3$, THF, 0 °C, N_2; (iv) aq. HCl, Δ.

SCHEME 1

tion has been provided by alkylation experiments on β-oxophosphoranes where the major products resulted from *O*-alkylation[11a,b]



SCHEME 2

The presence of an enolate structure is consistent with the observed additional data for (4), where the absorption band for the C=O stretch appears at 1539 cm^{-1} instead of the more typical range of 1705 – 1725 cm^{-1} for an acetyl C=O group[12]. Acidic hydrolysis of (4) gave, as expected, triphenylphosphine oxide and the acetyl compound (5), in which the C=O stretch is at 1710 cm^{-1}[13].

In our earlier paper, we were unable to assign the geometry of (4) by ^1H or ^{13}C NMR spectroscopy. It is clear from the crystallographic data[14] (Table I) that (4) is present as the (*Z*)-isomer as shown in Figure 1, a feature which is in agreement with the geometry reported for other β-oxophosphoranes[9a–c] The O-C-C-P unit of the ylide is essentially planar, consistent with sp^2 hybridisation and a trigonal planar configuration of the ylide carbanion. This planar enolate configuration facilitates the synthesis of alkynes by the high temperature thermolysis of β-oxophosphoranes which proceeds by the elimination of triphenylphosphine oxide through a proposed 1,2-oxaphosphetene intermediate[15].

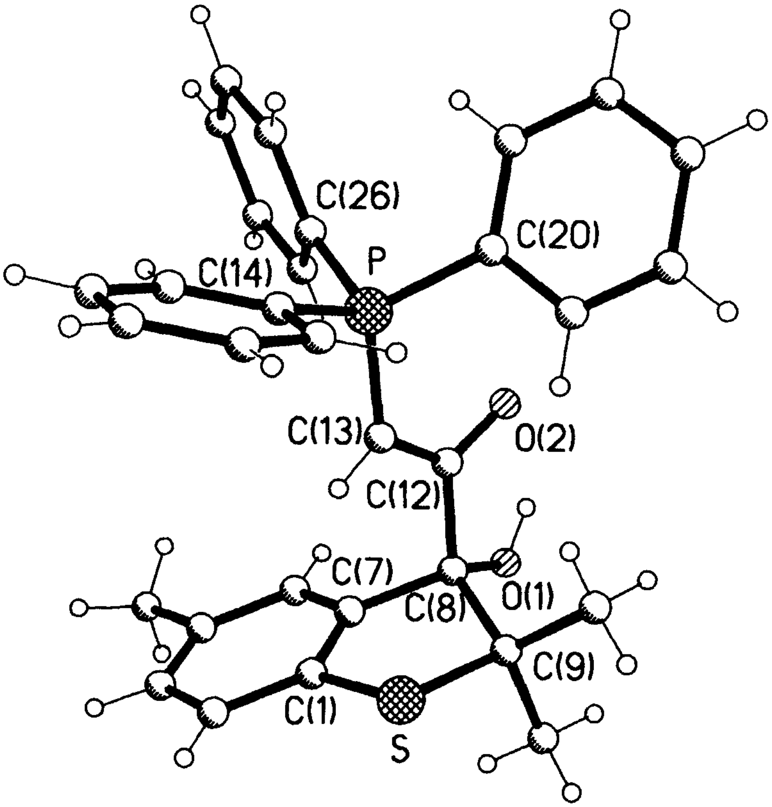


FIGURE 1 Perspective View and Key Atom Labelling of the Ylide (4)

TABLE I Selected Bond lengths (Å) and Angles (°) for the Ylide (4)

S-C(1)	1.768(2)	S-C(9)	1.863(3)
P-C(13)	1.723(2)	P-C(26)	1.798(2)
P-C(14)	1.810(2)	P-C(20)	1.811(2)
O(1)-C(8)	1.402(3)	O(2)-C(12)	1.252(3)
C(1)-C(7)	1.375(3)	C(7)-C(8)	1.525(3)
C(8)-C(9)	1.555(3)	C(8)-C(12)	1.577(3)
C(12)-C(13)	1.383(3)		

C(1)-S-C(9)	90.51(11)	C(13)-P-C(26)	114.72(12)
C(13)-P-C(14)	106.27(11)	C(26)-P-C(14)	106.52(11)
C(13)-P-C(20)	113.88(11)	C(26)-P-C(20)	107.83(11)
C(14)-P-C(20)	107.10(11)	C(7)-C(1)-S	113.41(18)
C(1)-C(7)-C(8)	113.9(2)	O(1)-C(8)-C(7)	111.63(18)
O(1)-C(8)-C(9)	109.06(18)	C(7)-C(8)-C(9)	104.97(18)
O(1)-C(8)-C(12)	106.37(18)	C(7)-C(8)-C(12)	110.78(170
C(9)-C(8)-C(12)	114.12(19)	C(8)-C(9)-S	104.42(15)
O(2)-C(12)-C(13)	124.2(2)	O(2)-C(12)-C(8)	114.6(2)
C(13)-C(12)-C(8)	121.21(19)	C(12)-C(13)-P	120.94(17)

The three phenyl groups on the P atom are oriented in a propeller-like manner with respect to the P-C(13) bond and the P-phenyl bond lengths are 1.798(2), 1.810(2) and 1.811(2) Å close to the P-C bond length of 1.82–1.83 Å in triphenylphosphine[16]. The C-P-C bond angles are around 107° and indicate that the P atom has adopted a tetrahedral geometry.

The ^{1}H NMR spectrum of (4) displays singlets at δ 1.47, 1.56 and 2.31 each accounting for three protons which are assigned to the diastereotopic C-2 methyl groups and the aromatic methyl group respectively. A doublet at δ 4.38 accounts for one proton and the magnitude of the coupling constant (*J* 24.5 Hz) is in accord with literature values for $^{2}J_{P\text{-}H}$[11b,17]. A slightly broadened singlet at δ 6.11 is attributable to the hydroxyl proton. Exchange with D_2O revealed that this proton and the proton on the carbon adjacent to the phosphorus atom are both labile. Partial ^{13}C NMR data for this ylide are presented in Figure 2. It is noteworthy that no P-C coupling to the carbonyl carbon (β-C) is observed, a feature that is common for other stabilised ylides[11b]. The remaining P-C coupling constants are comparable to those reported in the literature for various stabilised ylides [18]. The ^{31}P NMR spectrum of this compound displayed a doublet at δ 15.7, a chemical shift comparable with those of phosphorus atoms in other stabilised ylides[9g,11b,18,19,20]. The infrared spectrum of (4) displayed hydroxyl stretching band at 3308 cm^{-1}

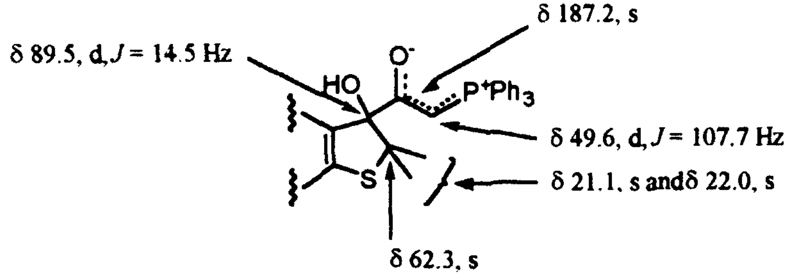
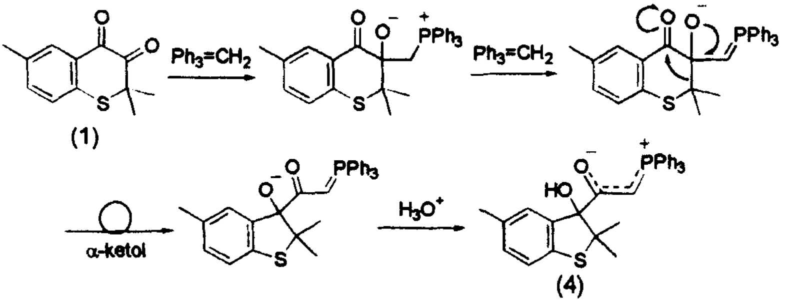


FIGURE 2 Partial ^{13}C NMR Data for (4)

The formation of (4) can be rationalised (Scheme 3) by attack of methylenetriphenylphosphorane on the more electrophilic 3-carbonyl group to afford a betaine. A second mole of methylenetriphenylphosphorane then behaves as a base and abstracts a proton α to the phosphonium function to generate a new ylide. This ylide cannot undergo the normal betaine → oxaphosphetane → alkene sequence of the Wittig reaction and instead favours an α-ketol rearrangement to afford (4) on acidic work-up.



SCHEME 3

EXPERIMENTAL

Melting points were determined in capillary tubes and are uncorrected. Distillations were performed using a Kugelrohr (Büchi GKR-50 Glass Tube Oven) and all boiling points quoted relate to the oven temperature at which the distillation commenced. Infrared spectra were recorded on a Mattson-Polaris Fourier Transform spectrophotometer. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker WM250 instrument for solutions in $CDCl_3$; coupling constants are given in Hz. Flash chromatographic separations were performed on Crossfields Sorbsil C60 silica gel (M.P.D. 60Å, 40–60μ, activated) according to the published procedure[21]. 2,2,6-Trimethylthiochroman-3,4-dione (1) was prepared according to the literature procedure[22].

Reaction of 2,2,6-Trimethylthiochroman-3,4-dione with Excess Methylenetriphenylphosphorane

n-Butyllithium (17 mmol) was added rapidly to a vigorously stirred suspension of methyltriphenylphosphonium bromide (16 mmol) in anhydrous THF (30 ml) cooled to −10 °C under an argon atmosphere. The resulting orange solution was stirred at room temperature for 45 minutes. 2,2,6-Trimethylthiochroman-3,4-dione (8 mmol) was added in a single portion followed by further THF (20 ml). After stirring at room temperature for 30 minutes, the solution was poured into water (200 ml) and extracted with ethyl acetate (3 × 50 ml). Removal of the dried (Na_2SO_4) solvent gave the crude product which was eluted from silica gel with 20% ethyl acetate in hexane to afford two fractions. Fraction 1 **3-Methylidene-2,2,6-trimethylthiochroman-4-one** (2) (17%) as a bright yellow oil, b.p. 125 °C at 7×10^{-2} mmHg; υ_{max}(Nujol)/cm^{-1} 1665; δ_H 1.58 (6H, s, 2-Me), 2.33 (3H, s, 6-Me), 5.45 (1H, s, alkenyl-H), 6.52 (1H, d, *J* 0.9, alkenyl-H), 7.09 (1H, d, *J* 7.8, 8-H), 7.20 (1H, dd, *J* 7.8 and 1.8, 7-H), 7.95 (1H, d, *J* 1.8, 5-H); δ_C 20.6 (6-Me), 27.2 (2-Me), 46.3 (2-C), 118.3 (3-CH_2), 150.5 (3-C), 186.5 (4-C), 127.5–136.8 (6 × C) (Found: C, 71.7; H, 6.6; S, 14.7. $C_{13}H_{14}OS$ requires C, 71.5; H, 6.5; S, 14.7%) and Fraction 2. **(Z)-2,2,5-Trimethyl-3-[(triphenylphosphoranylidene)acetyl]-2,3-dihydrobenzo[*b*]thiophen-3-ol** (4) (46%) as colourless crystals from ethyl acetate and hexane, m.p. 169.0–171.0 °C; υ_{max} (Nujol)/cm^{-1} 3308, 1539; δ_H 1.47 (3H, s, 2-Me), 1.56 (3H, s, 2-Me), 2.31 (3H, s, 5-Me), 4.38 (1H, d, *J* 24.5, alkenyl-H), 6.11 (1H, s, OH), 6.94–7.04 (3H, m, 4-H, 6-H, 7-H), 7.39–7.57 (15H, m, Ph_3P), D_2O treatment resulted in the collapse of signals at δ 4.38 and 6.11; δ_C 21.1 (2-Me), 22.0 (2-Me), 28.4 (5-Me), 49.6 (d, *J* 107.7, $3''$-C), 62.3 (2-C), 89.5 (d, *J*14.5, 3-C), 122.7 (Ar-C), 125.7 (d, *J* 7.2, Ar-C-*p*P), 127.2 (Ar-C), 128.8 (d, *J* 12.1, Ar-C-*m*P), 132.2 (Ar-C), 132.9 (d, *J* 9.8, Ar-C-*o*P), 134.8 (d, *J* 100.0, Ar-C-*ipso*P), 145.2 (Ar-C), 187.2 ($3'$-C); δ_P 15.7 (Found: MH^+ 497.1727; C, 75.1; H, 5.9; P, 6.4; S, 6.9. $C_{31}H_{29}O_2PS$ requires MH^+ 497.1704; C, 75.0; H, 5.9; P, 6.2; S, 6.5%).

A suspension of the foregoing ylide (4) (1.2 mmol) in dilute hydrochloric acid (4M, 40 ml) was refluxed for 1.5 hours. The cooled mixture was diluted with water (200 ml) and extracted with ethyl acetate (3 × 50 ml). The combined organic extracts were washed with water (100 ml), dried (Na_2SO_4) and evaporated to afford a pale yellow solid. Elution from silica with 20% ethyl acetate in hexane gave two fractions. Fraction 1. **3-Acetyl-2,2,5-trimethyl-2,3-dihydrobenzo[*b*]thiophen-3-ol** (5) (87%) as colourless crystals from hexane and ethyl acetate, m.p. 91.5–93.0 °C υ_{max} (Nujol)/cm^{-1} 3430, 1710; δ_H 1.31 (3H, s, 2-Me), 1.53 (3H, s, 2-Me), 2.27 (3H, s, 5-Me), 2.32 (3H, s, COMe), 4.76 (1H, s, OH), 6.87 (1H, s, 4-H), 7.06–7.08 (2H, m, 6-H, 7-H) (Found: C, 65.9; H, 6.8; S, 13.7. $C_{13}H_{16}O_2S$ requires C, 66.1; H, 6.8; S, 13.6%). Fraction 2. **Triphenylphosphine oxide** identical in all aspects with authentic material.

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