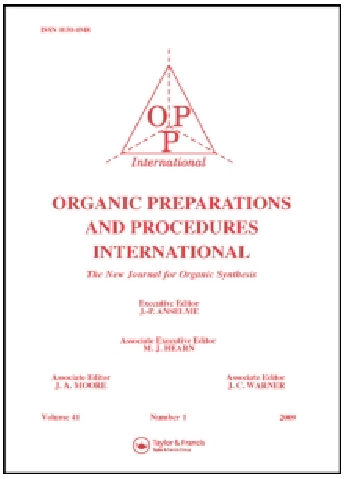

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NEW SYNTHESIS OF DIASTEREOMERIC (±)-13,17,21-TRIMETHYLPENTA- AND (±)-13,17,21-TRIMETHYLHEPTATRIACONTANES

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NEW SYNTHESIS OF DIASTEREOMERIC (±)-13,17,21-TRIMETHYLPENTA- AND (±)-13,17,21-TRIMETHYLHEPTATRIACONTANES

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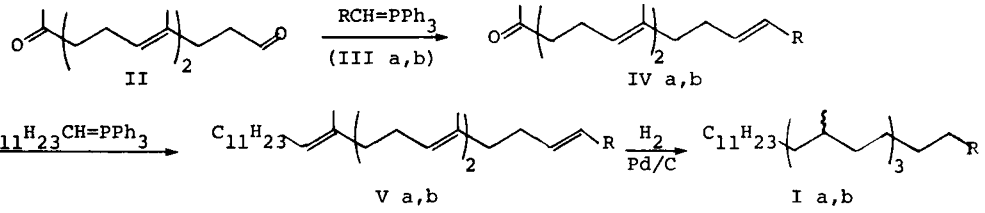
Recently a seven-step synthesis of the title hydrocarbons Ia and Ib starting from geranyl acetone was described in this Journal.[1] We now report a three-step preparation of the same compounds starting from keto aldehyde II, readily obtainable by selective ozonolysis of all-trans trimethylcyclododecatriene.[2]



a) $R = \underline{n}\text{-}C_{10}H_{21}$ b) $R = \underline{n}\text{-}C_{12}H_{25}$

We have previously shown[2] that the aldehyde group of II can be selectively olefinated. In the present case, monoolefination of II with phosphoranes IIIa and IIIb proceeds to give the keto trienes IVa and IVb in $\geq$ 60% yield as E/Z mixtures.[3]

In both cases, less than 10% diolefination products were formed; they were easily removed by column chromatography on silica gel. The treatment of IVa and IVb with n-dodecylidene triphenylphosphorane according to the procedure of Sonnet[1] afforded, after chromatography on silica gel, a $\geq$ 70% yield of the tetraenes Va and Vb as E/Z mixtures.[3] Hydrogenation of V over 5% Pd/C quantitatively gave the corresponding racemic alkanes I as mixtures of diastereomers.[1] Their structure as well as the structure of intermediate olefins IV and V were confirmed by spectral data; according to GLC data, all these compounds contain 2-4% of impurities. The mass spectra of I matched those reported for the natural hydrocarbons.[4]

Thus, successive olefination of II, serving as a source of the inner 1,5,9-trimethyl fragment of the target molecules I, provides a simple route to these alkanes using primary long chain alkyl bromides; the overall yield of the sequence is > 40%.

EXPERIMENTAL SECTION

NMR spectra were measured in CCl_4 on a Varian DA-60-IL spectrometer with TMS as an internal standard. Mass spectra were determined on a Varian MAT-CH-6 spectrometer at 120-170° and 70 ev. GLC-retention times (τ) were obtained using column with 5% of SE-30 on chromatone N-AW-DMCS at 270°.

Synthesis of 6,10-dimethyl-5(E),9(E),13-tetracosatriene-2-one (IVa).- To a stirred suspension of n-undecyltriphenylphosphonium bromide[5] (6.95 g, 14 mmoles) of THF (50 ml) under an argon atmosphere was added n-butyllithium (10.8 ml of 1.3 M in hexane) over 10 min at -70°; the reaction mixture was kept at this temperature for 0.5 hr. After addition (syringe) of the keto aldehyde II[2] (3.3 g, 14 mmoles) in THF (5 ml), the reaction mixture was stirred for 3 hrs at -70°; it was then treated at 10° with a saturated solution of NaCl (50 ml), and then extracted with light pet ether. The extract was washed with water, dried over Na_2SO_4, evaporated and the residue was chromatographed on silica gel (100 g). Gradient elution from hexane to hexane-ether (4:1 v/v) gave 3.35 g (64%) of triene IVa as an oil, n_D^{20} 1.4674, τ 7.6 min.

NMR: δ 0.80 (t, J = 6.5 Hz, 3H, $C\underline{H}_3CH_2$), 1.20 (m, 16H, 8 x CH_2), 1.50 (bs, 6H, $CH_3C=C$), 1.95 (m, 12H, $CH_2C=C$), 2.02 (s, 3H, CH_3-CO), 2.30 (m, 2H, CH_2CO), 4.8-5.3 (m, 4H, HC=C). MS (m/e, %): 3.74 (1.8, M^+), 316 (1.2), 248 (15.3), 193 (22.2), 180 (45.0), 125 (100).

Anal. Calcd for $C_{26}H_{46}O$: C, 83.3; H. 12.4

Found: C, 82.9; H, 12.2

Synthesis of 6,10-dimethyl-5(E),9(E),13-hexacosatriene-2-one (IVb). Similarly, starting from n-tridecyltriphenylphosphonium bromide[5] (7.32 g, 14 mmoles) and keto aldehyde II (3.3 g, 14 mmoles), the triene IVb was prepared (3.4 g, 60%) as an oil, n_D^{20} 1.4691, τ 8.0 min.

NMR: δ 0.82 (t, J = 6.5 Hz, 3H, $C\underline{H}_3CH_2$), 1.20 (m, 20H, 10 x CH_2), 1.50 (bs, 6H, $CH_3C=C$), 1.95 (m, 12H, $CH_2C=C$), 1.97 (s, 3H, CH_3CO), 2.22 (m, 2H, CH_2CO), 4.9-5.2 (m, 4H, HC=C). MS (m/e, %): 4.02 (1.0, M^+), 344 (0.8), 276 (20.8), 208 (95.5), 193 (15.6), 125 (100).

Anal. Calcd for $C_{28}H_{50}O$: C, 83.5; H, 12.5

Found: C, 83.5; H, 12.7

Synthesis of 13,17,21-trimethyl-12,16(E),20(E),24-pentatriacontatetraene (Va).- To a stirred suspension of n-dodecyltriphenylphosphonium bromide[5] (2.55 g; 5 mmoles) in THF (50 ml) under an argon atmosphere was added n-butyllithium (3.85 ml of 1.3 M in hexane) over 5 min at -30°; the reaction mixture was kept at this temperature for 0.5 hr. After addition (syringe) of the ketone IVa (1.85 g; 5 mmoes) in THF (5 ml), the reaction mixture was stirred for another two hrs at -30°. Further work-up as above and chromatography on silica gel (50 g; gradient elution from hexane to hexane-ether, 4:1 v/v) gave 2.0 g (76%) of tetraene Va as an oil, n_D^{20} 1.4682, τ 40.4 min.

NMR: δ 0.82 (t, J = 6.5 Hz, 6H, $C\underline{H}_3CH_2$), 1.20 (m, 34H, 17 x CH_2), 1.50 and 1.59 (bs, 9H, $CH_3C{=}C$), 1.95 (m, 16H, $CH_2C{=}C$), 4.9-5.2 (m, 5H, HC=C).

Anal. Calcd for $C_{38}H_{70}$: C, 86.6; H, 13.4
Found: C, 86.2; H, 13.0

Synthesis of 13,17,21-trimethyl-12,16(E),20(E),24-heptatriacontatetraene (Vb).- Similarly, starting from n-dodecyltriphenylphosphonium bromide (2.25 g, 5 mmoles) and ketone IVb (2.0 g, 5 mmoles), Vb (1.93 g, 70%) was obtained as an oil, n_D^{20} 1.4714.

NMR: δ 0.82 (t, J = 6.5 Hz, 6H, $C\underline{H}_3CH_2$), 1.20 (m, 38H, 19 x CH_2), 1.50 and 1.59 (bs, 9H, $CH_3C{=}C$), 1.95 (m, 16H, $CH_2C{=}C$), 4.9-5.2 (m, 5H, HC=C); τ 42.5 min.

Anal. Calcd for $C_{40}H_{74}$: C, 86.6; H, 13.4
Found: C, 86.2; H, 13.1

Hydrocarbons Ia and Ib.- A solution of tetraene Va (0.2 g) in ethanol (5 ml) was hydrogenated under the normal conditions over 50 mg of 5% Pd/C catalyst. The usual work-up gave 0.2 g of Ia as an oil, n_D^{20} 1.4568,[1] τ 29.9 min. Similarly, Vb was transformed into Ib as an oil, n_D^{20} 1.4597,[1] τ 31.5 min.

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