SIMPLE SYNTHESIS OF β-SILYLOXYACYLCYCLOPROPANES AND THE HOMOALLYL REARRANGEMENT OF CYCLOPROPYLCARBINOLS BY THE ACTION OF TRIMETHYLSILYL HALIDES IN THE PRESENCE OF ZINC HALIDES

B. A. Cheskis, N. M. Ivanova,
A. M. Moiseenkov, and O. M. Nefedov

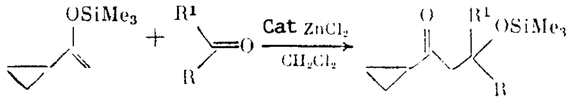
UDC 542.953:547.512'128:547.28:546.47'121

The $ZnCl_2$ catalyzed condensation of 1-trimethylsilyloxyvinylcyclopropane with aldehydes and ketones gave β-silyloxyacylcyclopropanes, which were converted by the action of TsOH in boiling benzene into 1-cyclopropyl-2E-alken-1-ones. Reduction of the latter gave saturated and allyl cyclopropylcarbinols, which by means of Me_3SiX and catalytic amounts of ZnX_2 (X = Cl, Br) were highly selectively converted into the corresponding linear mono- and dienic E-homoallyl halides. The sequence of reactions that was worked out provided an effective synthesis of 3E-dodecenyl acetate, a sex pheromone of the sugar beet moth.

One of the modern variants of carrying out the controlled cross-condensation of an aldol-crotonic type consists in the use of a silyloxyolefin as the key component of this reaction, usually proceeding in the presence of equimolar amounts of classical Lewis acids ($BF_3 \cdot OEt_2$, $SnCl_4$, $TiCl_4$, etc.) [1, 2], and also n-Bu_4NF [3], $TrClO_4$ [4], the $SnCl_2/Me_3SiCl$ pair [5], and certain other catalysts [6]. However, the most available of these were found to be only weakly effective with respect to the condensation of trimethylsilyloxyvinylcyclopropane (I) with aldehydes and ketones (II). On the other hand, the use in this specific case of catalytic amounts of $ZnCl_2$, which was not found to be very suitable for the related silyloxyolefins (cf. [7]), unexpectedly revealed a new and reliable method for the preparation of β-silyloxyacylcyclopropanes (III), the formation of which is not accompanied by the occurrence of the competing Michael reaction when conjugated aldehydes are used in the condensation (cf. [5]). In the present article, we discuss certain properties of the thus obtained cyclopropane ketoethers (III), including their three-stage stereospecific transition into linear homoallyl halides, as a result of the cyclopropyl carbinyl rearrangement (CPCR) of the corresponding alcohols by the action of trimethylsilyl halides, catalyzed by zinc halides.

The condensation of vinyl ether (I) with aldehydes (IIa-f) and ketones (IIg, h) (scheme 1) proceeds readily at —20-20°C in the presence of ~20 mole % of $ZnCl_2$ in a CH_2Cl_2 medium giving silyloxy ketones (IIIa-h) in a yield of 60-80% after 30 min-3 h (Table 1). The structure of the compounds obtained was confirmed by spectral methods. In particular, the PMR spectra contain signals of the Me_3SiO, cyclo-C_3H_5, and CH_2CO groups at δ 0.09-0.12, 0.8-2.1, and 2.6-2.7 ppm, respectively.

Scheme 1

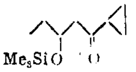
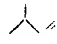
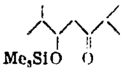
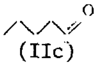
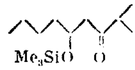
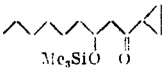
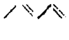
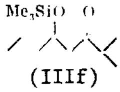
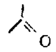
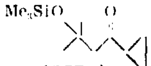
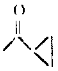
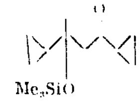


(I) (IIa—h) (IIIa—h)

R = H, R^1 = Et (a), i-Pr (b), n-Bu (c), n-C_6H_{13} (d), n-C_8H_{17} (e), E-MeCH=CH (f); R = R^1 = Me (g); R = Me, R^1-cyclo-C_3H_5 (h).

The N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2025-2036, September, 1990. Original article submitted September 11, 1989.

TABLE 1. β-Trimethylsilyloxyacylcyclopropanes (III) Obtained from Vinyl Ether (I) and Carbonyl Compounds (II)

Compound	Reaction conditions		Product	Yield, %*
	T, °C	time, h		
 (IIa)	−10	1	 (IIIa)	61
 (IIb)	20	1	 (IIIb)	81
 (IIc)	−10	0,7	 (IIIc)	81
 (IId)	20	2	 (IIId)	74
 (IIe)	−20	2,5	 (IIIe)	76
 (IIf)	−20	0,5	 (IIIf)	73
 (IIg)	−10	1	 (IIIg)	65
 (IIh)	20	3	 (IIIh)	70

---

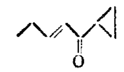
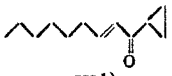
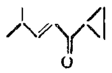
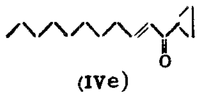
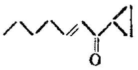
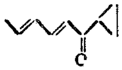
*Of a distilled product.

In accordance with our aim to carry out the synthesis of linear homoallylhalides from silyl ethers of aldols (III), ketoethers (IIIa-f) were first converted by the action of catalytic amounts of TsOH in boiling benzene (scheme 2) into their corresponding cyclopropyl ketones (IVa-f) (Table 2) the direct preparation of which by crotonic condensation of acetylcyclopropane with the corresponding aldehydes, for example with (IIb) [8], proceeds with low selectivity. The structure of the compounds thus prepared in a practically quantitative yield was confirmed spectrally, the SSCC of the vicinal protons of the HC=CHCO fragment with J = 16 Hz revealed in their PMR spectra, indicating its E-configuration. According to the PMR and GLC data, the stereochemical purity of the ketoolefins (IV) exceeds 99%.

The next step in the adopted scheme of transformations of aldol ethers (III) consists in the conversion of compounds (IV), which were found to be readily obtainable products of cross crotonic condensation, into their corresponding saturated or allyl cyclopropylcarbinols, which generally leads to the obtainment of the desired mono- or di- and trienic homoallyl halides.

In the first variant (scheme 2), the hydrogenation of (IVa, d, e) over Raney nickel gave the saturated ketones in almost quantitative yields, and these were reduced without additional purification with $NaBH_4$ into cyclopropylcarbinols (Va, d, e). In this case, the use of Pd/C as the catalyst at the intermediate stage of the hydrogenation causes partial opening of the trimembered ring.

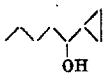
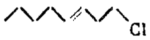
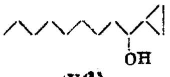
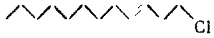
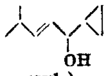
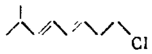
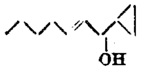
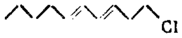
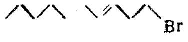
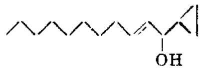
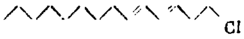
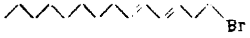
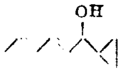
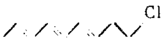
TABLE 2. Conjugated Ketones (IV)

Initial silyloxy ketone (III)	Time of reaction, min	Ketoolefin (IV)	Yield, %*	Initial silyloxy ketone (III)	Time of reaction, min	Ketoolefin (IV)	Yield, %*
(IIIa)	60	 (IVa)	93	(IIId)	20	 (IVd)	88
(IIIb)	60	 (IVb)	97	(IIIe)	45	 (IVe)	99
(IIIc)	40	 (IVc)	97	(IIIf)	90	 (IVf)	98

---

*Of distilled product.

TABLE 3. Homoallyl Halides (VII)-(X)

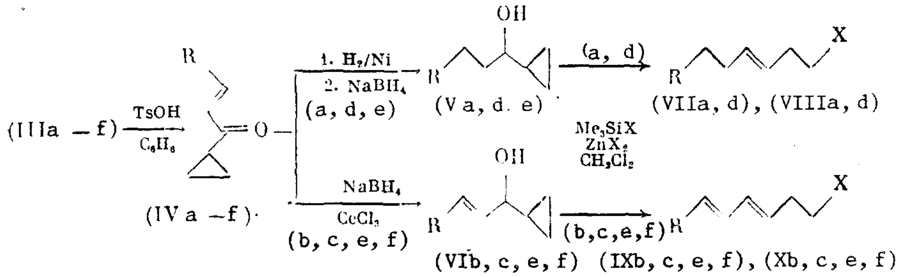
Alcohol	Reaction conditions		Homoallyl halide	Yield, %*
	T, °C	time, min		
 (Va)	−10	90	 (VIIa)	81
	−20	20	 (VIIIa)	90
 (Vd)	0	90	 (VIId)	85
	0	30	 (VIIId)	76
 (VIb)	−10	25	 (IXb)	79
	−20	15	 (Xb)	83
 (VIc)	−20	20	 (IXc)	89
	−40	10	 (Xc)	91
 (VIe)	−20	30	 (IXe)	85
	−20	30	 (Xe)	95 **
 (VIf)	−40	10	 (IXf)	65 **

---

*Of the reduced product.

**PMR and GLC data of a product chromatographically purified on SiO_2.

Scheme 2



R = Et (a), *i*-Pr (b), *n*-Bu (c), *n*-C_6H_{13} (d), *n*-C_8H_{17} (e), *E*-MeCH=CH (f).
X = Cl (VII, a, d), (IXb, c, e, f), Br (VIIIa, d), (Xb, c, e, f).

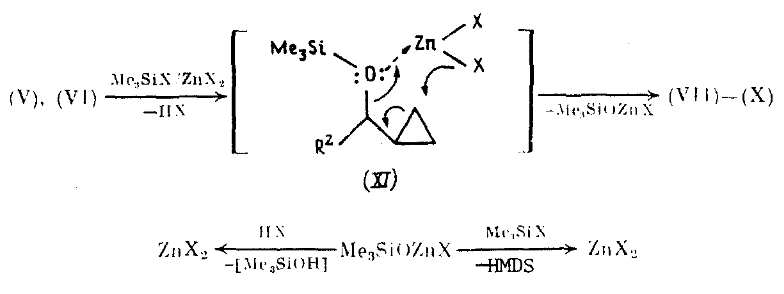
In the second variant (scheme 2), the hydride reduction of the conjugated ketones (IVb, c, e, f) by the $NaBH_4/CeCl_3$ pair [9] gives the corresponding allyl alcohols (VIb, c, e, f) in high yields. It was thus found that the use in this case of individual $NaBH_4$ or $LiAlH_4$ and also of the $LiAlH_4/CeCl_3$ pair [10] is accompanied by a high saturation of the C=C bond.

Alcohols (V), (VI), readily obtained in two stages from ketones (III), were further converted into the desired linear homoallyl halides by means of CPCR [11], usually realized by the action of HBr [12]; $ZnBr_2$ [13]; or magnesium halides [14]. A possibility was also demonstrated recently of carrying out the CPCR by means of the $Me_3SiCl/LiBr$ or Me_3SiCl/LiI reagents, which, however, is accompanied by a considerable contribution of the competing exchange of the hydroxyl group for the halogen atom [15]. Taking these facts into consideration, it appeared to be expedient to investigate other paths of introducing trimethylsilyl halides into the CPCR in the presence of a suitable Lewis acid. As a result, after several trial experiments, it was found that our object could be attained readily and under exceptionally mild conditions by using a combination of the Me_3SiX/ZnX_2 reagents (X = Cl, Br).

Thus (scheme 2), treatment of alcohols (Va, d) and (VIb, c, e, f) at —40-0°C in a CH_2Cl_2 medium with 2-2.2 mole-eq. of Me_3SiX in the presence of 10-20 mole % of ZnX_2 leads rapidly and in high yields to the corresponding homoallyl chlorides (VIIa, d) and (IXb, c, e, f) or bromides (VIIIa, d) and (Xb, c, e, f) (Table 3), of which the dienic (Xe) and in particular, the trienic (IXf) representatives were found to be thermally and chromatographically very labile compounds. The dienic (IXb, c, e), (Xb, c, e) and trienic (IXf) homoallyl halides thus prepared do not contain as by-products, the products of the allylic isomerization of the starting alcohols (VIb, c, e, f), which are characteristic, for example, when HBr is used in this reaction [16]. The *E*-configuration of all the compounds (VII)-(X) obtained, arising as a result of the rearrangement of the C=C bond follows from the SSCC value of the vicinal protons (J = 15 Hz) at this bond found in their PMR spectra. At the same time, according to the PMR and GLC data, the stereochemical purity of the compounds under consideration is 97-99%.

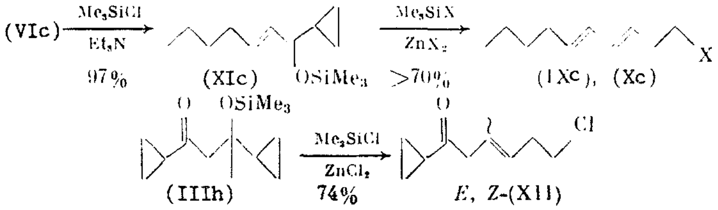
The (V), (VI) → (VII)-(X) rearrangement may possibly proceed via the intermediate stage of the silyl ether (XI) in the form of a complex with the ZnX_2 catalyst, the possible paths of regeneration of which are given in scheme 3.

Scheme 3



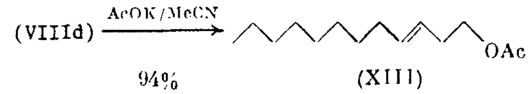
In accordance with these concepts, treatment under approximately the above described conditions of silyl ether (XIc) authentically prepared from alcohol (VIc), with ~1 mole-eq. of Me_3SiX gives homoallyl halides (IXc), (Xc) in a >70% yield. In a similar way (scheme 4), the β-silyloxy ketone (IIIh) was converted by the action of the $Me_3SiCl/ZnCl_2$ catalyst pair into a mixture of stereoisomeric 6-keto chlorides (XII) in a ratio of $E/Z \simeq 3{:}2$, found from a comparison of the integral intensities of single CH_3 signals at δ 1.68 and 1.78 ppm in the spectrum of this mixture and confirmed by its GLC analysis. It should be emphasized here that carrying out the reactions discussed in schemes 2-4 in the absence of the ZnX_2 catalyst leads to the formation of a complex mixture of compounds, among which the above discussed homoallyl halides (VII)-(X), (XII) are not the predominant products.

Scheme 4



Thus, the above sequence of transformations of the readily available [17] silyloxyvinylcyclopropane (I) into linear homoallyl halides (VII)-(X) reveals a simple, effective, and stereospecific path of the synthesis of various disubstituted *E*-olefins, many representatives of which form, in particular, part of the composition of pheromones of insects [18]. For example, compound (VIIIa) previously obtained from acetylenic precursors, was used to obtain the main constituent of "Gossyplure," the sex pheromone of the cotton pink bollworm *Rectinophora gossypiella* [19]. Starting from the now available bromide (VIIId), we carried out a simple synthesis of acetate (XIII), a sex pheromone of sugar beet moth *Scrobipalpa ocellatella* [20]; the overall yield of (XIII) was thus ~40%, based on the initial silyloxyvinylcyclopropane.

Scheme 5



The structure of all the compounds discussed above, which had not been previously described, was established from the data of their spectral and elemental analysis. The structures of the known compounds (IVb) [8], (Va) [21], (VIc) [22], (VIIIa) [19], (VIIId) [23], (Xc) [22], and (XIII) [20] were confirmed by comparison of the physicochemical characteristics found for them with previously published data for these compounds.

EXPERIMENTAL

The IR spectra were run on a UR-20 spectrophotometer in $CHCl_3$ (if not specifically noted otherwise), and the UV spectra of the alcoholic solutions were recorded on a "Specord UV VIS" spectrophotometer. The PMR spectra of solutions in $CDCl_3$ were measured relative to TMS on a "Bruker WM-250" spectrometer. The mass spectra were obtained on a "Varian MAT CH-6" spectrometer at an ionizing voltage of 70 eV. The GLC was carried out on a LKhM-80 chromatograph (a 3 m x 3 mm column filled with 15% Carbowax 20 M on Chromaton N-AW-HMDS).

Trimethylsilyoxy Ketones (III) (Table 1). 1-Cyclopropyl-3-trimethylsilyloxypentanone (IIIa). A 0.59 g (4.3 mmoles) portion of $ZnCl_2$ was added to a solution of 4.5 g (28.8 mmoles) of (I) [17] and 2.01 g (34.6 mmoles) of (IIa) in 20 ml of CH_2Cl_2 stirred at —30°C in an Ar atmosphere. The reaction mixture was stirred for 1 h at —10°C (a GLC control), and then treated at 0°C with a saturated aqueous solution of $NaHCO_3$ and extracted with ether. The extract was washed with a saturated solution of NaCl, dried over $MgSO_4$, evaporated, and the residue was distilled. Yield, 3.75 g (61%) of (IIIa), bp 88-89°C (6 mm), n_D^{20} 1.4390. IR spectrum (KBr, ν, cm^{-1}): 685, 750, 840, 940, 1005, 1055, 1190, 1250, 1385, 1450, 1700, 2960, 3010. PMR spectrum (δ, ppm, J, Hz): 0.11 s (9H, CH_3Si), 0.8-1.1 m (4H, the cyclopropane CH_2), 0.90 t (3H, CH_3, $J = 7.5$), 1.49 m (2H, CH_2), 1.95 m (1H, CH), 2.65 the AB part of the ABX spectrum ($\delta_A = 2.57$, $\delta_B = 2.73$, $J_{AB} = 15$, $J_{AX} = 5.5$, $J_{BX} = 7.5$, 2H, CH_2), 4.12 m (1H, OCH). Mass spectrum, m/z (I, %): M^+ 214(0.8), 199(10), 185(5), 141(12), 131(5), 99(10), 83(11), 75(15), 69(46), 55(13), 41(31), 40(100). Found: C 61.81; H 10.43; Si 12.77%. $C_{11}H_{22}O_2Si$. Calculated: C 61.63; H 10.34; Si 13.00%.

1-Cyclopropyl-4-methyl-3-trimethylsilyloxypentan-1-one (IIIb) was obtained from 1.06 g (14.7 mmoles) of (IIb), 2.0 g (12.8 mmoles) of (I) and 0.34 g (2.5 mmoles) of $ZnCl_2$ in 10 ml of CH_2Cl_2. Bp 66°C (1 mm), n_D^{21} 1.4430. IR spectrum (ν, cm^{-1}): 855, 955, 1080, 1265, 1395, 1470, 1700, 2880, 2970, 3020. PMR spectrum (δ, ppm, J, Hz): 0.09

s (9H, CH_3Si), 0.87 d (3H, CH_3, J = 7), 0.89 d (3H, CH_3, J = 7), 0.8-1.1 m (4H, the cyclopropane CH_2), 1.67 m (1H, HC^4), 1.96 m (1H, CH), 2.61 the AB part of the ABX spectrum (δ_A = 2.52, δ_B = 2.70, J_{AB} = 15, J_{AX} = 5, J_{BX} = 8, 2H, CH_2), 4.05 m (1H, OCH). Mass spectrum, m/z (I, %): M^+ 228(2), 213(45), 186(15), 185(83), 157(21), 141(54), 99(28), 75(67), 73(100), 71(17), 70(22), 57(13). Found: C 63.51; H 10.64%. $C_{12}H_{24}O_2Si$. Calculated: C 63.10; H 10.59%.

1-Cyclopropyl-3-trimethylsilyloxyheptan-1-one (IIIc) was obtained from 2.85 g (33.1 mmoles) of (IIc), 4.5 g (28.8 mmoles) of (I) and 0.78 g (5.7 mmoles) of $ZnCl_2$ in 20 ml of CH_2Cl_2. Bp 82-83°C (1 mm), n_D^{22} 1.4419. IR spectrum (ν, cm^{-1}): 845, 865, 950, 1060, 1080, 1130, 1255, 1390, 1695, 2870, 2940, 2960, 3000. PMR spectrum (δ, ppm, J, Hz): 0.10 s (9H, CH_3Si), 0.8-1.1 m (4H, the cyclopropane CH_2), 0.90 t (3H, CH_3, J = 7), 1.2-1.5 m (6H, CH_2), 1.95 m (1H, CH), 2.65 the AB part of the ABX spectrum (δ_A = 2.57, δ_B = 2.73, J_{AB} = 15, J_{AX} = 5, J_{BX} = 7, 2H, CH_2), 4.17 m (1H, OCH). Mass spectrum, m/z (I, %): M^+ 242(3), 227(100), 199(15), 185(58), 159(36), 141(78), 130(18), 99(33), 85(17), 75(61), 73(89), 69(21), 57(20), 55(23). Found: C 64.08; H 11.10; Si 11.29%. $C_{13}H_{26}O_2Si$. Calculated: C 64.41; H 10.81; Si 11.58%.

1-Cyclopropyl-3-trimethylsilyloxynonan-1-one (IIId) was obtained from 1.6 g (14.0 mmoles) of (IId), 2.0 g (12.8 mmoles) of (I) and 0.34 g (2.5 mmoles) of $ZnCl_2$ in 5 ml of CH_2Cl_2. Bp 84°C (1 mm), n_D^{22} 1.4464. IR spectrum (ν, cm^{-1}): 850, 955, 1070, 1135, 1260, 1395, 1465, 1700, 2865, 2950, 3020. PMR spectrum (δ, ppm, J, Hz): 0.11 s (9H, CH_3Si), 0.8-1.1 m (4H, the cyclopropane CH_2), 0.89 t (3H, CH_3, J = 7), 1.2-1.5 m (10H, CH_2), 1.95 m (1H, CH), 2.65 the AB part of the ABX spectrum (δ_A = 2.58, δ_B = 2.72, J_{AB} = 15, J_{AX} = 5, J_{BX} = 7, 2H, CH_2), 4.17 m (1H, OCH). Mass spectrum, m/z (I, %): M^+ 270(1), 255(47), 227(7), 187(10), 185(33), 141(45), 99(16), 75(31), 73(39), 69(100), 57(23), 55(20). Found: C 67.04; H 11.18%, $C_{15}H_{30}O_2Si$. Calculated: C 66.61; H 11.18%.

1-Cyclopropyl-3-trimethylsilyloxyundecan-1-one (IIIe) was obtained from 1.5 g (10.6 mmoles) of (IIe), 1.5 g (9.6 mmoles) of (I) and 0.26 g (1.9 mmoles) of $ZnCl_2$ in 7 ml of CH_2CL_2. Bp 98-99°C (0.03 mm), n_D^{22} 1.4464. IR spectrum (ν, cm^{-1}): 725, 840, 950, 1020, 1070, 1250, 1390, 1460, 1690, 2860, 2940, 3000. PMR spectrum (δ, ppm, J, Hz): 0.10 s (9H, CH_3Si), 0.8-1.1 m (4H, the cyclopropane CH_2), 0.89 t (3H, CH_3, J = 7), 1.2-1.5 m (14H, CH_2), 1.95 m (1H, CH), 2.64 the AB part of the ABX spectrum (δ_A = 2.57, δ_B = 2.71, J_{AB} = 15, J_{AX} = 5, J_{BX} = 7, 2H, CH_2), 4.17 m (1H, OCH). Mass spectrum, m/z (I, %): M^+ 298(0.8), 283(12), 282(60), 215(11), 185(62), 141(86), 113(24), 99(32), 83(22), 75(86), 73(100), 57(40), 55(38), 43(48). Found: C 68.37; H 11.50; Si 9.03%. $C_{17}H_{34}O_2Si$. Calculated: C 68.39; H 11.48; Si 9.11%.

1-Cyclopropyl-3-trimethylsilyloxy-4*E*-hexen-1-one (IIIf) was obtained from 0.52 g (7.4 mmoles) of (IIf), 1.0 g (6.4 mmoles) of (I) and 0.17 g (1.3 mmole) of $ZnCl_2$ in 10 ml of CH_2Cl_2. Bp 78-80°C (1 mm), n_D^{24} 1.4491. IR spectrum (ν, cm^{-1}): 850, 910, 970, 1010, 1030, 1075, 1220, 1260, 1395, 1450, 1600, 1640, 1695, 2920, 2970, 3010. PMR spectrum (δ, ppm, J, Hz): 0.10 s (9H, CH_3Si), 0.8-1.1 m (4H, the cyclopropane CH_2), 1.68 d (3H, CH_3, J = 6.5), 1.95 m (1H, CH), 2.68 the AB part of the ABX spectrum (δ_A = 2.57, δ_B = 2.79, J_{AB} = 15, J_{AX} = 6, J_{BX} = 8, 2H, CH_2), 4.58 m (1H, OCH), 5.45 d.d (1H, HC^4, J = 15 and 6), 5.62 d. q. (1H, HC^5, J = 15 and 6.5). Mass spectrum, m/z (I, %): M^+ 226(0.7), 205(2), 153(6), 136(6), 121(11), 84(15), 71(15), 69(100), 44(15), 43(15), 41(47). Found: C 63.43; H 9.80; Si 12.02%. $C_{12}H_{22}O_2Si$. Calculated: C 63.66; H 9.79; Si 12.41%.

1-Cyclopropyl-3-methyl-3-trimethylsilyloxybutan-1-one (IIIg) was obtained from 0.21 g (3.7 mmoles) of (IIg), 0.48 g (3.2 mmoles) of (I) and 90 mg (0.6 mmole) of $ZnCl_2$ in 3 ml of CH_2Cl_2. Bp 59-60°C (2 mm), n_D^{22} 1.4396. IR spectrum (ν, cm^{-1}): 725, 845, 1040, 1170, 1250, 1370, 1385, 1445, 1685, 2900, 2970, 3095. PMR spectrum (δ, ppm): 0.13 s (9H, CH_3Si), 0.8-1.1 m (4H, the cyclopropane CH_2), 1.34 s (6H, CH_3) 2.1 m (1H, CH), 2.67 s (2H, CH_2), Mass spectrum, m/z (I, %): M^+ 199(90), 141(95), 131(100), 115(17), 99(43), 75(48), 73(81), 69(86), 41(11). Found: C 62.00; H 10.36; Si 13.00%. $C_{11}H_{22}O_2Si$. Calculated: C 61.63; H 10.34; Si 13.10%.

1,3-Dicyclopropyl-3-methyl-3-trimethylsilyloxybutan-1-one (IIIh) was obtained from 0.54 g (6.4 mmoles) of (IIh), 1.0 g (6.4 mmoles) of (I) and 90 mg (0.66 mmole) of $ZnCl_2$ in 5 ml of CH_2Cl_2. Bp 78-79°C (1 mm), n_D^{21} 1.4557. IR spectrum (ν, cm^{-1}): 850, 910, 1020, 1070, 1165, 1260, 1390, 1450, 1690, 2905, 2970, 3020, 3090. PMR spectrum (δ, ppm): 0.12 s (9H, CH_3Si), 0.2-0.5 and 0.8-1.1 m (5H, the cyclopropane CH_2, CH), 1.23 s (3H, CH_3), 2.12 m (1H, CH), 2.73 s (2H, CH_2). Mass spectrum, m/z (I, %): 225(59), 157(100), 141(55), 75(14), 73(64), 69(68), 41(11). Found: C 65.30; H 10.25%. $C_{13}H_{24}O_2Si$. Calculated: C 64.95; H 10.68%.

Conjugated Ketones (IV) (Table 2). 1-Cyclopropyl-2*E*-penten-1-one (IVa). A solution of 1.97 g (9.2 mmoles) of (IIIa) and 0.1 g of $TsOH{\cdot}H_2O$ in 35 ml of benzene was boiled using a Dean—Stark adapter until no more water separated out (~1 h, GLC control), and then was washed with saturated aqueous solutions of $NaHCO_3$ and NaCl, dried over $MgSO_4$, evaporated, and the residue was distilled. Yield, 1.06 g (93%) of (IVa), bp 65°C (7 mm), n_D^{20} 1.4765. IR spectrum (KBr, ν, cm^{-1}): 820, 905, 975, 1010, 1090, 1115, 1145, 1190, 1205, 1280, 1390, 1440, 1630, 1660, 1680, 2880, 2985, 3095. UV spectrum (λ_{max}, nm): 200 (ε 4600). PMR spectrum (δ, ppm, *J*, Hz): 0.8-1.2 m (4H, the cyclopropane CH_2), 1.11 t (3H, CH_3, *J* = 7), 2.13 m (1H, CH), 2.28 br. q. (2H, $CH_2C{=}C$, *J* = 7), 6.23 br. d (1H, HC^2, *J* = 16), 6.97 d. t (1H, HC^3, *J* = 16 and 7). Mass spectrum, *m/z* (I, %): M^+ 124(35), 109(13), 95(15), 83(100), 69(54), 55(60), 44(44), 41(57), 39(48). Found: C 77.24; H 9.73%. $C_8H_{12}O$. Calculated: C 77.38; H 9.74%.

1-Cyclopropyl-4-methyl-2*E*-penten-1-one (IVb) [8] was obtained from 1.25 g (5.5 mmoles) of (IIIb) and 50 mg of $TsOH{\cdot}H_2O$ in 20 ml of benzene. Bp 80°C (10 mm), n_D^{18} 1.4759. IR spectrum (ν, cm^{-1}): 815, 910, 920, 980, 1025, 1095, 1190, 1270, 1340, 1390, 1445, 1465, 1625, 1660, 1680, 2875, 2985, 3000, 3095. UV spectrum (λ_{max}, nm): 226 (ε 19800). PMR spectrum (δ, ppm, *J*, Hz): 0.8-1.1 m (4H, the cyclopropane CH_2), 1.09 d (6H, CH_3, *J* = 7), 2.14 m (1H, CH), 2.49 m (1H, HC^4), 6.18 br. d (1H, CH^2, *J* = 16), 6.88 d. d (1H, HC^3, *J* = 16 and 7).

1-Cyclopropyl-2*E*-hepten-1-one (IVc) was obtained from 5.5 g (22.7 mmoles) of (IIIc) and 0.3 g of $TsOH{\cdot}H_2O$ in 70 ml of benzene. Bp 58-59°C (1 mm), n_D^{20} 1.4748. IR spectrum (ν, cm^{-1}): 905, 935, 980, 1095, 1180, 1200, 1220, 1395, 1445, 1465, 1630, 1660, 1680, 2870, 2940, 2960, 3005. UV spectrum (λ_{max}, nm): 226 (ε 15600), 280 (ε 106). PMR spectrum (δ, ppm, *J*, Hz): 0.8-1.1 m (4H, the cyclopropane CH_2), 0.91 t (3H, CH_3, *J* = 7), 1.3-1.5 m (4H, CH_2), 2.13 m (1H, CH), 2.23 br. q (2H, $CH_2C{=}C$, *J* = 7), 6.22 br. d (1H, HC^2, *J* = 16), 6.91 d. t (1H, HC^3, *J* = 16 and 7). Mass spectrum, *m/z* (I, %): M^+ 152(24), 123(17), 111(68), 97(16), 95(27), 81(21), 73(19), 69(100), 57(27), 55(100). Found: C 78.84; H 10.33%. $C_{10}H_{16}O$. Calculated: C 78.90; H 10.59%.

1-Cyclopropyl-2*E*-nonen-1-one (IVd) was obtained from 1.5 g (5.5 mmoles) of (IIId) and 50 mg of $TsOH{\cdot}H_2O$ in 20 ml of benzene. Bp 90°C (1 mm), n_D^{20} 1.4743. IR spectrum (ν, cm^{-1}): 820, 910, 980, 1030, 1100, 1210, 1390, 1420, 1445, 1625, 1660, 1680, 2865, 2940, 3020, 3100. UV spectrum (λ_{max}, nm): 227 (ε 20000). PMR spectrum (δ, ppm, *J*, Hz): 0.8-1.1 m (4H, the cyclopropane CH_2), 0.89 t (3H, CH_3, *J* = 7), 1.2-1.5 m (8H, CH_2), 2.13 m (1H, CH), 2.23 br. q (2H, $CH_2C{=}C$, *J* = 7), 6.22 br. d (1H, HC^2, *J* = 16), 6.91 d. t (1H, HC^3, *J* = 16 and 7). Mass spectrum, *m/z* (I, %): M^+ 180(4), 165(3), 139(12), 123(18), 109(9), 97(22), 95(21), 84(18), 81(18), 69(100), 55(63), 43(47), 41(77). Found: C 80.25; H 11.16%. $C_{12}H_{20}O$. Calculated: C 79.94; H 11.18%.

1-Cyclopropyl-2*E*-undecen-1-one (IVe) was obtained from 3.64 g (12.2 mmoles) of (IIIe) and 0.2 g of $TsOH{\cdot}H_2O$ in 50 ml of benzene. Bp 84-85°C (0.03 mm), n_D^{22} 1.4729. IR spectrum (ν, cm^{-1}): 915, 980, 1100, 1395, 1425, 1450, 1470, 1630, 1665, 1680, 2865, 2950, 3010. UV spectrum (λ_{max}, nm): 208 (ε 18600). PMR spectrum (δ, ppm, *J*, Hz): 0.8-1.1 m (4H, the cyclopropane CH_2), 0.89 t (3H, CH_3, *J* = 7), 1.2-1.5 m (12H, CH_2), 2.13 m (1H, CH), 2.23 br. q (2H, $CH_2C{=}C$, *J* = 7), 6.22 br. d (1H, HC^2, *J* = 16), 6.91 d. t (1H, HC^3, *J* = 16 and 7). Mass spectrum, *m/z* (I, %): M^+ 208(1), 165(19), 145(15), 143(16), 131(16), 122(18), 121(55), 120(21), 97(66), 95(48), 84(51), 83(39), 82(32), 81(46), 69(100), 67(36), 57(30), 55(87), 43(56). Found: C 80.65; H 11.59%. $C_{14}H_{24}O$. Calculated: C 80.71; H 11.61%.

1-Cyclopropyl-2*E*,4*E*-hexadien-1-one (IVf) was obtained from 1.11 g (4.9 mmoles) of (IIf) and 50 mg of $TsOH{\cdot}H_2O$ in 35 ml of benzene. Bp 65°C (1 mm), n_D^{23} 1.5450. IR spectrum (ν, cm^{-1}): 915, 985, 1030, 1090, 1120, 1395, 1450, 1635, 1690, 2850, 3020. UV spectrum (λ_{max}, nm): 220 (ε 18000), 275 (ε 6150). PMR spectrum (δ, ppm, *J*, Hz): 0.8-1.1 m (4H, the cyclopropane CH_2), 1.90 br. d (3H, CH_3, *J* = 6), 2.13 m (1H, CH), 6.16-6.24 and 7.14-7.26 m (4H, HC=CH). Mass spectrum, *m/z* (I, %): M^+ 136(42), 121(100), 95(63), 83(15), 79(15), 77(20), 69(54), 67(38), 65(17), 57(17), 55(30). Found: C 79.66; H 8.99%. $C_9H_{12}O$. Calculated: C 79.37; H 8.88%.

1-Cyclopropylpentan-1-ol (Va). A suspension of 1.25 g (10 mmoles) of (IVa) and 0.1 g of Raney-Ni in 15 ml of EtOH was hydrogenated at ~25°C and at atmospheric pressure until no more H_2 was absorbed (~4 h, GLC control). The mixture was filtered, the catalyst was washed with 15 ml of EtOH and 1.53 g (40 mmoles) of $NaBH_4$ was added to the combined filtrate. The reaction mixture was stirred for 3 h at ~25°C (GLC control), and was then diluted with water and extracted by an ether—hexane (3:1) mixture. The extract was washed with a saturated aqueous solution of NaCl, dried over $MgSO_4$, evaporated, and the residue was distilled under vacuum. Yield, 1.12 g (88%) of (Va) [21]. Bp 64°C (6 mm), n_D^{21} 1.4423. IR spectrum (KBr, ν, cm^{-1}): 820, 915, 1000, 1020, 1280, 1380, 1430, 1460, 2860, 2930, 2960, 3000, 3080, 3380. PMR spectrum (δ, ppm, *J*, Hz): 0.2-0.6 m (4H, the cyclopropane CH_2), 0.8-1.0 m (1H, CH), 0.92 t (3H, CH_3, *J* = 7), 1.2-1.7 m (6H, CH_2), 2.85 m (1H, OCH).

1-Cyclopropylnonan-1-ol (Vd). In a similar way, from 0.5 g (2.8 mmoles) of (IVd), 50 mg of Raney-Ni in 10 ml of EtOH, and further, 0.46 g (12 mmoles) of $NaBH_4$, 0.41 g (80%) of (Vd) was obtained, bp 79°C (1 mm), n_D^{20} 1.4510. IR spectrum (ν, cm^{-1}): 825, 920, 1000, 1025, 1050, 1070, 1245, 1380, 1415, 1435, 1470, 2855, 2925, 3010, 3080, 3605. PMR spectrum (δ, ppm, *J*, Hz): 0.2-0.6 m (4H, the cyclopropane CH_2), 0.8-1.0 m (1H, CH), 0.88 t (3H, CH_3, *J* = 7), 1.2-1.7 m (14H, CH_2), 2.86 m (1H, OCH). Mass spectrum, *m/z* (I, %): 166(2), 122(3), 121(5), 105(17), 96(7), 82(10), 77(9), 72(22), 71(100), 69(18), 67(17), 57(18), 55(20), 44(29), 43(83), 41(38). Found: C 78.28; H 13.01%. $C_{12}H_{24}O$. Calculated C 78.20; H 13.12%.

1-Cyclopropylundecan-1-ol (Ve). In a similar way, from 183 g (8.8 mmoles) of (IVe), 0.15 g of Raney-Ni in 25 ml of EtOH, and further, 1.34 g (35.2 mmoles) of $NaBH_4$, 1.77 g (95%), of (Ve) was obtained, bp 105-107°C (1 mm), n_D^{23} 1.4539. IR spectrum (ν, cm^{-1}): 830, 920, 965, 1000, 1050, 1075, 1245, 1380, 1415, 1470, 2865, 2930, 3010, 3610. PMR spectrum (δ, ppm, J, Hz): 0.2-0.6 m (4H, the cyclopropane CH_2), 0.8-1.0 m (1H, CH), 0.88 t (3H, CH_3, J = 7), 1.2-1.7 m (18H, CH_2) 2.86 m (1H, OCH). Mass spectrum, m/z (I, %): M^+ 212(0.5), 194(2), 169(3), 109(6), 97(12), 96(14), 95(14), 84(20), 82(21), 81(24), 71(29), 69(37), 68(31), 67(29), 57(42), 55(47), 43(100), 41(79). Found: C 79.32; H 13.30%. $C_{14}H_{28}O$. Calculated: C 79.18; H 13.29%.

1-Cyclopropyl-4-methyl-2*E*-penten-1-ol (VIb). A 0.55 g portion (14.5 mmoles) of $NaBH_4$ was added at 0°C to a stirred solution of 1.0 g (7.2 mmoles) of (IVb) and 2.68 g (7.2 mmoles) of $CeCl_3{\cdot}7H_2O$ in 30 ml of MeOH. The reaction mixture was stirred for 3 h at 0°C, and was then treated as in the preceding experiments. Yield, 0.68 g (67%) of (VIb), bp 71°C (6 mm), n_D^{20} 1.4580. IR spectrum (ν, cm^{-1}): 825, 870, 920, 970, 1000, 1020, 1220, 1365, 1385, 1465, 1670, 2870, 2960, 3080, 3450, 3600. PMR spectrum (δ, ppm, J, Hz): 0.2-0.6 m (4H, cyclopropane CH_2), 0.9-1.1 m (1H, CH), 1.01 d (6H, CH_3, J = 7), 2.30 m (1H, HC^4), 3.43 m (1H, HC^1), 5.56 the AB part of the ABX spectrum (δ_A = 5.49, δ_B = 5.63, J_{AB} = 15, J_{AX} = J_{BX} = 6, 2H, HC^2, HC^3). Mass spectrum, m/z (I, %): M^+ 140(2), 122(15), 107(23), 97(100), 91(31), 79(64), 69(79), 55(59), 43(67), 41(100), 39(49). Found: C 76.98; H 11.64%. $C_9H_{16}O$. Calculated: C 77.09; H 11.50%.

1-Cyclopropyl-2*E*-hepten-1-ol (VIc). In a similar way, from 3.29 g (21.6 mmoles) of (IVc), 8.05 g (21.6 mmoles) of $CeCl_3{\cdot}7H_2O$ and 1.23 g (32.5 mmoles) of $NaBH_4$ in 110 ml of MeOH, 2.57 g (77%) of (VIc) [22] was obtained, bp 65-71°C (1 mm), n_D^{21} 1.4610. IR spectrum (ν, cm^{-1}): 820, 970, 995, 1025, 1220, 1380, 1465, 2870, 2930, 2960, 3005, 3080, 3600. PMR spectrum (δ, ppm, J, Hz): 0.2-0.6 m (4H, cyclopropane CH_2), 0.9-1.1 m (1H, CH), 0.91 t (3H, CH_3, J = 7), 1.2-1.5 m (4H, CH_2), 2.05 br. q (2H, HC^4, J = 7), 3.45 br. t (1H, HC^1, J = 7), 5.54 d.d (1H, HC^2, J = 16 and 7), 5.68 d.t (1H, HC^3, J = 16 and 7).

1-Cyclopropyl-2*E*-undecen-1-ol (VIe). In a similar way, from 2.15 g (10.3 mmoles) of (IVe), 3.84 g (10.3 mmoles) of $CeCl_3{\cdot}7H_2O$ and 0.59 g (15.5 mmoles) of $NaBH_4$ in 40 ml of MeOH, 1.99 g (92%) of (VIe) was obtained, bp 110-111°C (1 mm), n_D^{21} 1.4640. IR spectrum (ν, cm^{-1}): 835, 870, 925, 975, 1005, 1030, 1055, 1095, 1230, 1385, 1470, 1675, 2870, 2960, 3020, 3090, 3460, 3615. PMR spectrum (δ, ppm, J, Hz): 0.2-0.6 m (4H, cyclopropane CH_2), 0.9-1.1 m (1H, CH), 0.89 t (3H, CH_3, J = 7), 1.2-1.5 m (12H, CH_2), 2.05 br. q (2H, HC^4, J = 7), 3.45 br. t (1H, HC^1, J = 7), 5.54 d.d (1H, HC^2, J = 16 and 7), 5.68 d.t (1H, HC^3, J = 16 and 7). Mass spectrum, m/z (I, %): 192(7), 182(20), 167(5), 153(5), 138(8), 111(13), 97(100), 84(47), 83(63), 70(53), 69(67), 55(75), 43(52), 41(82). Found: C 79.99; H 12.62%. $C_{14}H_{26}O$. Calculated: C 79.94; H 12.46%.

1-Cyclopropyl-2*E*,4*E*-hexadien-1-ol (VIf). In a similar way, from 0.71 g (5.2 mmoles) of (IVf), 1.94 g (5.2 mmoles) of $CeCl_3{\cdot}7H_2O$ and 0.3 g (7.8 mmoles) of $NaBH_4$ in 15 ml of MeOH, 0.59 g (82%) of (VIf) was obtained, bp 71°C (1 mm), n_D^{24} 1.5098. IR spectrum (ν, cm^{-1}): 825, 920, 990, 1025, 1050, 1220, 1380, 1440, 1630, 1690, 2880, 2920, 3005, 3080, 3450, 3600. UV spectrum (λ_{max}, nm): 229 (ε 15300), 276 (ε 690). PMR spectrum (δ, ppm, J, Hz): 0.2-0.6 m (4H, the cyclopropane CH_2), 0.9-1.1 m (1H, CH), 1.77 d (3H, CH_3, J = 7), 3.50 t (1H, HC^1, J = 7), 5.65 d.d (1H, HC^2, J = 15 and 7), 5.72 d.q (1H, HC^5, J = 15 and 7), 6.0-6.3 m (2H, HC^3, HC^4). Mass spectrum, m/z (I, %): M^+ 138(51), 121(42), 120(21), 109(33), 105(44), 95(100), 93(42), 91(60), 79(93), 77(70), 67(88). Found: C 79.66: H 8.99%. $C_9H_{14}O$. Calculated: C 79.37; H 8.88%.

Halides (VII)-(X) (Table 3). 1-Chloro-3*E*-octene (VIIa). A solution of 1.68 g (15.5 mmoles) of Me_3SiCl in 8 ml of CH_2Cl_2 was added in the course of 25 min to a suspension of 0.9 g (7.0 mmoles) of (Va) and 0.1 g (0.7 mmole) of $ZnCl_2$ in 20 ml of CH_2Cl_2, stirred at —10°C. The reaction mixture was stirred for 1.5 h at —10°C (GLC control), and was then treated at 0°C with a saturated aqueous solution of $NaHCO_3$, and extracted with ether. The extract was washed with a saturated aqueous solution of NaCl, dried over $MgSO_4$, evaporated, and the residue was distilled in vacuum. Yield 0.83 g (81%) of (VIIa), bp 50°C (6 mm) n_D^{20} 1.4451. IR spectrum (KBr, ν, cm^{-1}): 625, 720, 965, 1235, 1450, 2860, 2920, 2960. PMR spectrum (δ, ppm, J, Hz): 0.90 t (3H, CH_3, J = 7), 1.2-1.4 m (4H, HC^6, HC^7), 2.01 br. q (2H, HC^5, J = 7), 2.46 br. q (2H, HC^2, J = 7), 3.52 t (2H, HC^1, J = 7), 5.41 br.d.t (1H, HC^3, J = 15 and 7), 5.57 br.d.t (1H, HC^4, J = 15 and 7). Mass spectrum, m/z (I, %): M^+ 148(4) and 146(9), 106(7), 104(17), 81(21), 69(24), 68(28), 67(37), 56(46), 55(76), 43(22), 41(100), 39(33). Found: C 65.79; H 10.29; Cl 24.20%. $C_8H_{15}Cl$. Calculated: C 65.52; H 10.31; Cl 24.17%.

1-Bromo-3*E*-octene (VIIIa) [19] was obtained from 1.53 g (11.9 mmoles) of (Va), 0.61 g (2.7 mmoles) of $ZnBr_2$ and 4.02 g (26.3 mmoles) of Me_3SiBr in 45 ml of CH_2Cl_2. Bp 65°C (6 mm), n_D^{19} 1.4700. IR spectrum (ν, cm^{-1}): 640, 720, 825, 935, 970, 1020, 1150, 1205, 1260, 1380, 1455, 2870, 2930, 2960, 3005. PMR spectrum (δ, ppm, J, Hz): 0.90 t (3H, CH_3, J = 7), 1.2-1.4 m (4H, HC^6, HC^7), 2.02 br. q (2H, HC^5, J = 7), 2.55 br. q (2H, CH^2, J = 7), 3.38 t (2H, HC^1, J = 7), 5.39 br.d.t (1H, HC^3, J = 15 and 7), 5.55 br.d.t (1H, HC^4, J = 15 and 7).

1-Chloro-3*E*-dodecene (VIId) was obtained from 0.8 g (4.3 mmoles) of (Vd), 60 mg (0.4 mmole) of $ZnCl_2$ and 1.04 g (9.6 mmoles) of Me_3SiCl in 20 ml of CH_2Cl_2. Bp 75°C (1 mm), n_D^{22} 1.4515. IR spectrum (ν, cm^{-1}): 620, 975, 1080, 1115, 1245, 1300, 1380, 1465, 1675, 2860, 2950. PMR spectrum (δ, ppm, J, Hz): 0.90 t (3H, CH_3, J = 7), 1.2-1.4 m (12H, CH_2), 2.01 br. q (2H, HC^5, J = 7), 2.45 br. q (2H, HC^2, J = 7), 3.51 t (2H, HC^1, J = 7), 5.41 br.d.t (1H, HC^3, J = 15 and 7), 5.56 br. d.t (1H, HC^4, J = 15 and 7). Mass spectrum, m/z (I, %): M$^+$ 204(6) and 202(20), 137(4), 132(5), 125(6), 109(18), 104(26), 97(30), 84(30), 83(52), 81(40), 70(74), 69(83), 67(63), 57(74), 56(76), 55(94), 43(79), 41(100). Found: C 71.30; H 11.60; Cl 17.68%. $C_{12}H_{23}Cl$. Calculated: C 71.08; H 11.43; Cl 17.48%.

1-Bromo-3*E*-dodecene (VIIId) [23] was obtained from 0.61 g (3.3 mmoles) of (Vd), 0.16 g (0.7 mmole) of $ZnBr_2$, and 1.11 g (7.3 mmoles) of Me_3SiBr in 20 ml of CH_2CL_2. Bp 84°C (1 mm), n_D^{26} 1.4660. IR spectrum (ν, cm^{-1}): 640, 860, 975, 1270, 1380, 1465, 2860, 2935, 3015. PMR spectrum (δ, ppm, J, Hz): 0.89 t (3H, CH_3, J = 7), 1.2-1.4 m (12H, CH_2), 2.01 br. q (2H, HC^5, J = 7), 2.55 br. q (2H, HC^2, J = 7), 3.38 t (2H, HC^1, J = 7), 5.38 br.d.t (1H, HC^3, J = 15 and 7), 5.55 br.d.t (1H, HC^4, J = 15 and 7).

1-Chloro-7-methyl-3*E*,5*E*-octadiene (IXb) was obtained from 0.2 g (1.4 mmole) of (VIb), 20 mg (0.14 mmole) of $ZnCl_2$ and 0.34 g (3.1 mmoles) of Me_3SiCl in 9 ml of CH_2Cl_2. Bp 68°C (7 mm), n_D^{20} 1.4873. IR spectrum (ν, cm^{-1}): 650, 715, 945, 985, 1205, 1290, 1330, 1360, 1380, 1465, 1655, 2970, 2860. UV spectrum (λ_{max}, nm): 230 (ε 34200). PMR spectrum (δ, ppm, J, Hz): 1.01 d (6H, CH_3, J = 7), 2.33 m (1H, HC^7), 2.53 br. q (2H, HC^2, J = 7), 3.53 t (2H, HC^1, J = 7), 5.57 d.t (1H, HC^3, J = 15 and 7), 5.64 d.d (1H, HC^6, J = 15 and 7), 5.9-6.2 m (2H, HC^4, HC^5). Mass spectrum, m/z (I, %): M$^+$ 160(11) and 158(34), 143(20), 109(41), 107(30), 95(100), 91(38), 79(63), 67(61), 55(53), 43(39), 41(69). Found: C 68.18; H 9.75; Cl 22.20%. $C_9H_{15}Cl$. Calculated: C 68.13; H 9.53; Cl 22.34%.

1-Bromo-7-methyl-3*E*,5*E*-octadiene (Xb) was obtained from 0.2 g (1.4 mmole) of (VIb), 70 mg (0.3 mmole) of $ZnBr_2$ and 0.48 g (3.1 mmoles) of Me_3SiBr in 9 ml of CH_2Cl_2. Bp 82°C (6 mm), n_D^{20} 1.5064. IR spectrum (ν, cm^{-1}): 640, 720, 945, 990, 1265, 1360, 1385, 1460, 1650, 2870, 2960. UV spectrum (λ_{max}, nm): 231 (ε 34000). PMR spectrum (δ, ppm, J, Hz): 1.01 d (6H, CH_3, J = 7), 2.33 m (1H, HC^7), 2.63 br. q (2H, HC^2, J = 7), 3.39 t (2H, HC^1, J = 7), 5.55 d.t (1H, HC^3, J = 15 and 7), 5.64 d.d (1H, HC^6, J = 15 and 7), 5.9-6.2 m (2H, HC^4, HC^5). Mass spectrum, m/z (I, %): M$^+$ 204(27) and 202(28), 189(8), 187(8), 122(13), 95(88), 81(44), 79(58), 69(39), 67(100), 55(46), 43(40), 41(90). Found: C 53.57; H 7.65; Br 39.00%. $C_9H_{15}Br$. Calculated: C 53.22; H 7.44, Br 39.34%.

1-Chloro-3*E*,5*E*-decadiene (IXc) was obtained from 0.5 g (3.2 mmoles) of (VIc), 40 mg (0.3 mmole) of $ZnCl_2$, and 0.77 g (7.1 mmoles) of Me_3SiCl in 20 ml of CH_2Cl_2. Bp 55-56°C (1 mm), n_D^{20} 1.4889. IR spectrum (ν, cm^{-1}): 655, 705, 840, 985, 1220, 1290, 1380, 1460, 1655, 2870, 2930, 2960, 3010. UV spectrum (λ_{max}, nm): 231 (ε 24600). PMR spectrum (δ, ppm, J, Hz): 0.90 t (3H, CH_3, J = 7), 1.2-1.5 m (4H, CH_2), 2.08 br. q (2H, HC^7, J = 7), 2.53 br. q (2H, HC^2, J = 7), 3.53 t (2H, HC^1, J = 7), 5.55 d.t (1H, HC^3, J = 15 and 7), 5.65 d.t (1H, HC^6, J = 15 and 7), 5.9-6.2 m (2H, HC^4, HC^5). Mass spectrum, m/z (I, %): M$^+$ 174(11) and 172(39), 143(9), 129(14), 118(21), 116(63), 95(21), 93(26), 91(21), 82(23), 81(80), 79(37), 77(34), 69(79), 67(100), 55(13), 53(11), 43(11). Found: C 69.61; H 10.00; Cl 20.30%. $C_{10}H_{17}Cl$. Calculated: C 69.55; H 9.92; Cl 20.53%.

1-Bromo-3*E*,5*E*-decadiene (Xc) [22] was obtained from 0.5 g (3.2 mmoles) of (VIc), 0.16 g (0.7 mmole) of $ZnBr_2$, and 1.09 g (7.1 mmoles) of Me_3SiBr in 20 ml of CH_2Cl_2. Bp 77-78°C (1 mm), n_D^{22} 1.5080. IR spectrum (ν, cm^{-1}): 570, 640, 760, 985, 1270, 1380, 1460, 1655, 2870, 2930, 2960, 3010. UV spectrum (λ_{max}, nm): 233 (ε 26800). PMR spectrum (δ, ppm, J, Hz): 0.90 t (3H, CH_3, J = 7), 1.2-1.5 m (4H, CH_2), 2.08 br.q (2H, HC^7, J = 7), 2.62 br. q (2H, HC^2, J = 7), 3.40 t (2H, HC^1, J = 7), 5.53 d.t (1H, HC^3, J = 15 and 7), 5.66 d.t (1H, HC^6, J = 15 and 7), 5.9-6.2 m (2H, HC^4, HC^5).

1-Chloro-3*E*,5*E*-tetradecadiene (IXe) was obtained from 0.5 g (2.4 mmoles) of (VIe), 30 mg (0.2 mmole) of $ZnCl_2$, and 0.57 g (5.2 mmoles) of Me_3SiCl in 15 ml of CH_2Cl_2. Bp 88°C (0.02 mm), n_D^{22} 1.4836. IR spectrum (ν, cm^{-1}): 545, 655, 990, 1295, 1380, 1460, 1655, 1710, 2860, 2950, 3005. UV spectrum (λ_{max}, nm): 232 (ε 24300). PMR spectrum (δ, ppm, J, Hz): 0.89 t (3H, CH_3, J = 7), 1.2-1.5 m (12H, CH_2), 2.08 br. q (2H, HC^7, J = 7), 2.53 br. q (2H, HC^2, J = 7), 3.54 t (2H, HC^1, J = 7), 5.54 d.t (1H, HC^3, J = 15 and 7), 5.65 d.t (1H, HC^6, J = 15 and 7), 5.9-6.2 m (2H, HC^4, HC^5). Mass spectrum, m/z (I, %): M$^+$ 230(3) and 228(8), 138(5), 129(5), 118(12), 116(36), 93(17), 82(20), 81(51), 79(20), 67(41), 57(15), 55(17), 44(100), 43(19), 41(24). Found: C 73.73; H 11.38; Cl 15.44%. $C_{14}H_{25}Cl$. Calculated: C 73.49; H 11.10; Cl 15.49%.

1-Bromo-3*E*,5*E*-tetradecadiene (Xe) was obtained from 0.5 g (2.4 mmoles) of (VIe), 0.12 g (0.5 mmole) of $ZnBr_2$, and 0.8 g (5.2 mmoles) of Me_3SiBr in 20 ml of CH_2Cl_2. The compound was purified by flash chromatography on 10 g of cooled SiO_2 (elution with hexane). During distillation it partly resinifies. Bp 106°C (0.01 mm), n_D^{22} 1.4973. IR spectrum (ν, cm^{-1}): 545, 565, 650, 990, 1265, 1380, 1460, 1655, 1710, 2860, 2930, 3005. UV spectrum (λ_{max}, nm): 232 (ε 26500). PMR spectrum (δ, ppm, J, Hz): 0.89 t (3H, CH_3, J = 7), 1.2-1.5 m (12H, CH_2), 2.08 br.q(2H, HC^7, J = 7), 2.62 br. q (2H, HC^2, J = 7), 3.40 t (2H, HC^1, J = 7), 5.53 d.t (1H, HC^3, J = 15 and 7), 5.66 d.t (1H, HC^6, J = 15 and 7), 5.9-6.2 m (2H, HC^4, HC^5). Mass spectrum m/z (I, %): M^+ 274(12) and 272(13), 176(11), 174(12), 162(20), 160(24), 95(71), 93(29), 82(45), 81(85), 79(60), 67(100), 44(60), 41(73). Found: C 61.15; H 9.38; Br 28.62%. $C_{14}H_{25}Br$. Calculated: C 61.54; H 9.22; Br 29.24%.

1-Chloro-3*E*,5*E*,7*E*-nonatriene (IXf) was obtained from 0.5 g (3.6 mmoles) of (VIf), 50 mg (0.4 mmole) of $ZnBr_2$ and 0.69 g (6.4 mmoles) of Me_3SiCl in 25 ml of CH_2Cl_2. The compound was purified by flash chromatography on 10 g of cooled SiO_2 (elution with hexane). During distillation it partly resinifies. Bp 67°C (1 mm), n_D^{24} 1.5525. IR spectrum (ν, cm^{-1}): 665, 950, 1115, 1295, 1375, 1430, 1450, 1650, 1700, 1730, 2960, 2990, 3020. UV spectrum (λ_{max}, nm): 266. PMR spectrum (δ, ppm, J, Hz): 1.78 d (3H, CH_3, J = 7), 2.57 q (2H, HC^2, J = 7), 3.55 t (2H, HC^1, J = 7), 5.62 d.t (1H, HC^3, J = 15 and 7), 5.71 d.q (1H, HC^8, J = 15 and 7), 6.0-6.3 m (4H, HC^4, HC^5, HC^6, HC^7). Mass spectrum m/z (I, %): M^+ 158(19) and 156(50), 121(10), 119(10), 107(52), 105(33), 93(100), 91(59), 79(81), 77(33), 55(26), 46(23), 45(44). Found: C 69.09; H 8.44; Cl 22.35%. $C_9H_{13}Cl$. Calculated: C 69.00; H 8.36; Cl 22.63%.

1-Cyclopropyl-1-trimethylsilyloxy-2*E*-heptene (XIc). A solution of 0.27 (2.5 mmoles) of Me_3SiCl in 3 ml of CH_2Cl_2 was added in the course of 5 min to a solution of 0.35 g (2.3 mmoles) of (VIc) and 0.34 g (3.4 mmoles) of Et_3N in 10 ml of CH_2Cl_2 stirred at −20°C in an Ar atmosphere. After 15 min, the mixture was filtered off, the filtrate was evaporated and the residue was distilled under vacuum. Yield, 0.5 g (97%) of (XIc), bp 66°C (1 mm), n_D^{21} 1.4390. IR spectrum (ν, cm^{-1}): 840, 880, 945, 970, 1040, 1100, 1130, 1250, 1380, 1435, 1460, 1670, 2870, 2930, 2965, 3005, 3080. PMR spectrum (δ, ppm, J, Hz): 0.11 s (9H, CH_3Si), 0.15-0.25 m (4H, the cyclopropane CH_2), 0.9-1.0 m (1H, CH), 0.90 t (3H, CH_3, J = 7), 1.2-1.4 m (4H, CH_2), 2.03 br. q (2H, HC^4, J = 7), 3.49 br. t (1H, HC^1, J = 7), 5.5 m (2H, HC^2, HC^3). Mass spectrum, m/z (I, %): M^+ 226(1), 211(1), 198(4), 169(10), 155(8), 95(8), 93(9), 75(14), 73(50), 67(15), 43(100). Found: C 68.70; H 11.62; Si 12.01%. $C_{13}H_{26}OSi$. Calculated: C 68.96; H 11.57; Si 12.40%.

Chloride (IXc) (from ether (XIc)). A solution of 0.11 g (1.0 mmole) of Me_3SiCl in 1 ml, of CH_2Cl_2 was added in the course of 5 min to a suspension of 0.2 g (0.88 mmole) of (XIc) and 10 mg (0.088 mmole) of $ZnCl_2$ in 3 ml of CH_2Cl_2, stirred at −20°C in Ar atmosphere, and after 10 min the reaction mixture was subjected to the usual treatment. After distillation, 0.11 g (72%) of (IXc) was obtained, whose physicochemical characteristics (bp, n_D, PMR) were identical with those of the above described product.

Bromide (Xc) (from ether (XIc)). In a similar way, from 0.2 g (0.88 mmole) of (XIc), 20 mg (0.089 mmole) of $ZnBr_2$, and 0.15 g (0.97 mmole) of Me_3SiBr in 4 ml CH_2Cl_2, 0.14 g (73%) of (Xc) was obtained, which in its physicochemical characteristics (bp, n_D, PMR) was identical with the above described sample of this bromide.

1-Cyclopropyl-3-methyl-6-chloro-3*E*/*Z*-hexen-1-ones (XII). In a similar way, from 0.59 g (2.46 mmoles) of (IIIh), 40 mg (0.3 mmole) of $ZnCl_2$, and 0.29 g (2.7 mmoles) of Me_3SiCl in 15 ml of CH_2Cl_2, 0.34 g (74%) of (XII) was obtained, bp 91-92°C (1 mm), n_D^{19} 1.4903. IR spectrum (ν, cm^{-1}): 600, 660, 725, 905, 930, 1029, 1080, 1120, 1205, 1295, 1385, 1445, 1695, 2690, 3010. PMR spectrum (δ, ppm, J, Hz): 0.8-1.1 m (4H, the cyclopropane CH_2), 1.68 and 1.78 s (3H, CH_3), 1.9-2.1 m (1H, CH), 2.51 and 2.55 q (2H, HC^5, J = 7), 3.23 and 3.29 s (2H, HC^2), 3.52 and 3.55 t (2H, HC^1, J = 7), 5.36 and 5.43 t (1H, HC^4, J = 7). Mass spectrum, m/z (I, %): M^+ 188(4) and 186(7), 150(79), 135(26), 109(44), 96(30), 95(33), 91(30), 83(40), 81(53), 79(33), 71(33), 70(56), 69(58), 67(44), 57(49), 55(72), 45(100), 43(67). Found: C 63.91; H 8.31; Cl 19.32%. $C_{10}H_{15}ClO$. Calculated: C 64.34; H 8.30; Cl 18.99%.

3*E*-Dodecenyl Acetate (XIII). A mixture of 0.36 g (1.5 mmoles) of (VIIId), 0.7 g (8.5 mmoles) of AcOK and 50 mg (0.1 mmole) of dibenzo-18-crown-6 in 5 ml of MeCN was boiled for 4 h, then was filtered off, the filtrate was diluted with water, and extracted with ether. The extract was washed with a saturated solution of NaCl, dried over $MgSO_4$, evaporated, and the residue was distilled under vacuum. Yield, 0.32 g (94%) of (XIII) [20], bp 95°C (1 mm), n_D^{21} 1.4402. IR spectrum (ν, cm^{-1}): 975, 1035, 1250, 1370, 1390, 1445, 1470, 1730, 2860, 2935, 2965, 3035. PMR spectrum (δ, ppm, J, Hz): 0.89 t (3H, CH_3, J = 7), 1.2-1.4 m (12H, CH_2), 1.99 br. q (2H, HC^5, J = 7), 2.06 s (3H, CH_3CO), 2.31 br. q (2H, HC^2, J = 7), 4.07 t (2H, HC^1, J = 7), 5.36 d.t (1H, HC^3, J = 15 and 7), 5.52 d.t (1H, HC^4, J = 15 and 7).

LITERATURE CITED

1. J. K. Rasmussen, Synthesis, 91 (1977); T. Mukaiyama, Organic Reactions, **28**, 203 (1982); P. Brownbridge, Synthesis, 1 (1983).
2. Y. Naruse, J. Ukai, N. Ikeda, and H. Yamamoto, Chem. Lett, **29**, 1451 (1985); H. Ohki, M. Wada, and K. Akiba, Tetrahedron Lett., **29**, 4719 (1988).
3. E. Nakamura, M. Shimizu, I. Kuwajima, et al., J. Org. Chem., **48**, 932 (1983).
4. S. Kobayashi, M. Murakami, and T. Mukaiyama, Chem. Lett., 1535 (1985).
5. N. Iwasawa and T. Mukaiyama, Chem. Lett., 463 (1987).
6. R. Noyori, I. Nishida, and J. Sakata, J. Am. Chem. Soc., **105**, 1598 (1983); M. Kawai, M. Ozaka, and Y. Izumi, Chem. Lett., 1581 (1986); M. T. Reetz and A. E. Vougioukas, Tetrahedron Lett., **28**, 793 (1987); S. Sato, I. Matsuda, and Y. Izumi, J. Organometal. Chem., **352**, 223 (1988).
7. T. Mukaiyama, K. Banno, and K. Narasaka, J. Am. Chem. Soc., **96**, 7503 (1974).
8. A. T. Nielsen, D. W. Moore, and K. Highberg, J. Org. Chem., **26**, 3691 (1961).
9. A. L. Gemal and J.-L. Luche, J. Am. Chem. Soc., **103**, 5454 (1981).
10. S. Fukuzawa, T. Fujinami, and S. Sakai, J. Chem. Soc., Perkin Trans. 1, 1929 (1986).
11. A. S. Arora and I. K. Ugi, in: Methoden der Organischen Chemie (Houben-Weyl), Vol. V/1b, E. Miller, (ed.), Georg Thieme Verlag, Stuttgart (1972), p. 912.
12. M. Julia, S. Julia, and R. Guegan, Bull. Soc. Chim. France, 1072 (1960).
13. S. F. Brady, M. Ilton, and W. S. Johnson, J. Am. Chem. Soc., **90**, 2882 (1968).
14. J. P. McCormick and D. L. Barton, J. Org. Chem., **45**, 2566 (1980).
15. G. Balme, G. Fournet, and J. Gore, Tetrahedron Lett., **27**, 1907 (1986).
16. M. Julia, C. Descoins, and C. Risse, Tetrahedron Suppl., **8** (II), 443 (1966).
17. W. Weber and A. Meijere, Synth. Commun., **16**, 837 (1986).
18. H. J. Bestmann and O. Vostrowsky, Chemistry of Plant Protection and Pesticidal Agents [in German], Vol 6, R. Wegler (ed.), Springer-Verlag, Berlin—Heidelberg—NY (1981), p. 29.
19. H. Dissenkötterand K. Eiter, Tetrahedron, **32**, 1591 (1976); T. Ishihara and A. Yamamoto, Agric. Biol. Chem., **48**, 211 (1984).
20. L. Pop, I. Oprean, A. Barabas, and F. Hodosan, J. Prakt. Chem., **328**, 867 (1986).
21. R. T. Hrubiec and M. B. Smith, J. Org. Chem., **49**, 431 (1984).
22. P. I. Svirskaya, S. N. Maiti, A. J. Jones, et al., J. Chem. Ecol., **10**, 795 (1984).
23. R. A. Myrsina, N. V. Kuznetsov, and V. E. Makarenko, Ukr. Khim. Zh., **48**, 858 (1982).