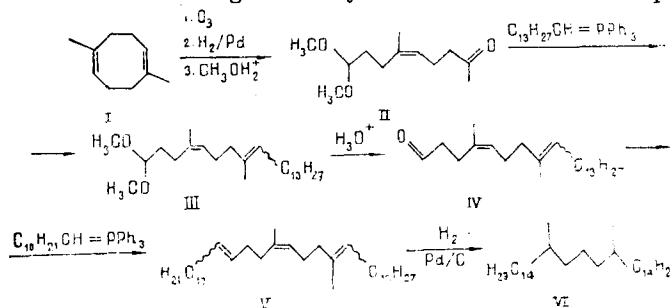


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( $\pm$ )-15,19-Dimethyltritriacontane (II) - a component of the pheromone of the stable fly - has been obtained by a five-stage synthesis from dimethylcyclooctadiene (I). The coupling of 1,1-dimethoxy-4-methyl-8-oxonon-4Z-ene [the product of the ozonolysis of (I)] with  $n\text{-C}_{13}\text{H}_{27}\text{CH=PPh}_3$  (THF;  $-30^\circ$ , 2 h;  $25^\circ$ , 15 h; Ar) gave 1,1-dimethoxy-4,8-dimethyldocosa-4Z,8Z(E)-diene (III). The hydrolysis of (III) ( $\text{TsOH}\cdot\text{Py}$ ,  $\text{H}_2\text{O}-\text{Ac}$ , boiling, 4 h) gave the corresponding aldehyde (IV). The condensation of (IV) with  $n\text{-C}_{10}\text{H}_{21}\text{CH=PPh}_3$  (THF;  $-60^\circ$  to  $-30^\circ\text{C}$ , 2 h,  $25^\circ\text{C}$ , 15 h) led to 15,19-dimethyltritriaconta-11Z(E),15Z,19Z(E)-triene (V), the exhaustive hydrogenation of which (ethanol,  $\text{H}_2$ , 5% Pd/C,  $25^\circ\text{C}$ ) gave (II). The substance, the yield in %, and  $R_f$  values are given, respectively: (II), 95, 0.92; (III), 29, 0.74; (IV), 80, 0.72; (V) 50, 0.8. The IR and PMR spectra of compounds (II)-(V) and the mass spectra of (II) and (III) are given.

15,19-Dimethyltritriacontane has been identified among the components of the pheromone of *Stomoxys calcitrans* (stable fly) [1]. To synthesize this compound we have used an approach to the synthesis of 1,5-dimethyl-branched long-chain alkanes developed previously [2]. The 1,1-dimethoxy-4-methyl-8-oxonon-4Z-ene (II) formed in high yield on the ozonolysis of 1,5-dimethylcycloocta-1Z,5Z-diene (I) [3] was coupled with  $n$ -tetradecylidenephosphorane in the Wittig reaction. The 1,1-dimethoxy-4,8-dimethyldocosa-4Z,8Z(E)-diene (III) formed, after hydrolysis to the aldehyde (IV) was again subjected to olefination with another Wittig reagent -  $n$ -undecylidenetriphosphorane, which led to 15,19-dimethyltritriaconta-11Z(E),19Z(E)-triene (V). Exhaustive hydrogenation of triene (V) gave ( $\pm$ )-15,19-dimethyltritriacontane (VI) the overall yield of which in the five stages of synthesis from the isoprene dimer (I) amounted to 9%.



#### EXPERIMENTAL

IR spectra were taken on a UR-20 spectrometer (in films). PMR spectra of solutions of the substances in  $\text{CDCl}_3$  were measured relative to RMS on a Tesla BS-487B instrument (100 MHz). Mass spectra were recorded on a MKh-1320 instrument with the aid of a system for direct introduction at a temperature of the ionization chamber of  $70\text{--}100^\circ\text{C}$  and an ionizing energy of 70 eV. GLC analysis was performed on a Chrom-4 instrument with the stationary phase SE-30 (5%) on Chromaton N-AW-DMCS (0.2-0.25 mm) at working temperatures of  $150\text{--}300^\circ\text{C}$  with helium as the carrier gas. The  $R_f$  values are given for a Silufol brand fixed layer of  $\text{SiO}_2$ , the revealing agent being iodine.

1,1-Dimethoxy-4-methyl-8-oxonon-4Z-ene (II) was obtained as in [3], and  $n$ -undecyl- and  $n$ -tetradecylphosphonium bromides as described in [4].

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1,1-Dimethoxy-4,8-dimethyldocosa-4Z,8Z(E)diene (III). At  $-70^{\circ}\text{C}$ , 10.7 ml of 1.3 N solution of  $n\text{-BuLi}$  in  $n\text{-hexane}$  was added to a stirred suspension of 7.5 g (13.9 mmole) of tetradecylphosphonium bromide in 70 ml of absolute THF. After 15-20 min at  $-30^{\circ}\text{C}$ , a solution of 2.0 g (9.35 mmole) of the ketoacetal (II) in 5 ml of THF was added. The reaction mixture was stirred for 2 h and was then gradually warmed to room temperature and was left for 15 h, after which it was diluted with 400 ml of  $n\text{-hexane}$  and was filtered through 15 g of  $\text{SiO}_2$ . The filtrate was evaporated in vacuum and the residue was chromatographed [45 g of  $\text{SiO}_2$ ; hexane-ether (9:1)] with the isolation of 1.07 g (29%) of the dienic acetal (III),  $R_f$  0.74,  $n_D^{20}$  1.4612.

IR spectrum ( $\nu$ ,  $\text{cm}^{-1}$ ): 725 m, 850 m, 890 m, 920 m, 960 m, 1020 m, 1070 vs, 1120 vs, 1200 s, 1380 s, 1460 s, 1660 w. Mass spectrum ( $m/z$ , %): 394 ( $M^+$ ), 393 (0.2), 376 (0.33), 362 ( $M - \text{CH}_3\text{OH}$ ) + (46.6), 347 (2.8), 330 ( $M^+ - 2\text{CH}_3\text{OH}$ ) + (38.0), 315 (36.7), 289 (22.7), 263 (10.0), 236 (6.0), 229 (7.34), 214 (4.0), 201 (15.3), 179 (14.7), 161 (11.32), 157 (5.53), 147 (23.3), 125 (66.6), 124 (53.3), 93 (100), 75 ( $\text{CH}_3\text{OCHOCH}_3$ ) + (93.5), 55 (28.6). PMR spectrum ( $\delta$ , ppm): 0.88 (3H, t,  $J = 5$  Hz,  $\text{CH}_3$ ), 1.26 (22H, narrow, m,  $\text{CH}_2$ ), 1.67 (6H, s,  $\text{CH}_3\text{C}=\text{C}$ ); 2.08 [10H, m,  $\text{CH}_2\text{C}=\text{C}$ ,  $\text{CH}_2\text{C} \begin{smallmatrix} \text{O} \\ \diagup \end{smallmatrix}$ ]; 3.3 (6H, s,  $\text{OCH}_3$ ), 4.3 (1H, t,  $J = 5$  Hz,  $\text{OCHO}$ ); 5.12 (2H, m,  $\text{CH}=\text{C}$ ).

4,8-Dimethyldocosa-4Z,8Z(E)-dien-1-al (IV). A mixture of 0.9 g (2.28 mmole) of the acetal (III), 0.63 ml of  $\text{H}_2\text{O}$ , 0.14 g of pyridinium tosylate, and 28 ml of acetone was boiled for 4 h, the solvent was evaporated off, and the residue was diluted with 70 ml of diethyl ether and was washed successively with  $\text{Na}_2\text{CO}_3$  and  $\text{NaCl}$  solutions, dried with  $\text{MgSO}_4$ , and evaporated in vacuum.

This gave 0.71 g (80%) of the aldehyde (IV),  $R_f$  0.72 [ $\text{SiO}_2$ , hexane-ether (4:1)]. IR spectrum ( $\nu$ ,  $\text{cm}^{-1}$ ): 740 w, 1070 m, 1120 m, 1180 m, 1370 s, 1380 s, 1460 s, 1720 vs, 2740 w. PMR spectrum ( $\delta$ , ppm): 0.88 (3H, t,  $J = 5$  Hz,  $\text{CH}_3$ ); 1.26 (22H, narrow, m,  $\text{CH}_2$ ); 1.58 and 1.68 (6H, s,  $\text{CH}_3\text{C}=\text{C}$ ); 2.03 (8H, m,  $\text{CH}_2\text{C}=\text{C}$ ); 2.4 (2H, m,  $\text{CH}_2\text{CO}$ ); and 5.16 (2H, m,  $\text{CH}=\text{C}$ ), 9.78 (1H, s,  $\text{CHO}$ ).

15,19-Dimethyltritriaconta-11Z(E),15Z,19Z(E)-triene (V). To a stirred (Ar,  $-70^{\circ}\text{C}$ ) suspension of 2.14 g (4.3 mmole) of undecylphosphonium bromide in 20 ml of absolute THF were added 3.3 ml of a solution of  $n\text{-BuLi}$  (1.3 N solution in  $n\text{-hexane}$ ) and, after 15-20 min, 0.5 g (1.43 mmole) of the aldehyde (IV) in 5 ml of THF, and the reaction mixture was kept at  $-60^{\circ}\text{C}$  for 2 h and was then gradually warmed to room temperature and was left for 15 h, after which it was diluted with 200 ml of  $n\text{-hexane}$  and was filtered through 10 g of  $\text{SiO}_2$ . The filtrate was evaporated in vacuum and the residue was chromatographed (10 g of  $\text{SiO}_2$ , hexane).

This gave 0.35 g (50%) of the triene (V),  $R_f$  0.8. IR spectrum ( $\nu$ ,  $\text{cm}^{-1}$ ): 740 m, 850 w, 1000 m, 1380 s, 1460 s, 1660 w. PMR spectrum ( $\delta$ , ppm): 0.88 (6H, t,  $J = 5$  Hz,  $\text{CH}_3$ ); 1.26 (38H, narrow, m,  $\text{CH}_2$ ); 1.59 and 1.69 (6H, s,  $\text{CH}_3\text{C}=\text{C}$ ); 2.06 (12H, m,  $\text{CH}_2\text{C}=\text{C}$ ), 5.13 and 5.37 (4H, m,  $\text{CH}=\text{C}$ ).

15,19-Dimethyltritriacontane (VI). A mixture of 0.2 g of the triene (V), 15 ml of ethanol, and 0.04 g of 5% Pd/C was stirred in an atmosphere of hydrogen until the absorption of hydrogen ceased (20 h), and it was then filtered and evaporated in vacuum, giving 0.19 g (95%) of the alkane (VI).  $R_f$  0.92 ( $\text{SiO}_2$ , hexane). IR spectrum ( $\nu$ ,  $\text{cm}^{-1}$ ): 1380, 1470. Mass spectrum ( $m/z$ , %): 492 ( $M^+$ ) (0.2), 491 (0.2), 477 ( $M^+ - \text{CH}_3$ )<sup>+</sup> (0.85), 463 (0.63), 449 (0.42), 420 (0.33), 392 (0.51), 366 (0.57), 334 (1.7), 295 ( $M^+ - \text{C}_{14}\text{H}_{29}$ )<sup>+</sup> (9.8), 281 (2.1), 267 ( $M^+ - \text{C}_{16}\text{H}_{33}$ )<sup>+</sup> (2.2), 253 (1.9), 225 ( $\text{C}_{16}\text{H}_{33}$ )<sup>+</sup> (6.3), 211 (6.8), 197 ( $\text{C}_{14}\text{H}_{29}$ )<sup>+</sup> (4.2), 183 (6.7), 169 (7.88), 155 (10.32), 141 (12.5), 127 (23.3), 85 (58.2), 71 (77.4), 57 ( $\text{C}_4\text{H}_9$ )<sup>+</sup> (100).

#### CONCLUSION

(±)-15,19-Dimethyltritriacontane - a component of the pheromone of Stomoxys calcitrans - has been synthesized from the readily accessible cyclodimer of isoprene.

#### LITERATURE CITED

1. E. Ade and G. Helmchen, *Tetrahedron Lett.*, 21, No. 12, 1137 (1980).

2. V. N. Odinokov, V. R. Akhmetova, G. A. Tolstikov, Dokl. Akad. Nauk SSSR, 271, No. 5, 1143 (1983).
3. G. A. Tolstikov, V. N. Odinokov, V. R. Akhunova, R. I. Galeeva, U. M. Dzhemilev, A. M. Moiseenkov, and A. V. Semenovskii, Izv. Akad. Nauk, No. 4, 887 (1978).
4. V. N. Odinokov, V. R. Akhmetova, G. A. Tolstikov, A. M. Moiseenkov, and A. V. Semenovskii, Zh. Obshch. Khim., 21, No. 3, 489 (1985).