INSECT PHEROMONES AND THEIR ANALOGS.
XXIV. METHYL-BRANCHED PHEROMONES DERIVED FROM 4-METHYLTETRAHYDROPYRAN. SYNTHESIS OF RACEMIC 14-METHYLOCTADEC-1-ENE - THE PHEROMONE OF *Lyonetia clerckella*

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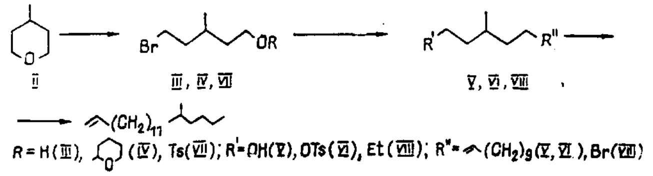
Racemic 14-methyloctadec-1-ene — the pheromone of the peach leafminer moth - has been synthesized from a bifunctional product of the cleavage of 4-methyltetrahydropyran.

Racemic 14-methyloctadec-1-ene (I), which exhibits attractive activity in relation to the peach leafminer moth *Lyonetia clerckella* [1, 2] has been obtained previously by multistage syntheses from 2-methylhexan-2-ol [3] or methyl butyl ketone [4].

A convenient starting compound for the synthesis of this pheromone may be 4-methyltetrahydropyran (II), the cleavage of which gives in high yield the tetrahydropyranyl ether of 5-bromo-3-methylpentan-1-ol (IV) [5]. The reaction of the Grignard reagent generated from the bromide (IV) with 1-bromoundec-10-ene under catalysis by the CuI—2,2 -bipyridyl system led to the corresponding coupling product, the acid hydrolysis of which gave 3-methylhexadec-15-en-1-ol. The latter was converted into the tosylate (VI) and combined in this form with diethyl lithiocuprate, which led to the desired pheromone (I). The yield of the latter, calculated on the pyran (II), amounted to 22%.



We have found conditions for the selective substitution of the tosyloxy group in 1-bromo-3-methyl-5-tosyloxypentane (VII) by its reaction with a dialkylcuprate reagent. As a result, 1-bromo-3-methylheptane (VIII) was obtained with a yield of 78%. Alkylation of the latter with the aid of undec-10-enylmagnesium bromide took place smoothly, as also in the case of the tosylate (VI). As we see, the second of the schemes developed was shorter than the first, and the yield of the pheromone (I) in this case was somewhat higher, amounting to 30% calculated on the initial pyran (II).

EXPERIMENTAL

IR spectra were taken on a UR-20 spectrometer (in films), and PMR spectra were recorded on a Tesla BS-467 instrument (working frequency 70 Hz, solvent CCl_4), the chemical shifts being given in the δ scale relative to the signal of HMDS (internal standard). GLC analysis was carried out on a Chrom-5 instrument with, as stationary phase, the silicone liquid SE-30 (5%) on Chromaton N-AW-DMCS (0.16-0.20 mm); working temperature 50-300°C, carrier gas helium.

3-Methylhexadec-15-en-1-ol (V). A stirred suspension of 0.63 g ($3.3 \cdot 10^{-3}$ mole) of CuI in 30 ml of absolute THF was treated with 0.52 g ($3.3 \cdot 10^{-3}$ mole) of 2,2'-bipyridyl, stirring (20°C, Ar) was continued for 0.5 h, and then the mixture was cooled to 2°C, a solution of 3.48 g ($15.6 \cdot 10^{-3}$ mole) of 1-bromoundec-10-ene in 30 ml of absolute THF was added, followed, after stirring for another 10 min, by a solution of the Grignard reagent obtained from 0.056 g ($23.3 \cdot 10^{-3}$ g-atom) of magnesium and 6.2 g ($23.4 \cdot 10^{-3}$ mole) of 1-bromo-3-methyl-5-(2-tetrahydropyranyloxy)pentane (III) in 5 ml of absolute THF, and the resulting mixture was stirred at 2°C for 2 h and was left at room temperature overnight. Then 60 ml of 10% HCl was added, stirring was carried out at 10°C for 1 h, and the products were extracted with diethyl ether (3 × 100 ml). The extract was

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evaporated and the residue was treated with 135 ml of methanol, 30 ml of water, and 0.23 g of TsOH, after which the mixture was stirred at room temperature for 20 h and was then evaporated. The residue was extracted with diethyl ether (3 × 100 ml) and the extract was washed successively with saturated solutions of $NaHCO_3$ and NaCl and was dried over Na_2SO_4 and evaporated. The residue was chromatographed (SiO_2, hexane—ethyl acetate, 1:1). This gave 2.70 g (68%) of the alcohol (V), n_D^{25} 1.4599. The IR spectrum and PMR spectrum were identical with those given in the literature [6].

1-Tosyloxy-3-methylhexadec-15-ene (VI). At 0°C, 1.06 g ($5.45 \cdot 10^{-3}$ mole) of p-toluenesulfonyl chloride was added to a solution of 1.28 g ($5.04 \cdot 10^{-3}$ mole) of the alcohol (V) in 16 ml of dry pyridine, and the mixture was stirred for 6 h and was then poured onto ice (10 g) and extracted with diethyl ether (3 × 80 ml). The ethereal solution was washed successively with 10% HCl and with saturated solutions of $NaHCO_3$ and NaCl, and was dried with $MgSO_4$ and evaporated. This gave 1.82 g (88%) of the tosylate (VI), its IR spectrum being identical with that reported in [6].

1-Bromo-3-methylheptane (VIII). At 0°C, 7.33 g ($38.5 \cdot 10^{-3}$ mole) of p-toluenesulfonyl chloride was added in portions to a solution of 6.41 g ($35.0 \cdot 10^{-3}$ mole) of 5-bromo-3-methylpentan-1-ol (III) in 11 ml of dry pyridine. Then the mixture was worked up as in the preceding experiment, giving 8.87 g (75%) of the tosylate (VII) [IR spectrum (ν, cm^{-1}): 570 s, 660 m (C—Br); 1180 s, 1350 s, 1600 m (OSO_2Ar)]. A solution of ethyllithium obtained at −35 to −20°C from 0.90 g ($129.6 \cdot 10^{-3}$ g-atom) of metallic lithium and 6.37 g ($58.4 \cdot 10^{-3}$ mole) of ethyl bromide in 50 ml of absolute diethyl ether was added dropwise (Ar) to a suspension of 5.47 g ($28.7 \cdot 10^{-3}$ mole) of CuI cooled to −78°C, and then the temperature was raised to −40°C and the mixture was stirred for 1 h. After this, the temperature of the reaction mixture was lowered to −68°C, a solution of 4.0 g ($11.9 \cdot 10^{-3}$ mole) of the tosylate (VII) in 10 ml of absolute diethyl ether was added, and the temperature was raised to −30°C; after being stirred for 2 h, the mixture was treated with 10 ml of 10% HCl and was extracted with diethyl ether (3 × 130 ml), after which the extract was washed with saturated NaCl solution, dried with $MgSO_4$, and evaporated. The residue was chromatographed (SiO_2, hexane), giving 1.8 g (78%) of the bromide (VIII), n_D^{20} 1.4518. IR spectrum (ν, cm^{-1}): 570 m, 640 m (C—Br); 1380 s ($C—CH_3$). PMR spectrum (δ, ppm): 0.67-1.02 (m, 6H, CH_3-3, H-7), 1.02-1.41 (m, 8H, H-2, H-4, H-5, H-6), 1.53-1.80 (m, 1H, H-3), 3.30 (t, 2H, J = 7 Hz, H-1). Found, %: C 49.61, H 8.83, Br 41.21, $C_8H_{17}Br$. Calculated, %: C 49.75, H 8.87, Br 41.38, M 193.14.

14-Methyloctadec-1-ene (I). A. A solution of ethyllithium, obtained from 0.34 g ($48.9 \cdot 10^{-3}$ g-atom) of metallic lithium and 2.39 g ($21.9 \cdot 10^{-3}$ mole) of ethyl bromide in 20 ml of absolute diethyl ether was added dropwise (Ar, −78°C) to a suspension of 1.99 g ($10.5 \cdot 10^{-3}$ mole) of CuI in 3 ml of diethyl ether, the temperature was raised to −40°C and the mixture was stirred for 1 h, and then a solution of 1.78 g ($4.4 \cdot 10^{-3}$ mole) of the tosylate (VI) in 5 ml of absolute diethyl ether was added, the resulting mixture was stirred at 0°C for 2 h and at room temperature for 2 h and, after the addition of 10 ml of saturated NH_4Cl solution, it was extracted with diethyl ether (3 × 50 ml), after which the extract was dried with $MgSO_4$ and evaporated. The residue was chromatographed (SiO_2, hexane), giving 0.69 g (59%) of compound (I), n_D^{20} 1.4430 [6]. The IR and PMR spectra were identical with those given in the literature [7].

B. A stirred suspension (Ar, 20°C) of 0.30 g ($1.56 \cdot 10^{-3}$ mole) of CuI in 16 ml of absolute THF was treated with 0.24 g ($1.56 \cdot 10^{-3}$ mole) of 2,2′-bipyridyl, and after 0.5 h the mixture was cooled to 2°C and a solution of 1.44 g ($7.47 \cdot 10^{-3}$ mole) of the bromide (VIII) in 8 ml of absolute THF was added; stirring was continued for 10 min, and then the Grignard reagent obtained from 0.40 g ($16.7 \cdot 10^{-3}$ g-atom) of magnesium and 2.5 g ($11.2 \cdot 10^{-3}$ mole) of 1-bromoundec-10-ene in 27 ml of absolute THF was added, and the reaction mixture was stirred at 2°C for 2 h and was left at room temperature for 15 h. After this, 20 ml of 10% HCl was added, the products were extracted with diethyl ether (3 × 100 ml), and the extract was washed successively with saturated solutions of $NaHCO_3$ and NaCl and was dried with $MgSO_4$ and evaporated. The residue was chromatographed (SiO_2, hexane), giving 1.41 g (71%) of compound (I), identical with that obtained in experiment A.

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