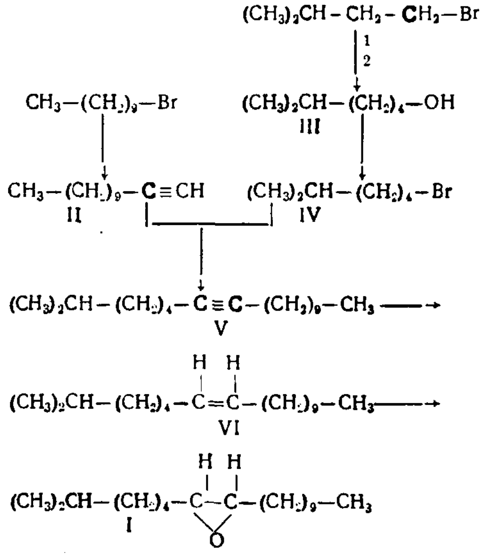
THE CHEMISTRY OF THE PHEROMONES

II.* A NEW SYNTHESIS OF DISPARLURE – THE SEX ATTRACTANT OF THE GYPSY MOTH

A. A. Shamshurin, M. A. Rekhter,
and L. A. Vlad

UDC 547,996:632.936

From females of Porthetria dispar (L.) (gypsy moth), M. Beroza et al. [2] isolated a sex attractant – disparlure – which was identified as 2-methyl-cis-7,8-epoxyoctadecane (I), and they synthesized it by the epoxidation of 2-methyloctadec-7-ene, obtained from isoheptyltriphenylphosphonium bromide and undecanal by the Wittig reaction. A defect of this method is the necessity for separating the mixture of cis and trans isomers at the stage of preparing the olefin. We have performed a stereodirected synthesis of disparlure in the following way:



As can be seen from the scheme, disparlure (I) was synthesized from 2-methyloctadec-7-yne (V), obtained from dodec-1-yne (II) and 1-bromo-5-methylhexane (IV). The dodec-1-yne (II) was obtained with a yield of 70% by condensing 1-bromodecane and lithium acetylide in dioxane. The method of obtaining the acetylene (II) described previously [3] gives a contaminated product in low yield (10-15%). The 1-bromo-5-methylhexane (IV) was synthesized from isoamyllithium and ethylene oxide with subsequent treatment of the alcohol (III) produced with phosphorus tribromide. Sodium dodecynide was obtained in the usual way [4] from dodec-1-yne and sodium methylsulfinylmethylide in DMSO and, without isolation, was alkylated with the 1-bromo-5-methylhexane.

2-Methyloctadec-7-yne (V) has a characteristic mass spectrum that confirms its structure (Fig. 1). The main peaks of the spectrum are those with m/e 264 (molecular ion), 43 (terminal isopropyl group) and 123 and 165, formed by α-cleavages at the triple bond and showing its position at C_7–C_8. Furthermore, the

---

* For Communication I, see [1].

Institute of Chemistry, Academy of Sciences of the Moldavian SSR. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 545-548, July-August, 1973. Original article submitted July 5, 1972.

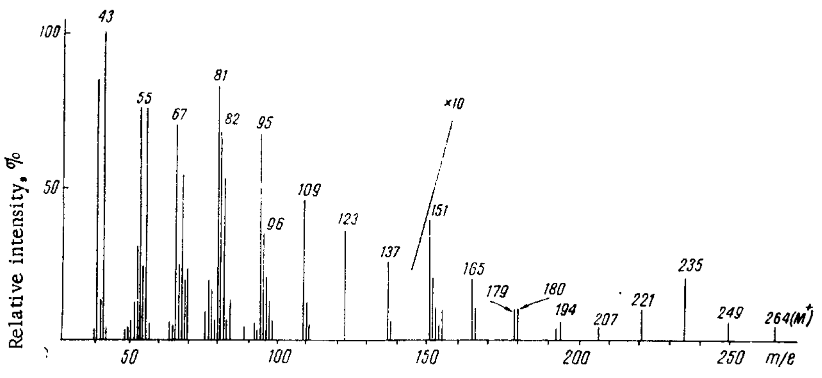
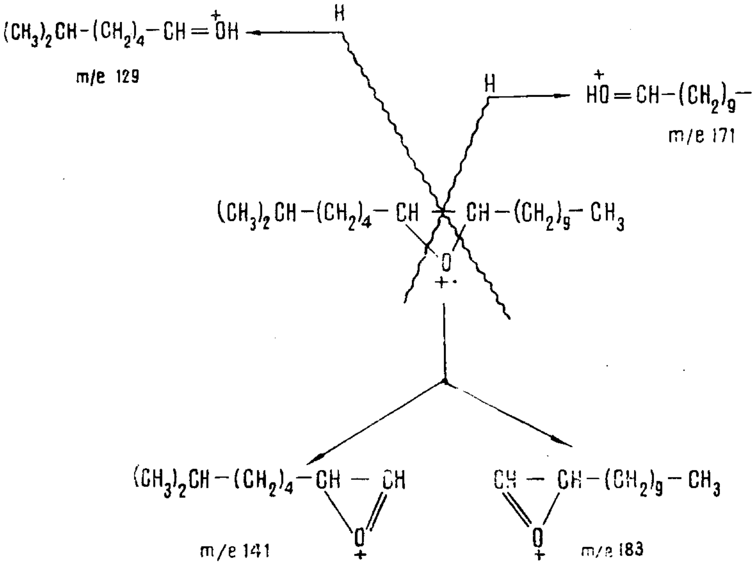


Fig. 1. Mass spectrum of 2-methyloctadec-7-yne.

mass spectrum contains peaks with m/e 55, 67, 81, 95, and 96, which are characteristic of dialkylacetylenes containing not less then eight carbon atoms in at least one alkyl residue [5].



The hydrogenation of the acetylene (V) over Lindlar's catalyst and the epoxidation of the olefin (VI) with monoperoxyphthalic acid (MPPA) gave disparlure* (I). The structure of the latter was confirmed by its mass spectrum, which had the fragmentation characteristic for epoxides [6, 7] (see scheme). As can be seen, the position of the epoxide ring at C_7-C_8 is unambiguously determined by the peaks with m/e 141 and 183 formed by cleavages in the α position to the epoxide ring, and also by fragments with m/e 129 and 171 formed as the result of the opening of the same ring.

EXPERIMENTAL

The purity of the starting materials and the analyses of the reaction products were checked by GLC in an instrument with a flame-ionization detector and glass columns (0.4 × 200 cm) under the following conditions:

a) 5% of SE-30 on Chromaton N-AW–HMDS at 80°C for the bromide (IV), 105°C for the alcohol (III), and 135 and 175°C, respectively, for the acetylenes (II) and (V);

b) 5% of NSKT-33 on Chromaton N-AW–HMDS at 175°C for disparlure (I).

The rate of flow of nitrogen for all the compounds was 40 ml/min. The mass spectra were obtained on an MKh-1303 mass spectrometer.

Dodec-1-yne (II). Over 1 h with continuous stirring and with a continuous passage through the reaction mixture of a current of purified acetylene, 3.5 g (0.5 mole) lithium was added in small portions to a

---

* When we had completed this work, another communication appeared [8] reporting a more complex variant of the synthesis of disparlure, also via 2-methyloctadec-7-yne (V).

flask containing 1.8 liter of liquid ammonia cooled with dry ice. After the lithium had been added, the mixture was stirred for another 3 h and then, without interruption of the passage of acetylene, 110 g (0.5 mole) of 1-bromodecane was added dropwise. After 4 h, 600 ml of dry dioxane was added to the flask, the flow of acetylene was stopped, and the mixture was left for 12 h. Then it was stirred at 25°C for 48 h, the dioxane was distilled off on a rotary evaporator, and the residue was decomposed with saturated ammonium chloride solution, and extracted with ether, and the extract was dried and distilled. The yield of (II) was 40.3 g (70%), bp 97-103°C (15 mm), n_D^{20} 1.4372. Literature data [9]: bp 95-97°C (15 mm), n_D^{20} 1.4375.

5-Methylhexan-1-ol (III). A flask fitted with a stirrer, dropping funnel, condenser, and tube for the introduction of nitrogen was charged with 2 g of finely cut lithium in 100 ml of absolute ether and 15 g of isoamyl bromide. After the reaction had begun, in a current of nitrogen at 20-30°C another 45 g (0.5 mole) of isoamyl bromide was slowly added, the mixture was stirred for 1 h, and then 10 g (0.3 mole) of ethylene oxide cooled with dry ice was added over 4 h. After all the oxide had been added, the reaction mixture was stirred at −20°C for another 2 h and was left for 12 h. The usual working up gave 15 g (43%) of a substance with bp 58°C (4 mm), n_D^{20} 1.4270. Literature data [10]: bp 170.5°C (755 mm), n_D^{20} 1.4254.

1-Bromo-5-methylhexane (IV). By the usual method, 8 g (0.07 mole) of the alcohol (III) and 5.7 g (0.02 mole) of phosphorus tribromide gave 4.8 g (39%) of (IV) with bp 39°C (3 mm), n_D^{20} 1.4490.

2-Methyloctadec-7-yne (V). To the sodium methylsulfinylmethylide obtained from 0.48 g (0.02 mole) of sodium hydride in 25 ml of absolute DMSO, 3.3 g (0.02 mole) of the acetylene (II) was added dropwise, the mixture was stirred at 20-25°C for 4 h, and then 4.25 g (0.025 mole) of the bromide (IV) was added. The reaction mixture was stirred at the same temperature for 10 h and was then heated at 60°C for 2 h, cooled, poured into 0.75 liter of water, and extracted with petroleum ether (bp 70-100°C). The solvent and compounds (II) and (IV) were eliminated by vacuum distillation, and the residue was chromatographed on a column of neutral alumina (2.5 × 30 cm) giving 1.1 g (20.8%) of (V), in the pure state according to GLC.

2-Methyloctadec-7-ene (VI). The acetylene (V) (0.8 g) was hydrogenated for 8 h in heptane over 0.5 g of Lindlar's catalyst to which 0.02 g of lead acetate had been added before hydrogenation. The yield of olefin (VI) was quantitative.

2-Methyl-cis-7,8-epoxyoctadecane (Disparlure, I). A mixture of 0.5 g of the olefin (VI) in 5 ml of ether and 0.7 g of monoperoxyphthalic acid was kept in the refrigerator for five days. According to GLC, the yield of disparlure (I) was 90%. After the usual working up, the product was purified additionally by TLC on silica gel using petroleum ether (bp 70-100°C) as the solvent. For the mass spectra, see Fig. 1.

SUMMARY

The stereodirected synthesis of 2-methyl-cis-7,8-epoxyoctadecane – the sex attractant of Porthetria dispar (L.) – has been effected.

LITERATURE CITED

1. A. A. Shamshurin, B. G. Kovalev, and A. P. Donya, Dokl. Akad. Nauk SSSR, 190, 1362 (1970).
2. B. A. Bierl, M. Beroza, and C. W. Collier, Science, 170, 87 (1970).
3. E. A. Bried and G. F. Hennion, J. Amer. Chem. Soc., 60, 1717 (1938).
4. K. Kříž, M. J. Benes, and J. Peska, Tetrahedron Lett., 2881 (1965); Collection Czech. Chem. Commun., 32, 358 (1967).
5. H. Luftmann and G. Spiteller, Org. Mass-Spectrom., 5, 1073 (1971).
6. R. T. Aplin and L. Coles, Chem. Commun., 858 (1967).
7. P. Brown, J. Kossanyi, and C. Djerassi, Tetrahedron Suppl., 8, Part 1, 241 (1966).
8. K. Eiter, Angew. Chem., 84, 67 (1972).
9. V. D. Yasnopol'skii, Physicochemical Constants of Organic Compounds with an Acetylenic Bond [in Russian], Baku (1966), p. 15.
10. I. Heilbron and R. M. Bunbury, Dictionary of Organic Compounds, 2nd ed., Eyre and Spottiswoode, London (1943-4).