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BRIEF COMMUNICATIONS

Preparative Synthesis of (Z)-5-Decenyl Acetate

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Abstract—A procedure was developed for preparative synthesis of (Z)-5-decenyl acetate, the sex hormone of *Agrotis Segetum*.

The use of pheromones for plant protection from pests became possible after preparation of synthetic analogs of these natural compounds. Since that time, the chemistry of synthetic pheromones has been receiving a considerable attention [1].

Agrotis Segetum is a pest damaging various cereals under natural conditions and in storehouses. The principal component of its pheromone is (Z)-5-decenyl acetate **I**.

Procedures have been developed for preparing I using the Wittig reaction to obtain the (Z)-alkene moiety [2–4], by selective ozonolysis of (Z,Z)-1,6-cyclooctadiene [5], and by metal interchange with di(1-hexenyl)mercury [6]. Medarde *et al.* [7] reported a general procedure for preparing components of *Agrotis Segetum* pheromone from 1,4-butanediol [7]. The above procedures are multistep, difficult in implementation, and time-consuming; they involve formation of undesirable by-products, and the yield of the target products is low. We have developed a new procedure for preparing pheromones of this type, which is free of the above drawbacks.

The procedure suggested starts from butylacetylene **II** and follows the $C_6 + C_4$ scheme. In the first step, sodium butylacetylenide reacts with 1-iodo-4-chlorobutane in liquid ammonia at -50 to -60°C (under these conditions, iodochloroalkanes react selectively, with only the iodine atom substituted) to form 1-chloro-5-decyne **III**. This compound is treated with sodium acetate in refluxing dimethylformamide (DMF). The resulting 5-decynyl acetate **IV** is hydrogenated in a flow of hydrogen in the presence of nickel acetate treated with ethylenediamine and sodium borohydride; the reaction gives (*Z*)-5-decenyl acetate **I**, overall yield 44%.

$$\begin{array}{c} CH_{3}(CH_{2})_{3}C \equiv CH \xrightarrow{\text{Na}, (CH_{2})_{4}CI, \text{NH}_{3}} CH_{3}(CH_{2})_{3}C \equiv C(CH_{2})_{4}CI \\ \mathbf{II} & \mathbf{III} \\ \end{array}$$

$$\xrightarrow{CH_{3}CO_{2}Na, CH_{3}CO_{2}H, DMF} CH_{3}(CH_{2})_{3}C \equiv C(CH_{2})_{4}OCOCH_{3} \xrightarrow{H_{2}, \text{Ni}(OCOCH_{3})_{2}} H \xrightarrow{CH_{3}(CH_{2})_{3}} H \xrightarrow{C=C} H \\ \mathbf{IV} & \mathbf{II} \\ \end{array}$$

N (CIL) CL NIL

The process efficiency and yield of **I** essentially depend on the reaction temperature. At temperatures above -50° C, side reactions occur (dehydrochlorination, disubstitution), and below -60° C, the yield of **I** does not change further.

In the synthesis of 1-chloro-5-decyne **III** and 5-decynyl acetate **IV**, we took the reactants in an

equimolar ratio, since an excess of any of the reactants had no appreciable effect on the product yield. The hydrogenation of 5-decynyl acetate IV to (*Z*)-5-decenyl acetate was performed according to [8].

According to GLC, the final product I contained the Z isomer only, which is confirmed by the IR data (presence of a medium-intensity band in the region of 730 cm⁻¹; absence of a band at 980 cm⁻¹, characteristic of the *E* configuration) and by a characteristic multiplet of the (*Z*)-CH=CH protons in the ¹H NMR spectrum at 5.1–5.35 ppm (J = 11.5 Hz).

EXPERIMENTAL

The ¹H NMR spectra were recorded on a Varian Mercury-300 spectrometer (300 MHz) in CDCl₃, internal reference TMS, and the IR spectra, on a UR-20 spectrometer (thin films). The GLC analysis was performed on a Chrom-5 chromatograph equipped with a flame ionization detector and $25\,000 \times 0.2$ -mm glass capillary column coated with SE-30, carrier gas nitrogen, flow rate 30 ml min⁻¹.

1-Chloro-5-decyne III. Alkyne **II** (12.8 g) was added over a period of 15 min at -60° C to sodium amide prepared from 3.45 g of Na and 0.5 l of liquid ammonia; the mixture was stirred for 3 h. Then 32.8 g of 1-iodo-4-chlorobutane was added dropwise over a period of 2 h. The mixture was stirred for an additional 2 h and allowed to warm up. After evaporation of ammonia (15 h), 200 ml of anhydrous diethyl ether was added to the residue, and the mixture was refluxed with stirring for 3 h. After cooling, dilute HCl (pH 3) was added, and the mixture was extracted with diethyl ether (3 × 50 ml). The combined ether extracts were washed with a Na₂S₂O₃ solution and dried over magnesium sulfate. Distillation gave 18.1 g (70%) of **III** [9], bp 75–76°C (2 mm Hg), $n_d^{20} = 1.4610$.

5-Decynyl acetate IV. Chloroalkyne **III** (3.45 g) was added to a mixture of 1.64 g of sodium acetate and 10 ml of acetic acid in 50 ml of anhydrous DMF. The mixture was stirred at the boiling point for 10 h, the solvent was distilled off, 15 ml of water was added to the residue, and the mixture was extracted with diethyl ether (3×50 ml). The extract was washed with water to pH 7 and dried over magnesium sulfate. The solvent was removed. Vacuum distillation gave 3.2 g (82%) of **IV**, bp 92°C (2 mm Hg), $n_d^{20} = 1.4460$. IR spectrum, v, cm⁻¹: 1745, 2250. ¹H NMR spectrum, δ , ppm: 0.9 t (3H, CH₃CH₂, J = 7 Hz), 1.4–1.7 m (8H, CH₂), 1.9–2.15 m (4H, CH₂C≡CCH₂), 1.85 s (3H, COCH₃), 4.1 t (2H, OCH₂, J = 6.8 Hz).

(Z)-5-Decenyl acetate I. A 0.32-g portion of $Ni(OAc)_2 \cdot 4H_2O$ in 10 ml of absolute ethanol was bubbled with hydrogen, after which 1.4 ml of a 1 M alcoholic solution of sodium borohydride was added in three portions. To the resulting black solution, we added 0.18 g of anhydrous ethylenediamine and 1.5 g of decynyl acetate IV; the mixture was stirred at 20°C in a flow of hydrogen. After the hydrogenation was complete, the catalyst was filtered off, the filtrate was evaporated, and the precipitate was diluted with 20 ml of water and extracted with diethyl ether $(3 \times 50 \text{ ml})$. The extract was washed with 10 ml of water and dried over magnesium sulfate; the solvent was distilled off. Yield of I 1.2 g (81%), bp 100-101°C (7 mm Hg), $n_d^{20} = 1.4400$. IR spectrum, v, cm⁻¹: 730 m, 1150 s, 1245 s, 1370 m, 1390 m, 1465 m, 1658 w, 1745 vs, 3015 m. ¹H NMR spectrum, δ, ppm: 0.89 t (3H, CH_3CH_2 , J = 7.1 Hz), 1.3–1.45 m (8H, CH₂), 1.95– 2.25 m (4H, CH₂CH=CHCH₂), 1.96 s (3H, COCH₃), 4.01 t (2H, OC H_2 , J = 6.8 Hz), 5.1–5.35 m (2H, CH=CH, J = 11.5 Hz).

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