Gel chromatography was carried out on a column 1.2 × 45 cm filled with G-75 gel in DMSO. V_e = 31 ml, V_0 = 9.8 ml in terms of dextran blue with a molecular mass of 2,000,000. The coefficients found previously [7] were used to calculate molecular masses.

SUMMARY

The dioxane lignin has been isolated from the ripe stems of the sea island cotton plant of variety S-6030, a developed semiempirical formula has been derived for it, its UV and IR spectra have been recorded, and its molecular mass has been determined (10,100).

LITERATURE CITED

1. J. M. Pepper and M. Siddequellan, Can. J. Chem., 39, 1454 (1961).
2. G. F. Zakis, L. N. Mozheiko, and G. M. Telysheva, Methods of Determining the Functional Groups of Lignin [in Russian], Riga (1975).
3. A. N. Belozerskii and N. I. Proskuryakov, A Practical Handbook on Plant Biochemistry [in Russian], Moscow (1951), p. 17.
4. N. A. Veksler, L. S. Smirnova, and Kh. A. Abduazimov, Khim. Prir. Soedin., 100 (1977).
5. B. Kh. Pulatov, Kh. A. Abduazimov, Khim. Prir. Soedin., 260 (1978).
6. V. B. Karklin' and P. P. Érin'sh, Khim. Drevesiny, No. 7, 83 (1971).
7. N. I. Babikova, B. D. Bogomolov, O. M. Sokolov, G. G. Kochergina, G. I. Popova, and V. I. Udal'tsova, Lesn. Zh., No. 3, 112 (1974).

INSECT PHEROMONES AND THEIR ANALOGS.

VIII. SYNTHESIS OF THE (Z) AND (E) ISOMERS OF 2-METHYLOCTADEC-7-ENE AND OF 2-METHYL-7,8-EPOXYOCTADECANE

V. N. Odinokov, G. G. Balezina,
U. M. Dzhemilev, G. Yu. Ishmuratov,
D. V. Amirkhanov, V. P. Krivonogov,
F. Kh. Sitnikova, and G. A. Tolstikov

UDC 547.31+547.422+632.78

A highly stereospecific method for the synthesis of racemic (Z)-disparlure has been developed which is based on the reduction of 2-methyloctadec-7-yne with the aid of 9-borabicyclo[3.3.1]nonane and the epoxidation of the resulting (Z)-2-methyloctadec-7-ene with p-methoxycarbonylperbenzoic acid. The ^{13}C NMR spectra of the (Z) and (E) isomers of 2-methyloctadec-7-ene and 2-methyl-7,8-epoxyoctadecane, which unambiguously confirm the structures of these compounds, are given. It has been established that (E)-2-methyloctadec-7-ene exhibits a moderate attractant activity while the (Z) isomer does not attract the gypsy moth. The addition of 5-25% of (E)-disparlure increases the biological activity of (Z)-disparlure.

In the synthesis of racemic (Z)-disparlure by the Witting olefin-forming reaction [1, 2], or by the hydrogenation of 2-methyloctadec-7-yne [3-6], from 2 to 15% of the (E) isomer is formed. Only a few methods permit d,*l*-disparlure exclusively of the (Z) configuration to be obtained [7-9]. Information on the influence of (Z)-2-methyloctadec-7-ene and (E)-2-methyl-7,8-epoxyoctadecane as impurities on the biological activity of the sex pheromone of the gypsy moth (*Lymantria dispar*), (Z)-2-methyl-7,8-epoxyoctadecane is inadequate. It is known, in particular, the (Z)-2-methyloctadec-7-ene is an inhibitor of the sex pheromone [10], while conversely, (E)-2-methyl-7,8-epoxyoctadecane in amounts not exceeding 10-15% enhances the attractant properties of (Z)-d,*l*-disparlure [11]. There is no information whatever on the action of (E)-2-methyloctadecene on the behavior of gypsy moth males.

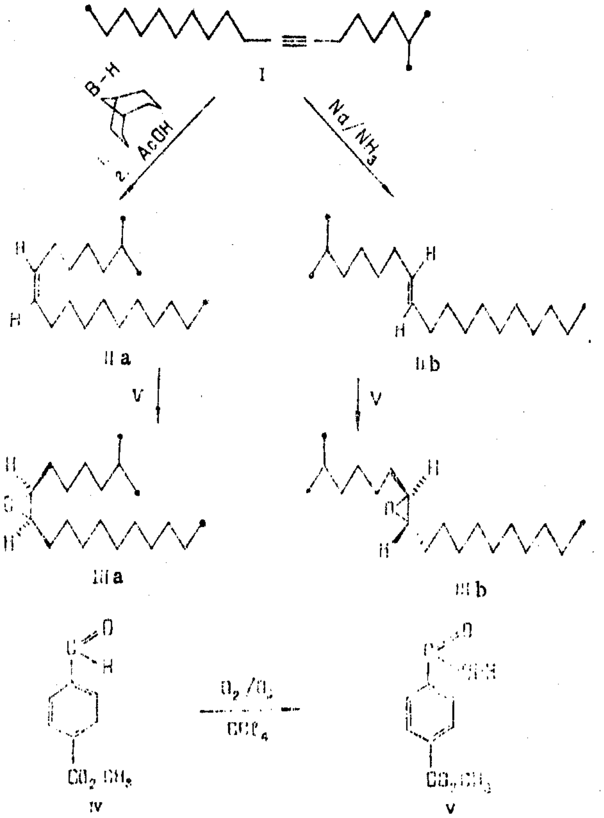
Institute of Chemistry, Bashkir Branch, Academy of Sciences of the USSR, Ufa. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 630-634, September-October, 1983. Original article submitted October 20, 1982.

0009-3130/83/1905-0593$07.50

In this connection, we have performed the synthesis of stereochemically individual (Z)- and (E)-2-methyloctadec-7-enes (IIa and b, respectively), which were converted with high selectivity into the stereochemically pure (Z) and (E)-2-methyl-7,8-epoxyoctadecanes (IIIa and b, respectively) with the aid of a new epoxidating agent — p-methoxycarbonylperbenzoic acid (V), which is readily obtainable from methyl p-formylbenzoate (IV) by oxidation with oxygen, initiated by ozone (0.5-1%), in carbon tetrachloride solution [12].

We have reported the synthesis of the stereochemically pure (Z)-olefin (IIa) by a scheme based on the selective ozonolysis of (Z,Z)-cyclooctadiene [7, 9]. We have now established that the (Z)-olefin (IIa) in a quality not inferior to that obtained by ozonolysis is formed in the reduction of 2-methyloctadec-7-yne (I) with the aid of 9-borabicyclo[3.3.1]nonane (9-BBN) — an effective reagent for the hydroboration of acetylenes [13]. The stereochemical individuality of the (Z)-olefin (IIa) was established by GLC analysis and PMR and ^{13}C NMR spectroscopy. The identification under the same conditions of the products of the hydrogenation of the alkyne (I) over Lindlar catalysts [4, 5] or over a nickel boride catalyst [6] showed the presence in the (Z)-olefin (IIa) of 5-7% or 1.5-2%, respectively, of the (E) isomer (IIb). The stereochemically pure (E)-olefin (IIb) was synthesized by the reduction of the triple bond in the dialkylacetylene derivative (I) with the aid of metallic sodium in liquid ammonia [4] (scheme 1).

Scheme 1



There are no differences in the PMR spectra of the (Z)- and (E)-olefins (IIa and b) which permit their stereochemical purity to be judged. However, in the products of their epoxidation (IIIa and b), the positions of the signals of the protons of the epoxide ring of the (Z) isomer (IIIa) (δ 2.88 ppm) are shifted appreciably downfield in comparison with those of the (E) isomer (IIIb) (δ 2.64 ppm). The ratio of the intensities of these signals can be used as a quantitative measure of the ratio of the geometric isomers in a sample of disparlure under investigation. However, a higher accuracy of analysis is attained with the aid of the GLC method using a stereospecific phase. An unambiguous confirmation of the assignment of the samples of the olefins (IIa and b) and the epoxides (IIIa and b) that have been synthesized to the (Z) and (E) series is given by their ^{13}C NMR spectra (Table 1). Evidence that the olefin (IIa) belongs to the (Z) series is provided by the chemical shifts of the vicinal (δ 129.2 ppm) and allyl (δ 27.25 ppm) carbon atoms, while the downfield shift

TABLE 1. ^{13}C NMR Spectra (δ, ppm) of the (Z) and (E) Isomers of 2-Methyloctadec-7-ene (IIa, b) and 2-Methyl-7,8-epoxyoctadecane (IIIa, b)

Carbon atom	Compound			
	IIa	IIb	IIIa	IIIb
C^1	22,66	22,72	22,66	22 66
C^2	27,25	28,10	27,45	28,03
C^3	39,04	39,04	39,04	39,04
C^4	27,25	27,06	27,45	27,38
C^5	30,09	29,84	27,12	26,54
C^6	27 25	32,69	28,03	32,30
C^7	129,2	132,5	55,87	57,55
C^8	129 2	132,5	55,87	57,55
C^9	27,25	32,69	28,03	32,30
C^{10}	29,78	29,84	26,87	26,28
C^{11}	29,45	29,33	29,71	29,78
C^{12}	29 78	29,84	29,71	29,78
C^{13}	29,78	29,84	29 71	29,78
C^{14}	29,78	29,84	29,71	29,78
C^{15}	29,45	29,52	29,71	29,78
C^{16}	32,04	32,04	32,04	32,04
C^{17}	22,66	22,72	22,66	22,66
C^{18}	14 11	14,18	14 18	14,18
CH_3	22,66	22,72	22,66	22,66

of the corresponding signals (δ 132.5 and 32.69 ppm) is evidence in favor of the (E) configuration of the olefin (IIb).

An analogous pattern is observed in the ^{13}C NMR spectra of the epoxides (IIIa and b). The signals of the epoxide ring of the (E) isomer (IIIb) (δ 57.55 ppm) are shifted by 1.68 ppm downfield in relation to the signal of the same carbon atoms in the spectrum of the (Z) isomer (IIIa), and the downfield shift for the C atoms adjacent to the epoxide ring of (E)-disparlure (IIIb) amounts to 4.27 ppm.

Biological tests on the attractant activity for the gypsy moth were carried out both on the individual (Z)- and (E)-isomeric olefins (IIa and b) and on (Z)- and (E)-disparlures (IIIa and b) and also on mixtures of (Z)-disparlure (IIIa) with the (Z)-olefin (IIa) in ratios (wt.%) of 95:5, 75:25, and 50:50; with the (E)-olefin (IIb) (95:5; 50:50; 25:75); and with (E)-disparlure (IIIb) (95:5; 90:10; 85:15; 75:25; 50:50). The trials showed that the highest biological activity of the individual compounds (IIa, b; IIIa, b) is possessed by (Z)-disparlure (IIIa) (in an amount of the preparation of 0.5-5 μg/trap). The activity of the (E)-olefin (IIb) is considerably lower and that of (E)-disparlure (IIIb) even lower. The (Z)-olefin (IIa) does not exhibit the properties of an attractant of the gypsy moth. At the same time, the addition of a small amount (5%) of the (Z)-olefin (IIa) to (Z)-disparlure (IIIa) does not lower the activity of the preparation. An increase activity is shown by a preparation of (Z)-disparlure containing 5% of the (E)-olefin or of (E)-disparlure (for a concentration of 0.5 μg/trap.). It is interesting to note the high attractant activity of a preparation of (Z)-disparlure containing 25% of the (E)-isomer (0.5 μg/trap) and 75% of the (E)-olefin.

EXPERIMENTAL

The IR spectra of the substances were taken on a UR-20 spectrometer in a thin layer, the PMR spectra on a Tesla BS-487B spectrometer at a working frequency of 80 MHz with $CDCl_3$ as the solvent and HMDS as internal standard, and the ^{13}C NMR spectra on a Bruker WH-90 instrument at a working frequency of 22.63 MHz with CCl_4 as solvent and internal standard (δ 96.0 ppm). Chemical shifts are given in the δ scale. Mass spectra were measured on a MKh-1306 instrument at a temperature of the ionization chamber of 200°C and with an ionizing voltage of 70 V. GLC analysis was carried out on a Chrom 5 instrument with a flame-ionization detector, the stationary phase being poly(ethylene succinate) (10%) on Chromosorb G-N-AW-DMCS (0.20-0.25 mm), column dimensions of 3.7 m × 3 mm, working temperature 176°C, carrier gas helium.

(Z)-2-Methyloctadec-7-ene (IIa). In an atmosphere of argon, 22 ml (11 mmole) of a 0,5 M solution of 9-BBN in absolute THF was added dropwise to a solution of 2.64 g (10 mmole) of 2-

methyloctadec-7-yne (I), obtained as described previously [4], at 0-2°C. The reaction mixture was kept at 0°C for 24 h, and then 5 ml of glacial AcOH was added and it was boiled for 5 h, cooled to 20°C, treated with 250 ml of a diethyl ether, and washed with 25 ml of 6 M NaOH and then with 20 ml of saturated NaCl solution, dried with $MgSO_4$, and evaporated. Chromatography of the residue (Al_2O_3, hexane) gave 2.53 g (95% of the (Z)-olefin (IIa), n_D^{20} 1.4488, bp 140-142°C (1 mm); its IR and PMR spectra were identical with those of an authentic sample [9]. Mass spectrum [m/z (I, %)]: M^+ 266(8.9), 251(0.5), 238(2.51), 223(0.5), 210(2.51), 196(0.55), 182(1.1), 167(1.66), 153(2.77), 139(5.0), 125(11.05), 111(27.7), 97(55.6 83(77.8), 69(97.5), 57(89.1), 43(100).

(E)-2-Methyloctadec-7-ene (IIb). A solution of 3.5 g (13.2 mmole) of compound (I) in 50 ml of absolute diethyl ether was added dropwise to a solution of 2 g (87 mg-atom) of metallic sodium in 300 ml of liquid ammonia. The reaction mixture was stirred at −35°C for 15 h, and then 200 ml of diethyl ether was added and, at 0-5°C, 50 ml of water. The ethereal layer was separated off, washed with 20 ml of saturated NaCl, dried with $MgSO_4$, and evaporated and the residue was distilled in vacuum. This gave 3.37 g (96%) of the (E)-olefin (IIb), bp 110-112°C (0.5 mm), n_D^{20} 1.4465 [6]. IR spectrum (ν, cm^{-1}): 980 m-s, 1130 m, 1370 m, 1385 m, 1470 s, 2870 v.s., 2935 v.s, 2965 infl., 3020 infl. PMR spectrum, (δ, ppm): 0.87 d (6 H, 2 $C\underline{H}_3CH$, J = 6 Hz); 0.88 t (3 H, CH_3CH_2, J = 6 Hz); 1.27 br.s (23 H, CH_2 and CH groups); 1.97 br.s (4 H, 2 $CH_2C{=}C$); 5.39 m (2 H, $\overline{CH{=}CH}$). Mass spectrum [m/z (I, %)]: M^+ 266(10.0), 251(0.97), 238(3.25), 223(0.65), 210(2.57), 196(0.65), 182(0.97), 167(1.61), 153(2.58), 139(3.25), 125(6.5), 111(12.8), 97(25.7), 83(38.7), 69(54.8), 57(84.2), 43(100).

(Z)-2-Methyl-7,8-epoxyoctadecane (IIIa). At 20°C with stirring, a solution of 2.4 g (9 mmole) of the (Z)-olefin (IIa) in 10 ml of chloroform was added to a suspension of 2 g (10 mmole) of the peracid (V) in 50 ml of dry chloroform, the mixture was stirred for 1 h, and the precipitate was filtered off and washed with chloroform. The solvent was distilled off from the filtrate and the residue was distilled in vacuum to give 2.44 g (96%) of the epoxide (IIIa), mp 138-140°C (0.5 mm), n_D^{20} 1.4472. The IR and PMR spectra were identical with those of an authentic sample [9]. Mass spectrum [m/z (I, %)]: M^+ 282(0.47), 267(0.18), 264(0.73), 239(0.22), 225(0.55), 211(1.27), 197(0.55), 183(8.05), 169(2.54), 152(3.6), 141(7.2), 110(21.7), 97(32.7), 95(25.4), 83(49.1), 82(51.0), 69(96.3), 55(100), 43(>100).

(E)-2-Methyl-7,8-epoxyoctadecane (IIIb) was obtained in a similar manner to the (Z)-epoxide (IIIa), with the exception of the fact that the reaction mixture was held for 5 h instead of 1 h. The yield of distilled epoxide (IIIb) was 2.36 g (93%), bp 135-137°C (0.5 mm), n_D^{20} 1.4465 [6]. IR spectrum (ν, cm^{-1}): 730 w, 905 m, 1080 w, 1130 w, 1370 m, 1380 m, 1470 s, 2870 v.s, 2930 v.s, 2965 infl. PMR spectrum (δ, ppm): 0.88 d (6 H, 2 $C\underline{H}_3CH$, J = 6 Hz), 0.89 t (3 H, $C\underline{H}_3CH_2$, J = 6 Hz); 1.28 and 1.47 m (27 H, CH_2 and CH groups) 2.64 t (2 H, $\underline{CH{-}CH{-}O}$, J = 4 Hz). Mass spectrum [m/z (I, %)]: M^+ 282(0.55), 267(0.22), 264(1.1), 239(0.22), 225(0.44), 211(1.1), 197(0.55), 183(7.78), 169(2.22), 152(4.42), 141(5.55), 123(7.75), 110(23.8), 97(31.1), 95(26.7), 83(52.1), 82(47.8), 69(91.2), 55(100), 43(>100).

p-Methoxycarbonylperbenzoic Acid (V). At 20-25°C, a mixture of ozone and oxygen (0.5-1% by weight of O_3) was passed through a solution of 16.4 g (0.1 mole) of p-methoxycarbonylbenzaldehyde (IV) in 600 ml of CCl_4. The resulting precipitate was filtered off, washed with 100 ml of CCl_4, and subjected to vacuum. This gave 16.3 g (83%) of the peracid (V), $C_9H_8O_5$.

SUMMARY

A highly stereospecific method of synthesizing racemic (Z)-disparlure has been developed which is based on the reduction of 2-methyloctadec-7-yne with the aid of 9-borabicyclo[3.3.1]-nonane and the epoxidation of the (Z)-2-methyloctadec-7-ene with p-methoxycarbonylperbenzoic acid.

LITERATURE CITED

1. B. A. Bierl, M. Beroza, and C. W. Collier, Science, 170, 87 (1970).
2. H. J. Bestmann, O. Vostrowsky, and W. Stransky, Chem. Ber., 109, 3375 (1976).
3. K. Eiter, Angew. Chem., 84, 67 (1972).
4. B. G. Kovalev, R. I. Ishchenko, V. A. Marchenko, and M. P. Filippova, Zh. Org. Khim., 9, 6 (1973).

5. A. A. Shamshurin, M. A. Rekhter, and L. A. Vlad, Khim. Prir. Soedin., 545 (1973).
6. A. N. Kost, B. G. Kovalev, E. D. Matveeva, V. V. Stan, L. G. Yudin, Yu. A. Elizarov, and M. N. Barybkina, Bioorg. Khim., 3, 934 (1977).
7. G. A. Tolstikov, V. N. Odinokov, R. I. Galeeva, and R. S. Bakeeva, Tetrahedron, Lett., 1857 (1978).
8. H. Klünenberg and H. Schafer, Angew. Chem., 90, 48 (1978).
9. V. N. Odinokov, R. I. Galeeva, R. S. Bakeeva, R. S. Grishova, and G. A. Tolsikov, Zh. Org. Khim., 15, 1403 (1979).
10. R. Carde and W. Roelofs, Nature (London), 241, 474 (1973).
11. M. Beroza, B. A. Bierl, I. Tardif, and D. Cook, J. Econ. Entomol., 64, 1499 (1971).
12. G. S. Bylina, G. A. Tolstikov, G. I. Rutman, P. N. Zernov, V. N. Odinokov, and U. M. Dzhemilev, USSR Inventor's Certificate No. 656,130, Byull. Izobret., No. 15, 21 (1979).
13. H. C. Brown, C. G. Scouten, and R. Liotta, J. Am. Chem. Soc., 101, 96 (1979).

SYNTHESIS AND MEMBRANE ACTIVITY OF NEW DERIVATIVES OF 2,3-BENZO-18-CROWN-6

A. V. Shkinev, M. I. Asrarov,
A. I. Gagel'gans, N. Zh. Saifullina,
E. A. Mukhamedzhanova, and A. K. Tashmukhamedova

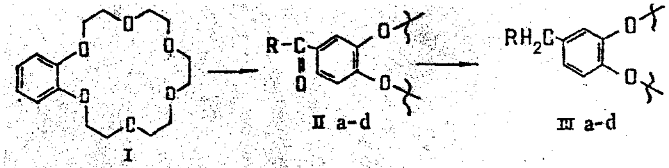
UDC 547.639.5.04+542.95+541.49

The acylation of 2,3-benzo-18-crown-6 with carboxylic acids in the presence of polyphosphoric acid has given new acyl derivatives which have been reduced to the corresponding alkyl derivatives. The ionophoric activities of the compounds have been investigated on mitochondrial membranes.

A distinguishing feature of the crown ethers is their capacity for forming complexes with ions of alkali metals and transporting them through artificial and biological membranes. An analysis of the interrelationship of structure and membrane-active properties of acyl and alkyl derivatives of cyclopolyethers performed previously [1-4] showed that the number and chemical nature of the substituents in the benzene rings largely determines the effective concentrations and cationic specificities of these synthetic ionophores. We simultaneously characterized the ionophoric properties of dialkyl derivatives of dibenzo-18-crown-6, but for the purposes of further structural-functional analysis interest is presented by information on the membrane activities of the alkyl derivatives of benzo-18-crown-6, and this is given in the present paper.

The benzo-18-crown-6 derivatives described in the literature were obtained by condensing pyrocatechol derivatives with pentaethyleneglycol dichloride [5]. The new acyl derivatives of benzo-18-crown-6 considered in the present paper were synthesized by a method we have described previously [6].

The alkyl derivatives were obtained by the Clemmensen reduction of the corresponding acyl derivatives. As for the other benzocrowns, the reaction took place with yields of 40-50%.


I; II a-d; III a-d

a $R=CH_3$; b $R=C_2H_5$; c $R=C_3H_7$; d $R=C_4H_9$

Institue of Biochemistry, Academy of Sciences of the Uzbek SSR, Tashkent. Institute of Bioorganic Chemistry, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 634-637, September-October, 1983. Original article submitted July 16, 1982.