The Chemistry of Organolead(IV) Tricarboxylates. Synthesis and Electrophilic Heteroarylation Reactions of 2- and 3-Thienyl-, and 2- and 3-Furyl-lead Tricarboxylates

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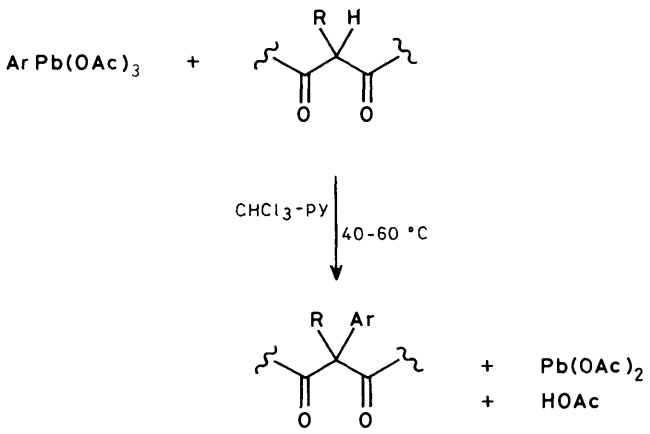
Tin(IV)–lead(IV) exchange and mercury(II)–lead(IV) exchange reactions have been used to obtain 2-thienyl-lead triacetate (**3**), 2-thienyl-lead tribenzoate (**4**), 3-thienyl-lead triacetate (**16**), 2-furyl-lead triacetate (**21**), and 3-furyl-lead triacetate (**31**). In reactions with the β-dicarbonyl compounds (**7**), (**11**), and (**13**), the above heteroaryl-lead compounds behaved as 2-thienyl, 3-thienyl, 2-furyl, and 3-furyl cation equivalents respectively, giving the α-heteroaryl β-dicarbonyl compounds (**8**), (**12**), (**14**), (**17**), (**18**), (**19**), (**25**), (**27**), (**28**), (**33**), (**34**), and (**35**) in synthetically useful yields.

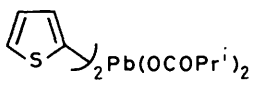
During the past 10 years we have shown that aryl-lead(IV) triacetates are useful reagents for the direct electrophilic *C*-arylation of carbon acids such as β-dicarbonyl compounds[1–3] (see Scheme 1). In view of the interest in the preparation of α-heteroaryl β-dicarbonyl compounds, especially α-thienylmalonates[4] and α-furylmalonates,[5] by the pharmaceutical industry, we sought to extend our method to include the synthesis of such compounds.



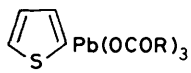
Scheme 1.

The first report of a heteroaryl-lead(IV) tricarboxylate was that of Panov and Kocheshkov,[6] who obtained bis(2-thienyl)lead di-isobutyrate (**1**) by treating thiophene with lead tetraisobutyrate. 2-Thienyl-lead tri-isobutyrate (**2**), the presumed intermediate in formation of (**1**), was not isolated, but it has been suggested[7] that such compounds may be relatively stable. In 1974, we reported[8] the preparation of 2-thienyl-lead triacetate (**3**) by the direct plumbation of thiophene with lead tetra-acetate in dichloroacetic acid, followed by treatment with acetic acid. This work was extended by de Vos and co-workers[9] to the synthesis of a variety of 4- and 5-substituted 2-thienyl-lead triacetates. The chemistry of 2-thienyl-lead triacetate has only been briefly examined; in trifluoroacetic acid it underwent protodemetallation to give thiophene,[8] while treatment with trifluoroacetic acid and durene† produced the 2,5-diarylthiophene (**5**) in low yield.[10]

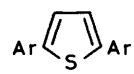
† 1,2,4,5-Tetramethylbenzene.



(**1**)



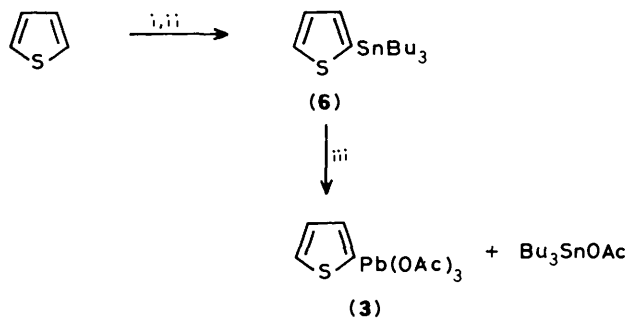
(**2**) R = Pr^i
(**3**) R = Me
(**4**) R = Ph



(**5**) Ar = 2,3,5,6-Me_4C_6H

Results and Discussion

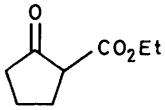
2-Thienyl-lead Tricarboxylates.—In the present work the direct plumbation route[8] to 2-thienyl-lead triacetate (**3**) was found to give variable results. This appeared to arise from its sensitivity to water, which is necessary in the reaction work-up. Since our more recent tin–lead exchange method[11] does not involve an aqueous work-up, we examined the preparation of (**3**) by this route, which is outlined in Scheme 2. The stannane (**6**)



(**3**)

Scheme 2. *Reagents:* i, BuLi–THF; ii, Bu_3SnCl; iii, $Pb(OAc)_4$–$Hg(OAc)_2$ catalyst

was produced in good yield, and with lead tetra-acetate in chloroform it underwent a clean metal–metal exchange. The reaction, which took *ca.* 2 h, could be accelerated (30 min) by catalysis with mercury(II) acetate. The lead compound (**3**) was simply obtained by precipitation with light petroleum containing some acetic acid for protection against moisture, and washing with light petroleum under dry nitrogen. The material prepared in this way darkened rapidly in a moist atmosphere, in contrast to the behaviour of analogous benzene derivatives,[8,11] which slowly polymerise in the presence of water.



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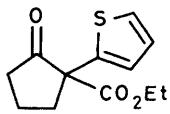
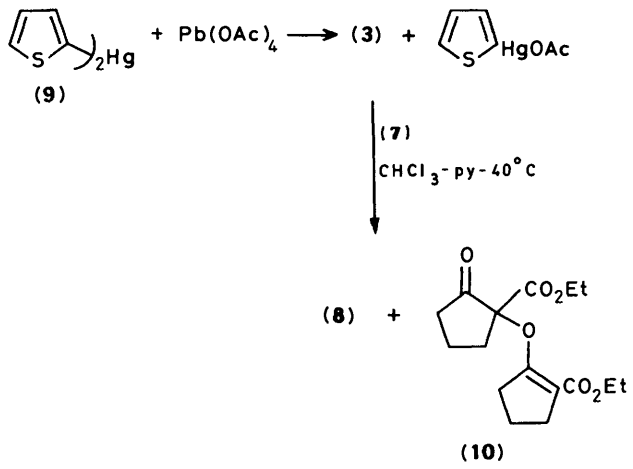


(8)

When 2-thienyl-lead triacetate (**3**) was treated with the β-keto ester (**7**) under the conditions indicated in Scheme 1, the expected α-thienyl β-keto ester (**8**) was obtained in only 9% yield, in contrast to the generally high yielding reaction of aryl-lead triacetates.[12] A similar low yield of (**8**) was produced when our method of *in situ* generation of (**3**) from bis(2-thienyl)-mercury (**9**)[3] was used (see Scheme 3). This route involved the



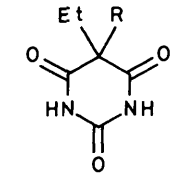
Scheme 3.

preparation of the mercury compound (**9**) by reaction of 2-thienyl-lithium with mercury(II) chloride. With lead tetra-acetate in chloroform (**9**) underwent rapid metal–metal exchange, which was complete (n.m.r. spectroscopy) within 15 min. Pyridine (2 equiv.) and the β-keto ester (**7**) were then added to the mixture at 40 °C. Accompanying (**8**) in the reaction was the keto diester (**10**), a product of radical coupling, which could be obtained in good yield by treatment of (**7**) with lead tetra-acetate.

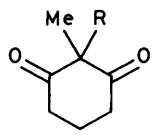
These results indicated that 2-thienyl-lead triacetate (**3**) was a stronger oxidant than previously investigated aryl-lead triacetates, and a means of suppressing this characteristic was sought. It appeared that this might be achieved simply by replacing the acetate ligands by benzoate, since lead tetrabenzoate is known to be a weaker oxidant than lead tetra-acetate.[13] This possibility was examined using the method outlined in Scheme 3. When lead tetrabenzoate[14] was added to bis(2-thienyl)mercury (**9**) in dry pyridine, the metal–metal exchange was complete within 0.5 h, and after having stirred the resulting mixture with the β-keto ester (**7**) for a further 0.5 h the thiophene derivative (**8**) was obtained in 76% yield. Lower yields were obtained when our usual conditions (chloroform–pyridine) were used. A complication in the use of lead tetrabenzoate was the separation of the product (**8**) from 2-thienylmercury benzoate, which was more soluble in organic solvents than the corresponding acetate. However, this was overcome by the addition of iodine, which converted it into 2-iodothiophene, readily removed by chromatography.

The above procedure, employing the *in situ* generation of 2-thienyl-lead tribenzoate (**4**), was also used to convert 5-ethylbarbituric acid (**11**) and 2-methylcyclohexane-1,3-dione (**13**) into the 2-thienyl derivatives (**12**) and (**14**) respectively.

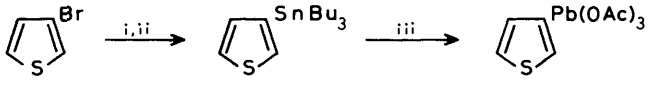
3-Thienyl-lead Triacetate.—3-Thienyl-lead triacetate (**16**) was considerably more stable than the 2-thienyl compound (**3**), behaving similarly to the corresponding benzene derivatives. Its synthesis was readily achieved in moderate yield *via* the stannane (**15**) as outlined in Scheme 4. Unlike 2-thienyl-lead



(**11**) R = H
(**12**) R = 2-Thienyl



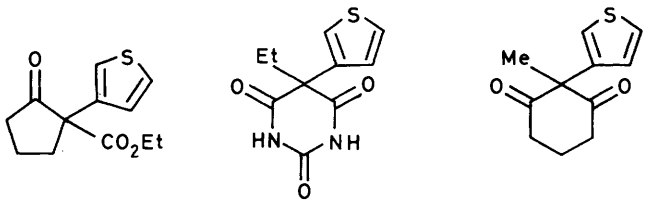
(**13**) R = H
(**14**) R = 2-Thienyl



(**15**) (**16**)

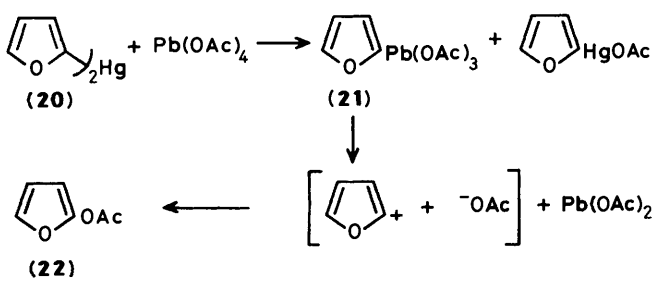
Scheme 4. *Reagents:* i, BuLi; ii, Bu_3SnCl; iii, $Pb(OAc)_4$, Hg(OAc) catalyst

triacetate (**3**), the lead compound (**16**) reacted smoothly with β-dicarbonyl compounds under the conditions developed for arylation with benzenoid aryl-lead triacetates.[12] In reactions with the β-dicarbonyls (**7**), (**11**), and (**13**), the 3-thienyl derivatives (**17**), (**18**), and (**19**) were obtained in yields of 79, 51, and 82%, respectively.



(**17**) (**18**) (**19**)

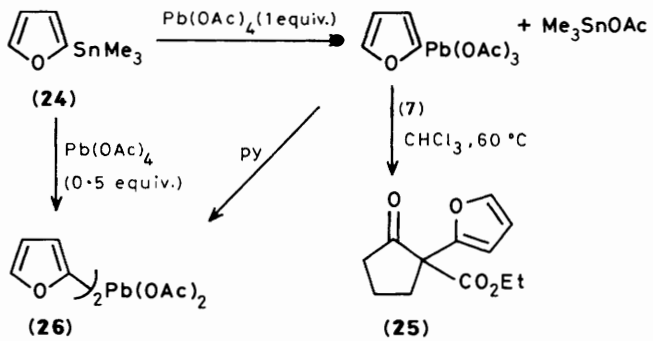
2-Furyl-lead Triacetate.—In the expectation that 2-furyl-lead triacetate (**21**) may behave similarly to the 2-thienyl compound (**3**), we first examined its generation by reaction of bis(2-furyl)-mercury (**20**) with lead tetra-acetate. For the synthesis of the required mercury compound (**20**), the method used above for the preparation of (**9**) was found to be more convenient than that previously reported.[15] The reaction between lead tetra-acetate and bis(2-furyl)mercury (**20**) was performed initially in deuteriochloroform and monitored by ^1H n.m.r. spectroscopy (see Scheme 5). The reaction was characterised by a rapid



Scheme 5.

appearance of aromatic signals downfield from those of compound (**20**), presumably due to the 2-furyl-lead compound (**21**). These signals were slowly replaced by a similar set of upfield signals, and after 15 min there was no further change in the spectrum of the mixture. The product of this decomposition was isolated, and identified as 2-furyl acetate (**22**).[16] We believe that the lead compound (**21**) breaks down to give lead(II) acetate, and 2-furyl cation and acetate ion, which combine to produce the acetate (**22**).

We have found that in the case of vinyl-lead triacetates generated from divinylmercury compounds, a similar breakdown occurs to yield vinyl acetates.[17] On the other hand, solutions of vinyl-lead triacetates generated by tin–lead exchange as in Scheme 2 are relatively more stable, and therefore we turned to this approach. Tributyl-2-furylstannane (**23**) was prepared by a route analogous to that used to obtain the stannane (**6**). Reaction of this compound (**23**) with lead tetra-acetate and a catalytic amount of mercury(II) trifluoroacetate in deuteriochloroform did, in fact, lead to a more stable solution of 2-furyl-lead triacetate (**21**), and after 1 h only a trace of 2-furyl acetate (**22**) could be detected by n.m.r. spectroscopy. Addition of the keto ester (**7**) to a solution of lead compound (**21**) generated in this way afforded the α-furyl β-keto ester (**25**) in modest yield (n.m.r. spectroscopy); however, the method was not synthetically useful, since separation from tributylstannyl acetate, the other product of the metal–metal exchange, could not be achieved. This problem was readily overcome by use of 2-furyltrimethylstannane (**24**), which on treatment with 1 equiv. of lead tetra-acetate rapidly gave lead compound (**21**) in high yield together with trimethylstannyl acetate,* a compound of low solubility in organic solvents (see Scheme 6). When this

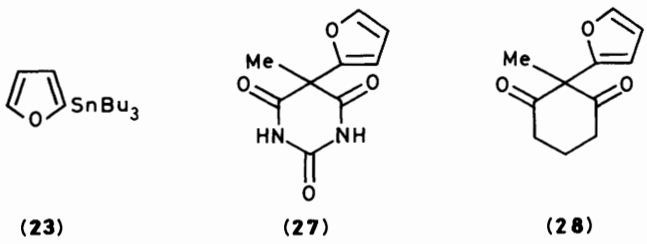


Scheme 6.

reaction mixture was treated with the keto ester (**7**) at 60 °C, the α-furyl β-keto ester (**25**) was isolated in 76% yield. Unlike the arylation of β-dicarbonyls by benzenoid aryl-lead triacetates, the addition of pyridine to the above mixture led to a lower yield of (**25**). This was shown to arise from the formation of bis(2-furyl)lead diacetate (**26**), which could be obtained in good yield by adding pyridine only to the solution containing (**21**). By way of confirmation of the structure of the lead compound (**26**), it was also produced in 96% yield by mixing (**24**) and lead tetra-acetate in a 2:1 ratio.

The above method for the preparation of the α-furyl derivative (**25**) was also used to obtain the α-furyl β-dicarbonyl compounds (**27**) and (**28**) from 5-ethylbarbituric acid (**11**) and 2-methylcyclohexane-1,3-dione (**13**) in yields of 33 and 28%, respectively. There would appear to be the potential to improve

* It should be noted that benzenoid aryltrimethylstannanes do not generally give high yields of aryl-lead triacetates with lead tetra-acetate owing to competing methyl–tin cleavage.[11]



(**23**) (**27**) (**28**)

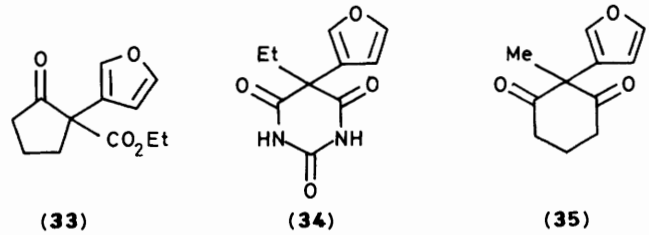
yields with the less reactive dicarbonyls such as (**13**) by using the enolate salts. Thus, when the reaction of stannane (**24**) and lead tetra-acetate was carried out in dry dimethyl sulphoxide, followed by the addition of the sodium salt of (**13**) in dimethyl sulphoxide, the β-diketone (**28**) was obtained in 42% yield.

3-*Furyl-lead Triacetate*.—As in the case of the thienyl-lead compounds (**3**) and (**16**), 3-furyl-lead triacetate (**31**) proved to be more stable than the 2-substituted compound (**21**); however, like 3-thienyl-lead triacetate (**16**), it was rather more moisture sensitive than the corresponding benzene derivatives. The synthesis of (**31**) from 3-bromofuran[18] was readily achieved by a route analogous to that outlined in Scheme 4 for compound (**16**), but with modification of the conditions used in the tin–lead exchange step. This was necessary since reaction of tributyl-3-furylstannane (**29**) with lead tetra-acetate and a mercury(II) catalyst gave a mixture of 3-furyl-lead triacetate (**31**) and the

(**29**) R = Bu (**31**) *n* = 1
(**30**) R = Me (**32**) *n* = 2

bis(3-furyl)lead compound (**32**). By the use of a 1:1 mixture of stannane (**29**) and lead tetra-acetate without a catalyst and a reaction time of 20 min, the required compound (**31**) was obtained free of (**32**). Alternatively, the latter compound (**32**) could be obtained in good yield with 2 equiv. of the tin compound (**29**) and catalysis by mercury(II) trifluoroacetate.

Unlike 2-furyl-lead triacetate (**21**), pyridine did not catalyse the disproportionation of the 3-furyl compound (**31**), and it was found to be necessary for the arylation of β-dicarbonyl compounds by (**31**). Using the conditions developed with benzenoid aryl–lead triacetates[12] [chloroform, pyridine (3



(**33**) (**34**) (**35**)

equiv.), 40 °C], the β-dicarbonyl compounds (**7**), (**11**), and (**13**) reacted with the lead compound (**31**) to give (**33**), (**34**), and (**35**) in yields of 70, 62, and 50%, respectively.

As in the case of arylation with 2-furyl-lead triacetate (**21**), isolation of the lead compound (**31**) may be avoided, resulting in a more convenient procedure. The required 3-furyltrimethylstannane (**30**) was readily obtained in the same way as the

tributyl compound (**29**), and underwent a rapid exchange (5 min) with lead tetra-acetate to generate a chloroform solution of lead compound (**31**). Addition of pyridine, followed by the β-keto ester (**7**), resulted in a 72% isolated yield of the 3-furyl derivative (**33**).

Experimental

The instruments employed for spectroscopic determinations and the general procedures have been noted previously,[8] except that flash chromatography was carried out on a column packed with Merck Kieselgel 60 (230—400 mesh), and n.m.r. spectra were recorded on either Varian XL 100 or Bruker MW 400 spectrometers. Lead tetrabenzoate[14] and 3-furyltrimethylstannane (**30**)[19] were prepared as previously described.

Tributyl(2-thienyl)stannane (**6**).—Butyl-lithium in hexane (1.5M; 22 ml, 33 mmol) was added to thiophene (5.04 g, 60 mmol) in anhydrous tetrahydrofuran (50 ml) at −30 °C and the mixture was stirred at this temperature under nitrogen for 2 h. Tributylchlorostannane (10.05 g, 30 mmol) was added and the mixture was stirred at −30 °C for a further 30 min. Saturated aqueous sodium hydrogen carbonate (50 ml) was added, and the organic phase was separated and washed with saturated aqueous sodium hydrogen carbonate (50 ml) and brine (30 ml). The solvent was evaporated from the dried (Na_2SO_4) extract, and the residue was chromatographed on a column of neutral alumina (light petroleum) to give the *title compound* (**6**) (8.4 g, 75%) as a colourless oil (Found: C, 51.6; H, 8.2; S, 9.0. $C_{16}H_{30}SSn$ requires C, 51.5; H, 8.1; S, 8.6%); $\lambda_{max.}$(hexane) 211 and 246 nm (ε 3 380 and 7 060); $\delta_H(CDCl_3)$ 0.7—1.8 (27 H, m, 3 × Bu), 7.19 (1 H, dd, $J_{3,4}$ 3.2, $J_{3,5}$ 4.4, $^{117Sn}J_{3,Sn}$ 20.6, $^{119Sn}J_{3,Sn}$ 21.8 Hz, 3-H), 7.26 (1 H, dd, $J_{3,4}$ 3.2, $J_{4,5}$ 4.4 Hz, 4-H), and 7.67 (1 H, dd, $J_{3,5}$ 1.0 Hz, $J_{4,5}$ 4.4, $^{117Sn}J_{5,Sn}$ 9.4, $^{119Sn}J_{5,Sn}$ 10.0 Hz, 5-H); $\delta_C(CDCl_3)$ 10.8 (t), 13.6 (q), 27.3 (t), 29.7 (t), 127.7 (d, C-4), 130.4 (d, C-5), 135.1 (d, C-3), and 135.9 (s, C-2); *m/z* 317 ($M^+ - C_4H_8$, 100%) and 315 (98).

Tributyl(3-thienyl)stannane (**15**).—Butyl-lithium in hexane (1.4M; 36 ml, 50 mmol) was added to 3-bromothiophene (8.15 g, 50 mmol) in anhydrous ether (50 ml) at −70 °C and the mixture was stirred under nitrogen for 15 min. Tributylchlorostannane (16.27 g, 50 mmol) was added and the mixture was stirred for 1 h at −70 °C. The temperature was allowed to rise to room temperature over a period of 2 h, and the reaction was worked up as above to yield the *title compound* (**15**) (6.0 g, 32%) as a colourless oil (Found: C, 51.8; H, 8.2; S, 8.6. $C_{16}H_{30}SSn$ requires C, 51.5; H, 8.1; S, 8.6%); $\lambda_{max.}$(cyclohexane) 247 nm (ε 4 500); $\delta_H(CDCl_3)$ 0.74—1.68 (27 H, m, 3 × Bu), 7.15 (1 H, dd, $J_{2,4}$ 1.0, $J_{4,5}$ 4.6 Hz, 4-H), 7.33 (1 H, dd, $J_{2,4}$ 1.0, $J_{2,5}$ 2.5 Hz, 2-H), and 7.43 (1 H, dd, $J_{2,5}$ 2.5, $J_{4,5}$ 4.6 Hz, 5-H); ^{117}Sn and ^{119}Sn satellites unresolved; $\delta_C(CDCl_3)$ 10.2 (t), 13.7 (q), 27.3 (t), 29.2 (t), 124.9 (d, C-4), 131.2 (d, C-5), 133.1 (d, C-2), and 137.4 (s, C-3); *m/z* 317 ($M^+ - C_4H_8$, 100%) and 315 (73).

Tributyl(2-furyl)stannane (**23**).—Butyl-lithium in hexane (1.4M; 47 ml, 66 mmol) was added to furan (8.16 g, 120 mmol) in anhydrous tetrahydrofuran (100 ml) at −30 °C and the mixture was stirred under nitrogen for 1.5 h. Tributyl(chloro)stannane (20.10 g, 60 mmol) was added and the mixture was stirred for 0.5 h under the same conditions. Work-up as for the preparation of compound (**6**) above gave the *title compound* (**23**) (16.5 g, 77%) as a colourless oil (Found: C, 53.8; H, 8.8. $C_{16}H_{30}OSn$ requires C, 53.8; H, 8.5%); $\lambda_{max.}$(cyclohexane) 228 nm (ε 12 600); $\delta_H(CDCl_3)$ 0.71—1.70 (27 H, m, 3 × Bu), 6.41 (1 H, dd, $J_{3,4}$ 3.2, $J_{4,5}$ 1.7, $^{117Sn}J_{4,Sn}$ 5.2, $^{119Sn}J_{4,Sn}$ 5.4 Hz, 4-H), 6.56 (1 H, dd, $J_{3,4}$ 3.2, $J_{3,5}$ 0.6, $^{117Sn}J_{3,Sn}$ 3.8, $^{119Sn}J_{3,Sn}$ 4.0 Hz, 3-H), and 7.73 (1 H, dd, $J_{3,5}$ 0.6, $J_{4,5}$ 1.7, $^{117Sn}J_{5,Sn}$ 6.5, $^{119Sn}J_{5,Sn}$ 6.9 Hz, 5-H); $\delta_C(CDCl_3)$ 10.1 (t), 13.7 (q), 27.2 (t), 29.0 (t), 109.0 (d, C-3), 121.2 (d, C-4), 147.0 (d, C-5), and 160.7 (s, C-2); *m/z* 301 ($M^+ - C_4H_8$, 100%) and 299 (94).

2-Furyltrimethylstannane (**24**).—Butyl-lithium in hexane (1.5M; 20 ml, 30 mmol) was added slowly with stirring to furan (4.08 g, 60 mmol) in dry ether (50 ml), and the mixture was stirred at room temperature under nitrogen for 3 h. A solution of chlorotrimethylstannane (5.98 g, 30 mmol) in dry ether (30 ml) was added and the mixture was stirred for a further 15 min. Dry light petroleum (100 ml) was added and the mixture was filtered under nitrogen. The solvent was evaporated and the residue was distilled to give the title compound (**24**) (5.88 g, 85%) as a colourless oil, b.p. 75—77 °C at 30 mmHg (lit.,[20] 65 °C at 15 mmHg).

*Tributyl(3-furyl)*stannane (**29**).—Butyl-lithium in hexane (1.5M; 28 ml, 41 mmol) was added to 3-bromofuran[18] (6.10 g, 41 mmol) in anhydrous ether (50 ml) at −70 °C, and the mixture was stirred under nitrogen for 15 min. Tributyl(chloro)stannane (13.49 g, 41 mmol) was added and the mixture was stirred for 1 h under the same conditions. The reaction was then worked up as for compound (**6**) above, to give the *title compound* (**29**) (13.55 g, 88%) as a colourless oil (Found: C, 54.1; H, 8.6. $C_{16}H_{30}OSn$ requires C, 53.8; H, 8.5%); $\lambda_{max.}$(cyclohexane) 220 nm (ε 3 850); $\delta_H(CDCl_3)$ 0.72—1.90 (27 H, m, 3 × Bu), 6.35 (1 H, dd, $J_{2,4}$ 0.7, $J_{4,5}$ 1.6, $^{117Sn}J_{4,Sn}$ 10.0, $^{119Sn}J_{4,Sn}$ 10.6 Hz, 4-H), 7.23 (1 H, dd, $J_{2,5}$ 1.3, $J_{2,4}$ 0.7, $^{117Sn}J_{2,Sn}$ 8.0, $^{119Sn}J_{2,Sn}$ 8.5 Hz, 2-H), and 7.55 (1 H, dd, $J_{2,5}$ 1.3, $J_{4,5}$ 1.6, $^{117Sn}J_{5,Sn}$ 4.7, $^{119Sn}J_{5,Sn}$ 5.0 Hz, 5-H); *m/z* 301 ($M^+ - C_4H_8$, 100%) and 299 (70).

Bis(2-thienyl)mercury (**9**).—Butyl-lithium in hexane (1.5M; 42 ml, 60 mmol) was added slowly with stirring to thiophene (5.54 g, 66 mmol) in dry tetrahydrofuran (50 ml) at −30 °C, and the mixture was stirred under nitrogen for 1 h. Mercuric chloride (8.15 g, 30 mmol) was added at −55 °C and the mixture was stirred at that temperature for 1 h. The mixture was allowed to warm to room temperature and then filtered at the pump. The precipitate was washed with tetrahydrofuran–light petroleum (1:1; 30 ml) and water (500 ml), and dried *in vacuo* to yield the title compound (**9**) (8.96 g, 81%) as pale yellow crystals, m.p. 198—200 °C (lit.,[21] m.p. 198—199 °C).

Bis(2-furyl)mercury (**20**).—Butyl-lithium in hexane (1.4M; 47 ml, 66 mmol) was added slowly with stirring to furan (8.16 g, 0.12 mol) in dry tetrahydrofuran (100 ml) at −30 °C, and the mixture was stirred under nitrogen for 1 h. Mercuric chloride (8.15 g, 30 mmol) was added at −30 °C and the mixture was stirred at that temperature under nitrogen for 1 h. The mixture was allowed to warm to room temperature and water (100 ml) was added. The organic phase was separated and washed with water (2 × 100 ml), brine (50 ml), dried (Na_2SO_4), and the solvent was evaporated. The residue crystallised from aqueous acetone to give the title compound (**20**) (9.19 g, 92%) as colourless crystals, m.p. 105—107 °C (lit.,[15] m.p. 114 °C).

2-Thienyl-lead Triacetate (**3**).—2-Thienyltributylstannane (**6**) (4.47 g, 12 mmol) was added to a solution of lead tetra-acetate (4.43 g, 10 mmol) and mercury(II) trifluoroacetate (0.21 g, 0.5 mmol) in dry chloroform (50 ml), and the mixture was stirred in a stoppered flask for 30 min. Acetic acid (5 ml) was added and the stirring was continued for a further 5 min. The solvent was evaporated and the residue was dissolved in a minimum volume of chloroform–acetic acid (19:1). The solution was poured slowly into dry light petroleum (100 ml), and the precipitated solid was collected at the pump under a stream of dry nitrogen. The material was dried *in vacuo* to yield the title compound (**3**) (2.58 g, 55%) as cream-coloured crystals, m.p. 61—65 °C (lit.,[8] m.p. 82—86 °C).

3-Thienyl-lead Triacetate (**16**).—Tributyl(3-thienyl)stannane (**15**) (11.2 g, 30 mmol) was added to a solution of lead tetra-acetate (11.0 g, 25 mmol) and mercury trifluoroacetate (0.52 g, 1.25 mmol) in dry chloroform and the mixture was stirred for 1 h in a stoppered flask. The reaction mixture was filtered through dried Celite and the solvent was evaporated. Light petroleum–acetic acid (97:3, 100 ml) was added, and the precipitate was collected at the pump under dry nitrogen and washed with the same solvent mixture (100 ml). The crude material was crystallised from chloroform–acetic acid (97:3) by the slow addition of light petroleum–acetic acid (97:3) to give the *title compound* (**16**) (8.09 g, 69%) as cream-coloured needles, m.p. 75—77 °C (Found: C, 25.0; H, 2.8; S, 6.7. $C_{10}H_{12}O_6PbS$ requires C, 25.7; H, 2.6; S, 6.9%); $\delta_H(CDCl_3)$ 2.16 (9 H, s, 3 × Me). 7.39 (1 H, dd, $J_{2,4}$ 1.0, $J_{4,5}$ 5.1, $^{207Pb}J_{4,Pb}$ 80 Hz, 4-H), 7.66 (1 H, dd, $J_{2,5}$ 2.9, $J_{4,5}$ 5.1, $^{207Pb}J_{5,Pb}$ 97 Hz, 5-H), and 7.86 (1 H, dd, $J_{2,4}$ 1.0, $J_{2,5}$ 2.9, $^{207Pb}J_{2,Pb}$ 198 Hz, 2-H).

3-Furyl-lead Triacetate (**31**).—Tributyl(3-furyl)stannane (**29**) (3.93 g, 11 mmol) was added to a solution of lead tetra-acetate (4.43 g, 10 mmol) in dry chloroform (50 ml), and the mixture was stirred for 20 min under dry nitrogen in a stoppered flask. The reaction mixture was poured slowly with stirring into dry light petroleum (300 ml) and the resulting solution was kept in a stoppered flask at 4 °C for 24 h. The precipitated material was collected at the pump, and crystallised by the technique used for (**16**) above to give the *title compound* (**31**) (2.57 g, 57%) as colourless crystals, m.p. 64—65 °C (Found: C, 24.8; H, 2.8. $C_{10}H_{12}O_7Pb$ requires C, 26.6; H, 2.7%);* $\delta_H(CDCl_3)$ 2.11 (9 H, s, 3 × Me), 6.72 (1 H, dd, $J_{2,4}$ 0.7, $J_{4,5}$ 1.9, $^{207Pb}J_{4,Pb}$ 76 Hz, 4-H), 7.69 (1 H, dd, $J_{2,4}$ 0.7, $J_{2,5}$ 1.4, $^{207Pb}J_{2,Pb}$ 74 Hz, 2-H), and 7.79 (1 H, dd, $J_{2,5}$ 1.4, $J_{4,5}$ 1.9, $^{207Pb}J_{5,Pb}$ 31 Hz, 5-H).

Bis(2-furyl)lead Diacetate (**26**).—Tributyl(2-furyl)stannane (**23**) (1.43 g, 4.0 mmol) was added to a solution of lead tetra-acetate (0.89 g, 2.0 mmol) and mercury trifluoroacetate (17 mg, 0.04 mmol) in dry chloroform and the mixture was stirred at room temperature for 1.5 h. Acetic acid (0.12 g, 4.0 mmol) was added and the mixture was stirred for a further 15 min. The solvent was evaporated and dry light petroleum (30 ml) was added. The precipitate was collected and crystallised from chloroform–light petroleum containing a small amount of acetic acid, to give the *title compound* (**26**) (0.88 g, 96%) as colourless needles, m.p. 156—159 °C (decomp.) (Found: C, 31.0; H, 2.6. $C_{12}H_{12}O_6Pb$ requires C, 31.4; H, 2.6%); $\delta_H(CDCl_3)$ 2.05 (6 H, s, 2 × Me), 6.56 (2 H, dd, $J_{3,4}$ 3.4, $J_{4,5}$ 1.8, $^{207Pb}J_{4,Pb}$ 44 Hz, 4-H), 6.77 (2 H, dd, $J_{3,4}$ 3.4, $J_{3,5}$ 0.7, $^{207Pb}J_{3,Pb}$ 44 Hz, 3-H), and 7.66 (2 H, dd, $J_{3,5}$ 0.7, $J_{4,5}$ 1.8, $^{207Pb}J_{5,Pb}$ 18 Hz, 5-H).

Bis(3-furyl)lead Diacetate (**32**).—Tributyl(3-furyl)stannane (**29**) (1.43 g, 4.0 mmol) was treated with lead tetra-acetate under the same conditions as for the synthesis of compound (**26**) above. The same crystallisation procedure afforded the *title compound* (**32**) (0.71 g, 77%) as colourless needles, m.p. 157—160 °C (decomp.) (Found: C, 31.7; H, 2.7. $C_{12}H_{12}O_6Pb$ requires C, 31.4: H, 2.6%); $\delta_H(CDCl_3)$ 2.00 (6 H, s, 2 × Me), 6.56 (2 H, dd, $J_{2,4}$ 0.8, $J_{4,5}$ 2.0 Hz, $^{207Pb}J_{4,Pb}$ 52 Hz, 4-H), 7.56 (2 H, dd, $J_{2,4}$ 0.8, $J_{2,5}$ 1.5, $^{207Pb}J_{2,Pb}$ 22 Hz, 2-H), 7.59 (2 H, dd, $J_{2,5}$ 1.5, $J_{4,5}$ 2.0, $^{207Pb}J_{5,Pb}$ 45 Hz, 5-H).

Ethyl 2-Oxo-1-(2-thienyl)cyclopentanecarboxylate (**8**).—Lead tetrabenzoate (84%; 2.71 g, 3.3 mmol) and bis(2-thienyl)mercury (1.58 g, 4.3 mmol) were dissolved in dry pyridine (15 ml), and the mixture was stirred at room temperature for 0.5 h with exclusion of moisture. Ethyl 2-oxocyclopentanecarboxylate (469 mg, 3.0 mmol) was added, and the mixture was stirred under the same conditions for 0.5 h. Ether (30 ml) was added, the mixture was filtered, and the residue was washed with ether (2 × 10 ml). The combined filtrates were washed with sulphuric acid (1.5M; 2 × 50 ml), and a solution of iodine in ether was added slowly until the ether solution remained coloured. The ether phase was washed in turn with aqueous sodium thiosulphate (5%; 10 ml), saturated aqueous sodium hydrogen carbonate (2 × 20 ml), and aqueous potassium iodide (10%; 20 ml), dried (Na_2SO_4), and the solvent evaporated. Fractionation of the product by preparative t.l.c. in ethyl acetate–light petroleum (1:4) gave the *title compound* (**8**) (545 mg, 76%) as a colourless oil (Found: C, 60.9; H, 6.2. $C_{12}H_{14}O_3S$ requires C, 60.5; H, 5.9%); $\lambda_{max.}$(EtOH) 241 nm (ε 7 420); $\nu_{max.}$(film) 1 760 and 1 735 cm^{-1}; $\delta_H(CDCl_3)$ 1.22 (3 H, t, *J* 7.0 Hz, Me), 1.84—2.20 (2 H, m), 2.32—2.68 (3 H, m), 2.78—3.10 (1 H, m), 4.18 (2 H, q, *J* 7.0 Hz, CH_2), 6.97 (1 H, dd, $J_{3,4}$ 3.6, $J_{4,5}$ 5.0 Hz, 4-H), 7.06 (1 H, dd, $J_{3,4}$ 3.6, $J_{3,5}$ 1.4 Hz, 3-H), and 7.26 (1 H, dd, $J_{4,5}$ 5.0, $J_{3,5}$ 1.4 Hz, 5-H); *m/z* 238 (M^+, 88%) and 119 (100).

5-Ethyl-5-(2-thienyl)barbituric Acid (**12**).—5-Ethylbarbituric acid (**11**) (468 mg, 3.0 mmol) was treated with 2-thienyl-lead tribenzoate by a procedure identical to that used in the preparation of (**8**) above. The crude product was fractionated by p.l.c. in ethyl acetate–benzene (1:19) to give the title compound (**12**) (362 mg, 51%) as colourless crystals (aqueous ethanol), m.p. 180—181 °C (lit.,[22] m.p. 179—180 °C) (Found: C, 50.2; H, 4.4. $C_{10}H_{10}N_2O_3S$ requires C, 50.4; H, 4.2%); $\nu_{max.}$(Nujol) 3 285, 3 190, 1 780, 1 710, and 1 670 cm^{-1}; $\delta_H(CDCl_3)$ 0.95 (3 H, t), 2.46 (2 H, q), 7.00 (1 H, dd, $J_{3,4}$ 5.0, $J_{4,5}$ 3.6 Hz, 4-H), 7.08 (1 H, dd, $J_{3,4}$ 5.0, $J_{3,5}$ 1.4 Hz, 3-H), and 7.45 (1 H, dd, $J_{4,5}$ 3.6, $J_{3,5}$ 1.4 Hz, 5-H); *m/z* 238 (M^+, 84%), 210 (M^+ − CO, 71), and 209 (M^+ − CHO, 100).

2-Methyl-2-(2-thienyl)cyclohexane-1,3-dione (**14**).—2-Methylcyclohexane-1,3-dione (**13**) (378 mg, 3.0 mmol) was treated with 2-thienyl-lead tribenzoate by the same procedure as that used in the preparation of (**8**) above, except that the reaction was carried out at 40 °C for 18 h. The crude product was fractionated by preparative t.l.c. in ethyl acetate–light petroleum (1:3) to give the *title compound* (**14**) (152 mg, 24%) as a viscous oil (Found: C, 63.4; H, 6.0; S, 15.4. $C_{11}H_{12}O_2S$ requires C, 63.4; H, 5.8; S, 15.4%); $\lambda_{max.}(CHCl_3)$ 257 and 273 nm (ε 4 000 and 650); $\delta_H(CDCl_3)$ 1.55 (3 H, s, Me), 1.56—2.19 (2 H, m), 2.41—2.99 (4 H, m), 6.71 (1 H, dd, $J_{3,4}$ 3.6, $J_{3,5}$ 1.2 Hz, 3-H), 6.97 (1 H, dd, $J_{3,4}$ 3.6, $J_{4,5}$ 5.2 Hz, 4-H), and 7.28 (1 H, dd, $J_{4,5}$ 5.2, $J_{3,5}$ 1.2 Hz, 5-H); *m/z* 208 (M^+, 60%) and 105 (100).

Ethyl 2-Oxo-1-(3-thienyl)cyclopentanecarboxylate (**17**).—Ethyl 2-oxocyclopentanecarboxylate (**7**) (235 mg, 1.5 mmol) was added to a solution of 3-thienyl-lead triacetate (0.77 g, 1.65 mmol) and pyridine (0.39 g, 5.0 mmol) in dry chloroform, and the mixture was stirred for 2 h at room temperature in a stoppered flask with protection from moisture. Ether (20 ml) was added and the mixture was filtered. The residue was washed with ether (2 × 10 ml), and the combined filtrates were washed with sulphuric acid (1.5M; 2 × 20 ml), water (2 × 20 ml), and brine (10 ml), dried (Na_2SO_4), and evaporated. The crude product was chromatographed on a column of silica gel in light petroleum–ether (1:1) to give the *title compound* (**17**) (284 mg, 79%) as a colourless oil (Found: C, 60.5; H, 5.7; S, 13.8. $C_{12}H_{14}O_3S$ requires C, 60.5; H, 5.9; S, 13.5%); $\lambda_{max.}$(cyclohexane) 237 nm (ε 5 700); $\delta_H(CDCl_3)$ 1.23 (3 H, t), 1.83—3.03 (6 H, m), 4.21 (2 H, q), 7.18 (1 H, dd, $J_{2,4}$ 2.3, $J_{4,5}$ 4.3 Hz, 4-H), and 7.24—7.37 (2 H, m, 2- and 5-H); *m/z* 238 (M^+, 71%), 181 (52), 123 (100), and 109 (99).

* A tendency to polymerise in the presence of moisture often results in low percentage carbon figures for aryl-lead triacetates.[8]

5-Ethyl-5-(3-thienyl)barbituric Acid (**18**).—5-Ethylbarbituric acid (**11**) (235 mg, 1.5 mmol) was treated with 3-thienyl-lead triacetate by the same procedure as that used in the preparation of (**17**) above. The crude product was purified by chromatography on a column of silica gel in light petroleum–ether (1:4) to afford the title compound (**18**) (182 mg, 51%) as colourless crystals, m.p. 189—192 °C (lit.,[23] m.p. 192—194 °C); $\lambda_{max.}$(CHCl$_3$) 245 nm (ε 4 700); δ_H[(CD$_3$)$_2$SO] 0.86 (3 H, t), 2.32 (2 H, q), 7.03 (1 H, dd, $J_{2.4}$ 1.5, $J_{4.5}$ 5.1 Hz, 4-H), 7.41 (1 H, dd, $J_{2.4}$ 1.5, $J_{2.5}$ 2.9 Hz, 2-H), 7.52 (1 H, dd, $J_{2.5}$ 2.9, $J_{4.5}$ 5.1 Hz, 5-H), and 11.64 (2 H, br s, 2 × NH); *m/z* 238 (M^+, 43%) and 210 (M^+ − CO, 100).

2-Methyl-2-(3-thienyl)cyclohexane-1,3-dione (**19**).—2-Methylcyclohexane-1,3-dione (**13**) (235 mg, 1.5 mmol) was treated with 3-thienyl-lead triacetate by the same procedure as that used in the preparation of (**17**) above, except that the reaction was carried out at 40 °C for 18 h. The crude product was purified by preparative t.l.c. in light petroleum–ethyl acetate (4:1) to yield the *title compound* (**19**) (256 mg, 82%) as colourless crystals, m.p. 44—47 °C (Found: C, 63.7; H, 6.1. C$_{11}$H$_{12}$O$_2$S requires C, 63.4; H, 5.8%); $\lambda_{max.}$(cyclohexane) 239 and 243 nm (ε 5 700 and 5 800); δ_H(CDCl$_3$) 1.46 (3 H, s), 1.60—2.16 (2 H, m), 2.43—3.00 (4 H, m), 6.77 (1 H, dd, $J_{4.5}$ 5.1, $J_{2.4}$ 1.4 Hz, 4-H), 6.91 (1 H, dd, $J_{2.4}$ 1.4, $J_{2.5}$ 2.9 Hz, 2-H), and 7.35 (1 H, dd, $J_{4.5}$, $J_{2.5}$ 2.9 Hz, 5-H); *m/z* 208 (M^+, 100%).

Ethyl 1-(2-Furyl)-2-oxocyclopentanecarboxylate (**25**).—2-Furyltrimethylstannane (**24**) (1.15 g, 5.0 mmol) was added to lead tetra-acetate (2.0 g, 4.5 mmol) in dry chloroform (5 ml), and the mixture was stirred for 5 min at room temperature in a stoppered flask. A solution of ethyl 2-oxocyclopentanecarboxylate (**7**) (469 mg, 3.0 mmol) in dry chloroform (1 ml) was added, and the mixture was stirred at 60 °C for 1.5 h with exclusion of moisture. The reaction was worked up as for the preparation of (**17**) above, and the product was purified by preparative t.l.c. in light petroleum–ethyl acetate (4:1). The *title compound* (**25**) (506 mg, 76%) was obtained as a colourless oil (Found: C, 64.7; H, 6.7. C$_{12}$H$_{14}$O$_4$ requires C, 64.9; H, 6.4%); $\lambda_{max.}$(EtOH) 221 nm (ε 5 300); $\nu_{max.}$(CHCl$_3$) 1 760 and 1 730 cm^{-1}; δ_H(CDCl$_3$) 1.23 (3 H, t), 1.80—2.90 (6 H, m), 4.19 (2 H, q), 6.32 (2 H, m, 3- and 4-H), and 7.38 (1 H, m, 5-H); *m/z* 222 (M^+, 88%), 149 (M^+ − CO$_2$Et, 98), and 107 (149 − C$_2$H$_2$O, 100).

5-Ethyl-5-(2-furyl)barbituric Acid (**27**).—5-Ethylbarbituric acid (**11**) (469 mg, 3.0 mmol) was treated with 2-furyl-lead triacetate (**21**) by the same procedure as that used in the preparation of (**25**) above, except that the reaction time was 3 h. The crude product was purified by preparative t.l.c. in benzene–ethyl acetate (3:2) to yield the title compound (**27**) (219 mg, 33%) as pale yellow crystals, m.p. 180—182 °C (from aqueous ethanol) (lit.,[24] m.p. 188—189 °C); $\nu_{max.}$(Nujol) 3 240, 1 750, 1 730, and 1 705 cm^{-1}; δ_H[(CD$_3$)$_2$SO] 0.86 (3 H, t), 2.30 (2 H, q), 6.44 (1 H, dd, $J_{3.4}$ 3.4, $J_{4.5}$ 1.6 Hz, 4-H), 6.48 (1 H, dd, $J_{3.4}$ 3.4, $J_{3.5}$ 1.0 Hz, 3-H), 7.60 (1 H, dd, $J_{3.5}$ 1.0, $J_{4.5}$ 1.6 Hz, 5-H), and 11.7 (2 H, br s, 2 × NH); *m/z* 222 (M^+, 80%), 194 (M^+ − CO, 97), 193 (M^+ − CHO, 36), and 162 (100).

2-(2-Furyl)-2-methylcyclohexane-1,3-dione (**28**).—(*a*) 2-Methylcyclohexane-1,3-dione (**13**) (378 mg, 3.0 mmol) was treated with 2-furyl-lead triacetate by the same procedure as that used in the preparation of (**25**) above, except that the reaction was carried out at 60 °C for 4 h. The crude product was purified by p.l.c. in light petroleum–ethyl acetate (4:1) to afford the *title compound* (**28**) (161 mg, 28%) as a viscous oil (Found: C, 68.6; H, 6.3. C$_{11}$H$_{12}$O$_3$ requires C, 68.7; H, 6.3%); $\lambda_{max.}$(EtOH) 243 and 247sh nm (ε 1 800 and 800); $\nu_{max.}$(film) 1 730 and 1 705 cm^{-1}; δ_H(CDCl$_3$) 1.51 (3 H, s), 1.59—2.22 (2 H, m), 2.42—3.07 (4 H, m), 6.10 (1 H, dd, $J_{3.4}$ 3.4, $J_{3.5}$ 0.8 Hz, 3-H), 6.36 (1 H, dd, $J_{3.4}$ 3.4, $J_{4.5}$ 1.9 Hz, 4-H), and 7.37 (1 H, dd, $J_{3.5}$ 0.8, $J_{4.5}$ 1.9 Hz, 5-H); *m/z* 192 (M^+, 100%).

(*b*) A solution of 2-furyltrimethylstannane (**24**) (0.76 g, 3.3 mmol) in dry dimethyl sulphoxide (1 ml) was added to lead tetra-acetate (1.33 g, 3.0 mmol) in dry dimethyl sulphoxide (2 ml), and the mixture was stirred at room temperature in a stoppered flask. A solution of the sodium enolate of 2-methylcyclohexane-1,3-dione [prepared from (**13**) (252 mg, 2.0 mmol) and sodium hydride (48 mg, 2.0 mmol) in dry dimethyl sulphoxide (1 ml)] was added, and the mixture was stirred at room temperature for 0.5 h in a stoppered flask. The reaction was worked up and the product purified as above to give compound (**28**) (162 mg, 42%), identical with the material obtained in (*a*) above.

Ethyl 1-(3-Furyl)-2-oxocyclopentanecarboxylate (**33**).—(*a*) A solution of the keto ester (**7**) (235 mg, 1.5 mmol) in dry chloroform (1 ml) was added to 3-furyl-lead triacetate (**31**) (0.81 g, 1.8 mmol) and pyridine (0.42 g, 5.4 mmol) in dry chloroform (3 ml), and the mixture was stirred at 40 °C for 18 h. The reaction was worked up as for the preparation of (**17**) above, and the product was purified by preparative t.l.c. in light petroleum–ether (4:1). The *title compound* (**33**) (233 mg, 70%) was obtained as a colourless oil (Found: C, 65.0; H, 6.5. C$_{12}$H$_{14}$O$_4$ requires C, 64.8; H, 6.4%); $\lambda_{max.}$(cyclohexane) 226 nm (ε 1 600); δ_H(CDCl$_3$) 1.24 (3 H, t), 1.84—2.94 (6 H, m), 4.18 (2 H, q), 6.46 (1 H, dd, $J_{2.4}$ 0.8, $J_{4.5}$ 1.8 Hz, 4-H), 7.39 (1 H, dd, $J_{2.5}$ 1.5, $J_{4.5}$ 1.8 Hz), and 7.43 (1 H, dd, $J_{2.4}$ 0.8, $J_{2.5}$ 1.5 Hz, 2-H); *m/z* 222 (M^+, 92%) and 107 (100).

(*b*) A solution of the stannane (**30**) (0.28 g, 1.2 mmol) in dry chloroform (1 ml) was added to lead tetra-acetate (0.48 g, 1.1 mmol) in dry chloroform (1 ml), and the mixture was stirred at room temperature for 5 min in a stoppered flask. A solution of pyridine (0.26 g, 3.3 mmol) and the keto ester (**7**) (152 mg, 1.0 mmol) in dry chloroform (1 ml) was then added and the mixture was stirred at 40 °C for 21 h. The reaction was worked up and the product was purified as in (*a*) above to yield keto ester (**33**) (159 mg, 72%), identical with the above material.

5-Ethyl-5-(3-furyl)barbituric Acid (**34**).—5-Ethylbarbituric acid (**11**) (235 mg, 1.5 mmol) was treated with 3-furyl-lead triacetate (**31**) by the same procedure as that used in the preparation of (**33**) [method (*a*)] above. The crude product was purified by preparative t.l.c. in benzene–ethyl acetate (4:1) to give the *title compound* (**34**) (206 mg, 62%) as colourless plates, m.p. 166—168 °C (from aqueous ethanol) (Found: C, 54.5; H, 4.6. C$_{10}$H$_{10}$N$_2$O$_4$ requires C, 54.1; H, 4.5%); $\nu_{max.}$(CHCl$_3$) 3 382, 1 740, and 1 718 cm^{-1}; δ_H[(CD$_3$)SO] 0.83 (3 H, t), 2.21 (2 H, q), 6.44 (1 H, dd, $J_{2.4}$ 0.8, $J_{4.5}$ 1.8 Hz, 4-H), 7.60 (1 H, dd, $J_{2.5}$ 1.3, $J_{4.5}$ 1.8 Hz, 5-H), 7.63 (1 H, dd, $J_{2.4}$ 0.8, $J_{2.5}$ 1.3 Hz, 2-H), and 11.6 (2 H, br s, 2 × NH); *m/z* 222 (M^+, 41%), 194 (M^+ − CO, 41), 193 (M^+ − CHO, 13), and 166 (100).

2-(3-Furyl)-2-methylcyclohexane-1,3-dione (**35**).—2-Methylcyclohexane-1,3-dione (**13**) (189 mg, 1.5 mmol) was treated with 3-furyl-lead triacetate (**31**) by the same procedure as that used in the preparation of (**33**) [method (*a*)] above. The crude product was purified by p.l.c. in light petroleum–ethyl acetate (4:1) to afford the *title compound* (**35**) (143 mg, 50%) as a colourless oil (Found: C, 69.0; H, 6.0. C$_{11}$H$_{12}$O$_3$ requires C, 68.7; H, 6.3%); $\lambda_{max.}$(cyclohexane) 221 nm (ε 1 800); δ_H(CDCl$_3$) 1.45 (3 H, s), 1.69—2.91 (6 H, m), 6.15 (1 H, dd, $J_{2.4}$ 1.0, $J_{4.5}$ 1.8 Hz, 4-H), 7.15 (1 H, dd, $J_{2.4}$ 1.0, $J_{2.5}$ 1.5 Hz, 2-H), and 7.40 (1 H, dd, $J_{2.5}$ 1.5, $J_{4.5}$ 1.8 Hz, 5-H); *m/z* 192 (M^+, 100%).

Ethyl 1-(2-Ethoxycarbonylcyclopent-1-enyloxy)-2-oxocyclopentane-carboxylate (**10**).—The keto ester (**7**) (2.96 g, 19 mmol) was added to lead tetra-acetate (4.21 g, 9.5 mmol) in dry

chloroform (20 ml), and the mixture was stirred at room temperature for 1 h. The reaction was worked up as in the preparation of (**17**) above, and the crude product was purified by radial chromatography (Chromatotron) in light petroleum–ether (1:1). The *title compound* (**10**) was obtained as a colourless oil (Found: C, 62.0; H, 6.8. $C_{16}H_{22}O_6$ requires C, 61.9; H, 7.1%); $\lambda_{max.}$(cyclohexane) 246 nm (ε 5 800); $\nu_{max.}$(film) 1 749, 1 724, 1 690, and 1 632 cm^{-1}; $\delta_H(CDCl_3)$ 1.26 (3 H, t), 1.31 (3 H, t), 1.78—2.64 (12 H, m), 4.15 (2 H, q), and 4.28 (2 H, q); $\delta_C(CDCl_3)$ 13.9 (q), 14.1 (q), 17.9 (t), 19.8 (t), 28.8 (t), 33.0 (t), 35.4 (t), 36.1 (t), 59.2 (t), 61.9 (t), 85.0 (s, C-1), 112.4 (s, C-1′), 164.4 (s, 2′-CO_2Et and C-2′), 169.1 (s, 1-CO_2Et), and 207.3 (s, C-2).

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