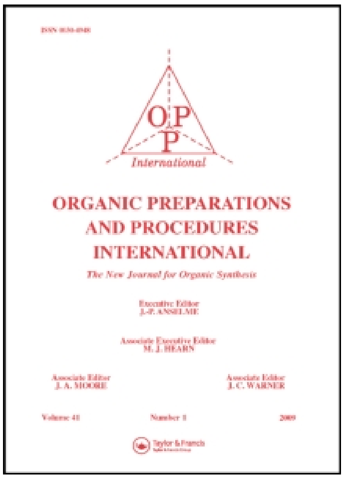

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A SIMPLE SYNTHESIS OF (+)-*trans*-VERBENYL PROPIONATE, A PHEROMONE ANALOG OF AMERICAN COCKROACH USING LEAD(IV) PROPIONATE

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A SIMPLE SYNTHESIS OF (+)-trans-VERBENYL PROPIONATE, A PHEROMONE ANALOG OF AMERICAN COCKROACH USING LEAD(IV) PROPIONATE[†]

Submitted by
(03/21/88)

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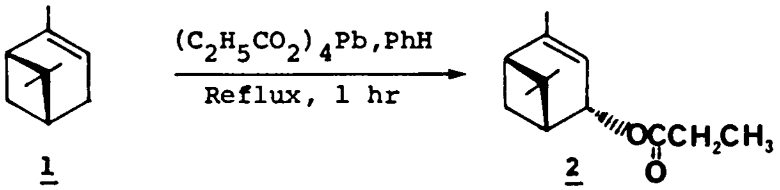
(+)-trans-Verbenyl propionate (1) is a synthetic attractant of the American cockroach (Periplaneta americana)[1]. Although the activity of this compound is less than that of periplanone B, the true sex excitant pheromone (2×10^{-2} mg and 10^{-8} mg, respectively), its preparation is much simpler.[2] Compound 1 has been previously prepared by Nishino and Takayanagi from (+)-α-pinene (2) in 20% overall yield.[1] Because of our interest in the use of 1 for cockroach control, we report an improved one-pot version of this synthesis.



1 2

The use of lead(IV)propionate[3] as acyloxylation reagents gave (+)-trans-verbenyl propionate (1) directly from (+)-α-pinene (2) in excellent yield (90%). The synthesis of lead(IV) propionate has also been modified.

EXPERIMENTAL SECTION

IR spectra were recorded on SPECORD IR75 spectrometer. ^{1}H-NMR (100 MHz) and ^{13}C-NMR (25.5 MHz) spectra were determined on a VARIAN XL-100-15 instrument using deuterochloroform as solvent. All signals are expressed by the ppm downfield from TMS used as an internal standard. The MS spectra were made by HEWLETT-PACKARD 5985A instrument at 70 eV.

Lead(IV) Propionate.- To a hot mixture (80°) of propionic acid (40 ml) and propionic anhydride (10 ml) was added lead(II,III)oxide (10 g) in small portions under vigorous stirring waiting for the total dissolution of each portions. (The addition of Pb_3O_4 portions should not last more than 20 minutes!). The mixture was cooled to 10-20°C and the white precipitate was filtered off to yield 6.5 g (90%) lead(IV)propionate as a white cotton wool-like compound. It is very sensitive to moisture, turning brown on exposure to moisture.

Anal. Calcd for $C_{12}H_{20}O_8Pb$: C, 28.9; O, 25.6; H, 4.0 Found: C, 28.5; O, 25.7, H, 4.2

(+)-trans-Verbenyl Propionate (1).- To a stirred solution of (+)-α-pinene (2; 10 ml, 0.063 mol; $[\alpha]_D^{23.8}$= +45.9(neat)) in dry benzene (200 ml) was added lead(IV)propionate (63 g; 0.126 mol) and the resulting mixture was refluxed for 1 hr. The cooled mixture was diluted with benzene (400 ml) and washed successively with water (10 x 50 ml), 5% $NaHCO_3$ (3 x 50 ml) and brine (2 x 50 ml). After drying ($MgSO_4$) the solution was concentrated in vacuo and the residue fractionated to yield 11.8 g (90%) of 1 as colorless oil, bp. 116°/15 torr; $[\alpha]_D^{21.7}$= +134.5 (c = 0.81; $CHCl_3$), lit.[1] $[\alpha]_D^{25}$= +132.0 (c = 0.5; benzene).

IR(film): 3030, 1740, 1650, 1181 cm^{-1}; ^{1}H-NMR: δ 5.35 (m, 2H, C = CH- + -CHO-), 1.9-2.45 (m, 3H, $-CH_2-$ and -CH-C=C), 1.75 (s, 3H, = $C-CH_3$), 1.47 (d, 1H, J = 8Hz, $-C\underline{H}-CHO-$), 1.35 and 0.92 (2xs, 2x3H, CH_3-C-CH_3), 1.13 (t, J = 7Hz, 3H, $O=CCH_2C\underline{H}_3$), 2.30 (q, J = 7Hz, 2H, $CH_2C=O$); ^{13}C-NMR: δ 174.2 (C=O), 27.9 ($O=C\underline{C}H_2$), 9.2 ($O=CCH_2\underline{C}H_3$), 73.5 (CH-O), 115.5 (-CH=), 150.3 ($-\underline{C}=CH-$), 47.7 ($-\underline{C}H-C=$), 29.4 ($-CH-\underline{C}H_2-CH-$), 44.5 ($\underline{-C}H-CH-O$), 46.2 ($CH_3-\underline{C}-CH_3$), 20.6 + 26.5 ($\underline{C}H_3-C-\underline{C}H_3$), 22.7 ($=C-\underline{C}H_3$); MS: 208.2 (0.2), 152.2 (19.3), 134.2 (10.6), 119.2 (100.0), 109.2 (24.1), 105.2 (18.7), 94.2 (11.7), 93.2 (37.7), 91.2 (60.9), 82.2 (15.5), 79.2 (19.8), 77.2 (36.5), 65.2 (14.4), 57.1 (49.2), 53.1 (12.5), 43.1 (33.8), 41.1 (28.3), 39.1(21.5).

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SYNTHESIS OF (2-BUTYL-3-BENZOFURANYL){4-[2-(DIETHYLAMINO)ETHOXY]-3,5-DIIODOPHENYL}METHANE DERIVATIVES

Submitted by (04/25/88)
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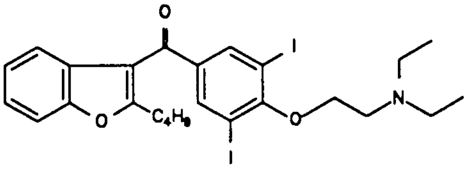
The mechanism of toxicity of synthesis of (2-butyl-3-benzofuranyl){4-[2-(diethylamino) ethoxy]-3,5-diiodophenyl}methane derivatives is unknown. However, certain evidence supports the postulation that the molecule is enzymatically oxidized to free radical intermediates.[1] The extended π conjugation available to the amiodarone molecule could facilitate free-radical reactions by stabilizing the radical intermediates. This conjugation could be interrupted by eliminating the bridging sp^2 hybridized carbonyl carbon and, presumably, reduce the toxicity of the agent. We wish to report the synthesis of a series of benzofuranyl agents in which the bridging carbonyl is replaced by a methylene derivatives of the general structure, 2.

Synthesis of the (2-butyl-3-benzofuranyl){4-[2-diethylamino)ethoxyl]-3,5-diiodophenyl} methane derivatives involved the conversion of the alcohol (2a) to the corresponding ester (2b), ether (2c) and hydrocarbon (2d) of amiodarone. Formation of the pivalate (2b) was achieved by treatment of the alcohol (2a) with excess pivaloyl chloride in pyridine at 65°.[2] The pivalate ester was synthesized for steric reasons; it was felt that the bulky t-butyl group would effectively block the reactive benzylic position. Since ether derivatives would be expected to be even more stable



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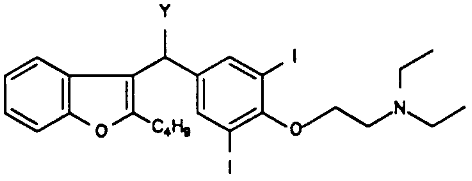

2

a) Y = OH b) Y = $OCCMe_3$ c) Y = OCH_3 d) Y = H_2