A NEW VARIANT OF THE SYNTHESIS OF DISPARLURE VIA ACETYLENIC INTERMEDIATES

Jaroslav JONAS, Pavel SLANINA, Otakar HUMPA and Ctibor MAZAL

Department of Organic Chemistry, J. E. Purkyně University, 611 37 Brno

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Disparlure, the sexual feromone of the Gypsy Moth, has been prepared via the known intermediate 2-methyl-7-octadecyne, using a new constructional principle: $C_9 + C_{10} \rightarrow C_{19}$. The so far undescribed 7-methyl-1-octyne was used as the C_9 component. The advantages of this procedure consist in higher yields of disparlure and in a substantial simplification of the method of purification of 2-methyl-7-octadecyne.

The sexual feromone of the Gypsy Moth (*Lymantria dispar* L.) – disparlure (*I*), used for fighting the Nun or Black Archer (*Lymantria monacha* L.), was isolated for the first time by Bierl, Beroza and Collier[1] who also determined its structure as *cis*-2-decyl-3-(5-methylhexyl)-oxirane (*I*). The methods of synthesis of disparlure (*I*) published so far (cf. ref.[2]) may be divided into those leading to the key acetylenic intermediate 2-methyl-7-octadecyne[3-12] (*II*), and others. The constructional principles used so far for the synthesis of *II* can be divided into three groups:

a) $C_{12} + C_7 \rightarrow II$ (refs[3-10]),

b) $C_{15} + C_4 \rightarrow II$ (ref.[11]), and

c) $C_{13} + C_6 \rightarrow II$ (ref.[12]).

We prepared disparlure (*I*) via the key acetylenic intermediate *II* using the following constructional principle[13]

d) $C_9 + C_{10} \rightarrow II$,

where the so far undescribed 7-methyl-1-octyne[14] (*III*) served as one component, while the second C_{10} component was 1-bromodecane, and we found that this procedure brought advantages both with respect to the yields of compound *II* and the ease of its purification.

EXPERIMENTAL

The 1-bromo-5-methylhexane (*IV*) used was prepared from 5-methylhexanol, prepared according to ref.[4]. The ^{1}H NMR and ^{13}C NMR spectra were measured on a Tesla BS 567 instrument at 100 and 25 MHz, respectively, using tetramethylsilane as internal reference. The chemical shifts are given in δ-scale. The purity of the products was checked by gas chromatography on a Chrom V instrument, with flame-ionization detection and a column packed with Carbowax 20 M, at 198°C.

7-Methyl-1-octyne (*III*)

Cooled dimethylformamide (200 ml) was added to a mixture of sodium acetylide and liquid ammonia (prepared by introduction of purified acetylene into a solution of 13·5 g, i.e. 0·54 mol, of sodium in 400 ml of liquid ammonia), followed by a solution of 89·6 g (0·5 mol) of 1-bromo-5-methylhexane (*IV*) in 70 ml of dimethylformamide, added dropwise over 10 min. The mixture was stirred for 1 h and allowed to stand overnight. After addition of 1·5 l of water the organic layer was separated, the aqueous layer extracted with three 150 ml portions of diethyl ether and the combined organic layers were dried over magnesium sulfate, filtered and the solvent distilled off. Yield, 45·3 g (0·36 mol, 72·3%) of compound *III*, b.p. 39—41°C/1·33 kPa, 48—50°C/1·99 kPa, n_D^{20} 1·4218. ^{1}H NMR (C^2HCl_3): 0·79 (d, CH); 2·52 (s, 1 H); 3·31 (t, 2 H). ^{13}C NMR (without solvent): 18·92; 23·06; 27·17; 28·51; 29·44; 39·11; 69·05; 84·32. IR spectrum ($\tilde{\nu}$, cm^{-1}): 3 280, 2 120, 630.

2-Methyl-7-octadecyne (*II*)

A calculated amount of n-butyllithium in hexane was added to a solution of 24·3 g (0·18 mol) of 7-methyl-1-octyne (*III*) in 300 ml of diglyme, hexane was distilled off and the mixture heated under stirring at 80—90°C for 6 h. Then, 44·3 g (0·2 mol) of 1-bromodecane in 50 ml of diglyme were added at once to the mixture which was stirred and heated at 130—140°C for 60 h. Diglyme was distilled off under reduced pressure and the distillation residue was fractionated using a rotatory vacuum evaporator and a water pump, with a Hickman flask inserted between the distillation flask and the evaporator. At temperatures from 195 to 205°C (oil bath) 29 g (63%) of compound *II* were obtained, with a purity higher than 97%. The ^{1}H NMR spectrum of this product was in agreement with the literature (ref.[6]), and the mass spectrum agreed with that in ref.[5]. ^{13}C NMR spectrum (without solvent): 14·66; 19·48; 23·17; 23·51; 27·39; 28·70; 29·67; 30·08; 30·27; 30·49; 31·39; 32·17; 32·80; 39·37; 80·10; 80·18.

cis-2-Decyl-3-(5-methylhexyl)-oxirane — Disparlure (*I*)

Compound *II* was hydrogenated over Lindlar catalyst in ethanol at room temperature and converted to (*Z*)-2-methyl-7-octadecene in an almost quantitative yield (chromatographically pure, with a ^{1}H NMR spectrum corresponding to the data in ref.[6]). This was converted to disparlure *I* in an almost quantitative yield by epoxidation with *m*-chloroperoxybenzoic acid in dichloromethane at 0°C (on epoxidation in diethyl ether the presence of acids leads to isomerization of compound *I* to an equilibrium mixture of compound *I* and its (*E*)-isomer, which is biologically inactive[15]). The mass spectrum of the disparlure obtained is in agreement with the fragmentation published in ref.[5]. The IR and ^{1}H NMR spectra are in agreement with the data from ref.[6].

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