

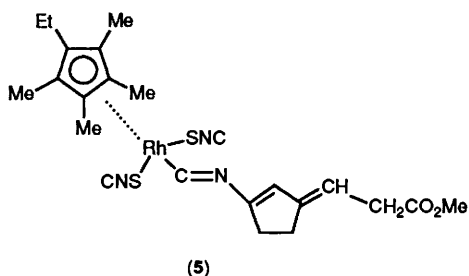
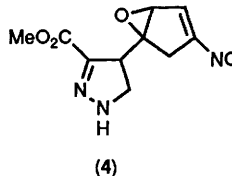
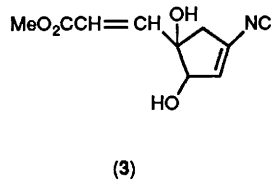
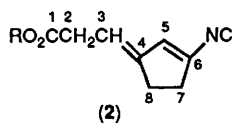
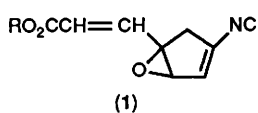
## Esterification of Isocyanide Carboxylic Acids and Hydrolysis of their Esters †

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The naturally occurring isocyanide carboxylic acids dermadin (1; R = H) and 3-[3-isocyano-(Z)-cyclopent-2-enylidene]propionic acid (2; R = H) have been esterified in 45–70% yields by reaction with alcohols and phenols in the presence of dicyclohexylcarbodi-imide and a trace of 4-dimethylaminopyridine. The phenyl esters are hydrolysed in methyl alcohol–carbonate buffer pH 10 to the parent isocyanide acids with retention of full biological activity, in *ca.* 60% yield. The isocyanide esters have been characterised as their stable crystalline  $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{SCN})_2]$  complexes, most of which have sharp, characteristic melting points.

Many species of the genus *Trichoderma* produce unstable metabolites characterised by the presence of carboxylic acid and isocyanide functionalities.<sup>1</sup> Three of these compounds (1; R = H) (2; R = H), and (3) have been characterised and most of our knowledge of their chemistry depends on stabilisation as their methyl esters, prepared by reaction with diazomethane. This reaction has two disadvantages. First, the diazomethane may add to the unsaturated systems present in the metabolites to give a complex mixture of products. One such unstable product isolated from dermadin (1; R = H), has infrared and <sup>1</sup>H NMR spectra consistent with (4). Secondly, it has proved difficult to regenerate the parent acids from their methyl esters, and one may deduce from those instances that have been reported<sup>2</sup> that the yields are low.



We have therefore sought an alternative method of esterifying these acids and have found that a variety of esters can be prepared under the conditions described by Neises and Steglich.<sup>3</sup> The reactions proceeded without isomerisation of the unsaturated systems as demonstrated by NOE of the

side-chain protons with those on the cyclopentene ring.<sup>4</sup> Yields were in the range 45–70%. We chose alcohols and phenols which would improve the stability of the metabolites, and also be expected to hydrolyse under neutral or mildly alkaline conditions. All of the esters gave crystalline, stable complexes when treated with bis( $\eta^5$ -pentamethylcyclopentadienyl)di- $\mu$ -thiocyanato-dithiocyanatodirhodium(III).<sup>5</sup> These complexes had sharp melting points, could be easily recrystallised and gave acceptable elemental analyses when combustions were performed in the presence of vanadium pentoxide. The corresponding ethyltetramethylcyclopentadienylrhodium complex of (2; R = Me), (5), was also prepared. As expected, it was more soluble in non-polar solvents, but proved more difficult to recrystallise than its pentamethyl analogue.

The trimethylsilyl ethyl ester of dermadin (1; R = Me<sub>3</sub>Si-C<sub>2</sub>H<sub>4</sub>) did not react with fluoride ion<sup>6</sup> under a variety of conditions except when the generated dermadin polymerised. Similarly, the 4-methoxyphenyl ester of the isocyanide (2; R = MeOC<sub>6</sub>H<sub>4</sub>), though more stable on chromatography than its phenyl analogue, could not be selectively oxidised with ceric ammonium nitrate at pH 7–9.<sup>7</sup> It was hydrolysed in carbonate buffer at pH 10 but the reaction was sluggish. By contrast, the phenyl esters were converted into their parent acids at pH 10 at room temperature in about 18 h. Hydrolysis of these esters in borate buffer (pH 10) gave a number of products which were not characterised; initially, a single component of the same *R<sub>F</sub>* as that of an intermediate observed in the carbonate–hydrogen carbonate hydrolysis was observed. The nature of these intermediates is unknown, but their subsequent reactions in the two buffers differ; the best yields of the desired acids were obtained in carbonate buffer. These isocyanides, obtained in *ca.* 60% yield, had UV, IR, and <sup>1</sup>H NMR spectra identical with the corresponding metabolites (1; R = H) and (2; R = H). The concentrations at which they inhibited the growth of rumen bacteria<sup>8</sup> were also comparable to those of the metabolites.

### Experimental

M.p.s are not corrected. Optical rotations were measured on a Rudolph polarimeter. UV spectra were recorded on a Cary spectrometer and IR spectra on a Perkin-Elmer 283 instrument. Mass spectra were obtained on a VG Analytical ZAB-EQ mass spectrometer with a VG 11-250 data system. Accurate mass measurements were made by the peak matching method using an appropriate ion in the spectrum of perfluorokerosene as a reference. NMR spectra were measured at 20 °C in carbon tetrachloride or chloroform (CDCl<sub>3</sub>) as

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solvents on a Bruker MSC-300 instrument at 300 MHz for proton spectra and 75.5 MHz for  $^{13}\text{C}$  spectra. All samples were examined in 5 mm tubes. Except where stated otherwise, chemical shifts refer to single protons [locant numbers refer to formula (2)] and are given in ppm downfield from the signal of tetramethylsilane. Coupling connectivities were determined as indicated, by  $^1\text{H}$  COSY and  $^1\text{H}$ - $^{13}\text{C}$  heterocorrelation experiments; nuclear Overhauser effects (NOE) on the *Z*- and *E*-isomers were measured in the usual way.<sup>4</sup>

Solutions of isocyanides were stored in peroxide-free ether at  $-15^\circ\text{C}$ . Dichloromethane was stored over calcium hydride and distilled therefrom before use. Tetrahydrofuran (THF) was stirred with lithium aluminium hydride ( $5\text{ g dm}^{-3}$ ) for 18 h and was distilled from this mixture before use. Dicyclohexylcarbodi-imide (DCC) was distilled (b.p.  $108$ – $109^\circ\text{C}$  at 1 mmHg) and aliquots (1 g) sealed into glass ampoules which were kept at  $4^\circ\text{C}$ . The ampoules were opened before use, the DCC was melted, dissolved in a known volume of dichloromethane and the appropriate quantity transferred to the reaction mixture (lower yields were obtained if these precautions were not taken). All other chemicals were of reagent grade and were used as received. All elemental analyses of rhodium derivatives for C, H, N, and S were combustions in the presence of vanadium pentoxide. High pressure liquid chromatography was done at  $20^\circ\text{C}$  using a reversed phase column ( $20 \times 0.3\text{ cm}$ , RP18, Merck) and methyl alcohol–ammonium acetate buffer (0.01M; pH 4.2) as the developing solvent in the equipment previously described.<sup>9</sup> Analytical thin layer chromatography was carried out on commercially prepared glass plates (0.025 cm thick, Kieselgel 60F<sub>254</sub>, Merck) and isocyanides were detected on the plates by spraying them with nickel(II) chloride (0.001%).

*Procedure for the Preparation of Isocyanide Esters.*—The isocyanide (1 mmol) in carbon tetrachloride or dichloromethane ( $10\text{ cm}^3$ ) was treated at  $-15^\circ\text{C}$  with a solution of the alcohol (1.1 mmol) and DCC (1.2 mmol) in dichloromethane ( $2\text{ cm}^3$ ). 4-Dimethylaminopyridine (20 mg) was added and the reaction mixture stirred at  $-15^\circ\text{C}$  for 24 h. The precipitated urea, collected by filtration, was washed ( $3 \times 1\text{ cm}^3$ ) with dichloromethane at  $-15^\circ\text{C}$  and the filtrate and washings were evaporated to  $2\text{ cm}^3$ . The concentrate was applied to a silica gel column (Merck, Kieselgel 60H,  $10 \times 4.5\text{ cm}$ , allowed to settle under gravity for 18 h) prepared with diethyl ether–light petroleum (b.p.  $40$ – $60^\circ\text{C}$ ) (1:4). The esters, eluted at  $4^\circ\text{C}$  with mixtures of ether–light petroleum (proportions given under individual compounds), were detected by spotting the fractions ( $15\text{ cm}^3$ ) on filter paper and spraying the paper with nickel(II) chloride. Appropriate fractions were combined, evaporated to  $ca. 5\text{ cm}^3$ , and transferred into appropriate solvents for spectroscopy or for preparation of the rhodium complexes.

*Procedure for the Reaction of Isocyanides with* [ $\{\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{SCN})_2\}_2$ ].—The isocyanide (0.2 mmol) in dichloromethane ( $10\text{ cm}^3$ ) was treated with a solution ( $5\text{ cm}^3$ ) of the rhodium complex (0.15 mmol) in dichloromethane. The solution was kept at  $4^\circ\text{C}$  for 3 h, and then evaporated to  $0.5\text{ cm}^3$  and the concentrate applied to a silica gel (Merck, Kieselgel 60H) column ( $8 \times 2\text{ cm}$ ) packed with the aid of dichloromethane. The yellow–orange isocyanide complex was eluted at  $4^\circ\text{C}$  from this column with methyl alcohol–dichloromethane (1:99).

*Hydrolysis of the Phenyl Esters of Isocyanides* (1; R = Ph) (2; R = Ph).—The phenyl ester (0.1 mmol) in methyl alcohol ( $5\text{ cm}^3$ ) was treated with sodium carbonate buffer {pH 11, [ $\text{Na}_2\text{CO}_3$  (0.7 g) in water ( $50\text{ cm}^3$ ) treated with  $\text{NaHCO}_3$  to pH 10 and the solution diluted to  $100\text{ cm}^3$ ]  $5\text{ cm}^3$ } at ambient

temperature. The progress of the reaction was followed by HPLC; under the chromatography conditions the retention volumes ( $\text{cm}^3$ ) of the components were: dermadin, 4.33; phenol, 5.94; phenyl dermadinate, 7.59; (2; R = H), 2.87; (2; R = Ph), 9.74. When the reaction was complete (*ca.* 18 h), the reaction mixture was concentrated ( $<5^\circ\text{C}$ , at 10 mmHg) to  $2\text{ cm}^3$  in such a way that the concentrate did not freeze. The concentrate was acidified to pH 4.6 with hydrochloric acid ( $6\text{ mol dm}^{-3}$ ) and was extracted with ether ( $4 \times 2\text{ cm}^3$ ). The ether extracts were dried and the acid transferred to solvents suitable for spectroscopic measurements.

( $\eta^5$ -Ethyltetramethylcyclopentadienyl)di- $\mu$ -thiocyanato-bis-dithiocyanatodirrhodium(III).—Di- $\mu$ -chloro-(dichloro)bis( $\eta^5$ -ethyltetramethylcyclopentadienyl)dirrhodium(III)<sup>10</sup> (1.63 g) was dissolved in acetone–dichloromethane (4:1;  $50\text{ cm}^3$ ) and the solution treated with a warm solution of sodium thiocyanate (4.86 g) in acetone ( $60\text{ cm}^3$ ). The mixture was stirred at room temperature for 1 h when a fine precipitate was deposited. The reaction mixture was evaporated, the residue treated with dichloromethane, and the mixture washed with water ( $2 \times 75\text{ cm}^3$ ). The dry ( $\text{Na}_2\text{SO}_4$ ) dichloromethane solution was evaporated and the residue (1.69 g) applied to preparative silica gel plates (PLC,  $20 \times 20 \times 0.1\text{ cm}$ ) which were developed with methyl alcohol–dichloromethane (3:97). The main orange–red band was eluted with acetone and the eluate evaporated. The residual gum was taken up in dichloromethane ( $20\text{ cm}^3$ ) and diethyl ether (*ca.*  $10\text{ cm}^3$ ) was added. The mixture was stirred for 1 week at room temperature by which time the separated gum solidified. The solid was collected, washed with ether, and dried (1.24 g, 67%; m.p.  $165$ – $168^\circ\text{C}$ ). The rhodium complex separated from THF as orange needles, m.p.  $168$ – $169^\circ\text{C}$  (Found: C, 42.5; H, 4.7; Rh, 27.4; S, 17.1.  $\text{C}_{26}\text{H}_{34}\text{N}_4\text{Rh}_2\text{S}_4$  requires C, 42.4; H, 4.65; Rh, 27.9; S, 17.4%).

*Methyl 3-[3-Isocyano-(Z)-cyclopent-2-enylidene]propionate* ( $\eta^5$ -ethyltetramethylcyclopentadienyl)dithiocyanato-NC-rhodium (5).—The isocyanide<sup>11</sup> (120 mg) in dichloromethane ( $50\text{ cm}^3$ ) was treated with methyl alcohol ( $0.18\text{ cm}^3$ ) and DCC (0.872 g) at  $-15^\circ\text{C}$ . 4-Dimethylaminopyridine (20 mg) was added and the stirred mixture kept at  $-15^\circ\text{C}$  for 24 h when the precipitated urea was collected, washed with dichloromethane ( $-15^\circ\text{C}$ ;  $2 \times 10\text{ cm}^3$ ), and the combined filtrate and washings were concentrated to  $5\text{ cm}^3$ . The resulting brown solution was applied to a silica gel column ( $12 \times 4.5\text{ cm}$ ) which was eluted with ether–light petroleum (1:1). The first  $100\text{ cm}^3$  of eluate was discarded and the next  $100\text{ cm}^3$  collected. The eluate was concentrated to  $5\text{ cm}^3$ , diluted with carbon tetrachloride ( $30\text{ cm}^3$ ), and the solution concentrated in diffuse light at  $<10^\circ\text{C}$  to *ca.*  $5\text{ cm}^3$ ; it was then diluted with carbon tetrachloride as before. This process was repeated and the final  $\text{CCl}_4$  solution had IR and  $^1\text{H}$  NMR spectra identical with those of the ester previously reported.<sup>4</sup> This solution containing about 25 mg (determined by its UV absorption at 270 nm) of the ester was added to a solution of the rhodium complex (44.5 mg) described in the preceding paragraph, in dichloromethane. After 1 h, the reaction mixture was concentrated to  $1\text{ cm}^3$  and the solution applied to a PLC plate which was developed with dichloromethane–methyl alcohol (3:97). The main orange band was eluted with acetone and the resulting gum crystallised on trituration with ether. The complex separated from dichloromethane–ether (4:1) at  $-15^\circ\text{C}$  as orange needles, m.p.  $126$ – $127^\circ\text{C}$  (Found: C, 49.7; H, 5.2; N, 7.55; S, 11.6.  $\text{C}_{23}\text{H}_{28}\text{N}_3\text{O}_2\text{RhS}_2$  requires C, 50.6; H, 5.2; N, 7.7; S, 11.8%).

*Methyl 3-[3-Isocyano-(E)-cyclopent-2-enylidene]propionate.*—The methyl ester (2; R = Me) (25 mg) in benzene ( $3\text{ cm}^3$ )

was treated with a solution (0.2 cm<sup>3</sup>) of iodine (3 mg) in benzene (1 cm<sup>3</sup>). The reaction mixture was kept in the dark at 4 °C for 18 h, and then concentrated to 0.5 cm<sup>3</sup> and applied to 2 PLC plates (20 × 20 × 0.05 cm). The plates were developed with ether–light petroleum (2:3) until partial but discernable separation (UV reflectance) was obtained. The band of lower *R<sub>F</sub>* was eluted and then rechromatographed when complete separation occurred. The band of lower *R<sub>F</sub>* was eluted and had the following properties:  $\lambda_{\max}(\text{Et}_2\text{O})$  263 nm ( $\epsilon$  20 400 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>); *m/z* 177.0797, C<sub>10</sub>H<sub>11</sub>NO<sub>2</sub> requires 177.0790, 145, 118, 91;  $\nu_{\max}(\text{CCl}_4)$  2 105 and 1 745 cm<sup>-1</sup>;  $\delta_{\text{H}}(\text{CDCl}_3)$  6.30 (5-H), 5.65 (m, 3-H), 3.70 (3 H), 3.09 (2 H, <sup>3</sup>*J* 7.3 Hz), 2.76–2.66 (2 H, m), 2.64–2.55 (2 H, m); 3-H–5-H NOE *ca.* 9%. The [Rh( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)(SCN)<sub>2</sub>] complex, prepared by the standard method, recrystallised from dichloromethane–ether as orange needles, m.p. 115–117 °C (Found: C, 49.4; H, 5.0; N, 7.9; O, 6.1; Rh, 19.8; S, 11.7. C<sub>22</sub>H<sub>26</sub>N<sub>3</sub>O<sub>2</sub>RhS<sub>2</sub> requires C, 49.7; H, 4.9; N, 7.9; O, 6.0; Rh, 19.4; S, 12.1%),  $\delta_{\text{C}}(\text{CDCl}_3)$  171.3 (ester CO), 144.9 (quat. olefin C), 136.25 (olefin CH), 131.0 (CNS), 121.3 (*N*-sub. olefin C), 118.7 (olefin CH), *ca.* 103 (cyclopent. quat. C), 51.95 (ester Me), 34.9 (side chain CH<sub>2</sub>), 33.4 (CH<sub>2</sub>), 25.7 (CH<sub>2</sub>), and 9.2 (5 Me).

*Phenyl 3-[3-Isocyano-(Z)-cyclopent-2-enylidene]propionate*.—This ester was eluted from the silica gel column [with considerable polymerisation (*ca.* 40%)] with ether–light petroleum (7:18), yield 45%; *m/z* 239.0948. C<sub>15</sub>H<sub>13</sub>NO<sub>2</sub> requires 239.0946;  $\lambda_{\max}(\text{Et}_2\text{O})$  269 nm ( $\epsilon$  13 500 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>),  $\nu_{\max}(\text{CCl}_4)$  3 050, 3 020, 2 109, and 1 769 cm<sup>-1</sup>;  $\delta_{\text{H}}(\text{CCl}_4)$  7.5–7.0 (5 H, m), 6.66 (5-H), 5.51 (3-H, <sup>3</sup>*J* 7.5 Hz), 3.30 (2 H, <sup>3</sup>*J* 7.5 Hz), 2.72 [4 H, 8-H (7-H)]; 2-H–5-H NOE *ca.* 8%, 3-H–8-H NOE *ca.* 17%. The rhodium complex separated from dichloromethane–ether (1:1) as orange needles, m.p. 161–163 °C (Found: C, 53.6; H, 4.8; N, 7.1; O, 7.0; Rh, 17.1; S, 10.5). C<sub>27</sub>H<sub>28</sub>N<sub>3</sub>O<sub>2</sub>RhS<sub>2</sub>·0.5H<sub>2</sub>O requires C, 53.8; H, 4.85; N, 7.0; O, 6.6; Rh, 17.1; S, 10.6%),  $\delta_{\text{C}}(\text{CDCl}_3)$  169.5 (ester CO), 150.89, 144.15, 131.8 (cyclopent. CH), 129.45 (aromatic CH), 125.92 (aromatic CH), 121.5 (aromatic CH), 121.3 (quat. C side chain subs.), 116.41 (side chain olefin CH), 103.5 (quat. cyclopentadiene C), 35.15 (side chain CH<sub>2</sub>), 33.07 (CH<sub>2</sub>), 28.83 (CH<sub>2</sub>), and 9.19 (5 Me).

*4-Methoxyphenyl 3-[3-Isocyano-(Z)-cyclopent-2-enylidene]propionate*.—This ester was eluted from the silica gel column with ether–light petroleum (1:4), yield 70%; *m/z* 269.1059. C<sub>16</sub>H<sub>15</sub>NO<sub>2</sub> requires 269.1052;  $\lambda_{\max}(\text{Et}_2\text{O})$  270 nm ( $\epsilon$  12 000 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>);  $\nu_{\max}(\text{CCl}_4)$  2 110 and 1 765 cm<sup>-1</sup>;  $\delta_{\text{H}}(\text{CCl}_4)$  6.90 (<sup>3</sup>*J* 9 Hz), 6.79 (<sup>2</sup>*J* 9 Hz), 6.54, 5.48 (t, <sup>3</sup>*J* 7.5 Hz), 3.77 (3 H), 3.25 (2 H, <sup>3</sup>*J* 7.5 Hz), and 2.71 (4 H). The rhodium complex was recrystallised by dissolution in the minimum volume of dichloromethane and dilution to turbidity with *t*-butyl methyl ether, m.p. (132 °C) 138 °C (Found: C, 53.2; H, 4.75; Rh, 16.3; S, 10.3. C<sub>28</sub>H<sub>30</sub>N<sub>3</sub>O<sub>3</sub>RhS<sub>2</sub> requires C, 53.9; H, 4.85; Rh, 16.3; S, 10.3%),  $\delta_{\text{H}}(\text{CDCl}_3)$  7.61 (<sup>3</sup>*J* 9 Hz), 6.88 (<sup>3</sup>*J* 9 Hz), 6.86, 5.62 (t, <sup>3</sup>*J* 7.5 Hz), 3.79 (3 H), 3.39 (2 H, <sup>3</sup>*J* 7.5 Hz), 2.87 (2 H, m), 2.75 (2 H, m), and 1.9 (15-H);  $\delta_{\text{C}}(\text{CDCl}_3)$  169.9 (ester CO), 157.5, 144.4, 144.1, 133.1 (CNS), 131.8 (cyclopentene CH), 122.2 (arom. CH), 121.3 (quat. C, side chain subs.), 116.5 (side chain olefin CH), 114.6 (aromatic CH), 103.5 (quat. C cyclopentadiene), 55.7 (OMe), 35.1 (side chain CH<sub>2</sub>), 33.05 (CH<sub>2</sub>), 28.8 (CH<sub>2</sub>), and 9.2 (5 Me).

*Methyl Dermadinate*.—Dermadin<sup>11</sup> (55.4 mg) was dissolved in dichloromethane (3 cm<sup>3</sup>) and the solution treated successively at –15 °C with methyl alcohol (0.01 cm<sup>3</sup>), DCC (45 mg), and 4-dimethylaminopyridine (5 mg). The mixture was stirred at –15 °C for 24 h after which time the precipitated urea was collected, washed with dichloromethane (2 × 2 cm<sup>3</sup>),

and the filtrate and washings concentrated to 2 cm<sup>3</sup>. The concentrate was applied to a silica gel column (20 × 2 cm) which was developed at 4 °C with diethyl ether–light petroleum (b.p. 40–60 °C) (1:1). Fractions (15 cm<sup>3</sup>) were collected and their absorption at 220 nm determined. By this means, fractions 8–15 were combined, evaporated to 2 cm<sup>3</sup>, and the solution was diluted with light petroleum (3 cm<sup>3</sup>), cooled to –15 °C and slowly evaporated until crystallisation began. The crystals (50 mg), m.p. 70–71 °C, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +115° (*c* 0.3 in Et<sub>2</sub>O);  $\lambda_{\max}(\text{Et}_2\text{O})$  221 nm ( $\epsilon$  15 500 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>); IR and <sup>1</sup>H NMR spectra identical with the material obtained by the reaction of diazomethane with dermadin,<sup>11</sup> were collected, taken up in dichloromethane (2 cm<sup>3</sup>) and the rhodium complex prepared by the standard method. The complex separated from acetone–ether (1:1) as clumps of orange needles, m.p. 80–90 °C (Found: C, 48.4; H, 4.45; N, 7.9; O, 9.0, Rh, 18.6; S, 11.4. C<sub>22</sub>H<sub>24</sub>N<sub>3</sub>O<sub>3</sub>RhS<sub>2</sub> requires C, 48.4; H, 4.4; N, 7.7; O, 8.8; Rh, 18.9; S, 11.8%),  $\delta_{\text{H}}(\text{CDCl}_3)$  6.86 (<sup>3</sup>*J* 15.8 Hz), 6.67, 6.16 (<sup>3</sup>*J* 15.8 Hz), 3.89, 3.77 (3 H), 3.14 (<sup>2</sup>*J* 18 Hz), 3.06 (<sup>2</sup>*J* 18 Hz), and 1.89 (15 H).

*Reaction of Diazomethane with Methyl Dermadinate*.—Methyl dermadinate (40 mg) dissolved in ether (10 cm<sup>3</sup>) was treated with a solution (20 cm<sup>3</sup>) of diazomethane (12 mg) in ether. After 24 h at 4 °C the reaction solution was colourless. It was evaporated to 2 cm<sup>3</sup> and the concentrate applied to a silica gel column (Kieselgel 60H, 10 × 2.4 cm) which was eluted with ether–light petroleum (3:2; 150 cm<sup>3</sup>) and then with ether–light petroleum (4:1). The first 150 cm<sup>3</sup> of the latter eluate was discarded and the next 50 cm<sup>3</sup> collected, concentrated, and applied to a PLC plate (20 × 20 × 0.05 cm) which was developed with ether–THF (9:1); the main band reacted with nickel(II) chloride<sup>9</sup> and was eluted with acetone. The acetone eluate was evaporated at –20 °C at 0.2 mmHg to provide a gum that rapidly decomposed. The gum was digested with chloroform (CDCl<sub>3</sub>) and the solution which filtered through a 1 × 0.5 cm pad of silica gel had the following spectroscopic properties:  $\nu_{\max}$  3 411, 2 125, 1 702, and 1 616 cm<sup>-1</sup>;  $\delta_{\text{H}}$  6.46 (e), 6.28 (*J* 1.6 Hz), 3.93, 3.85 (3 H), 3.9–3.8 (2 H, m, coupled to  $\delta_{\text{H}}$  6.46 and 3.42), 3.42, 2.81 (2 H, *J* 18 Hz), and 2.48 (2 H, *J* 18 Hz).

*Phenyl dermadinate*. This ester was eluted from the silica gel column with ether–light petroleum (1:1), yield 70%; [ $\alpha$ ]<sub>D</sub><sup>23</sup> +145° (*c* 0.4 in Et<sub>2</sub>O); *m/z* 253.0737. C<sub>15</sub>H<sub>11</sub>NO<sub>3</sub> requires 253.0739;  $\lambda_{\max}(\text{Et}_2\text{O})$  225, 234 nm ( $\epsilon$  15 200 and 15 000 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>);  $\nu_{\max}(\text{CHCl}_3)$  2 130 and 1 745 cm<sup>-1</sup>;  $\delta_{\text{H}}(\text{CDCl}_3)$  7.5–6.9 (5 H, m), 6.97 (<sup>3</sup>*J* 15 Hz), 6.26 (<sup>3</sup>*J* 15 Hz), 6.27, 3.82, and 2.87 (2 H). The rhodium complex separated from tetrahydropyran–*t*-butyl methyl ether (1:1) as orange needles, m.p. 144–145 °C (Found: C, 53.4; H, 4.35; N, 6.9; O, 7.9. C<sub>27</sub>H<sub>26</sub>N<sub>3</sub>O<sub>3</sub>RhS<sub>2</sub> requires C, 53.4; H, 4.3; N, 6.9; O, 7.9%),  $\delta_{\text{H}}(\text{CDCl}_3)$  7.5–7.0 (5 H, m), 7.06 (<sup>3</sup>*J* 16 Hz), 6.69, 6.37 (<sup>3</sup>*J* 16 Hz), 3.96, 3.18 (2 H, m), and 1.90 (15 H).

*Trimethylsilylethyl dermadinate*. This ester was eluted from the silica gel column with ether–light petroleum (13:50), yield 55%;  $\nu_{\max}(\text{CCl}_4)$  2 925, 2 115, 1 728, and 1 660 cm<sup>-1</sup>;  $\delta_{\text{H}}(\text{CCl}_4)$  referred to the signal of SiMe<sub>3</sub> in the compound) 6.69 (<sup>3</sup>*J* 15.8 Hz), 6.20, 5.95 (<sup>3</sup>*J* 15.8 Hz), 4.10 (2 H, m, <sup>3</sup>*J* 8.4 Hz), 3.67, 2.84 (<sup>2</sup>*J* 19 Hz), 2.76 (<sup>2</sup>*J* 19 Hz), 0.92 (2 H, t, <sup>2</sup>*J* 8.4 Hz), and 0.00 (9 H). The rhodium complex (0.27 g) was taken up in warm tetrahydropyran (2 cm<sup>3</sup>) and the solution allowed to evaporate at room temperature over 72 h when yellow needles separated, m.p. (170) 185 °C (Found: C, 49.7; H, 5.4; N, 6.9; O, 8.9; Rh, 15.5; Si, 4.4. C<sub>26</sub>H<sub>34</sub>N<sub>3</sub>O<sub>3</sub>RhS<sub>2</sub>Si requires C, 49.5; H, 5.4; N, 6.7; O, 7.6; Rh, 16.3; Si, 4.4%),  $\delta_{\text{H}}(\text{CDCl}_3)$  6.78 (<sup>3</sup>*J* 15.8 Hz), 6.61 (<sup>4</sup>*J* 1.5 Hz, <sup>4</sup>*J* 1.5 Hz), 6.09 (<sup>3</sup>*J* 15.8 Hz), 4.20 (2 H, m, <sup>2</sup>*J* 8.5 Hz), 3.83, 3.09 (<sup>2</sup>*J* 18.5 Hz, <sup>4</sup>*J* 1.5 Hz), 3.01 (<sup>2</sup>*J* 18.5 Hz, <sup>4</sup>*J* 1.5 Hz), 1.84 (15 H), 0.97 (2 H, m, <sup>2</sup>*J* 8.5 Hz), and 0.00 (9 H).

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