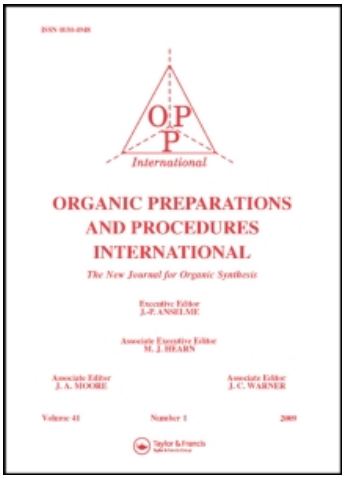

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AN IMPROVED ELECTROSYNTHETIC PREPARATION OF THE FEMALE HOUSEFLY SEX PHEROMONE

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12. Extreme caution should be exercised when working with potassium; small unreacted pieces coming in contact with water will cause a fire. We found that cutting the potassium under pentane and destroying it in methanol worked the best in our lab.

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AN IMPROVED ELECTROSYNTHETIC PREPARATION OF THE FEMALE HOUSEFLY SEX PHEROMONE

Submitted by (03/11/94)

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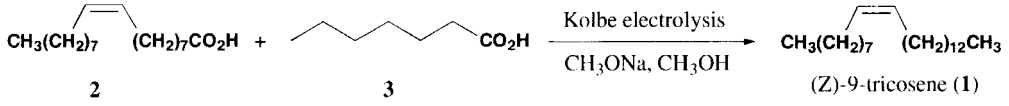
The housefly *(Musca domestica)* pheromone, (Z)-9-tricosene (**1**), has been prepared in a number of different ways. Most of the chemical syntheses suffer from being multistep processes.[1] In Brazil, this compound is sold in two commercial formulations associated with traditional insecticide to control flies in household and poultry applications. Gribble and co-workers[2] described a one step synthesis of this pheromone using a mixed Kolbe electrolysis of oleic acid (**2**) and heptanoic acid (**3**),

in methanol, to afford the title compound in 14% yield (after separation). This paper presents an improvement of the previous preparation of this important pheromone, based on the calculation of the dimerization rate constant of the radicals generated from each individual acid.

The determination of the dimerization constant was carried out according to the procedure described by Andrieux *et al.*[3], using the cyclic voltammetry, by measuring the peak potential with the sweep rate for each acid individually. The rate constants are 4.2×10^5 M^{-1} s^{-1} and 7.6×105 M^{-1} s^{-1} for the oleic and heptanoic acids respectively.



2 3 (Z)-9-tricosene (1)

An extensive study of the system, including changing solvent, degree of neutralization of the acids, use of supporting electrolytes, and analysis of the influence of the acid concentrations in the product distribution, allowed us to obtain a 100% improvement, starting with a *two-fold* excess of oleic acid at the beginning of the electrolysis and adding the remaining heptanoic acid as the electrolysis proceeds. At the end, an equimolar quantity of both acids was used.

EXPERIMENTAL SECTION

The oleic acid tech. grade was obtained from Aldrich and the methanol was freshly refluxed over magnesium for 4 hrs and then distilled just before being used in the reaction. IR spectrum was recorded on a Perkin Elmer 735 spectrometer. ^{1}H NMR spectrum was obtained on a Varian FT-80 spectrometer and mass spectrum was recorded on a gas chromatograph/mass spectrometer HP 5995 (70 eV).

(Z)-9-Tricosene.- A solution of oleic acid (2.825g, 10 mmol) in methanol (15 mL) and another solution of heptanoic acid (1.302g, 10 mmol) in methanol (15 mL) were neutralized (3 mol %) by addition of sodium methoxide. The solution of oleic acid (15 mL) and half (7.5 mL) of the solution of heptanoic acid were mixed in the electrolytic cell and the electrolysis was performed under constant current (0.4A). During the electrolysis, the remaining 7.5 mL of heptanoic acid solution was added dropwise into the electrolytic cell, over a 50 min period, under a nitrogen stream while the temperature of the system was kept at 15°. After 2 hrs, the reaction mixture was transferred to a 100 mL round bottom flask and the methanol was removed under reduced pressure. The crude product was filtered through a short silica gel column using petroleum ether as eluent. The petroleum ether was evaporated and the residue was vacuum distilled to give dodecane (450 mg, 26%, bp. 70-90°/0.1 mmHg, lit.[4] bp. 216°/760 mmHg), (Z)-9-tricosene (890 mg, 28%, lit.[2] bp. 150-152°/0.1 mmHg, lit.[4] bp. 300°/760 mmHg) and a residue (285 mg, 6%) of the oleic acid dimer.
IR: (film): 3011, 2920, 1640, 1460, 1370, 710. ^{1}H NMR ($CDCl_3$): δ 0.7-2.1 (m, 44H), 5.1-5.5 (m, 2H). Mass spectrum (70 eV) showed M^+ at m/e 322.

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THE SYNTHESIS OF 6-PROPYL-2-SELENOURACIL, THE SELENIUM ANALOGUE OF THE ANTI-THYROID DRUG PTU

Submitted by (04/28/94)

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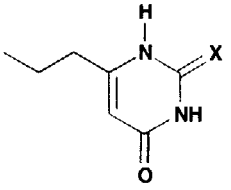
Despite the fact that thiocarbonyl compounds have often proved to be important therapeutic agents, the corresponding selenocarbonyl compounds are much less well known. One such important thiocarbonyl compound is 6-propyl-2-thiouracil (**1**), commonly referred to as PTU, a thiourylene drug useful as an anti-thyroid agent.[1] For a number of years the mechanism of action of these drugs was presumed to involve inhibition of a key thyroid enzyme, 5'-iodothyronine deiodinase, (ID-1) by formation of a mixed disulfide between a cysteine residue on the enzyme and the sulfur atom of the thiourylene.[2,3] Recently, it was discovered that ID-1 is, in fact, a seleno-enzyme containing a selenocysteine residue which is necessary for full biological activity.[4,5] Because of our interest in the chemistry of both selenocarbonyl compounds[6,7] and anti-thyroid therapeutic agents,[8] we sought to prepare 6-propyl-2-selenouracil (**2**), the selenium analogue of PTU to determine whether this compound could be a more effective inhibitor of ID-1, in particular because of the very mild conditions necessary for forming diselenide bonds.



1, X = S
2, X = Se