α-Octadecylamide of 2-Acetamido-2-deoxy-D-glucopyranosyl-(3→O)-D-lactoyl-L-alanyl-D-glutamic Acid (VII C). The diol (VI C) (0.15 g; 0.16 mmole) was dissolved in 12 ml of THF–ethanol–water (10:1:1) and was subjected to hydrogenolysis at room temperature over 0.2 g of 10% Pd/C. After 72 h, the catalyst was filtered off and was washed with 5 ml of ethanol. The filtrate was evaporated, and the addition of 25 ml of ether precipitated 0.075 g of compound (VII C). Glycopeptides (VII A and B) were synthesized similarly.

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OXIDATION OF HEXADEC-11Z-EN-1-OL BY Cr(VI) REAGENTS ON POLYMERIC SUPPORTS

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A method is proposed for the oxidation of hexadec-11Z-en-1-ol to hexadec-11Z-enal by Cr(VI) reagents on polymeric supports.

Recently, pyridinium chlorochromate, proposed by Corey [1], has been widely used as a mild oxidizing agent for converting alcohols into the corresponding carbonyl compounds. A disadvantage of this reagent is the necessity for the careful purification of the reaction mixture to eliminate compounds of low-valence chromium from the desired carbonyl compound.

The use of a polymeric analogue of pyridinium chlorochromate for the oxidation of a number of alcohols is known [2]. An advantage of polymeric reagents is the easy purification of the final product by filtration, and also the possibility of their repeated use after regeneration.

We have studied the oxidation of hexadec-11Z-en-1-ol to hexadec-11Z-enal – the main component of the pheromone of the cotton bollworm – by chromium(VI) reagents on polymeric supports.

As the polymeric supports we have used graft copolymers of polypropylene and Ftorlon [a polyfluoroethylene] with 4-vinylpyridine (Kh-53 and Kh-54, respectively) and also of polyacrylonitrile with 2-methyl-5-vinylpyridine (Kh-52) [3, 4].

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TABLE 1. Oxidation of Hexadec-11Z-en-1-ol (I) to Hexadec-11Z-enal (II) by the Kh-53 Chlorochromate in Methylene Chloride at Room Temperature and in Cyclohexane at 80°C

Reaction time, h	Amounts of reaction products (%) at the following reagent: substrate ratios (by weight)							
	1:0,12		1:0,06		1:0,03		1:0,03	
	I	II	I	II	I	II	I	II
	in methylene chloride						in cyclohexane	
2	98,3	1,6	98,3	1,7	94.2	5,7	85.7	12.8
4	95.7	4.2	96,4	3,4	89,5	10,4	65,5	34 4
6	94,1	5,8	70,5	29.4	85,7	14,3	52 0	48,0
8	91,8	8.2	69,7	30,2	65.9	33,9	47,0	52,9
10	89,5	10,5	67,8	32,1	64,3	35.6	41,2	58,8
12	87,8	12.1	64,5	35,5	60,5	39,4	33,9	66,0
14	82.8	17,2	58.3	41.6	55,8	44,1	32,2	67,7
16	79,5	20,4	52,1	46,8	39,6	60,3	29,5	70,0
18	78.1	21,8	50,7	49.1	35,7	64,3	27,1	71,7
20	76,8	23.1	47,8	52.3	33,8	66.2	21,0	77,1
22	73,3	26,7	43,1	56,8	27,4	72.5	15,2	82,5
24	68,6	31.3	39,9	60.0	21,7	78,3	15,3	82,4
26	67,1	32,9	35,7	64.2	17.6	82,3	15,3	82.4
28	—	—	32,1	67,9	14,6	85,3	—	—
30	—	—	28,3	71,7	11,1	88,9	—	—
32	67,1	32,9	28,1	71,8	7,2	92,7	—	—
34	67,1	32,9	28,1	71,8	4,2	95,8	—	—

Samples of the following polymeric fibers were studied: Kh-53 containing 59% of poly-4-vinylpyridine, Kh-54 with 36% of poly-4-vinylpyridine, and Kh-52 with 40% of poly-2-methyl-5-vinylpyridine. Chlorochromates of graft poly(4-vinylpyridinium) and poly(2-methyl-5-vinylpyridinium) were obtained by the action of equimolar amounts of CrO_3 and concentrated HCl on suspensions of the polymeric supports in water. The orange-colored polymeric oxidation reagents were washed with water and dried in vacuum.

The oxidation of hexadec-11Z-en-1-ol was conducted in methylene chloride at room temperature or in cyclohexane at 80°C. The course of the reaction was followed by the GLC method. The liquid phase used was the methylsilicone elastomer E-301 deposited on Chromaton N-AW-HMDS (0.50-0.25 mm fraction). The hexadec-11Z-en-1-ol was analyzed every 2 h.

It was found that the reagents obtained possessed different oxidizing capacities. Thus, at room temperature in methylene chloride with a ratio (by weight) reagent:substrate = 1.0:0.12, the reaction scarcely proceeded when the reagent based on the polymer Kh-52 was used. The oxidant based on the polymeric support Kh-54 gave 7.7% of the aldehyde in 12 h and then the reaction stopped. The best results were obtained with the reagent based on the polymeric support Kh-53. After 12 h, the aldehyde content was 12.1% and the subsequent experiments were therefore performed with this oxidation reagent. By varying the reagent:substrate ratio it was possible to obtain the desired aldehyde in practically quantitative (96%) yield (Table 1).

The black spent polymeric reagent was readily regenerated by successive washings with solutions of HCl and NaOH and then possessed the same activity as the freshly obtained material. The yield of hexadec-11Z-enal at a ratio of reagent used to hexadec-11Z-en-1-ol of 1.0:0.03 (room temperature, 36 h) was 95.8%.

At the same ratio of reactants the rate of oxidation rose considerably in cyclohexane with a rise in the temperature to 80°C — the amount of hexadec-11Z-enal reached 66% after 12 h. On further oxidation the reaction slowed down and additional peaks, which have not been identified, appeared on a chromatogram. At the end of the reaction the amount of by-products was 1.8%. The oxidation reaction was complete after 22 h with an 82.5% yield of hexadec-11Z-enal (see Table 1).

EXPERIMENTAL

The products of the oxidation of hexadec-11Z-en-1-ol were separated on a Chrom-5 gas chromatograph (Czechoslovakia) with a flame-ionization detector. The amount of the stationary liquid phase E-301 was 10% of the weight of the solid support Chromaton N-AW-HMDS. A 3.5 × 3 mm [sic] column was used. Separation was carried out at a column temperature of 180°C and temperatures of the evaporator and detector of 250 and 180°C. The rate of flow of the carrier gas, helium, was 30 ml/min, the sensitivity of the detector 100:10,000/128, and the volume of sample injected 0.02 μl. The sample was injected with a MSh-10M syringe.

The percentages of the products of the oxidation of hexadec-11Z-en-1-ol were calculated from the ratios of the areas of the peaks of the components being determined to the total area of all the peaks [5].

The Kh-52 polymeric support was a sample of an anion-exchange fiber based on a copolymer of acrylonitrile and 2-methylpyridine (VION AN-1) [4].

Preparation of the Graft Copolymers Kh-53 and Kh-54. Copolymers of polypropylene and Ftorlon with 4-vinylpyridine (Kh-53 and Kh-54, respectively) were obtained by radiation graft polymerization of the monomer from the vapor phase. A weighted amount of polymeric support (fiber) present in the upper chamber of a two-chamber ampul was subjected to the action of ^{60}Co γ-radiation at a dose rate of 40 rad/s for 20 h at 80°C. The vapor pressure of the monomer was constant. Before irradiation, air was eliminated from the reaction ampul by the freezing-thawing method to a residual pressure of 10^{-4} mm Hg. The modified Kh-53 fiber obtained in this way contained 50%, and the Kh-54 fiber 36% of poly-4-vinylpyridine.

Preparation of Polymeric Oxidation Reagents from Kh-52, Kh-53, and Kh-54. The ground polymeric material (1.0 g) was suspended in 4 ml of water for 2 h, and then 1 ml of conc. HCl and 0.9 g of CrO_3 were added. The mixture was stirred at room temperature for 2 h, and the polymer was filtered off and was washed with distilled water until the filtrate had become clear. The polymer was dried in vacuum (2 mm Hg, 60°C, 2 h). A dry dark orange-colored reagent was obtained.

Oxidation of Hexadec-11Z-en-1-ol. To a suspension of 1.0 g of a polymeric reagent in 10 ml of dry methylene chloride was added 0.12, 0.06, or 0.03 g of hexadec-11Z-en-1-ol, and the mixture was stirred with a magnetic stirrer at room temperature. Samples were taken from the reaction mixture for GLC analysis after predetermined intervals of time. The oxidation reaction in cyclohexane at 80°C was conducted similarly. The results are given in Table 1.

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