

The *in situ* generation of alk-1-ynyllead triacetates from terminal acetylenes by zinc–lead exchange and crystal structure of 2,4,7,9,13-pentamethyl-9-phenylethynyl-7,10-ethenospiro[5.5]undeca-1,4-diene-3,8-dione

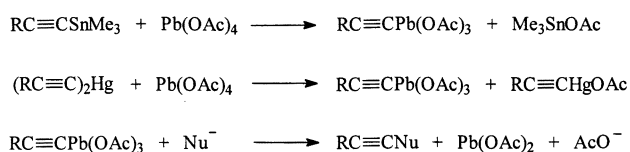
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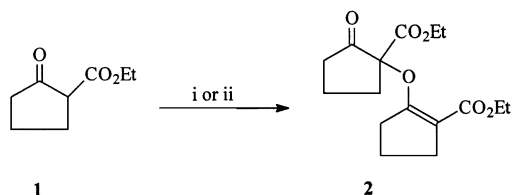
Methods involving zinc–lead exchange for the one-pot conversion of terminal acetylenes into alk-1-ynyllead(IV) triacetates have been developed, and examples of the *in situ* C-alkynylation of a number of carbon nucleophiles are reported. An attempt to extend the reaction to phenols by treating 2,4,6-trimethylphenol with phenylethynyllead triacetate led to formation of the spiro dienone **16**, the structure of which was determined by X-ray diffraction.

In an earlier paper we reported a new general method for the C-alkynylation of soft carbon nucleophiles such as β -dicarbonyl compounds and sodium nitronates.¹ The procedure involved the treatment of the nucleophile with an alk-1-ynyllead triacetate, unstable compounds which may be produced in solution by the reaction of either an alk-1-ynyl(trimethyl)stannane or a di(alk-1-ynyl)mercury compound with lead tetraacetate (LTA) (Scheme 1).



Scheme 1

The development of a one-pot procedure for converting an acetylene into an alkynyllead triacetate *in situ* was recognised by us as a potentially useful extension of the method, especially because of the moisture sensitivity of alk-1-ynyl(trimethyl)stannanes. Such a method was later reported by Ikegami,² who found that, if a tetrahydrofuran solution of a lithium acetylide was added at low temperature to LTA in methylene dichloride, the resulting mixture reacted at room temperature with a range of β -keto benzyl esters to give good yields of the corresponding α -alkynylated keto esters. We have attempted to use this procedure to produce the α -hex-1-ynyl β -keto ester **11**; however, we found that reaction of ethyl 2-oxocyclopentanecarboxylate **1** under the conditions reported, resulted in formation of the dimer **2** in approximately 72% yield and recovery of about 9% of the keto ester **1** (see Scheme 2). None of the hexynyl deriv-

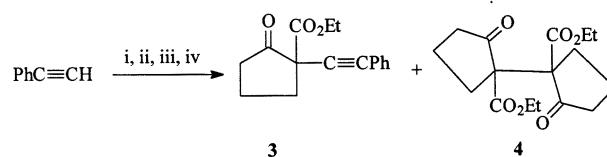


Scheme 2 Reagents and conditions: i, Mixture from reaction of $\text{C}_4\text{H}_9\text{C}\equiv\text{CLi}$ and Pb(OAc)_4 at -20°C then 15 min at RT; ii, Pb(OAc)_4

ative **11** could be detected in the reaction mixture. Compound **2** is readily formed by treatment of the β -keto ester **1** with LTA,³ which would indicate that the relatively fast disproportionation of the alkynyllead triacetate to the tetraalkynyllead and LTA,

which we had noted previously,¹ had occurred [eqn. (1)]. This would suggest that in the case of the β -keto ethyl ester **1** alkylation is slower than for the corresponding benzyl ester. In previous work it has been noted by ourselves⁴ and by Ikegami and co-workers⁵ that the reactivity of β -keto esters towards organolead triacetates is dependent on the nature of the ester group; methyl esters and benzyl esters were found to be more reactive than ethyl esters.

At about the same time as the communication of Ikegami, we had found that alkynylzinc chlorides reacted with LTA to give a solution which had the capacity to carry out the electrophilic alkylation of β -keto esters. This reaction, which has been developed into a useful one-pot method for the C-alkynylation of soft carbon nucleophiles, is outlined for the synthesis of the keto ester **3** (see Scheme 3). The most efficient and readily



Scheme 3 Reagents and conditions: i, BuLi, THF, -78°C ; ii, ZnCl_2 ; iii, LTA, CHCl_3 , -10°C then RT, 0.25 min; iv, compound **1**

reproduced procedure, which afforded a 73% yield of the phenylethynyl derivative **3**, involved the treatment of phenylacetylene (1.2 mol equiv.) in tetrahydrofuran with butyllithium at -78°C . Zinc chloride (1.2 mol equiv.) was added to the solution which was then stirred at -10°C for 20 min. A solution of LTA (1.1 mol equiv.) in chloroform was then added at -10°C to the solution which was then stirred for 15 s. After this the substrate **1** (1.0 mol equiv.) in chloroform was added to the mixture which was then stirred at -10°C for 1 h and a further 2 h at room temperature.

As we found previously in the case of Sn–Pb and Hg–Pb exchange reactions,¹ the time allowed for Zn–Pb exchange is most important for the success of the reaction. This, as indicated above, is due to disproportionation of the alkynyllead triacetate which is outlined in eqn. (1). As can be seen from Table 1, the optimum yield of compound **3** was obtained after a Zn–Pb exchange time of 15 s; any increase in this time resulted in formation of more of the dimer **4**, and with a delay of 15 min

Table 1 Effect of Zn–Pb exchange time on the ratio of the acetylene derivative **3** to dimer **4** in the reaction of Scheme 3 conducted at -10°C

Zn–Pb exchange time (min)	Molar ratio of (3):(4)	Total yield (%)
0.25	9.5:1	88
0.5	8.1:1	83
2.0	4.3:1	75
15.0	2:1	78

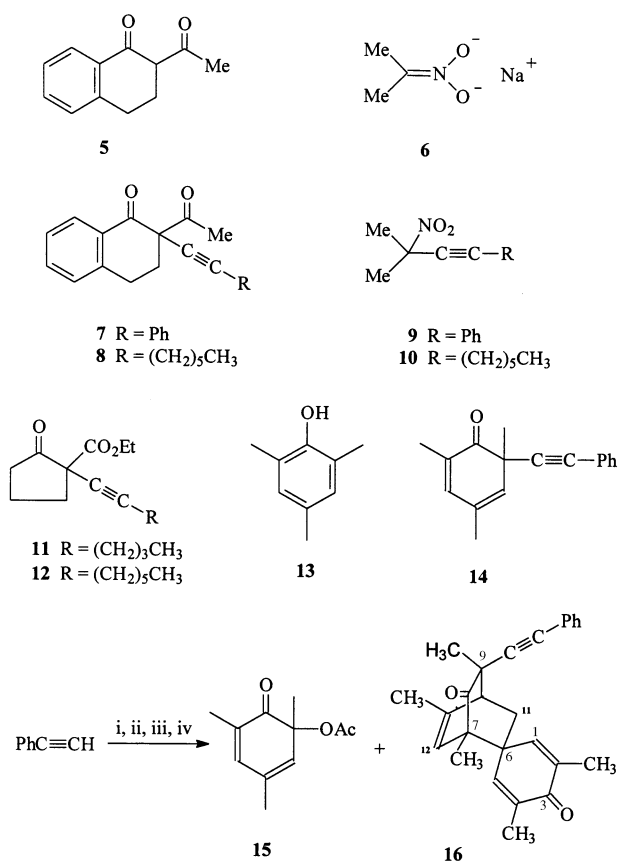
before addition of the substrate **1**, the product contained 33% of compound **4**.

The formation of the dimer **4** in the above reaction (Scheme 3) is noteworthy, since the C–O linked dimer **2** is the product of LTA oxidation of the keto ester **1**.³ It appeared likely that the presence of zinc chloride caused the change in the mode of oxidative dimerisation, and this was examined by treating the keto ester **1** with LTA (0.5 mol equiv.) and zinc chloride in chloroform. The C–C linked dimer **4** was produced in 67% yield as a single diastereoisomer, suggesting that the product arises in a radical coupling of two molecules complexed to a zinc ion through oxygen.

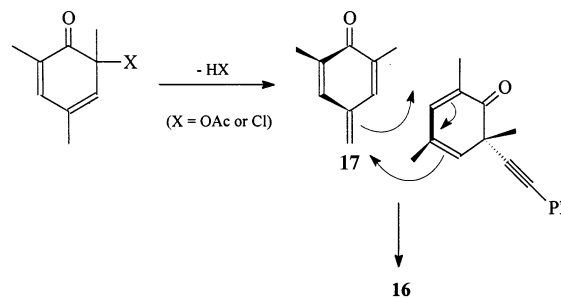
In exploring the generality of the above one-pot alkylation method, the β -diketone **5** and the sodium nitronate **6** were found to react readily under the conditions indicated in Scheme 3 to give the phenylethynyl derivatives **7** and **9** in yields of 59 and 58%, respectively. An initial attempt to extend the method, by replacing phenylacetylene with oct-1-yne in Scheme 3, resulted in production of some of the expected keto ester **12**; however, there was significant dimer **4** formation. This problem was readily overcome by introducing a catalytic amount of mercury(II) acetate (0.1 mol equiv.) with the LTA and maintaining all other conditions as in Scheme 3. The modified method resulted in a 52% yield of the keto ester **12** and it would appear to be potentially useful for the introduction of a variety of alkynyl groups, since the nucleophiles **5** and **6** behaved similarly to the β -keto ester **1**, affording the octynyl derivatives **8** (52%) and **10** (41%), respectively, in synthetically useful yields.

Although yields in five of the six alkylation reactions were below those which we reported for alkynyllead triacetates generated for alkynyl(trimethyl)stannanes,¹ the method offers greater efficiency in the use of the acetylene, and its simplicity is a considerable advantage. The need to employ a catalytic amount of mercury(II) acetate for the octynylation reactions requires some comment. We had found in previous work⁶ that arylboronic acids react with LTA to give diaryllead diacetates, whereas the same reaction conducted with a catalytic amount of mercury(II) acetate produced the aryllead triacetate in high yield. Thus, we reasoned that the octynylzinc reagent may be reacting in a similar way with LTA to yield octynyllead triacetate and dioctynyllead diacetate, but only the former lead compound with LTA–Hg(OAc)₂. Thus, in the absence of Hg(OAc)₂ unchanged LTA would be available to produce the dimer **4**.

An attempt to extend the method to include the alkylation of phenols was not successful, and we attribute this to their lower reactivity towards organolead triacetates as found by us in earlier work.^{7–9} When 2,4,6-trimethylphenol (mesitol) **13** was added to the mixture produced by use of the above conditions for Zn–Pb exchange with phenylacetylene, none of the 6-phenylethynyl dienone **14** (or its dimer)⁸ was detected. The product of Wessely acetoxylation, compound **15**, was present in 11% yield (see Scheme 4); however, the major product of the reaction was the novel spirodienone **16**, the structure of which was determined by X-ray diffraction (see below). The pathway to compound **16** no doubt involves a Diels–Alder condensation between the 6-phenylethynylcyclohexadienone **14** and the mesitol oxidation product **17** (see Scheme 5). This latter compound could arise by elimination of HX from either the 6-acetoxy-



Scheme 4 Reagents and conditions: i, BuLi, THF, -78°C ; ii, ZnCl₂; iii, LTA, CHCl₃, -10°C then RT, 0.25 min; iv, compound **13**



Scheme 5

cyclohexadienone **15** or the corresponding chloride as shown. The fact that compound **16** is obtained as a single diastereoisomer is readily explicable in terms of the least hindered approach of the dienophile in the condensation.

A single-crystal X-ray analysis (see Experimental section) of the spiro compound **16** showed that the structure consists of neutral molecules packed with no contacts shorter than those expected on the basis of the van der Waals radii as shown in Fig. 1. There is a triple bond between C(19) and C(20) and double bonds between C(4) and C(5), C(9) and C(10), C(12) and C(13), C(2) and O(1), and between C(11) and O(2). The phenylacetylene and cyclohexa-2,5-dienone moieties are both planar to within 0.05 Å. Long bonds between C(3) and C(8) [1.61(1) Å] and between C(7) and C(8) [1.57(1) Å] reflect the strain about the quaternary atom C(8).

Experimental

Mps were determined on a Kofler hot-stage and are uncorrected. Column chromatography was carried out on Merck Kieselgel 60 (230–240 mesh). IR spectra were recorded on a Digilab FTS-80 spectrometer, and NMR spectra were deter-

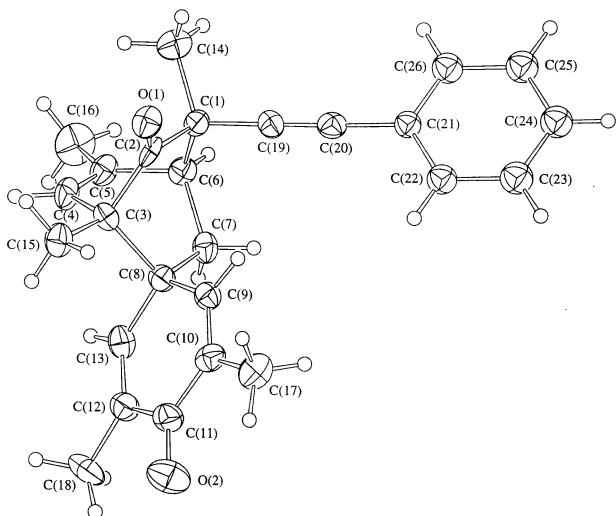


Fig. 1 X-Ray molecular structure of spirocyclohexa-2,5-dienone **16** (with atomic numbering used in the crystallographic data)

mined with SiMe₄ as internal standard on Bruker AMX-400 and AC-200B spectrometers. *J* Values are given in Hz. Microanalyses were performed by the microanalytical unit of the School of Chemistry, University of New South Wales, and mass spectra were recorded on an AEI model MS902 double focusing instrument.

General method for the reaction of carbon nucleophiles with phenylethylnyllead triacetate generated *in situ* by Zn–Pb exchange

Phenylacetylene (0.51 g, 5.0 mmol) was dissolved in dry tetrahydrofuran (5 cm³). Butyllithium solution (2.0 M; 2.5 cm³, 5.0 mmol) in hexane was added at –78 °C to the mixture which was then stirred for 20 min under nitrogen. Zinc chloride (0.68 g, 5.0 mmol) was added to the mixture after which it was allowed to warm to –10 °C; after being stirred at –10 °C for 30 min the mixture was diluted with chloroform (20 cm³) at –10 °C. Lead tetraacetate (2.03 g, 4.58 mol) in chloroform (20 cm³) was added to the mixture after which it was stirred at –10 °C for 15 s. The substrate (4.17 mmol) in chloroform (4 cm³) (for **1** and **5**) or THF (8 cm³) (for **6**) was added to the solution which was then stirred at –10 °C for 1 h, followed by 2 h at room temperature. The mixture was then poured into diethyl ether (200 cm³), filtered through Celite and evaporated to give the crude product.

The following compounds were synthesised by the above method.

(i) **Ethyl 2-oxo-1-(phenylethynyl)cyclopentanecarboxylate 3 (0.78 g, 73%)**. Separated by HPLC (Whatman Partisil 10 M20) in ethyl acetate–light petroleum (1 : 49) as a colourless oil. It had ¹H NMR and IR spectroscopic data in accord with literature values.¹

(ii) **2-Acetyl-2-(phenylethynyl)-3,4-dihydronaphthalen-1(2H)-one 7**. Separated as an oil (0.71 g, 59%) by flash chromatography in ethyl acetate–light petroleum (1 : 19). The ¹H NMR and IR spectra were identical with those obtained previously.¹

(iii) **3-Methyl-3-nitro-1-phenylbut-1-yne 9**. Obtained as an oil (0.46 g, 58%) by flash chromatography in ethyl acetate–light petroleum (1 : 19). The ¹H NMR and IR spectra correspond with those obtained previously.¹

General method for the reaction of carbon nucleophiles with oct-1-ynyllead triacetate *in situ* by Zn–Pb exchange

Oct-1-yne (0.55 g, 5.0 mmol) was dissolved in dry tetrahydrofuran (5 cm³). A solution of butyllithium (2.2 M; 2.25 ml, 5.0 mmol) in hexane was added at –78 °C to the mixture which was then stirred for 20 min under nitrogen. Zinc chloride (0.68 g, 5.0 mmol) was added to the solution after which it was

allowed to warm to –10 °C, at which temperature it was stirred for 30 min; it was then diluted with chloroform (10 cm³) at –10 °C. Lead tetraacetate (2.03 g, 4.58 mmol) and mercuric acetate (0.15 g, 0.46 mmol) in chloroform (20 cm³) were added to the solution after which it was stirred at –10 °C for 15 s. The substrate (4.17 mmol) in chloroform (3 cm³) (for **1** and **5**) or tetrahydrofuran (8 cm³) (for **6**) was added to the solution which was then stirred at –10 °C for 1 h, followed by 2 h at room temperature. The mixture was finally poured into diethyl ether (200 ml), filtered through Celite, and evaporated to give the crude product.

The following compounds were obtained by the above method.

(i) **Ethyl 1-(oct-1-ynyl)-2-oxocyclopentanecarboxylate 12**. Separated by flash chromatography in ethyl acetate–light petroleum (7 : 95) as a colourless oil (0.57 g, 52%). The ¹H NMR and IR spectroscopic data were identical with those obtained previously.¹

(ii) **2-Acetyl-2-(oct-1-ynyl)-3,4-dihydronaphthalen-1(2H)-one 8**. Obtained by flash chromatography in ethyl acetate–light petroleum (1 : 19) as an oil (0.64 g, 52%). The ¹H NMR and IR spectroscopic data were in accord with literature values.¹

(iii) **2-Methyl-2-nitrodec-3-yne 10**. Separated by flash chromatography in ethyl acetate–light petroleum (3 : 97) as an oil (0.34 g, 41%). The ¹H NMR and IR spectroscopic data were identical with those previously reported.¹⁰

Oxidation of ethyl 2-oxocyclopentanecarboxylate 1 by LTA in the presence of ZnCl₂

Lead tetraacetate (2.42 g, 5.46 mol) in chloroform (10 cm³) was added to a solution of ethyl 2-oxocyclopentanecarboxylate (1.53 g, 9.83 mmol) in chloroform (10 cm³) and tetrahydrofuran (10 cm³) at –10 °C, and the mixture was stirred at –10 °C for 1 h, followed by 2 h at room temperature. The mixture was then poured into diethyl ether (200 cm³), filtered through Celite and evaporated. The crude material was fractionated by flash chromatography (ethyl acetate–light petroleum, 2 : 23) to yield the *dimer 4* as a colourless oil (1.025 g, 67%) (Found: C, 61.7; H, 7.4. C₁₆H₂₂O₆ requires C, 61.9; H, 7.1%); δ_H(CDCl₃) 4.29 (4 H, q, *J* 7.1, 2 × CO₂CH₂CH₃), 2.86–2.72 (2 H, dt, *J* 14.1, 10.4, 3-H and 3'-H), 2.71–2.27 (6-H, m, 3-H, 3'-H, 5-H₂ and 5'-H₂), 2.26–2.07 (4-H, m, 4-H₂ and 4'-H₂) and 1.32 (6 H, t, *J* 7.1, 2 × CO₂CH₂CH₃); δ_C(CHCl₃) 205.9 (C-2 and C-2'), 166.9 (2 × CO₂Et), 69.4 (C-1 and C-1'), 62.7 (2 × CO₂CH₂CH₃), 38.1 (C-3 and C-3'), 35.0 (C-5 and C-5'), 18.8 (2 × CH₃) and 13.6 (C-4 and C-4'); ν_{max}(CHCl₃)/cm⁻¹ 1768 and 1723; *m/z* 164 (M – 2 × CO₂Et, 13%), 162 (26), 145 (13), 135 (25), 134 (18), 132 (14), 123 (13), 122 (26), 120 (20), 117 (28), 109 (66), 108 (34), 107 (76), 99 (32), 89 (28), 82 (41), 81 (26), 73 (20) and 55 (100).

Reaction of 2,4,6-trimethylphenol (mesitol) 13 with phenylethylnyllead triacetate produced by Zn–Pb exchange

Butyllithium in hexane (2.0 M; 3.5 cm³, 7.06 mmol) was added to phenylacetylene (0.72 g, 7.06 mmol) in dry THF (7.0 cm³) at –78 °C, and the mixture was stirred for 20 min under N₂. Zinc chloride (0.96 g, 7.06 mmol) was added to the solution which was then allowed to warm to –10 °C, at which temperature it was stirred for 30 min. Chloroform (25 cm³) was added to the mixture followed by LTA (2.84 g, 6.42 mmol) in chloroform (25 cm³); the mixture was then stirred at –10 °C for 15 s. Mesitol **13** (0.80 g, 5.88 mmol) in chloroform (6 cm³) and pyridine (1.01 g, 12.8 mol) were then added to the mixture after which it was stirred at –10 °C for 1 h followed by 3 h at room temperature. After this the mixture was poured into diethyl ether (200 cm³), filtered through Celite, and the filtrate washed in turn with dilute sulfuric acid (1.0 M; 2 × 100 cm³), water (2 × 100 cm³) and saturated brine (100 cm³) and then dried (Na₂SO₄) and evaporated. The residue was chromatographed on a column of silica gel in ethyl acetate–light petroleum (1 : 19) to yield

2,4,7,9,13-pentamethyl-9-phenylethynyl-7,10-etheno[5.5]-undeca-1,4-diene-3,8-dione **16** (0.89 g, 41%) as pale yellow crystals (from ethyl acetate–light petroleum), mp 132–133 °C (Found: C, 84.4; H, 7.2. $C_{26}H_{26}O_2$ requires C, 84.3; H, 7.1%); δ_H ($CDCl_3$) 0.98 (3 H, s, 7-Me), 1.55 (3 H, s, 9-Me), 1.80 (1 H, dd, J 14.2, 3.0, 11-H), 1.85 (3-H, d, J 1.5, 4-Me), 1.89 (3 H, J 1.0, 2-Me), 2.00 (3-H, d, J 1.7, 13-Me), 2.70 (1 H, dd, J 14.2, 2.5, 11-H), 2.83 (1 H, m, 10-H), 5.47 (1 H, dq, J 1.7, 1.2, 12-H), 6.46 (1 H, dq, J 3.3, 1.0, 1-H), 6.82 (1 H, dq, J 3.3, 1.5, 5-H), 7.28–7.35 (3 H, m, phenyl-H) and 7.39–7.43 (2 H, m, phenyl-H); δ_C ($CDCl_3$) 13.6 (7-Me), 16.1 (9-Me), 16.4 (9-Me or 13-Me), 21.8 (4-Me), 25.3 (2-Me), 33.6 (C-11), 44.4 (C-6), 48.0 (C-9), 48.4 (C-10), 55.5 (C-7), 84.4 (C=C), 90.7 (C=C), 122.6 (phenyl C-1), 124.1 (C-12), 128.3 (phenyl C-4), 128.4 (phenyl C-3 and C-5), 131.5 (phenyl C-2 and C-6), 134.5 (C-13), 135.2 (C-2), 146.1 (C-4), 147.9 (C-1), 148.0 (C-5), 186.7 (C-3) and 208.0 (C-8); ν_{max} ($CHCl_3$)/ cm^{-1} 1727, 1686, 1633, 1491, 1449, 1378 and 1231; λ_{max} (EtOH)/nm 254 and 243 ($\epsilon/dm^3 mol^{-1} cm^{-1}$ 26 480 and 27 690); m/z (370, 1%) 236 (62), 235 (30), 221 (54), 207 (25), 193 (85), 192 (50), 191 (30), 179 (18), 178 (64), 165 (31), 135 (33), 134 (100), 115 (24), 106 (20), 105 (32), 91 (94), 77 (35), 65 (26) and 63 (20).

Crystal structure analysis of the spirocyclohexa-2,5-dienone **16**

For diffractometry a crystal was mounted on a glass fibre with cyanoacrylate resin. Lattice parameters at 21 °C were determined by a least-squares fit to the setting parameters of 25 independent reflections, measured and refined on an Enraf-Nonius CAD4F four-circle diffractometer employing graphite monochromated Mo-K α radiation.

Crystal data. Formula $C_{26}H_{26}O_2$; M , 370.49, monoclinic, space group $P2_1/n$, a 12.979(4), b 9.423(4), c 18.129(3) Å; β 108.32(2)°, V 2104.8(9) Å³, Z 4, D_c 1.169 g cm⁻³, μ (Mo-K α) 0.39 cm⁻¹, λ (Mo-K α) 0.7107 Å, $F(000)$ 792 electrons.

Data collection and processing. Intensity data were collected in the range $1 < \theta < 22.5^\circ$ using an ω - θ scan. The scan widths and horizontal counter apertures employed were (1.00 + 0.35 tan θ)° and (2.70 + 1.05 tan θ) mm respectively. Data reduction and application of Lorentz and polarisation corrections were carried out using the Enraf-Nonius Structure Determination Package.¹¹ Of the 3060 reflections collected, 889 with $I > 2.5\sigma(I)$ were considered observed and used in the calculations.

Structure analysis and refinement. The structure was solved by direct methods using SHELXS-86¹² and the solution was extended by difference Fourier methods. The phenyl group was included as a rigid group (C–C 1.395 Å) with isotropically refined thermal parameters, hydrogen atoms were included at calculated sites (C–H 0.97 Å) and all other atoms were refined anisotropically. The use of these constraints allowed for a satisfactory refinement despite the small number of observed reflections available from the small and weakly diffracting crystals.

Full-matrix least-squares refinement of an overall scale factor, positional and thermal parameters converged (all

shifts $< 0.07\sigma$) with R^{\dagger} 0.052, R_w 0.051 and $w = 2.19/[\sigma^2(F_o) + 0.000 11F_o^2]$. Maximum excursions in a final difference map were +0.2 e Å⁻³ and -0.2 e Å⁻³. Scattering factors and anomalous dispersion terms used were those supplied in SHELX-76.¹³ All calculations were carried out using SHELX-76¹³ and plots were drawn using ORTEP.¹⁴ The atom numbering scheme is given in Fig. 1. Atomic coordinates, bond lengths and bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors (1997), *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/99.

Acknowledgements

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$$\dagger R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|, R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w_o^2]^{\frac{1}{2}}$$

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