Tetrahedron Letters No. 22, pp 1917 - 1918, 1977. Pergamon Press. Printed in Great Britain.

A SIMPLE SYNTHESIS OF PELLITORINE (N-ISOBUTYL-E,E-2,4-DECADIENEAMIDE) FROM THE BUTADIENE TELOMER

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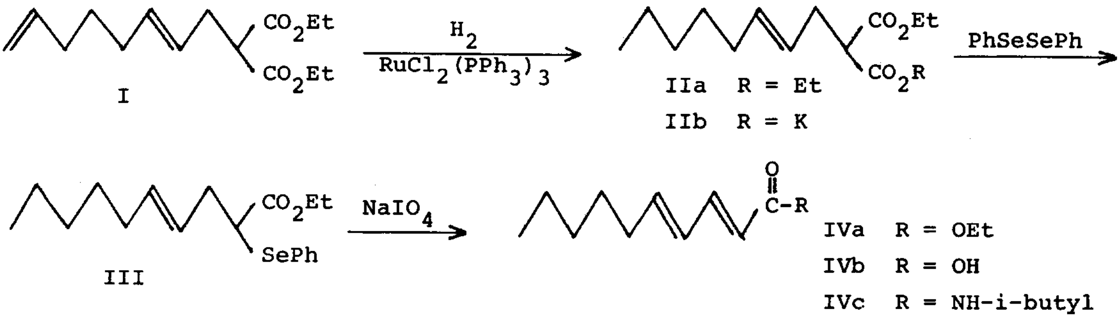
(Received in Japan 7 March 1977; received in UK for publication 21 April 1977)

Pellitorine is an insecticidal compound isolated from *Anacyckus pyrethrum* roots. Its structure was determinded as N-isobutyl-E,E-2,4-decadieneamide (IVc), which was prepared easily from E,E-2,4-decadienoic acid,[1] and hence the preparation of the acid means the synthesis of pellitorine. Crombie[1] and Jacobson[2] synthesized the acid by the Knoevenagel reaction of 2-octenal. Also Ohloff[3] and Näf[4] obtained a mixture of stereoisomers of the ester. We now wish to report the better synthetic method of E,E-2,4-decadienoic acid starting from an easily available butadiene telomer. Various telomers produced by the palladium catalyzed dimerization of butadiene with incorporation of nucleophiles[5] are useful starting materials for natural product syntheses.[6] The telomer obtained by the reaction of diethyl malonate and butadiene[7] is the starting material for the pellitorine synthesis, which was achieved by the following sequences.



I

IIa R = Et
IIb R = K

III

IVa R = OEt
IVb R = OH
IVc R = NH-i-butyl

Diethyl 2,7-octadienylmalonate (I) was prepared in a high yield by the reaction of diethyl malonate and butadiene catalyzed by palladium acetate and triphenylphosphine.[7] The selective homogeneous hydrogenation of the terminal double bond of I was achieved using $RuCl_2(PPh_3)_3$ (3 mol%) as a catalyst in a mixed solvent of benzene and ethanol (1:1) under hydrogen pressure (10-30 atm) at a room temperature. The gas absorption nearly stopped after taking up one equivalent of hydrogen, and 2-octenylmalonate (IIa) was isolated by distillation (102-104°C/2 mmHg) in 88% yield with nearly 100% selectivity. [nmr (CCl_4): δ 5.35 (m, 2H, olefin), 4.12 (q, 4H, J = 7.0 Hz), 3.22 (t, 1H, J = 7.0 Hz), 2.50 (m, 2H), 2.0 (m, 2H), 1.6-0.8 (m, 15H)].

Diester (IIa) was converted to solid monopotassium salt (IIb) by treatment with one equivalent of KOH in dry ethanol and subsequent complete removal of the solvent. IIb was treated with diphenyldiselenide in refluxing dry toluene for 5 hr and III was obtained in 74% yield as an oil. [nmr (CCl_4): δ 7.1-7.7 (m, 5H), 5.35 (m, 2H, olefin), 4.0 (q, 2H, J = 7.0 Hz), 3.48 (t, 1H, J = 7.0 Hz), 2.45 (m, 2H), 2.0 (m, 2H), 1.6-0.8 (m, 12H), IR: 1730, 970 cm^{-1}]. The oxidative removal of the phenylselenyl group with $NaIO_4$ by an established method[8,9] afforded ethyl E,E-2,4-decadienoate (IVa) in 91% yield. The E,E structure of the conjugated diene system was fully confirmed by its nmr and IR spectra[3]; [nmr (CCl_4): δ 6.8-7.5 (m, 1H, olefin), 5.9-6.1 (m, 2H, olefin), 5.60 (d, 1H, J = 15 Hz, olefin), 4.10 (q, 2H, J = 7.0 Hz), 1.9-2.4 (m, 2H), 0.8-1.5 (m, 12H), IR: 1720, 1640, 1620, 1000 cm^{-1}]. Hydrolysis of the ester (IVa) in aqueous methanolic KOH produced E,E-2,4-decadienoic acid (IVb) as colorless crystals. The acid was recrystallized from petroleum ether and identified by its melting point (49-51°C, reported, 49-50°C) and mass spectrum (M^+ = 168, calcd. for $C_{10}H_{16}O_2$, 168).

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