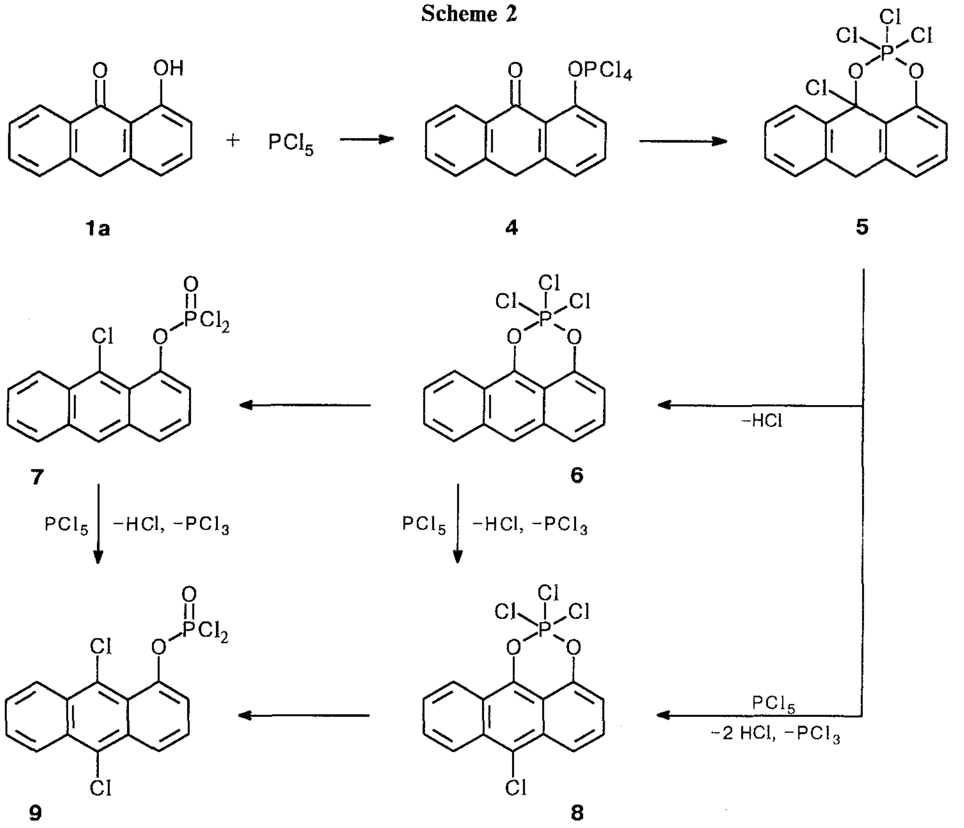
Scheme 2



344 $[M]^+$, 346 $[M+2]^+$,and 348 $[M+4]^+$ (compound **7**) were present. During removal of the solvent the organic compounds were resinified, and only the signal at δ 219.32 (PCl_3) was present in the ^{31}P NMR spectrum of the distillate.

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3-Aza-Cope rearrangement as a route to higher branched aliphatic aldehydes from telomers of isoprene with secondary amines

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Higher branched aliphatic aldehydes and the C_8—C_{14} alcohols derived from them are valuable fragrant substances.[1] In order to synthesize such aldehydes we used the 3-aza-Cope rearrangement of telomers of isoprene with secondary amines, which can be easily prepared on palladium,[2] nickel,[3] or lithium[4] catalysts. The reaction of allyl bromide with *N,N*-diethylnerylamine (**1**), synthesized from isoprene and diethylamine on a

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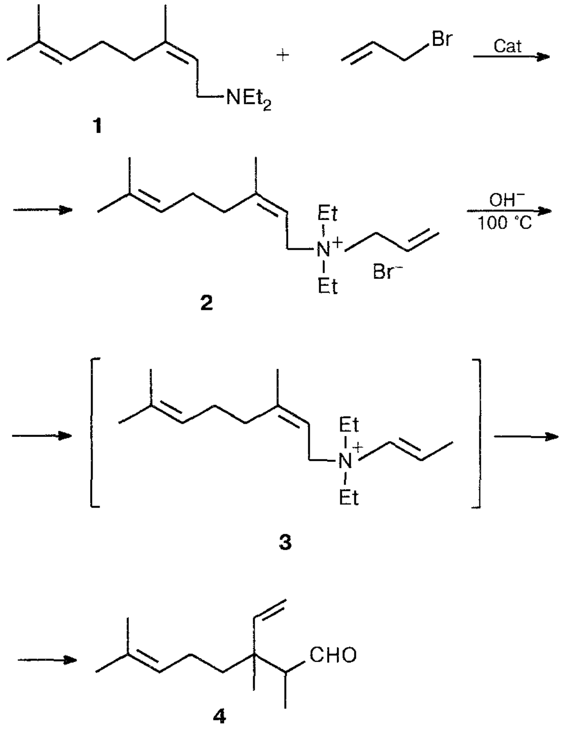
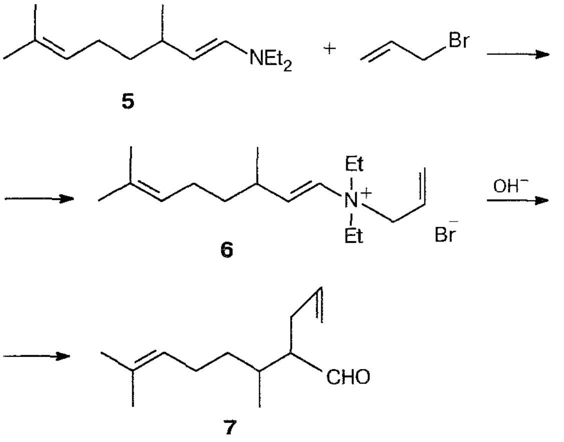
lithium catalyst,[4] affords tertiary salt **2**; the allyl group of the latter isomerizes to the propenyl group when treated with aqueous or alcoholic alkali. The obtained quaternary (*N*-allyl)enamine base **3** undergoes the 3-aza-Cope rearrangement when heated; the subsequent hydrolysis of the imine that forms gives 2,3,6-trimethyl-3-vinylocten-6-al (**4**).

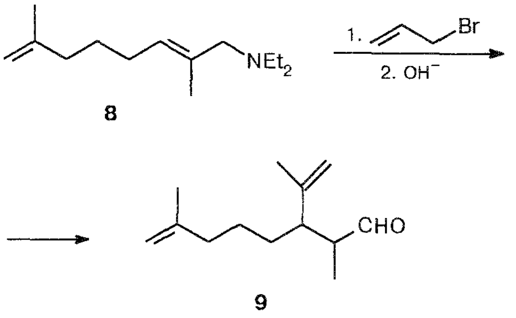


Aldehyde 4: b.p. 98—100 °C (8 Torr), n_D^{20} 1.4712; the corresponding 2,4-dinitrophenylhydrazone: m.p. 65—66 °C. IR, ν/cm^{-1}: 1725 (CHO). An aldehyde with the same skeleton was obtained from *N*,*N*-diethylgeranylamine. To confirm the structure of compound **4**, the quaternary salt of citronellaldiethylallylenamine (**6**) isomeric to salt **3** was obtained from citronellal-(*E*)-diethylenamine[5] (**5**) and allyl bromide; this salt was transformed to 2-allyl-3,7-dimethylocten-6-al (**7**) which is different from aldehyde **4**, *via* the 3-aza-Cope rearrangement.



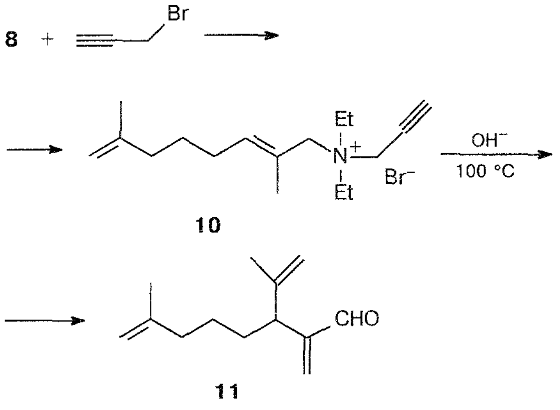
Aldehyde 7: b.p. 101—103 °C (8 Torr), n_D^{20} 1.4705; the corresponding 2,4-dinitrophenylhydrazone: m.p. 70—71 °C. IR, ν/cm^{-1}: 1725 (CHO).

Analogously, 2,7-dimethyl-3-isopropenylocten-7-al (**9**) was prepared from *N*,*N*-dialkyl-2,7-dimethyloctadien-2,7-ylamine (**8**) (the telomer of isoprene with dialkylamines formed on complex palladium catalysts [2,6]).



Aldehyde 9: b.p. 112—114 C (13 Torr), n_D^{20} 1.4652; the corresponding 2,4-dinitrophenylhydrazone: m.p. 60—61 °C. IR, ν/cm^{-1}: 1725 (CHO).

Using the same route, 2-methylene-3-isopropenyl-7-methylocten-7-al (**11**) was prepared from compound **8** and propargyl bromide *via* quaternary salt **10**.



Aldehyde 11: b.p. 101—103 °C (10 Torr), n_D^{20} 1.4770; the corresponding 2,4-dinitrophenylhydrazone: m.p. 94—95 °C. IR, ν/cm^{-1}: 1700 (CHO).

2,3,7-Trimethyl-2-ethyloctanol (b.p. 132—134 °C (12 Torr), n_D^{20} 1.4601) and 2,7-dimethyl-3-isopropyloctanol (b.p. 137—138 °C (12 Torr), n_D^{20} 1.4590) were obtained by hydrogenation of compounds **4** and **9**, respectively, over Raney nickel. All of the described compounds were prepared in 60—65 % yields. The use of different allyl- and propargyl halides in the reaction with telomers of isoprene with dialkylamines allows one to synthesize branched aliphatic aldehydes, alcohols, and acids *via* the 3-aza-Cope rearrangement.[7]

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