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The Chemistry of 2-Alkoxy-3,4-dihydro-2*H*-pyrans. III. Synthesis and Solvolysis of the Dichlorocarbene Adducts 3-Alkoxy-2-oxa-7,7-dichloronorcaranes

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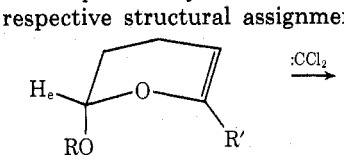
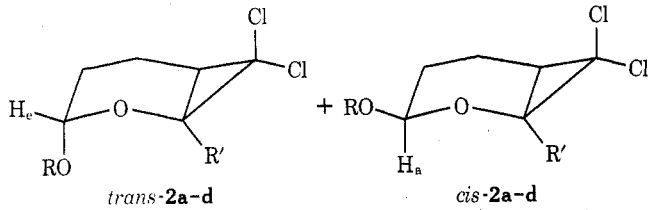
trans- and *cis*-3-alkoxy-2-oxa-7,7-dichloronorcaranes (**2a,b**) and *trans*- and *cis*-3-alkoxy-1-methyl-2-oxa-7,7-dichloronorcaranes (**2c,d**) were prepared by the addition of dichlorocarbene to 2-alkoxy-3,4-dihydro-2*H*-pyrans (**1a,b**) and 2-alkoxy-6-methyl-3,4-dihydro-2*H*-pyrans (**1c,d**), respectively. The addition, which is rather stereoselective owing primarily to the steric interactions of the axial 2-alkoxy group on the 3,4-dihydro-2*H*-pyran ring, yields predominantly the trans product. Subsequent solvolysis of the trans–*cis* mixtures **2a** and **2b** in alcoholic silver nitrate yielded 2-chloro-1,1,6,6-tetramethoxy-*cis*-2-hexene (**3a**) and 2-chloro-1,1,6,6-tetraethoxy-*cis*-2-hexene (**3b**), respectively. Similar treatment of **2c** and **2d** resulted in the formation of 3-chloro-7,7-dimethoxy-*cis*-3-hepten-2-one (**4a**) and 3-chloro-7,7-diethoxy-*cis*-3-hepten-2-one (**4b**), respectively. Evidence is presented that the electrocyclic ring opening requires the synchronous assistance of the equatorial 3-alkoxy substituent.

For some time we have been interested in the rather unusual effect of ring substituents on the chemistry of 3,4-dihydro-2*H*-pyrans.[2] In particular, an alkoxy group at the C-2 position seems to play a significant role in the outcome of electrophilic additions to the dihydropyran **1**.[2,3] We now describe the influence of the 2-alkoxy group on the addition of dichlorocarbene to the title compounds **1a–d**, and the subsequent solvolytic rearrangement studies of the dichlorocarbene adducts **2a–d** in alcoholic silver nitrate solutions.

Addition of dichlorocarbene, generated by the decomposition of ethyl trichloroacetate with sodium methoxide,[4] to 2-alkoxy-3,4-dihydro-2*H*-pyrans (**1a,b**)[5] and 2-alkoxy-6-methyl-3,4-dihydro-2*H*-pyrans (**1c,d**)[5] yielded a trans–cis mixture of the corresponding 3-alkoxy-2-oxa-7,7-dichloronorcaranes (**2a,b**) and 3-alkoxy-1-methyl-2-oxa-7,7-dichloronorcaranes (**2c,d**), respectively. The trans–cis mixtures were separated by careful column chromatography, and the respective structural assignments were based on spectral data and composition analyses. The stereochemical and conformational assignments of the adducts **2a–d** were made by analyzing the 100-MHz NMR spectra of the products (see Table I) and are consistent with the assigned conformation of the substituted dihydropyrans **1a–d**.

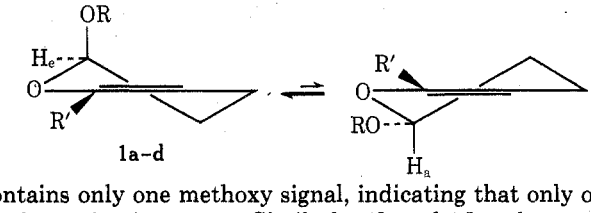


1a, R = CH_3; R′ = H
b, R = C_2H_5; R′ = H
c, R = CH_3; R′ = CH_3
d, R = C_2H_5; R′ = CH_3



trans-**2a–d** *cis*-**2a–d**

The conformations of the 2-alkoxy-3,4-dihydro-2*H*-pyrans (**1a–d**) were assigned by inspection of the 100-MHz NMR spectra. Two conformations for the 2-alkoxy-3,4-dihydro-2*H*-pyrans (**1a–d**) are possible, one with an equatorial anomeric proton (H_e) and another with an axial anomeric proton (H_a). The NMR spectrum of **1a** and **1c** each



1a–d

contains only one methoxy signal, indicating that only one conformation is present. Similarly, **1b** and **1d** each contain only one ethoxy triplet (see Table II). Since the anomeric proton of each 2-alkoxy-3,4-dihydro-2*H*-pyran (**1a–d**) is clearly a triplet, where $J_{ae} = J_{ee}$, the dihydropyrans **1a–d** exist predominantly (greater than 90%) in the conformation where the anomeric proton (H_e) is equatorial. Such a conformation is also predicted by the anomeric effect (Edward–Lemieux effect)[6] and makes the rather stereoselective addition of the dichlorocarbene to the olefins **1a–d** understandable.

The presence of a bulky axial group (the alkoxy substituent of the C-2 position) would result in a preferential trans addition to the dihydropyran **1**, yielding *trans*-**2** as the predominant product containing an anomeric equatorial proton (see Table I). Addition to the less favored sterically hindered side of the molecule would yield the minor product *cis*-**2**, which would assume a conformation containing

Table I

Adduct	R	R	Trans:cis	Trans H_e proton, δ	Cis H_a proton, δ
2a	CH_3	H	73:27	4.54 (t, J = 3 Hz)[a]	4.32 (dd, J = 4, 7 Hz)[a]
2b	C_2H_5	H	74:26	4.64 (t, J = 3 Hz)[a]	4.38 (dd, J = 4, 7 Hz)[a]
2c	CH_3	CH_3	80:20	4.70 (t, J = 3 Hz)[b]	4.36 (dd, J = 5, 7 Hz)[b]
2d	C_2H_5	CH_3	95:5	4.78 (t, J = 3 Hz)[b]	4.43 (dd, J = 5, 7 Hz)[b]

[a] 100 MHz, CCl_4. [b] 100 MHz, $CDCl_3$.

Table II[a]

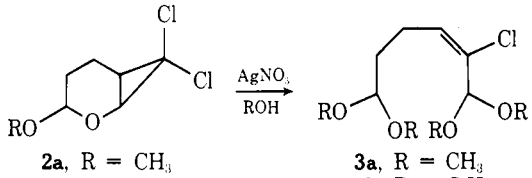
Dihydropyran	R	R	H_e anomeric proton, δ	CH_3O–, δ	CH_3CH_2O–, δ
1a	CH_3	H	4.77 (t, J = 3 Hz)	3.37 (s)	
1b	C_2H_5	H	4.86 (t, J = 3 Hz)		1.16 (t)
1c	CH_3	CH_3	4.82 (t, J = 3 Hz)[b]	3.37 (s)	
1d	C_2H_5	CH_3	4.93 (t, J = 3 Hz)[b,c]		1.18 (t)

[a] 100 MHz, CCl_4. [b] Similar results in CD_3CN. [c] Similar results in $CDCl_3$.

an anomeric axial proton (see Table I) to minimize steric interactions.

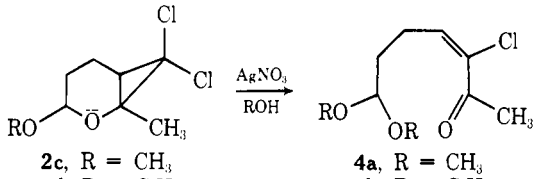
The successful preparation of the *trans*- and *cis*-3-alkoxy-2-oxa-7,7-dichloronorcaranes (**2a–d**) gave us an excellent opportunity to study the effect of the 3-alkoxy group on the electrocyclic ring opening of this system, which should proceed in a stereospecific disrotatory fashion.[7] Some previous ring openings of dihalocarbene adducts which have led to interesting results include thermolysis of 2-oxa-7,7-dichloronorcarane (**5**) with quinoline at reduced pressure,[4b] thermal rearrangement of 6,6-dichloro-2-oxabicyclo[3.1.0]hexane and its 3,3-dimethyl derivative,[8] and the silver ion assisted methanolysis of 11,11-dibromotricyclo[4.4.1.$0^{1,6}$]undecane.[9] We chose the latter less drastic conditions for our present study of the rather labile compounds **2a–d.**

Solvolysis of the trans–cis mixtures **2a** and **2b** in alcoholic silver nitrate yielded 2-chloro-1,1,6,6-tetramethoxy-*cis*-2-hexene (**3a**) and 2-chloro-1,1,6,6-tetraethoxy-*cis*-2-hexene (**3b**), respectively. Similar treatment of **2c** and **2d** re-



2a, R = CH_3 **3a**, R = CH_3
b, R = C_2H_5 **b**, R = C_2H_5

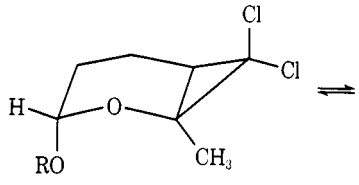
sulted in the formation of 3-chloro-7,7-dimethoxy-*cis*-3-hepten-2-one (**4a**) and 3-chloro-7,7-diethoxy-*cis*-3-hepten-2-one (**4b**), respectively. The isolated yield of each product



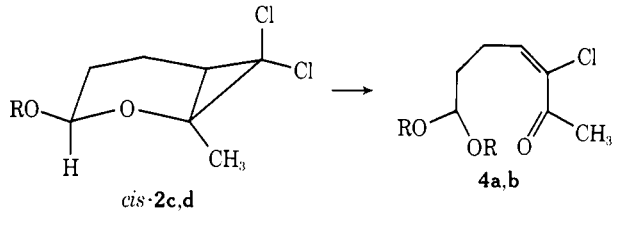
2c, R = CH_3 **4a**, R = CH_3
d, R = C_2H_5 **b**, R = C_2H_5

was respectable (78–86%). The assigned structures for the solvolysis products **3a, 3b, 4a,** and **4b** are all consistent with the spectral data and composition analyses.

Solvolysis of the pure *cis*-**2d** and *trans*-**2d** dichlorocarbene adducts turned out to be extremely important in understanding the mechanism of this rearrangement. Treatment of *cis*-3-ethoxy-1-methyl-2-oxa-7,7-dichloronorcarane (*cis*-**2d**) with ethanolic silver nitrate at 25° immediately produced the silver chloride precipitate, indicating a rather fast reaction. On the other hand, no precipitate was detected for several hours when *trans*-3-ethoxy-1-methyl-2-oxa-7,7-dichloronorcarane (*trans*-**2d**) was subjected to these conditions, suggesting a very slow reaction. The rate could be enhanced by gently warming the reaction mixture. Premature quenching of a solvolytic experiment using *trans*-**2d,** where trace amounts of silver nitrate were used in a very dilute system, yielded a mixture composed of *trans*-**2d,** product **4b,** and trace quantities of *cis*-**2d** which were isolated and identified. The presence of small amounts of *cis*-**2d** implies that *trans*-**2d** epimerizes to *cis*-**2d** and that it is the latter which undergoes electrocyclic ring opening. Similar empirical rate observations were evi-



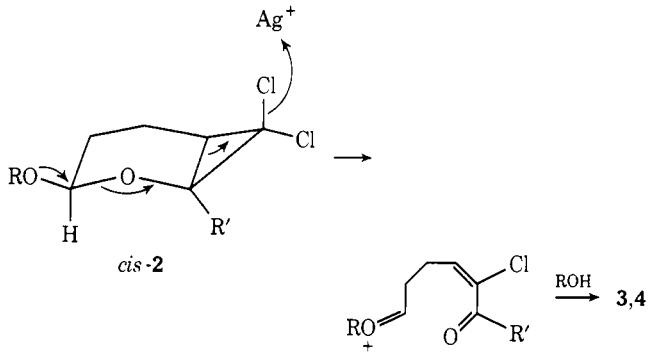
trans-**2c,d**



cis-**2c,d** **4a,b**

dent with *cis*- and *trans*-3-methoxy-1-methyl-2-oxa-7,7-dichloronorcarane (**2c**), although not quite as dramatic; which probably mean that the trans to cis epimerization is somewhat faster in this system.[10]

Consequently, it appears that the solvolysis of the syn substituent,[8,11] which results in a concerted disrotatory ring opening of the dichloroadducts **2** yielding the cis double bond[7,12] products **3** and **4,** requires the synchronous as-



cis-**2**

sistance[13] of the equatorial 3-alkoxy substituent. It was thus not surprising to find that the parent 2-oxa-7,7-dichloronorcarane (**5**), the dichlorocarbene adduct of 3,4-dihydro-2*H*-pyran,[4b,c] was inert to these and even more vigorous conditions.

Experimental Section[15]

The 2-alkoxy-3,4-dihydro-2*H*-pyrans (**1a, 1b**) and the 2-alkoxy-6-methyl-3,4-dihydro-2*H*-pyrans (**1c, 1d**) were prepared by a method previously described.[5a,b] Pyran **1b** is also available from Aldrich Chemical Co. Two of the commercial reagents require some special attention: the ethyl trichloroacetate must be distilled just prior to use and the sodium methoxide should be a freshly opened sample. Both solvents, methanol and the olefin-free pentane, were reagent grade. The pentane was passed through a Woelm neutral aluminum oxide (activity grade I) column just prior to use. All reactions were performed in dry glassware under a static nitrogen atmosphere. Gas chromatography (GLC) was performed on a Hewlett-Packard Model 7610A high-efficiency chromatograph (flame detector) using a 4 ft × 6 mm (all glass) 5% Carbowax 20M on 60–80 Chromosorb W column. Distillations were accomplished with short-path or Büchi Kugelrohr bulb-to-bulb apparatus. All boiling points are uncorrected. Column chromatography was performed on Woelm neutral aluminum oxide (activity grade III), Matheson Coleman and Bell activated alumina (chromatographic grade, 80–325 mesh), and Floridin magnesium silicate (Florisil, 60–100 mesh) columns by eluting with petroleum ether and petroleum ether–Et_2O.

3-Methoxy-2-oxa-7,7-dichloronorcarane (2a). To a stirred and cooled (0°) slurry of 2-methoxy-3,4-dihydro-2*H*-pyran (**1a,** 7.22 g, 0.063 mol) and sodium methoxide (5.0 g, 0.088 mol) in pentane (40 ml) was slowly added (ca. 10 min) 16.5 g (0.086 mol) of ethyl trichloroacetate. The mixture was stirred for 6 hr at 0° and then for 16 hr at 25°, after which the reaction mixture was partitioned between water and petroleum ether. The organic layer was separated and dried ($MgSO_4$), and the solvent was removed in vacuo affording a yellow oil (13.2 g). Analysis (GLC) of the yellow oil indicated a 73:27 mixture of trans and cis isomers of **2a,** which distilled together yielding a colorless oil (6.38 g, 52%): bp 105–107° (10 mm); ir (film) 2936, 1450, 1365, 1216, 1142, 1116, 1083, 1039, 1022, 905, 835, 711 cm^{-1}; mass spectrum *m/e* (rel intensity) 169 (8), 167 (23), 165 (19), 161 (8), 138 (10), 136 (10), 133 (13), 131 (10), 111 (37), 109 (62), 101 (27), 97 (19), 71 (100), 65 (29), 58 (65), 45 (29), 43 (21), 41 (27), 39 (27).

Anal. Calcd for $C_7H_{10}Cl_2O_2$: C, 42.67; H, 5.11; Cl, 35.98. Found: C, 42.73; H, 5.02; Cl, 36.03.

Column chromatography of distillate **2a** on alumina (Matheson Coleman and Bell) yielded 4.85 g (39%) of *trans*-**2a** (colorless oil), NMR (100 MHz, CCl_4) δ 4.54 (1 H, t, J = 3 Hz, equatorial anomeric proton), 3.50 (1 H, d, J = 8 Hz), 3.39 (3 H, s), 2.26–1.23 (5 H, m); a mixture which contained 415 mg (3%) of *trans*- and *cis*-**2a;** and 479 mg (4%) of *cis*-**2a** (colorless oil), NMR (100 MHz, CCl_4) δ 4.32 (1 H, d of d, J = 4 and 7 Hz, axial anomeric proton), 3.71 (1 H, d, J = 8 Hz), 3.41 (3 H, s), 2.22–1.99 (2 H, m), 1.80–1.40 (3 H, m).

3-Ethoxy-2-oxa-7,7-dichloronorcarane (2b). To a stirred and cooled (0°) slurry of 2-ethoxy-3,4-dihydro-2*H*-pyran (**1b,** 12.8 g, 0.10 mol) and sodium methoxide (7.4 g, 0.13 mol) in pentane (75 ml) was slowly added (*ca.* 15 min) 22.7 g (0.12 mol) of ethyl trichloroacetate. The mixture was stirred for 6 hr at 0° and then for 16 hr at 25°. Normal work-up, as described above for **2a,** afforded a yellow oil (11.8 g). Analysis (GLC) of the yellow oil indicated a 74:26 mixture of trans and cis isomers of **2b,** which distilled together yielding a colorless oil (9.7 g, 46%): bp 64–66° (12 mm); ir (film) 2975, 2930, 1445, 1370, 1228, 1210, 1145, 1114, 1085, 1046, 1024, 952, 876, 836, 814, 717 cm^{-1}; mass spectrum *m/e* (rel intensity) 185 (1), 183 (5), 181 (10), 177 (2), 175 (8), 169 (5), 167 (14), 165 (22), 149 (9), 147 (32), 145 (12), 138 (10), 136 (12), 129 (8), 128 (13), 125 (11), 111 (33), 109 (53), 101 (36), 85 (100), 83 (33), 72 (81), 65 (28), 57 (58), 44 (71), 39 (32).

Anal. Calcd for $C_8H_{12}Cl_2O_2$: C, 45.52; H, 5.73; Cl, 33.59. Found: C, 45.81; H, 5.91; Cl, 33.38.

Column chromatography of distillate **2b** on alumina (Matheson Coleman and Bell) yielded 5.72 g (27%) of *trans*-**2b** (colorless oil), NMR (100 MHz, CCl_4) δ 4.64 (1 H, t, J = 3 Hz, equatorial anomeric proton), 3.46 (1 H, d, J = 8 Hz) superimposed on four overlapping quartets centered at 3.76 (1 H, two overlapping quartets, J = 7 and 10 Hz) and 3.45 (1 H, two overlapping quartets, J = 7 and 10 Hz), 2.34–1.29 (5 H, complex m), 1.19 (3 H, t, J = 7 Hz); a mixture which contained 2.23 g (11%) of *trans*- and *cis*-**2b;** and 291 mg (1.5%) of *cis*-**2b** (colorless oil), NMR (100 MHz, CCl_4) δ 4.38 (1 H, d of d, J = 4 and 7 Hz, axial anomeric proton), 3.88 (1 H, two overlapping quartets, J = 7 and 9 Hz) on which is superimposed a doublet at 3.68 (1 H, d, J = 8 Hz), 3.40 (1 H, two overlapping quartets, J = 7 and 9 Hz), 2.34–1.93 (2 H, m), 1.92–1 25 (3 H, m), 1.17 (3 H, t, J = 7 Hz).

3-Methoxy-1-methyl-2-oxa-7,7-dichloronorcarane (2c). To a stirred and cooled (0°) slurry of 2-methoxy-6-methyl-3,4-dihydro-2*H*-pyran (**1c,** 19.2 g, 0.12 mol) and sodium methoxide (9.7 g, 0.18 mol) in pentane (100 ml) was slowly added (*ca.* 20 min) 32.5 g (0.17 mol) of ethyl trichloracetate. The mixture was stirred for 6 hr at 0° and then for 16 hr at 25°. Normal work-up, as described above for **2a,** afforded a yellow oil (35 g). Analysis (GLC) of the yellow oil indicated a 80:20 mixture of trans and cis isomers of **2c,** which distilled together yielding a colorless oil (19.0 g, 60%): bp 73–75° (1 mm); ir (film) 2925, 2830, 1440, 1375, 1220, 1112, 1055, 1030, 920, 895, 845, 700 cm^{-1}.

Anal. Calcd for $C_8H_{12}Cl_2O_2$: C, 45.52; H, 5.73; Cl, 33.59. Found: C, 45.78; H, 5.88; Cl, 33.51.

Column chromatography of distillate **2c** on aluminum oxide (Woelm) yielded 13.68 g (43%) of *trans*-**2c** (colorless oil), NMR (100 MHz, $CDCl_3$) δ 4.70 (1 H, t, J = 3 Hz, equatorial anomeric proton), 3.48 (3 H, s), 1.64 (3 H, s) superimposed on a multiplet at 2.40–1.35 (5 H, m), mass spectrum *m/e* (rel intensity) 183 (0.2), 181 (1), 179 (1), 177 (0.3), 175 (1), 169 (0.6), 167 (1), 143 (1), 141 (3), 139 (7), 111 (23), 109 (38), 97 (12), 79 (19), 72 (17), 71 (85), 58 (40), 43 (100); a mixture which contained 2.66 g (8%) of *trans*- and *cis*-**2c;** and 2.09 g (7%) of *cis*-**2c** (colorless oil), NMR (100 MHz, $CDCl_3$) δ 4.36 (1 H, d of d, J = 5 and 7 Hz, axial anomeric proton), 3.50 (3 H, s), 2.30–2.04 (2 H, m), 1.63 (3 H, s) superimposed on a multiplet at 1.70–1.37 (3 H, m), mass spectrum *m/e* (rel intensity) 181 (0.3), 179 (0.4), 177 (0.4), 175 (1), 171 (0.2), 169 (1), 167 (1), 143 (1), 141 (4), 139 (8), 111 (28), 109 (44), 97 (12), 79 (17), 72 (22), 71 (84), 58 (45), 43 (100).

3-Ethoxy-1-methyl-2-oxa-7,7-dichloronorcarane (2d). To a stirred and cooled (0°) slurry of 2-ethoxy-6-methyl-3,4-dihydro-2*H*-pyran (**1d,** 15.0 g, 0.105 mol) and sodium methoxide (7.2 g, 0.13 mol) in pentane (75 ml) was slowly added (ca. 15 min) 23.0 g (0.116 mol) of ethyl trichloroacetate. The mixture was stirred for 6 hr at 0° and then for 16 hr at 25°. Normal work-up, as described above for **2a,** afforded a yellow oil (15.8 g). Analysis (GLC) of the yellow oil indicated a 95:5 mixture of trans and cis isomers of **2d,** which distilled together yielding a colorless oil (12 g, 51%): bp 76–78° (1 mm); ir (film) 2980, 2935, 1445, 1375, 1245, 1212, 1110, 1060, 1030, 960, 895, 880, 845, 700 cm^{-1}.

Anal. Calcd for $C_9H_{14}Cl_2O_2$: C, 48.02; H, 6.27; Cl, 31.50. Found: C, 48.31; H, 6.28; Cl, 30.59.

Column chromatography of distillate **2d** on alumina (Matheson Coleman and Bell) yielded 9.0 g (38%) of *trans*-**2d** (colorless oil), NMR (100 MHz, $CDCl_3$) δ 4.78 (1 H, t, J = 3 Hz, equatorial anomeric proton), 3.89 (1 H, two overlapping quartets, J = 7 and 10 Hz), 3.52 (1 H, two overlapping quartets, J = 7 and 10 Hz), 1.59 (3 H, s) superimposed on a complex multiplet at 2.28–1.32 (5 H, m), 1.20 (3 H, t, J = 7 Hz), mass spectrum *m/e* (rel intensity) 193 (0.1), 191 (0.6), 189 (2), 183 (2), 181 (3), 179 (3), 145 (7), 141 (10), 139 (7), 117 (13), 115 (14), 111 (28), 109 (38), 89 (27), 85 (74), 57 (66), 53 (27), 43 (100); a mixture which contained 360 mg (1.5%) of *trans*- and *cis*-**2d;** and 360 mg (1.5%) of *cis*-**2d** (colorless oil), NMR (100 MHz, $CDCl_3$) δ 4.43 (1 H, d of d, J = 5 and 7 Hz, axial anomeric proton), 3.99 (1 H, two overlapping quartets, J = 7 and 10 Hz), 3.52 (1 H, two overlapping quartets, J = 7 and 10 Hz), 2.28–1.94 (2 H, m), a singlet at 1.61 (3 H, s) and a triplet at 1.21 (3 H, t, J = 7 Hz) superimposed on a complex multiplet at 1.92–1.20 (3 H, m), mass spectrum *m/e* (rel intensity) 191 (0.3), 189 (0.8), 183 (0.9), 181 (2), 179 (0.4), 145 (3), 141 (6), 139 (4), 117 (6), 115 (5), 111 (17), 109 (24), 89 (12), 85 (30), 57 (38), 53 (13), 43 (100).

2-Chloro-1,1,6,6-tetramethoxy-*cis*-2-hexene (3a). A solution of 3-methoxy-2-oxa-7,7-dichloronorcarane (**2a,** trans and cis mixture, 262 mg, 1.33 mmol) in 2 ml of methanol was added to a stirred solution of silver nitrate (249 mg, 1.46 mmol) in 5 ml of methanol; subsequently a white precipitate gradually appeared. After 24 hr the mixture was partitioned between petroleum ether and water; then the organic phase was separated, washed with brine, dried ($MgSO_4$), and concentrated in vacuo, affording a pale yellow oil (ca. 320 mg). Analysis (GLC) indicated one product. Further purification of the oil by column chromatography on Florisil yielded 2-chloro-1,1,6,6-tetramethoxy-*cis*-2-hexene (**3a**) as a colorless oil (247 mg, 78%): ir (film) 2970, 2915, 2810, 1660, 1450,

1360, 1190, 1130, 1060, 975, 915, 735 cm^{-1}; NMR (60 MHz, $CDCl_3$) δ 6.10 (1 H, t, J = 7 Hz with further fine splitting), 4.76 (1 H, perturbed s), 4.40 (1 H, t, J = 6 Hz), 3.39 (12 H, s), 2.36 (2 H, q, J = 7 Hz), 1.98–1.52 (2 H, m); mass spectrum m/e (rel intensity) 209 (3), 207 (8), 177 (2), 175 (4), 149 (9), 148 (9), 139 (5), 101 (4), 88 (5), 75 (100), 71 (4), 47 (5).

Anal. Calcd $C_{10}H_{19}ClO_4$: C, 50.32; H, 8.02; Cl, 14.85. Found: C, 50.61; H, 8.19; Cl, 14.99.

2-Chloro-1,1,6,6-tetraethoxy-*cis*-2-hexene (3b). A solution of 3-ethoxy-2-oxa-7,7-dichloronorcarane (**2b**, trans and cis mixture, 492 mg, 2.33 mmol) in 5 ml of ethanol was added to a stirred solution of silver nitrate (420 mg, 2.47 mmol) in 10 ml of ethanol; subsequently a white precipitate gradually appeared. Normal work-up, as described above for **3a**, after 24 hr afforded a pale yellow oil (ca. 670 mg). Analysis (GLC) indicated one product. Further purification of the oil by column chromatography on Florisil yielded 2-chloro-1,1,6,6-tetraethoxy-*cis*-2-hexene (**3b**) as a colorless oil (585 mg, 85%): ir (film) 2985, 2940, 2890, 1662, 1442, 1370, 1270, 1120, 1050 cm^{-1}; NMR (60 MHz, CCl_4) δ 5.98 (1 H, t, J = 7 Hz with further fine splitting), 4.72 (1 H, perturbed s), 4.37 (1 H, t, J = 6 Hz), 3.85–3.11 (8 H, complex m which appears to be a series of overlapping quartets, J = 7 Hz), 2.24 (2 H, q, J = 7 Hz), 1.88–1.41 (2 H, m), and two overlapping triplets at 1.18 (6 H, t, J = 7 Hz) and 1.15 (6 H, t, J = 7 Hz); mass spectrum m/e (rel intensity) 251 (4), 249 (12), 205 (2), 203 (3), 178 (3), 177 (4), 176 (10), 175 (6), 111 (9), 103 (100), 83 (12), 75 (38), 47 (32).

Anal. Calcd $C_{14}H_{27}ClO_4$: C, 57.04; H, 9.23; Cl, 12.03. Found: C, 56.88; H, 9.03; Cl, 12.34.

3-Chloro-7,7-dimethoxy-*cis*-3-hepten-2-one (4a). A solution of 3-methoxy-1-methyl-2-oxa-7,7-dichloronorcarane (**2c**, trans and cis mixture, 615 mg, 2.91 mmol) in 12 ml of methanol was added to a stirred solution of silver nitrate (551 mg, 3.24 mmol) in 30 ml of methanol; subsequently a white precipitate gradually appeared. Normal work-up, as described above for **3a**, after 24 hr afforded a pale yellow oil (581 mg). Analysis (GLC) indicated a major component (**4a**, 94%) and minor component (**6**, 6%).[14] Purification of the oil by column chromatography on Florisil yielded a mixture which contained 77 mg of **6** and **4a** and 518 mg (86%) of 3-chloro-7,7-dimethoxy-*cis*-3-hepten-2-one (**4a**) as a colorless oil: ir (film) 2930, 2820, 1685, 1615, 1435, 1355, 1245, 1220, 1125, 1065, 895 cm^{-1}; NMR (60 MHz, CCl_4) δ 6.85 (1 H, t, J = 7 Hz), 4.28 (1 H, t, J = 5.5 Hz), 3.26 (6 H, s), 2.34 (3 H, s) superimposed on 2.30 (2 H, q, J = 7 Hz), 1.93–1.50 (2 H, m); mass spectrum m/e (rel intensity) 177 (5), 175 (16), 162 (2), 160 (6), 137 (6), 135 (28), 133 (3), 131 (14), 101 (14), 89 (15), 75 (89), 58 (26), 53 (43), 43 (100).

Anal. Calcd for $C_9H_{15}ClO_3$: C, 52.31; H, 7.32; Cl, 17.15. Found: C, 52.10; H, 7.61; Cl, 16.85.

3-Chloro-7,7-diethoxy-*cis*-3-hepten-2-one (4b). A solution of 3-ethoxy-1-methyl-2-oxa-7,7-dichloronorcarane (**2d**, trans and cis mixture, 1.20 g, 5.33 mmol) in 5 ml of ethanol was added to a stirred solution of silver nitrate (1.02 g, 6.00 mmol) in 75 ml of ethanol; after some time a white precipitate gradually appeared. After 24 hr the mixture was filtered and the supernate was concentrated in vacuo to ca. 20 ml and then partitioned between hexane and water. The organic phase was separated, washed with brine, dried (Na_2SO_4), and concentrated in vacuo, affording a pale yellow oil (1.10 g). Analysis (GLC) indicated one product. Further purification of the oil by column chromatography on Florisil yielded 3-chloro-7,7-diethoxy-*cis*-3-hepten-2-one (**4b**) as a colorless oil (1.08 g, 86%): ir (film) 2965, 2920, 2870, 1685, 1613, 1355, 1365, 1240, 1220, 1120, 1060 cm^{-1}; NMR (100 MHz, $CDCl_3$) δ 7.02 (1 H, t, J = 7 Hz), 4.52 (1 H, t, J = 5.3 Hz), 3.68 (2 H, two overlapping quartets, J = 7 and 9.5 Hz), 3.49 (2 H, two overlapping quartets, J = 7 and 9.5 Hz), 2.40 (3 H, s) superimposed on 2.49 (2 H, q, J = 7 Hz), 1.82 (2 H, two overlapping triplets, J = 5.3 and 7 Hz), 1.20 (6 H, t, J = 7 Hz); mass spectrum m/e (rel intensity) 236 (M^+, 0.2), 234 (M^+, 0.7), 191 (15), 189 (47), 161 (2), 159 (6), 151 (13), 149 (40), 125 (10), 115 (24), 103 (100), 85 (13), 75 (40), 47 (33), 43 (74).

Anal. Calcd for $C_{11}H_{19}ClO_3$: C, 56.29; H, 8.16; Cl, 15.10. Found: C, 56.55; H, 8.43; Cl, 14.82.

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References and Notes

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(14) 3-Chloro-2,2,7,7-tetramethoxy-*cis*-3-heptene (**6**): ir (film) 2990, 2950, 2830, 1650, 1450, 1370, 1275, 1240, 1185, 1125, 1050, 875, 805, 670 cm^{-1}; NMR (60 MHz, $CDCl_3$) δ 6.10 (1 H, t, J = 7 Hz), 4.22 (1 H, t, J = 5.5 Hz), 3.28 (6 H, s), 3.14 (6 H, s), 2.28 (2 H, q, J = 7 Hz), 1.93–1.50 (2 H, m), 1.44 (3 H, s); mass spectrum m/e (rel intensity) 223 (8), 222 (6), 221 (24), 220 (10), 191 (2), 189 (6), 165 (5), 163 (13), 95 (14), 93 (19), 89 (62), 75 (100), 43 (24).
Anal. Calcd for $C_{11}H_{21}ClO_4$: C, 52.28; H, 8.38; Cl, 14.03. Found: C, 52.58; H, 8.11; Cl, 13.91.
(15) The ir spectra were determined with a Perkin-Elmer Model 237B infrared recording spectrophotometer and a Beckman Model IR-10 infrared recording spectrophotometer. The NMR spectra were determined at 60 MHz with a Varian Associates Model T-60 NMR spectrometer and at 100 MHz with a Varian Associates Model HA-100 NMR spectrometer. The chemical shifts are expressed in δ values (parts per million) relative to a Me_4Si internal standard. The mass spectra were obtained with a Consolidated Electronics Corp. Model 110-21B mass spectrometer.