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AN IMPROVED SYNTHESIS OF INSECT SEX ATTRACTANT: *CIS*-8-DODECEN -1-OL ACETATE

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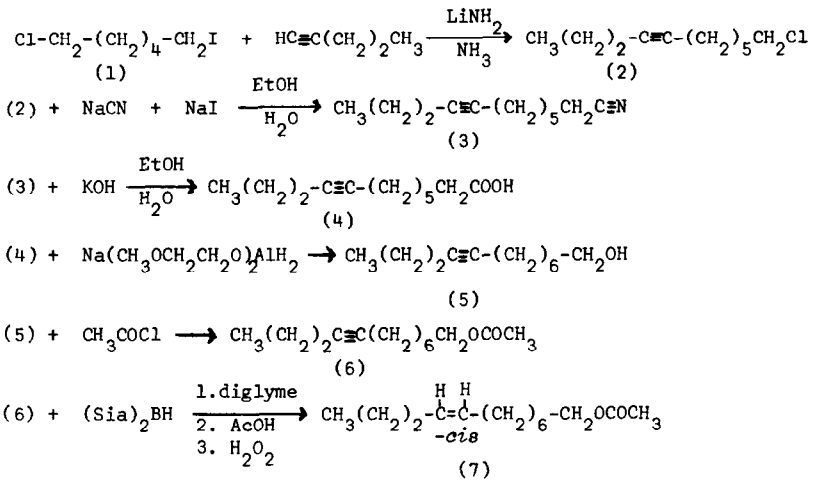
Larger amounts of the title compound were required for field trapping trials of the male oriental fruit-moth, *Cydia molesta*[1]. This compound was first reported by Roelofs[2] as a male sex attractant of the related fruit moth *Grapholitha molesta*.

We found the reported syntheses of structurally related pheromones[3,4,5] to be more suited for the preparation of small laboratory amounts of this compound. Moreover all the reported methods also yielded significant amounts of the *trans*-isomer and other impurities which were identified as strong biological inhibitors of the active *cis*-isomer.[6]

The advantage of the outlined synthesis of the title compound is also based on the ready availability of starting materials and its suitability for large scale syntheses.



The use of an *in situ* reaction of the chloro-iodohexane (1) with lithium and 1-pentyne avoided the handling of large amounts of lithium acetylide required by other methods. The catalysis by sodium iodide in the conversion of the chloroacetylene (2) to the nitrile (3) reduced the long time conventionally required for this reaction.

The steps (2) → (3) → (4) were carried out in an overall yield of 91%. When this sequence of reactions was carried out without the isolation of the intermediates the yield of acid (4) was 96%. Most impurities carried over from the previous steps were removed by solvent extraction of the acetylenic acid salt (4). The homogeneous reduction of this acid in benzene using sodium bis-(methoxyethoxy)aluminium hydride gave the acetylenic carbinol in a high yield

without any marked reduction of the triple bond. In the conversion of (2) to (6) the only purification requiring distillation was in the isolation of the acetoxy acetylene (6).

Using "disiamyl borane"[7] reduction of the acetoxy acetylene followed by hydrogen peroxide treatment to remove boron containing impurities, yielded the final product in a 66% overall yield (on 1) which assayed >98% *cis*-.

Table 1 lists physical constants of isolated intermediates. Laboratory preparations in several hundred grammes quantities could be conveniently carried out by the described method.

Table 1. Physical data for intermediate products.[(a)]

Compound	b.p. °C	Refrac.Index	I.r. ν_{max} (cm^{-1})	PMR (δ)[(b)] ppm	Yield (%)
(2)	60-1 @ 0.2mm[(c)]	n_D^{21} = 1.4605	-	t; 2.20	86
(3)	-	n_D^{20} = 1.4600	2280 (C≡N)	t; 2.15	94
(4)	-	n_D^{20} = 1.4588	-	t; 3.50	97
(5)	-	n_D^{24} = 1.4610	3340(OH)	t; 2.10	96
(6)	103-3.5 @ 0.2mm	n_D^{19} = 1.4495	1730 (C=O)	t; 4.00	93
(7)	65-70 @ 0.01mm	n_D^{19} = 1.4439[(d)]	-	t; 4.11 -CH=CH-,m;5.43,J=4.8Hz	90

(a) Analyses and mass spectra of all the intermediates conformed to theoretical calculations.

(b) Shifts listed for methylene protons adjacent to:-Cl in(2); -C≡N in (3);-COOH in (4) -OH in (5);-$OCOCH_3$ in (6) and (7). Solvent $CDCl_3$, with tetramethyl silane as an internal standard.

(c) Lit.[8] b.p. 82-3° @ 1.0mm.

(d) n_D^{25}=1.4426[9]. Product assayed on 300' capillary column coated with OV 17 liquid phase using an FID detector. Rf compared with an authentic sample of *cis*-8-dodecen -1-ol acetate.

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Patent applied for by CSIRO.

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