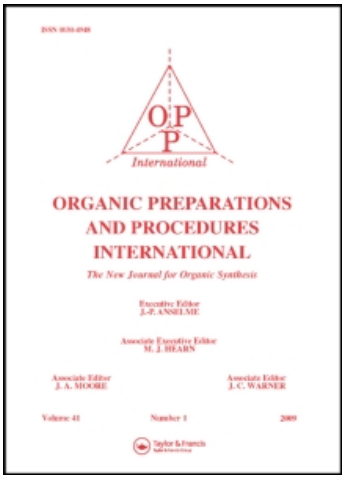

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SYNTHESIS AND REACTIONS OF β-SILYLOXYACYLCYCLOPROPANES TRIMETHYLSILYL HALIDE-ZINC HALIDE INDUCED CYCLOPROPYLCARBINYL REARRANGEMENT

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SYNTHESIS AND REACTIONS OF β-SILYLOXYACYLCYCLOPROPANES. TRIMETHYLSILYL HALIDE-ZINC HALIDE INDUCED CYCLOPROPYLCARBINYL REARRANGEMENT

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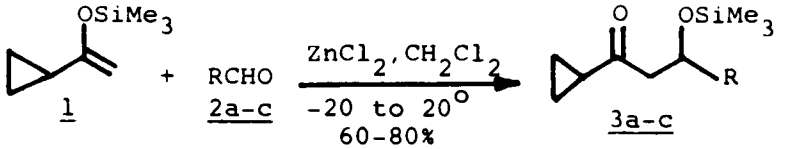
Condensation of silyl enol ethers with aldehydes and ketones in the presence of equimolar amounts of titanium tetrachloride, boron trifluoride etherate, and tin(IV) chloride is a convenient route to β-hydroxycarbonyl compounds.[1] However, when applied to the similar reaction of trimethylsilyloxyvinylcyclopropane (1) with aldehydes (2), the above, as well as some other catalysts like dimethylaluminum chloride,[2] trityl perchlorate,[3] or trimethylsilyl chloride-tin(II) chloride,[4] were found to be unsatisfactory. On the contrary, the use in this specific case of zinc chloride in catalytic amount gave unexpectedly good results. Herein, we discuss some properties of compounds 3 thus prepared, including their conversion into homoallylic halides.



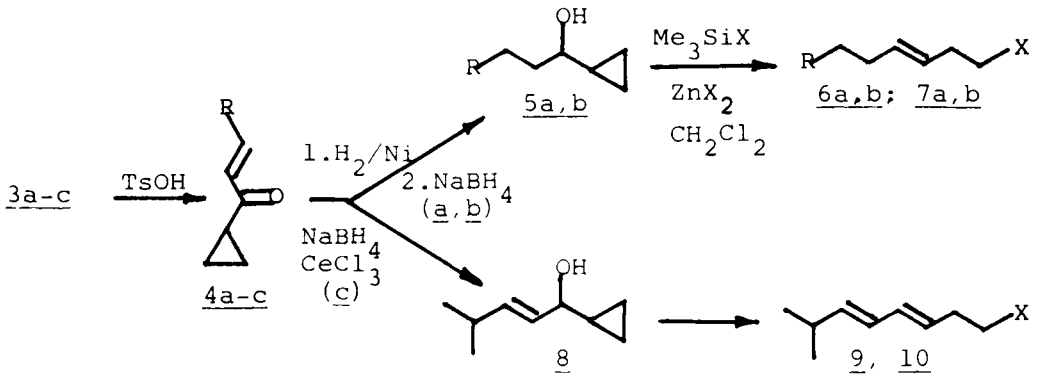
1 2a-c 3a-c

a) R = Et b) R = n-C_6H_{13} c) R = i-Pr

Condensation of 1 and 2a-c in the presence of $ZnCl_2$ (15-20 mol %) in methylene chloride at room temperature for 2-3 hrs led to the respective aldol ethers 3a-c in high yields. The struc-

tures of new compounds 3 were confirmed by their spectral data. Thus, the ^1H NMR spectra of these products displayed signals for Me_3SiO (δ 0.1 ppm), cyclo-C_3H_5 (δ 0.8-1.1 and 1.9-2.0 ppm), CH_2CO (δ 2.5-2.8 ppm), and HCOSi (δ 4.0-4.2 ppm) groups.

Among a series of possible transformations with the participation of β-silyloxyketones 3, we chose the conversion into corresponding linear homoallylic derivatives by means of cyclopropylcarbinyl rearrangement as a key step.



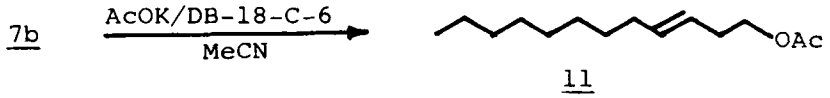
a) R = Et b) R = n-C_6H_{13} c) R = i-Pr

6a,b, 9) X = Cl 7a,b, 10) X = Br

Thus, the aldol ethers 3a-c were easily transformed by the action of TsOH in boiling benzene into the respective unsaturated ketones 4a-c which are normally difficultly available by direct condensation of acetylcyclopropane with aldehydes, e.g., 4c from isobutyraldehyde.[5] Unsaturated ketones 4a,b on hydrogenation over Ra-Ni followed by sodium borohydride reduction, without isolation of intermediate ketones, smoothly gave the cyclopropyl alcohols 5a,b.

Homoallylic rearrangement[6] of alcohols like 5 into the cor-

Compounds 6, 7, 9, 10 thus prepared from readily available enol ether 1 may serve as versatile building blocks for the construction of some acetogenin insect pheromones.[12] For example, the bromide 7a has been already used in the synthesis of one of the "gossyplure" components.[13] In the present study, dibenzo-18-crown-6 (DB-18-C-6) mediated acetolysis of the bromide 7b led quantitatively to the sex pheromone (11) of sugar beet moth, Scrobipalpa ocellatella.[14]



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The structures of the products discussed above were confirmed by their spectral and elemental analysis data (except for the known compounds 4c,[5] 5a,[15] 7a,[13] 7b,[16] and 11.[14]

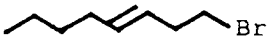
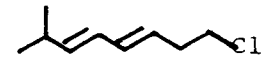
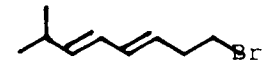
EXPERIMENTAL SECTION

Boiling points are uncorrected. IR spectra were recorded with a Zeiss Specord-75 IR apparatus. UV spectra were measured on a Zeiss Specord UV-VIS spectrophotometer in EtOH. ^{1}H NMR spectra were recorded with a Bruker WM-250 (250 MHz) spectrometer in $CDCl_3$ with TMS as an internal standard. GLC analyses were performed with a LHM-80 gas chromatograph equipped with a column (3.0 m x 3 mm) of Carbowax 20M on Chromaton N-AW-DMCS.

1-Cyclopropyl-3-trimethylsilyloxypentanone-1 (3a).- To a stirred solution of the silyl ether 1[17] (4.5 g, 28.8 mmol) and propanal (2a) (2.01 g, 34.6 mmol) in CH_2Cl_2 (20 ml) under argon and cooled to -30°, $ZnCl_2$ (0.59 g, 4.3 mmol) was added in one portion. The reaction mixture was stirred at -20° for 2 hrs then treated at 0° with a saturated solution of $NaHCO_3$ (10 ml) and extracted with Et_2O (3 x 40 ml). The extract was washed with a saturated aqueous solution of NaCl (3 x 20 ml), dried with $MgSO_4$, evaporated in vacuo, and distilled to give 3.75 g (61%) of 3a as a co-

responding halides is usually carried out by the action of HBr,[7] $ZnBr_2$,[8] or magnesium halides.[9] It was shown recently that similar results could be achieved by using a combination of Me_3SiCl with LiBr or LiI.[10] Thus, isomerization of alcohols 5 was found to proceed smoothly under mild conditions with Me_3SiCl or Me_3SiBr in presence of the corresponding zinc halide. Thus, treatment of 5a,b with Me_3SiX (~2.2 equiv.) and ZnX_2 (~0.15 equiv.) in methylene chloride at -20 to 0° stereoselectively gave allylic chlorides 6a,b or bromides 7a,b in high yields (Table).

TABLE. Homoallylic halides obtained

Starting alcohol	Reaction temp. (°C)	Reaction time (hrs)	Halide	Yield[a] (%)
5a	-10	2	6a 	81
	-20	0.75	7a 	90
5b	0	1.5	6b 	85
	0	0.5	7b 	78
8	-10	0.5	9 	79
	-20	0.25	10 	83

a) Of distilled products.

The (E)-configuration of the olefins thus obtained was determined from the ^1H NMR coupling constans, $^{1,3}J_{H,H}$ = 15 Hz, indicating at the same time a greater than 95% stereochemical purity of these compounds. Application of the above sequence to allylic cyclopropyl alcohols is illustrated by the effective conversion of 8 (easily prepared in turn by $CeCl_3$ mediated[11] sodium borohydride reduction of the unsaturated ketone 4c) into (E,E)-diene chloride 9 or bromide 10 (Table).

lorless liquid, bp. 88-89°/6 mm Hg, n_D^{20} 1.4390. IR (KBr): 685, 750, 840, 940, 1005, 1055, 1190, 1250, 1385, 1450, 1700, 2960, 3010 cm^{-1}. ^1H NMR: δ 0.11 (s, 9H, CH_3Si), 0.8-1.1 (m, 4H, CH_2 of cyclopropane), 0.90 (t, J = 7.5 Hz, 3H, CH_3), 1.49 (m, 2H, CH_2), 1.95 (m, 1H, CH), 2.65 (AB part of ABX system, δ_A = 2.57, δ_B = 2.73, J_{AB} = 15 Hz, J_{AX} = 5.5 Hz, J_{BX} = 7.5 Hz, 2H, CH_2), 4.12 (m, 1H, OCH).

Anal. Calcd. for $C_{11}H_{22}O_2Si$: C, 61.63; H, 10.34; Si, 13.00

Found: C, 61.81; H, 10.43; Si, 12.77

1-Cyclopropyl-3-trimethylsilyloxynonanone-1 (3b).- To a stirred solution of 1 (2.0 g, 12.8 mmol) and heptanal (2b) (1.6 g, 14.0 mmol) in CH_2Cl_2 (10 ml) under argon and cooled to 0°, $ZnCl_2$ (0.34 g, 2.5 mmol) was added in one portion. The reaction mixture was stirred at 20° for 3 hrs and worked-up as above to give 2.56 g (74%) of 3b as a colorless liquid, bp. 84°/1 mm Hg, n_D^{20} 1.4464. IR ($CHCl_3$): 850, 955, 1070, 1135, 1260, 1395, 1465, 1700, 2865, 2950, 3020 cm^{-1}. ^1H NMR: δ 0.11 (s, 9H, CH_3Si), 0.8-1.1 (m, 4H, CH_2 of cyclopropane), 0.89 (t, J = 7 Hz, 3H, CH_3), 1.2--1.5 (m, 10H, CH_2), 1.95 (m, 1H, CH), 2.65 (AB part of ABX system, δ_A = 2.58, δ_B = 2.72, J_{AB} = 15 Hz, J_{AX} = 5 Hz, J_{BX} = 7 Hz, 2H, CH_2), 4.17 (m, 1H, OCH).

Anal. Calcd. for $C_{15}H_{30}O_2Si$: C, 66.61; H, 11.18

Found: C, 67.04; H, 11.18

1-Cyclopropyl-4-methyl-3-trimethylsilyloxypentanone-1 (3c).- Similarly, starting from 1 (2.0 g, 12.8 mmol), 2-methylpropanal (2c) (1.06 g, 14.7 mmol), and $ZnCl_2$ (0.34 g, 2.5 mmol) in CH_2Cl_2 (10 ml) the compound 3c (2.36 g, 81%) was obtained as a colorless liquid, bp. 66°/1 mm Hg, n_D^{21} 1.4430. IR ($CHCl_3$): 855, 955, 1080, 1265, 1395, 1470, 1700, 2880, 2970, 3020 cm^{-1}. ^1H NMR: δ

0.09 (s, 9H, CH_3Si), 0.87 (d, J = 7 Hz, 3H, CH_3), 0.89 (d, J = 7 Hz, 3H, CH_3), 0.8-1.1 (m, 4H, CH_2 of cyclopropane), 1.67 (m, 1H, HC-4), 1.96 (m, 1H, CH), 2.61 (AB part of ABX system, δ_A = 2.52, δ_B = 2.70, J_{AB} = 15 Hz, J_{AX} = 5 Hz, J_{BX} = 8 Hz, 2H, CH_2), 4.05 (m, 1H, OCH).

Anal. Calcd. for $C_{12}H_{24}O_2Si$: C, 63.10; H, 10.59
Found: C, 63,51; H, 10.64

1-Cyclopropyl-2E-pentenone-1 (4a).- A solution of 3a (1.97 g, 9.2 mmol) and $TsOH \cdot H_2O$ (0.1 g) in benzene (35 ml) was refluxed with azeotropic removal of water (Dean-Stark water separator) for ca. 1 hr (GLC monitoring). The reaction mixture was washed successively with a saturated aqueous solution of $NaHCO_3$ (2 x 5 ml) and NaCl (3 x 7 ml), dried ($MgSO_4$), evaporated in vacuo, and distilled to give 1.06 g (93%) of 4a as a colorless liquid, bp. 65°/7 mm Hg, n_D^{20} 1.4765. IR (KBr): 820, 905, 975, 1010, 1090, 1115, 1145, 1190, 1205, 1280, 1390, 1440, 1630, 1660, 1680, 2880, 2985, 3095 cm^{-1}. UV: λ_{max} 200 nm (ε 4600). ^1H NMR: δ 0.8-1.2 (m, 4H, CH_2 of cyclopropane), 1.11 (t, J = 7 Hz, 3H, CH_3), 2.13 (m, 1H, CH), 2.28 (br.quint, J = 7 Hz, 2H, H_2C=C), 6.23 (br.d, J = 16 Hz, 1H, HC-2), 6.97 (dt, J = 16 and 7 Hz, 1H, HC-3).

Anal. Calcd. for $C_8H_{12}O$: C, 77.38; H, 9.74
Found: C, 77.24; H, 9.73

1-Cyclopropyl-2E-nonenone-1 (4b).- Similarly, starting from 3b (1.5 g, 5.5 mmol) and $TsOH \cdot H_2O$ (50 mg) in benzene (20 ml) the compound 4b (0.87 g, 88%) was obtained as a colorless liquid, bp. 90°/1 mm Hg, n_D^{20} 1.4743. IR ($CHCl_3$): 820, 910, 980, 1030, 1100, 1210, 1390, 1420, 1445, 1625, 1660, 1680, 2865, 2940, 3020, 3100 cm^{-1}. UV: λ_{max} 227 nm (ε 20000). ^1H NMR: δ 0.8-1.1

(m, 4H, CH_2 of cyclopropane), 0.89 (t, J = 7 Hz, 3H, CH_3), 1.2-1.5 (m, 8H, CH_2), 2.13 (m, 1H, CH), 2.23 (br.q, J = 7 Hz, 2H, $CH_2C=C$), 6.22 (br.d, J = 16 Hz, 1H, HC-2), 6.91 (dt, J = 16 and 7 Hz, 1H, HC-3).

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.94; H, 11.18
Found: C, 80.25; H, 11.16

1-Cyclopropyl-4-methyl-2E-pentenone-1 (4c).- In the same way, starting from 3c (1.25 g, 5.5 mmol) and $TsOH \cdot H_2O$ (50 mg) in benzene (20 ml) the compound 4c[5] (0.74 g, 97%) was obtained as a colorless liquid, bp. 80°/10 mm Hg, n_D^{18} 1.4759. IR ($CHCl_3$): 815, 910, 920, 980, 1025, 1095, 1190, 1270, 1340, 1390, 1445, 1465, 1625, 1660, 1680, 2875, 2985, 3000, 3095 cm^{-1}. UV: λ_{max} 226 nm (ε 19800). ^1H NMR: δ 0.8-1.1 (m, 4H, CH_2 of cyclopropane), 1.09 (d, J = 7 Hz, 6H, CH_3), 2.14 (m, 1H, CH), 2.49 (m, 1H, HC-4), 6.18 (br.d, J = 16 Hz, 1H, HC-2), 6.88 (dd, J = 16 and 7 Hz, 1H, HC-3).

1-Cyclopropylpentanol-1 (5a).- A suspension of 4a (1.25 g, 10 mmol) and Raney nickel (0.1 g) in ethanol (15 ml) was stirred at ~25° and atmospheric pressure of H_2 for ca. 4 hrs (GLC monitoring). The catalyst was filtered off and washed with ethanol (3 x 5 ml). To the combined solution $NaBH_4$ (1.53 g, 40 mmol) was added. The reaction mixture was stirred at ~25° for 3 hrs, then was diluted with H_2O (5 ml) and extracted with Et_2O-hexane (3:1) mixture. The extract was washed with a saturated aqueous solution of NaCl (3 x 10 ml), dried ($MgSO_4$), evaporated in vacuo, and distilled to give the compound 5a[15] (1.12 g, 88%) as a colorless liquid, bp. 64°/5 mm Hg, n_D^{21} 1.4423. IR (KBr): 820, 915, 1000, 1020, 1280, 1380, 1430, 1460, 2860, 2930, 2960, 3000, 3080, 3380 cm^{-1}. ^1H NMR: δ 0.2-0.6 (m, 4H, CH_2 of cyclopropane),

0.8-1.0 (m, 1H, CH), 0.92 (t, J = 7 Hz, 3H, CH_3), 1.2-1.7 (m, 6H, CH_2), 2.85 (m, 1H, OCH).

1-Cyclopropylnonanol-1 (5b).- Similarly, starting from 4b (0.5 g, 2.8 mmol), Raney nickel catalyst (50 mg) in ethanol (10 ml), and, then, after ca. 2.5 hrs, $NaBH_4$ (0.46 g, 12 mmol) in ethanol (10 ml) at ~25° for 4 hrs, the compound 5b (0.41 g, 80%) was obtained as a colorless liquid, bp. 79°/1 mm Hg, n_D^{20} 1.4510. IR ($CHCl_3$): 825, 920, 1000, 1025, 1050, 1070, 1245, 1380, 1415, 1435, 1470, 2855, 2925, 3010, 3080, 3605 cm^{-1}. ^1H NMR: δ 0.2-0.6 (m, 4H, CH_2 of cyclopropane), 0.8-1.0 (m, 1H, CH), 0.88 (t, J = 7 Hz, 3H, CH_3), 1.2-1.7 (m, 14H, CH_2), 2.86 (m, 1H, OCH).

Anal. Calcd. for $C_{12}H_{24}O$: C, 78.20; H, 13.12

Found: C, 78.28; H, 13.01

1-Cyclopropyl-4-methyl-2E-pentenol-1 (8).- To a stirred solution of 4c (1.0 g, 7.2 mmol) and $CeCl_3 \cdot 7H_2O$ (2.68 g, 7.2 mmol) in methanol (30 ml) under argon at ~25°, $NaBH_4$ (0.55 g, 14.5 mmol) was added. The reaction mixture was kept at this temperature for ca. 3 hrs (GLC monitoring) then was diluted with H_2O (10 ml) and extracted with Et_2O (3 x 20 ml). The extract was washed with a saturated aqueous solution of NaCl (3 x 10 ml), dried ($MgSO_4$), evaporated in vacuo, and distilled to give 8 (0.68 g, 67%) as a colorless liquid, bp. 71°/6 mm Hg, n_D^{20} 1.4580. IR ($CHCl_3$): 825, 870, 920, 970, 1000, 1020, 1220, 1365, 1385, 1465, 1670, 2870, 2960, 3080, 3450, 3600 cm^{-1}. ^1H NMR: δ 0.2-0.6 (m, 4H, CH_2 of cyclopropane), 0.9-1.1 (m, 1H, CH), 1.01 (d, J = 7 Hz, 6H, CH_3), 2.30 (m, 1H, HC-4), 3.43 (m, 1H, HC-1), 5.56 (AB part of ABX system, δ_A = 5.49, δ_B = 5.63, J_{AB} = 15 Hz, $J_{AX} = J_{BX}$ = 6 Hz, 2H, HC-2, HC-3).

Anal. Calcd. for $C_{12}H_{23}Cl$: C, 71.08; H, 11.43; Cl, 17.48

Found: C, 71.30; H, 11.60; Cl, 17.68

1-Chloro-7-methyl-3E,5E-octadiene (9).- In the same way (Table), starting from 8 (0.2 g, 1.4 mmol), $ZnCl_2$ (20 mg, 0.14 mmol), and Me_3SiCl (0.34 g, 3.1 mmol) in CH_2Cl_2 (9 ml) the chloride 9 was obtained (0.18 g) as a colorless liquid, bp. 68°/7 mm Hg, n_D^{20} 1.4873. IR ($CHCl_3$): 650, 715, 945, 985, 1205, 1290, 1330, 1360, 1380, 1465, 1655, 2870, 2960 cm^{-1}. UV: λ_{max} 230 nm (ε 34200). ^1H NMR: δ 1.01 (d, J = 7 Hz, 6H, CH_3), 2.33 (m, 1H, HC-7), 2.53 (br.q, J = 7 Hz, 2H, HC-2), 3.53 (t, J = 7 Hz, 2H, HC-1), 5.5-5.7 (m, 2H, HC-3, HC-6), 5.9-6.2 (m, 2H, HC-4, HC-5).

Anal. Calcd. for $C_9H_{15}Cl$: C, 68.13; H, 9.53; Cl, 22.34

Found: C, 68.18; H, 9.75; Cl, 22.20

1-Bromo-3E-octene (7a).- To a vigorously stirred suspension of 5a (1.53 g, 11.9 mmol) and $ZnBr_2$ (0.61 g, 2.7 mmol) in CH_2Cl_2 (30 ml) under argon and cooled to -20°, a solution of Me_3SiBr (4.02 g, 26.3 mmol) in CH_2Cl_2 (15 ml) was added for 30 min. The reaction mixture was kept at this temperature for 15 min (GLC monitoring) then was treated at -10° with a saturated aqueous solution of $NaHCO_3$ (10 ml) and extracted with Et_2O (3 x 20 ml). The extract was washed with a saturated aqueous solution of NaCl (2 x 10 ml), dried ($MgSO_4$), evaporated in vacuo, and distilled to give 7a[13] (2.06 g, 90%) as a colorless liquid, bp. 65°/6 mm Hg, n_D^{19} 1.4700. IR ($CHCl_3$): 640, 720, 825, 935, 970, 1020, 1150, 1205, 1260, 1380, 1435, 1455, 2870, 2930, 2960, 3005 cm^{-1}. ^1H NMR: δ 0.90 (t, J = 7 Hz, 3H, CH_3), 1.2-1.4 (m, 4H, HC-6, HC-7), 2.02 (br.q, J = 7 Hz, 2H, HC-5), 2.55 (br.q, J = 7 Hz, 2H, HC-2), 3.38 (t, J = 7 Hz, 2H, HC-1), 5.39 (br.dt, J = 15 and 7 Hz, 1H, HC-3), 5.55 (br.dt, J = 15 and 7 Hz, 1H, HC-4).

Anal. Calcd. for $C_9H_{16}O$: C, 77.09; H, 11.50

Found: C, 76.98; H, 11.64

1-Chloro-3E-octene (6a).- To a vigorously stirred suspension of 5a (0.9 g, 7.0 mmol) and $ZnCl_2$ (0.1 g, 0.7 mmol) in CH_2Cl_2 (20 ml) under argon and cooled to -10°, Me_3SiCl (1.68 g, 15.5 mmol) in CH_2Cl_2 (8 ml) was added for 25 min. The reaction mixture was kept at this temperature for 1.5 hrs (GLC monitoring) then was treated at 0° with a saturated aqueous solution of $NaHCO_3$ (2 x 5 ml) and extracted with Et_2O (3 x 10 ml). The extract was washed with a saturated aqueous solution of NaCl (2 x 7 ml), dried ($MgSO_4$), evaporated in vacuo, and distilled to give 6a (0.83 g, 81%) as a colorless liquid, bp. 50°/6 mm Hg, n_D^{20} 1.4451. IR (KBr): 625, 720, 965, 1235, 1450, 2860, 2920, 2960 cm^{-1}. ^1H NMR: δ 0.90 (t, J = 7 Hz, 3H, CH_3), 1.2-1.4 (m, 4H, HC-6, HC-7), 2.01 (br.q, J = 7 Hz, 2H, HC-5), 2.46 (br.q, J = 7 Hz, 2H, HC-2), 3.52 (t, J = 7 Hz, 2H, HC-1), 5.41 (br.dt, J = 15 and 7 Hz, 1H, HC-3), 5.57 (br.dt, J = 15 and 7 Hz, 1H, HC-4).

Anal. Calcd. for $C_8H_{15}Cl$: C, 65.52; H, 10.31; Cl, 24.17

Found: C, 65.79; H, 10.29; Cl, 24.20

1-Chloro-3E-dodecene (6b).- Similarly (Table), starting from 5b (0.8 g, 4.3 mmol), $ZnCl_2$ (60 mg, 0.4 mmol), and Me_3SiCl (1.04 g, 9.6 mmol) in CH_2Cl_2 (20 ml) the chloride 6b was obtained (0.74 g) as a colorless liquid, bp. 75°/1 mm Hg, n_D^{22} 1.4515. IR ($CHCl_3$): 620, 975, 1080, 1115, 1245, 1300, 1380, 1465, 1675, 2860, 2950 cm^{-1}. ^1H NMR: δ 0.90 (t, J = 7 Hz, 3H, CH_3), 1.2-1.4 (m, 12H, CH_2), 2.01 (br.q, J = 7 Hz, 2H, HC-5), 2.45 (br.q, J = 7 Hz, 2H, HC-2), 3.51 (t, J = 7 Hz, 2H, HC-1), 5.41 (br.dt, J = 15 and 7 Hz, 1H, HC-3), 5.56 (br.dt, J = 15 and 7 Hz, 1H, HC-4).

1-Bromo-3E-dodecene (7b).- Similarly (Table), starting from 5b (0.61 g, 3.3 mmol), $ZnBr_2$ (0.16 g, 0.7 mmol), and Me_3SiBr (1.11 g, 7.3 mmol) in CH_2Cl_2 (20 ml) the bromide 7b[16] was obtained (o.64 g) as a colorless liquid, bp. 84°/1 mm Hg, n_D^{26} 1.4660. IR ($CHCl_3$): 640, 860, 975, 1270, 1380, 1465, 2860, 2935, 3015 cm^{-1}. ^1H NMR: δ 0.89 (t, J = 7 Hz, 3H, CH_3), 1.2-1.4 (m, 12H, CH_2), 2.01 (br.q, J = 7 Hz, 2H, HC-5), 2.55 (br.q, J = 7 Hz, 2H, HC-2), 3.38 (t, J = 7 Hz, 2H, HC-1), 5.38 (br.dt, J = 15 and 7 Hz, 1H, HC-3), 5.55 (br.dt, J = 15 and 7 Hz, 1H, HC-4).

1-Bromo-7-methyl-3E,5E-octadiene (10).- In the same way (Table), starting from 8 (0.2 g, 1.4 mmol), $ZnBr_2$ (70 mg, 0.3 mmol), and Me_3SiBr (0.48 g, 3.1 mmol) in CH_2Cl_2 (9 ml) the bromide 10 was obtained (0.24 g) as a colorless liquid, bp. 82°/6 mm Hg, n_D^{20} 1.5064. IR ($CHCl_3$): 640, 720, 945, 990, 1265, 1360, 1385, 1460, 1650, 2870, 2960 cm^{-1}. UV: λ_{max} 231 (ε 34000). ^1H NMR: δ 1.01 (d, J = 7 Hz, 6H, CH_3), 2.33 (m, 1H, HC-7), 2.63 (br.q, J = 7 Hz, 2H, HC-2), 3.39 (t, J = 7 Hz, 2H, HC-1), 5.5-5.7 (m, 2H, HC-3, HC-6), 5.9-6.2 (m, 2H, HC-4, HC-5).

Anal. Calcd. for $C_9H_{15}Br$: C, 53.22; H, 7.44; Br, 39.34
Found: C, 53.57; H, 7.65; Br, 39.00

1-Acetoxy-3E-dodecene (11).- A mixture of 7b (0.36 g, 1.5 mmol), AcOK (0.7 g, 8.5 mmol), and dibenzo-18-crown-6 (50 mg, 0.1 mmol) in acetonitrile (5 ml) was refluxed under argon for 4 hrs then was diluted with H_2O (5 ml) and extracted with Et_2O (3 x 10 ml). The extract was washed with a saturated aqueous solution of NaCl (2 x 5 ml), dried ($MgSO_4$), evaporated in vacuo, and distilled to give 11[14] (0.32 g, 94%) as a colorless liquid, bp. 95°/1 mm Hg, n_D^{21} 1.4402. IR ($CHCl_3$): 975, 1035, 1250, 1370, 1390, 1445, 1470, 1730, 2860, 2935, 2965, 3035 cm^{-1}. ^1H NMR: δ 0.89

(t, J = 7 Hz, 3H, CH_3), 1.2-1.4 (m, 12H, CH_2), 1.99 (br.q, J = 7 Hz, 2H, HC-5), 2.06 (s, 3H, CH_3CO), 2.31 (br.q, J = 7 Hz, 2H, HC-2), 4.07 (t, J = 7 Hz, 2H, HC-1), 5.36 (dt, J = 15 and 7 Hz, 1H, HC-3), 5.52 (dt, J = 15 and 7 Hz, 1H, HC-4).

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