pH 7.2. A freshly prepared solution of fluorescein isothiocyanate in dimethyl sulfoxide (10 mg/ml) was added to a solution of the DNA (I) in 20-fold excess. The mixture was incubated in the dark at 37°C for 3 h. The complete washing out of the reagent that had not become bound to the DNA required eight precipitations with 80% ethanol. The completeness of the elimination was checked spectrofluorometrically. The degree of modification of the DNA by the fluorescein was calculated as described in [7].

Immobilization of DNA on Nitrocellulose Filters. A filter was washed twenty times with buffer A (0.15 M NaCl, 0.015 M sodium citrate, pH 7.0) and dried, a solution of DNA in 0.1 mM EDTA was added and it was again dried and was baked at 80°C for 3 h.

Analysis of Biotinylated DNA on Filters. A published method [11] was used with the difference that the filters were treated with avidin, after which they were washed additionally with buffer A (3 × 5 min). After the filters had been treated with biotinylated alkaline phosphatase, they were additionally washed with a buffer containing 3 M NaCl, 1 mM $MgCl_2$, 0.1 mM $ZnCl_2$, and 0.03 M triethanolamine, pH 7.7.

LITERATURE CITED

1. H. Bayley and J. R. Knowles, Meth. Enzymol., 46, 69 (1977).
2. J. V. Staros, Trends Biochem. Sci., 5, 320 (1980).
3. A. S. Girshovich, E. S. Bochkareva, V. M. Kramarov, and Y. A. Ovchinnikov, FEBS Lett., 45, No. 1, 213 (1974).
4. A. S. Forster, J. L. Meinnes, D. C. Skingle, R. H. Symons, Nucleic Acids Res., 13, No. 3, 748 (1985).
5. E. A. Bayer and M. Wilchek, Meth. Biochem. Anal., 26, 2 (1980).
6. J. J. Leary, D. L. Brigati, and D. C. Ward, Chromosomes and Cancer, Academic Press, New York (1983), p. 273.
7. S. A. Reines and La Donne H. Schulman, Meth. Enzymol., 59, 146 (1979).
8. T. Maniatis, E. Fritsch, and J. Sambrook, Molecular Cloning, Cold Spring Harbor Laboratory, Cold Spring Harbor, N.Y. (1982).
9. H. Becker, W. Berger, G. Domschke, et al., Organicum, Pergamon Press, Oxford (1973) [Russian translation from the German, Mir, Moscow (1979), p. 399].
10. F. Seela and F. Hansske, Z. Naturforsch. C, 31, 263 (1976).

SYNTHESIS OF THE ACETATE OF OCTADECA-trans-2,cis-13-DIEN-1-OL, A COMPONENT OF THE SEX PHEROMONES OF Synanthedon tipuliformis AND Zeuzera pyrina

A. M. Sorochinskaya and B. G. Kovalev

UDC 547.594:632.936.2

A new synthesis of the acetate of octadeca-trans-2,cis-13-dien-1-ol based on the alkylation of propargyl alcohol with pentadec-cis-10-enyl bromide, obtained from the readily accessible decamethylene bromohydrin, has been effected.

The sex pheromone of the current clearwing moth Synanthedon tipuliformis, one of the main pests of redcurrants and blackcurrants has been identified as a mixture of the acetates of octadeca-trans-2,cis-13-dien-1-ol (VII) and of octadec-cis-13-en-1-ol (VIII) in a ratio of 93:7 [1, 2]. A mixture of the two acetates is attractive for males of the pests under field conditions, and so also is the dienic acetate (VII) alone.

The sex pheromone of the leopard moth Z. pyrina, a dangerous trunk pest of apple and pear trees and other fruit crops, has been identified as a mixture of the dienic and

---

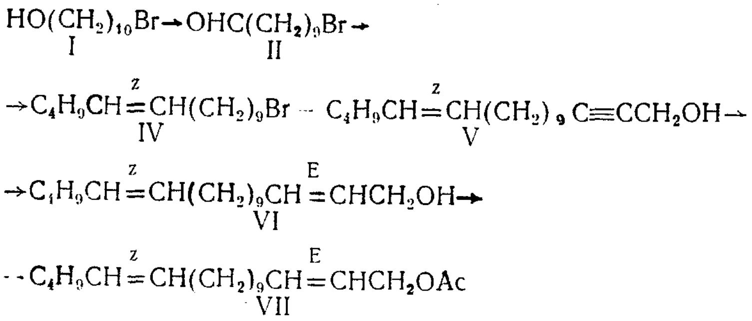
All-Union Scientific-Research Institute of Biological Methods of Plant Protection, Kishinev. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 264-266, March-April, 1989. Original article submitted January 21, 1988.

0009-3130/89/2502-0228$12.50

monoenic acetates (VII and VIII) and the acetate of octadecan-1-ol, the main component being the dienic acetate (VII) [3].

The schemes for the synthesis of the acetate (VII) known in the literature are based on the alkylation of propargyl alcohol with 1-bromopentadec-10-yne [4] or 1-bromopentadec-cis-10-ene (IV) [1, 3] and differ by the methods of obtaining these bromides. The acetylenic bromide is obtained by the alkylation of butyl bromide with tetrahydropyranyloxyundec-10-yne to tetrahydropyranyloxypentadec-10-yne with its subsequent bromination [4]. The synthesis of the ethylene bromide has also been carried out by the alkylation of hex-1-yne with 9-tetrahydropyranyloxynonyl halide [1, 3].

We have effected a new synthesis of the dienic acetate (VII) by a scheme which is likewise based on the alkylation of propargyl alcohol with pentadec-cis-10-enyl bromide (IV):



$$\underset{I}{HO(CH_2)_{10}Br} \rightarrow \underset{II}{OHC(CH_2)_9Br} \rightarrow$$

$$\rightarrow \underset{IV}{C_4H_9CH\overset{z}{=}CH(CH_2)_9Br} \rightarrow \underset{V}{C_4H_9CH\overset{z}{=}CH(CH_2)_9C{\equiv}CCH_2OH} \rightarrow$$

$$\rightarrow \underset{VI}{C_4H_9CH\overset{z}{=}CH(CH_2)_9CH\overset{E}{=}CHCH_2OH} \rightarrow$$

$$\rightarrow \underset{VII}{C_4H_9CH\overset{z}{=}CH(CH_2)_9CH\overset{E}{=}CHCH_2OAc}$$

We obtained the latter from the readily obtainable decamethylene bromohydrin (I) which was oxidized with pyridinium chlorochromate to 10-bromodecanal (II) with a yield of 70%. The bromoaldehyde (II) was converted by reaction with butylmethylenetriphenylphosphorane (III) under cis-olefination conditions [5] with a yield of 57% into the key bromide (IV), the isomeric purity of which was 98%. The alkylation of propargyl alcohol with the bromide (IV) in a mixture of liquid ammonia and diethyl ether took place fairly smoothly, and the acetylenic alcohol (V) was obtained with a yield of 40%. Its reduction with lithium, tetrahydroaluminate in ether gave a 90% yield of octadeca-trans-2,cis-13-dien-1-ol (VI), the acetylation of which led to the final dienic acetate (VII) with an overall yield of 13.3% calculated on the bromohydrin (I) and with a content of the trans,cis-isomer of 97%.

EXPERIMENTAL

The IR spectra of solutions of the substances in CCl_4 were taken on a IR-75 instrument with an NaCl cell and diffraction gratings at a layer thickness of 0.125 µm. PMR spectra were obtained on a BS-467A spectrometer in CCl_4 at a working frequency of 60 MHz with hexamethyldisiloxane as internal standard. The isomeric compositions of the compounds were determined by GLC on a Chrom-5 instrument using a stainless steel column (0.25 mm × 50 m) with the phase SP-2340 at a temperature of 170°C. The results of analyses of compounds (II), (IV), (VI), and (VII) corresponded to the calculated figures.

10-Bromodecanal (II). A solution of 2.37 g of decamethylene bromohydrin in 10 ml of methylene chloride was added dropwise to a suspension of 3.23 g of pyridinium chlorochromate in 60 ml of methylene chloride, and the mixture was stirred at 20-23°C for 4 h. Then 150 ml of diethyl ether was added and, after filtration through a layer of silica gel, the solution was evaporated and the residue was distilled. This gave 1.69 g (70%) of the bromoaldehyde (II), $C_{10}H_{19}BrO$, bp 120-125°C (2 mm), n_D^{20} 1.4710. IR spectrum, ν, cm^{-1}: 1720, 2720.

1-Bromopentadec-cis-10-ene (IV). A solution of 7.87 g of sodium bis(trimethylsilyl)-amide in 30 ml of absolute tetrahydrofuran was added dropwise to a suspension of 17.67 g of pentyltriphenylphosphonium bromide in 50 ml of absolute tetrahydrofuran at 25°C. The reaction mixture, which had a bright red color, was heated at the boiling point of the solvent for 40 min and was then cooled to −78°C and, at this temperature, a solution of 6.7 g of the aldehyde (II) in 10 ml of tetrahydrofuran was added. The resulting mixture was stirred at −78°C for 1 h and at 20°C for 12 h. The solvent was evaporated off at atmospheric pressure and the residue was treated with 70 ml of hexane–diethyl ether (1:1) and was washed with 20 ml of water. The organic layer was separated off and dried with Na_2SO_4

and it was then evaporated and the residue was distilled. This gave 4.7 g (57%) of the bromide (IV), $C_{15}H_{29}Br$, bp 141-142°C (1.5-2 mm), n_D^{20} 1.4720. IR spectrum (ν, cm^{-1}) 3001. PMR spectrum (ppm): 0.85 (3 H, CH_3, t), 1.27 (18 H, CH_2, br.s), 1.90 (4 H, $C\underline{H}_2CH{=}CHCH_2$, m), 3.30 (2 H, CH_2Br, t), 5.23 (2 H, $CH{=}CH$, m).

Octadec-cis-13-en-2-yne-1-ol (V). To a suspension of lithium amide obtained from 0.7 g of lithium in 200 ml of liquid ammonia was added 2.58 g of propargyl alcohol, and the mixture was stirred for 1 h. Then a solution of 8.0 g of the bromide (IV) in 30 ml of absolute diethyl ether was added dropwise. The reaction mixture was stirred for 12 h and was decomposed with saturated aqueous NH_4Cl; 100 ml of diethyl ether was added, the organic layer was separated off, dried with Na_2SO_4, and evaporated, and the residue was distilled. This gave 3.14 g (40%) of the alcohol (V) $C_{18}H_{32}O$, bp 220°C (bath temperature) (2 mm), n_D^{20} 1.4731. IR spectrum (ν, cm^{-1}): 1001, 3001, 3600. PMR spectrum (ppm): 0.82 (3 H, CH_3, t, J = 5 Hz), 1.26 (18 H, CH_2, br.s), 2.00 (6 H, $CH_2CH{=}CHCH_2\ldots CH_2C{=}C$, m), 3.5 (1 H, OH, s), 4.1 ($CH_2C{=}CC\underline{H}_2OH$, 2 H, J = 2 Hz, t), 5.2 (2 H, $CH{=}CH$, m).

Octadeca-trans-2,cis-13-dien-1-ol (VI). A solution of 2.0 g of the alcohol (V) in 10 ml of absolute diethyl ether was added to a suspension of 0.22 g of lithium tetrahydroaluminate in 60 ml of absolute diethyl ether at −70°C. The mixture was brought to 20°C and was then heated at the boiling point of the diethyl ether for 4 h and was cooled, and the excess of reducing agent was decomposed with ethyl acetate and then with water. The organic layer was separated off, dried with Na_2SO_4, and evaporated, and the residue was distilled. The yield of the alcohol (VI) was 1.8 g (90%), $C_{18}H_{34}O$, bp 174-175°C (2 mm), n_D^{20} 1.4693; IR spectrum (ν, cm^{-1}): 980, 1005, 1640, 1660, 3002, 3620. PMR spectrum (ppm): 0.82 (3 H, CH_3, m), 1.26 (18 H, CH_2, br.s), 2.00 (6 H, $CH_2CH{=}CHCH_2\ldots CH_2CH{=}CH$, m), 2.85 (1 H, OH, s), 4.00 (2 H, $CH{=}CHCH_2OH$, J = 4 Hz, d), 5.2-5.6 (4 H, $CH{=}CH\ldots CH{=}CH$, m).

Acetate of Octadeca-trans-2,cis-13-dien-1-ol (VII). A solution of 0.27 g of acetyl chloride in 5 ml of absolute benzene was added dropwise to a solution of 0.76 g of the alcohol (VI) and 0.23 g of pyridine in 20 ml of absolute benzene. The mixture was stirred at 20-23°C for 12 h and was then treated with water, and the organic layer was separated off and was washed with 5% HCl and with water, was dried with Na_2SO_4 and evaporated, and the residue was distilled. This gave 0.80 g (93%) of the acetate (VII), $C_{20}H_{36}O_2$, bp 195°C (bath temperature) (1 mm), n_D^{20} 1.4593. IR spectrum (ν, cm^{-1}): 970, 1730, 3001. PMR spectrum (ppm): 0.90 (3 H, CH_3, t), 1.26 (18 H, CH_2, br.s), 2.07 (9 H, $C\underline{H}_2CH{=}CHC\underline{H}_2\ldots C\underline{H}_2CH{=}CH$, $COCH_3$, m), 4.53 (2 H, $CH{=}CHC\underline{H}_2OAc$, d), 5.35-5.66 (4 H, $CH{=}CH\ldots CH{=}CH$, m).

SUMMARY

A new synthesis has been effected of the acetate of octadeca-trans-2,cis-13-dien-1-ol on the basis of the alkylation of propargyl alcohol with pentadec-cis-10-enyl bromide, obtained from the readily available decamethylene bromohydrin.

LITERATURE CITED

1. S. Voerman, C. J. Persoons, and E. Priesner, J. Chem. Ecol., 10, No. 9, 1371 (1984).
2. G. Szocs, M. Schwarz, G. Sziraki, M. Toth, J. A. Klun, and B. A. Leonhardt, Entomol. Exp. Appl., 39, 131 (1985).
3. C. Tonini, G. Gassani, P. Massardo, G. Guglielmetti, and L. Gastellari, J. Chem. Ecol., 12, No. 6, 1545 (1986).
4. M. Schwarz, J. A. Klun, B. A. Leonhardt, and D. T. Johnson, Tetrahedron Lett., 24, No. 10, 1007 (1983).
5. H. J. Bestmann, W. Stransky, and O. Vostrowsky, Chem. Ber., 109, 1694 (1976).