INSECT PHEROMONES AND THEIR ANALOGS

II. SYNTHESIS OF THE SEX ATTRACTANT OF THE GYPSY MOTH — d,*l*-DISPARLURE

G. A. Tolstikov, U. M. Dzhemilev,
G. G. Balezina, and V. P. Krivonogov

UDC 547.364

The development of methods of synthesizing disparlure has been the subject of considerable attention in recent years, which is due to the promising nature of the use of this compound for regulating the numbers of gypsy moths [1-5].

Continuing previous work [6, 7] on the use of the linear and cyclic oligomers formed as the result of the metal-complex-catalyzed transformations of 1,3-dienes for the synthesis of insect pheromones, we have found a new route to d,*l*-disparlure. The synthesis is based on the Wittig reaction, by means of which 2-methyloctadec-Z-7-ene (VII) has been obtained from undecanal (III) and 6-methylheptyltriphenylphosphonium bromide (VII). To obtain the undecanal we have recourse to a three-stage conversion of methyl undeca-E,E-2,5,10-trienoic acid (I), which was formed with high yield by the reaction of butadiene with methyl acrylate in the presence of nickel complexes [8]. The hydrogenation of the ester (I) on Raney nickel gave methyl undecanoate, which was reduced to undecan-1-ol (II) with the aid of $LiAlH_4$ in ether. The oxidation of (II) with the Corey reagent [9] gave undecanal (III) with a yield of ∼80% calculated on the ester (I). It is interesting to note that, in addition to undecanal, undecyl undecanoate (IV) was formed, its yield varying between 20 and 50% according to the reaction temperature. By performing oxidation at 0-20°C we obtained a mixture of aldehyde (III) and of ester (IV) in which the amount of the latter did not exceed 15%.

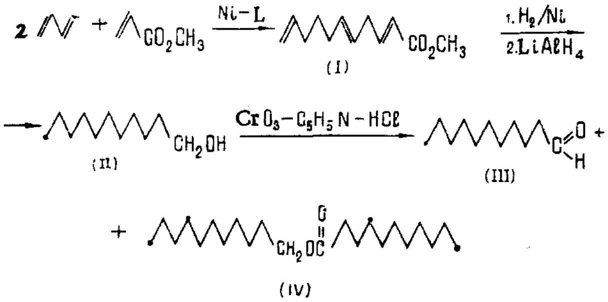
1-Bromo-6-methylheptane (X) was synthesized in three stages from a mixture of the esters (V) and (VI) formed by the codimerization of isoprene with methyl acrylate on homogeneous cobalt-containing catalysts [10]. The phosphonium salt (VII) was obtained by heating the bromide (X) with triphenylphosphine in acetonitrile.

It has been established that the maximum amount of the cis olefin (VIII) is obtained when the reaction between the aldehyde (III) and the salt (VII) is performed in hexamethylphosphoramide solution using potassium tert-butanolate as the alkaline reagent. Under these conditions the selectivity with respect to (VIII) amounts to ∼95%.

As can be seen from Table 1, fairly similar results were obtained when using other alkaline reagents. The oxidation of (VIII) with m-chloroperbenzoic acid in chloroform gave the epoxide (IX) quantitatively.

EXPERIMENTAL

The esters (I, V, and VI) and also the undecan-1-ol (II) and the 2-methylheptan-7-ol (XI) were obtained as described previously [8, 10]. The PMR spectra were recorded on a



Institute of Chemistry, Bashkir Branch of the Academy of Sciences of the USSR, Ufa.
Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 792-795, November-December, 1978. Original article submitted July 25, 1978.

0009-3130/78/1406-0674$07.50

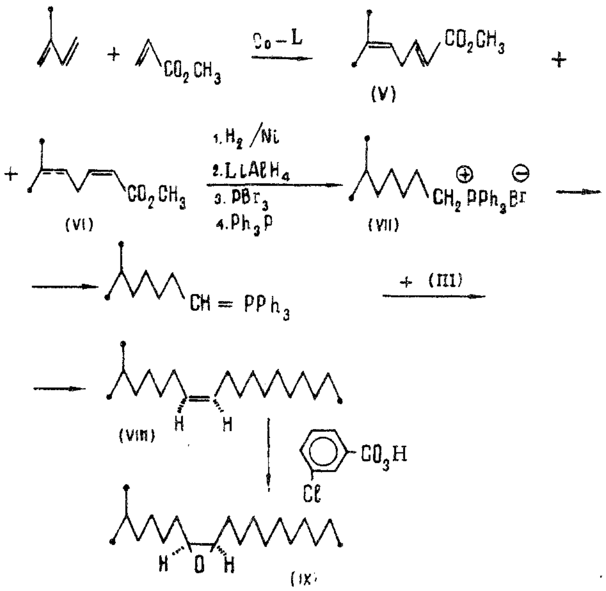


TABLE 1. Influence of the Nature of the Solvent and of the Alkaline Reaction on the Stereospecificity of the Reaction of Undecanal (III) with (6-Methylheptyl)triphenylphosphonium Bromide (VII)

Alkaline reagent	Solvent	Reaction temperature, °C	Overall yield of (VIII), %	Ratio of the isomers	
				cis-(VIII)	trans-(VIII)
LiBu	DMFA	–20	50,6	85	15
LiNEt$_2$	DMFA	–25	45,1	87,5	12,5
NaN(Me$_3$Si)$_2$	DMFA	–25	67,2	93,5	6,5
NaOEt	DMFA	–20	60	89	11
NaOEt	Hempa	– 5	63,5	91,5	8,5
KOCMe$_3$	DMFA	–20	69,5	89,5	10,5
KOCMe$_3$	DMSO	– 5	64	91,2	8,8
KOCMe$_3$	Hempa	– 5	72,5	94,7	5,3

Tesla-BS-480B spectrometer (internal standard HMDS; solvent CCl$_4$). The IR spectra were recorded on a UR-20 instrument (film). The compounds obtained analyzed on a Chrom-41 chromatograph with a flame-ionization detector using a column 2.4 m long and 0.3 m in diameter; PEGA (15 wt.%) on Chromaton (0.20 × 0.25 mm), carrier gas helium, 100 ml/min, temperature 160-180°C.

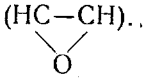
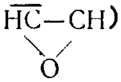
1-Bromo-6-methylheptane (X). With stirring at 15°C, 16 g (0.06 mole) of PBr$_3$ was added dropwise over 0.5 h to 19.5 g (0.15 mole) of the alcohol (X). The reaction mixture was heated at 80°C and was stirred at this temperature for another 5 h, after which it was left overnight. Then 200 ml of diethyl ether was added, and the organic layer was separated off, washed with 5% Na$_2$CO$_3$ solution and with water, and was dried over MgSO$_4$. Elimination of the solvent yielded 27.2 g (94%) of the bromide (XI) with mp 80-82°C (10 mm), n_D^{20} 1.4518, which corresponds to the literature [4].

6-Methylheptyltriphenylphosphonium Bromide (VII). A solution of 26.2 g (0.1 mole) of triphenylphosphine and 19.3 g (0.1 mole) of the bromide (X) in 100 ml of acetonitrile was heated at 75-80°C for 12 h with stirring. After the elimination of the acetonitrile, the crystalline residue was washed with benzene and was dried in vacuum at 50-60°C. This gave 34.4 g (76%) of the salt (VII) with mp 169-170°C (literature figures: mp 170-172°C [5]).

Undecanal (III). Over 1.5 h at 0.5°C, a solution of 43 g (0.25 mole) of undecan-1-ol in 100 ml of CH$_2$Cl$_2$ was added dropwise to a suspension of 100 g of the Corey reagent [9] in 150 ml of freshly distilled CH$_2$Cl$_2$, the mixture was stirred at room temperature for another 1 h, and it was then diluted with 0.5 liter of dry ether and the precipitate was washed with ether (3 × 200 ml). The ethereal extracts were washed with water to neutrality and were dried over MgSO$_4$. After the solvent had been eliminated and the residue had been distilled, 35 g of (III) was obtained with bp 78-80°C (1 mm), n_D^{20} 1.4320, which corresponds to literature information [3]. Yield 82.5%.

In addition to (III), 6 g (14%) of the ester $C_{22}H_{44}O_2$ (IV) with bp 180-183°C (1 mm), n_D^{20} 1.4435, was obtained. IR spectrum (ν, cm^{-1}): 1070, 1120 (C—O—), 1740 (C=O). PMR spectrum (δ, ppm): 0.83 (6 H, CH_3—CH_2); 1.25 (34 H, CH_2), 2.17 (2 H, CH_2—COO); 3.93 (2 H, CH_2OCO); m/e 340.

2-Methyloctadec-Z-7-ene (VIII). Over 1 h in an atmosphere of argon, 10 g (0.022 mole) of the salt (VII) in 60 ml of dimethylformamide was added to a solution of potassium tert-butanolate in tert-butanol (0.9 g of metallic potassium in 25 g of tert-butanol) cooled to −20°C. The mixture was stirred at room temperature for 2 h by which time the orange coloration characteristic for an ylide had appeared, and it was then cooled to −20°C, and 3.8 g (0.022 mole) of the aldehyde (III) in 10 ml of dimethylformamide was added over 1 h. The mixture was stirred for 3 h and was left overnight at room temperature, after which 200 ml of hexane and 150 ml of ice water were added. The organic layer was separated off, and the aqueous layer was extracted with hexane (3 × 50 ml). The combined extracts were washed with water, dried over $MgSO_4$, and distilled. This gave 4.1 g (69.5%) of the olefin $C_{19}H_{38}$ (VIII), with bp 105-107°C (0.5 mm), n_D^{20} 1.4485 [1, 7]. IR spectrum (ν, cm^{-1}) 1658 (Z-C=C); 3012 (Z-CH=). PMR spectrum (δ, ppm): 0.80 (6 H, CH_3CH); 0.87 (3 H, CH_3CH_2); 1.24 (23 H, CH_2, CH); 1.92 (4 H, CH_2C=C); 5.02 (2 H, triplet, J = 4 Hz); m/e 266.

2-Methyl-Z-7,8-epoxyoctadecane (IX). A solution of 8 g (0.03 mole) of the olefin (VIII) in 100 ml of dry $CHCl_3$ was cooled to −20°C and 50 ml of a 0.6 M solution of m-chloroperbenzoic acid in chloroform was added in small portions over 0.5 h [4]. The mixture was kept at −10°C for 2 h and was left overnight. Then it was washed with aqueous $NaHCO_3$ solution in water and was dried over Na_2SO_4. After elimination of the $CHCl_3$, the residue was chromatographed on Al_2O_3 (activity grade II) [hexane—diethyl ether (10:1)]. Distillation of the residue gave 7.6 g of (IX) with the composition $C_{19}H_{38}O$, bp 138-140°C (1 mm), n_D^{20} 1.4472 [2, 7]. Yield 89%. IR spectrum (ν, cm^{-1}): 840, 860, 1080, 1270,  $\underset{O}{(HC-CH)}$. PMR spectrum (δ, ppm) 0.80 (6 H, CH_3CH), 0.85 (3 H, CH_3CH_2), 1.23 (26 H, CH_2), 1.32 (1 H, CH), 2.62 (2 H,  $\underset{O}{HC-CH}$); m/e 282.

SUMMARY

A new route for the synthesis of 2-methyl-Z-7,8-epoxyoctadecane — the attractant of *Porthetria dispar* — has been developed which uses as the starting compounds linear oligomers of butadiene and isoprene with methyl acrylate.

LITERATURE CITED

1. B. G. Kovalev, R. I. Ishchenko, and V. A. Marchenko, Zh. Org. Khim., 9, 6 (1973).
2. A. A. Shamshurin, M. A. Rekhter, and L. A. Vlad, Khim. Prirodn. Soedin., 545 (1973).
3. H. Bestmann and O. Vostrowsky, Tetrahedron. Lett., 207 (1974).
4. H. Bestmann and O. Vostrowsky, Chem. Ber., 109, 3375 (1976).
5. W. Micheilowsky and T. Chan, Tetrahedron Lett., 49, 4439 (1976).
6. G. A. Tolstikov, U. M. Dzhemilev, and R. I. Khusnutdinov, Khim. Prirodn. Soedin., 126 (1978).
7. G. A. Tolstikov, V. N. Odinokov, R. I. Galeeva, and S. R. Rafikov, Dokl. Akad. Nauk SSSR, 239, 1377 (1978).
8. U. M. Dzhemilev, O. S. Vostrikova, and G. A. Tolstikov, Izv. Akad. Nauk SSSR, Ser. Khim., 2018 (1975).
9. E. Corey and J. Suggs, Tetrahedron Lett., 31, 2647 (1975).
10. G. A. Tolstikov, U. M. Dzhemilev, and R. I. Khusnutdinov, Zh. Org. Khim., 12, 315 (1976).