Addition of *tert*-Butyl Hypohalites to 3,4-Dihydro-2*H*-pyran and Its 2-Alkoxy and 2-Alkoxy-6-methyl Derivatives in Hydroxylic Solvents[1]

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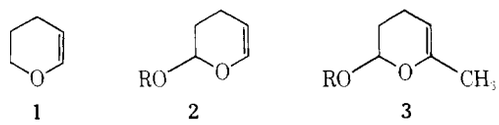
Electrophilic addition of *tert*-butyl hypochlorite and hypobromite to 3,4-dihydro-2*H*-pyran (1) in alcohol and organic acid solvents yielded cis/trans mixtures of the 1,2-addition products 3-halo-2-alkoxytetrahydropyrans (**4a–k**). Addition of these reagents to 2-alkoxy-3,4-dihydro-2*H*-pyrans (**2a** and **2b**) in the corresponding alcohol solvents yielded cis/trans mixtures of the 1,2-addition products 3-halo-2,6-dialkoxytetrahydropyrans (**5a–d**). In contrast, additions to 2-alkoxy-6-methyl-3,4-dihydro-2*H*-pyrans (**3a** and **3b**) yielded cis/trans mixtures of the 1,2-addition products 3-halo-2,6-dialkoxy-2-methyltetrahydropyrans (**6a–d**) and the 1,4-addition products 3-halo-6,6-dialkoxy-2-hexanone (**7a–d**). The important influence of the axial 2-alkoxy group and the 6-methyl group on the course of these reactions is discussed, as well as the stereochemistry of the products and the mechanisms of the reactions.

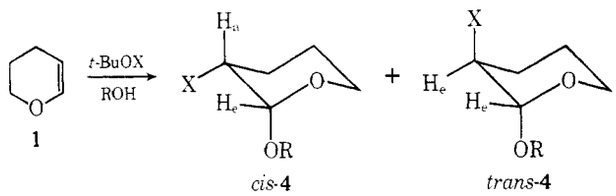
A comparison of electrophilic additions to 2-alkoxy-3,4-dihydro-2*H*-pyrans (**2**) vis-à-vis the unsubstituted compound 3,4-dihydro-2*H*-pyran (**1**) indicates the instrumental role of the 2-alkoxy group on the outcome of the reaction.[3] In addition, it is becoming apparent that the introduction of an alkyl group at the C-6 position, such as with the 2-alkoxy-6-methyl-3,4-dihydro-2*H*-pyrans (**3**), substantially enhances the reactivity of the dihydropyran ring system.[3a,b,4] We now wish to describe the electrophilic addition of *tert*-butyl hypohalite reagents[5] to these dihydropyrans **1–3** in hydroxylic



1 **2** **3**

solvents that demonstrates the unique synergistic effect of the 6-alkyl group coupled with the 2-alkoxy group on the course of the reaction.

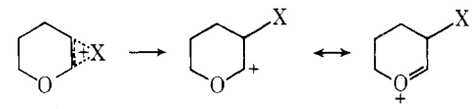
Addition of *tert*-butyl hypohalites (hypochlorite and hypobromite) to the unsubstituted 3,4-dihydro-2*H*-pyran (**1**) in hydroxylic solvents (alcohols and acids) yielded cis/trans mixtures of the corresponding 1,2-addition products **4a–k** (see



1 *cis*-**4** *trans*-**4**

Table I). Analysis of the product mixtures by 100-MHz NMR spectroscopy confirmed the configurations (and predominant conformations) for the cis- and trans-addition products. The alkoxy group at the newly developed anomeric center (C-2) is axial as is predicted by the anomeric effect[6,7] and confirmed by NMR analysis since the vicinal coupling constants are small (J_{ea} = 3.0–3.5 Hz, cis isomer, and J_{ee} = 3.2–4.9 Hz, trans isomer). The cis and trans isomers are resolvable on GLC analysis and distinguishable by NMR analysis[6,8] since the equatorial anomeric proton (C-2) for the cis diastereomer is always shifted further downfield than that of the trans and its coupling constant is usually smaller ($J_{ea} < J_{ee}$).

The mechanism of 1,2-additions of *tert*-butyl hypohalites to olefins is known to involve the electrophilic addition of X^+ to the double bond followed by the nucleophilic solvent.[5c,9] Halogen addition to 3,4-dihydro-2*H*-pyran has been discussed previously in detail,[6,8c] so we will only reiterate here that all products, especially when X is Cl, are derived principally from the oxocarbonium ion **1b.**



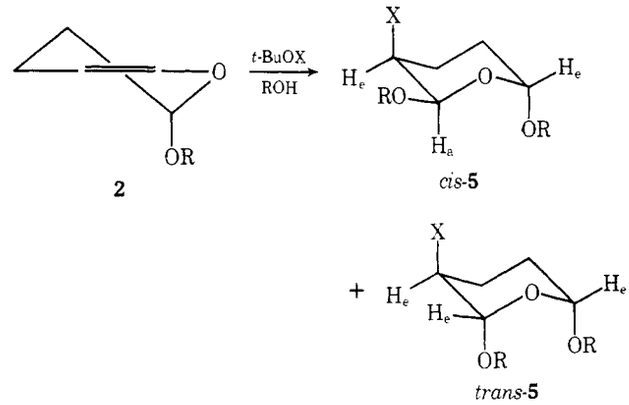
1a **1b**

For all of the alkyl alcohol solvents the ratio of cis:trans products was ca. 15:85 with *tert*-butyl hypochlorite. However, with the other nucleophilic solvents such as benzyl alcohol and the organic acids, which perhaps can more effectively stabilize the oxocarbonium ion **1b,** there was an appreciable increase in the formation of the cis isomer. Attempts to use other protic solvents such as alkylamines failed, presumably because of the competing N-chlorination of the solvent.[10]

Addition of *tert*-butyl hypobromite to 3,4-dihydro-2*H*-pyran (**1**) yielded similar results[11] as those with *tert*-butyl hypochlorite; however, it is necessary to add traces of a free-radical inhibitor such as dihydroquinone to minimize competing side reactions. There is also more trans isomer formed with *tert*-butyl hypobromite, reflecting the increased importance of the intermediate halonium ion **1a** when X is Br.

Although the addition of *tert*-butyl hypohalites to acyclic vinyl ethers in alcohol solvents has been evaluated,[5c,9c] we have found using the conditions described in the Experimental Section marked improvements in the isolated yields.[12]

Addition of the *tert*-butyl hypohalites to the 2-alkoxy-3,4-dihydro-2*H*-pyrans **2a** and **2b** in the respective alcohol solvent yielded the corresponding 1,2-addition products **5a–d**



2 *cis*-**5** *trans*-**5**

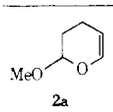
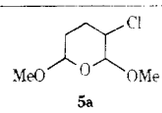
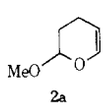
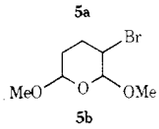
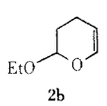
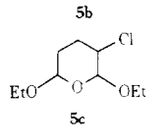
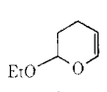
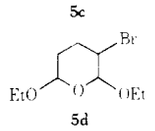
(see Table II). In these examples, however, the diastereomeric mixture is ca. a 50:50 cis:trans mixture with *tert*-butyl hypo-

Table I. *tert*-Butyl Hypohalite Addition to 3,4-Dihydro-2*H*-pyran

Hypohalite/solvent	Product	Cis/trans[a]	Isolated yield,[b] %
t-BuOCl/CH_3OH[c]	3-Chloro-2-methoxytetrahydropyran (**4a**)	15/85	72
t-BuOCl/C_2H_5OH[c]	3-Chloro-2-ethoxytetrahydropyran (**4b**)	15/85	67
t-BuOCl/*n*-C_3H_7OH[c]	3-Chloro-2-*n*-propoxytetrahydropyran (**4c**)	15/85	64
t-BuOCl/*i*-C_3H_7OH[c]	3-Chloro-2-isopropoxytetrahydropyran (**4d**)	15/85	50
t-BuOCl/*n*-C_4H_9OH[c]	3-Chloro-2-*n*-butoxytetrahydropyran (**4e**)	15/85	69
t-BuOBr/*n*-C_4H_9OH[d]	3-Bromo-2-*n*-butoxytetrahydropyran (**4f**)	10/90	75[i]
t-BuOCl/*sec*-C_4H_9OH[e]	3-Chloro-2-*sec*-butoxytetrahydropyran (**4g**)	20/80	60
t-BuOCl/*t*-C_4H_9OH[f]	3-Chloro-2-*tert*-butoxytetrahydropyran (**4h**)	15/85	35
t-BuOCl/$C_6H_5CH_2OH$[e]	3-Chloro-2-benzyloxytetrahydropyran (**4i**)	33/67	70
t-BuOCl/CH_3CO_2H[g]	3-Chloro-2-acetoxytetrahydropyran (**4j**)	32/68	85
t-BuOCl/$C_2H_5CO_2H$[h]	3-Chloro-2-propionoxytetrahydropyran (**4k**)	45/55	80

[a] Determined by GLC analysis and confirmed by 100-MHz NMR spectroscopy. [b] Isolated yield after distillation. [c] Reaction conditions are described in Experimental Section for **4e**. [d] Reaction conditions are described in Experimental Section for **4f**. [e] Same reaction conditions as **4e** except temperature (0 °C). [f] Same reaction conditions as **4e** except temperature (20 °C). [g] Reaction conditions are described in Experimental Section for **4j**. [h] Same reaction conditions as **4j** except temperature (0 °C). [i] Isolated yield after column chromatography.

Table II. *tert*-Butyl Hypohalite Addition to 2-Alkoxy-3,4-dihydro-2*H*-pyrans

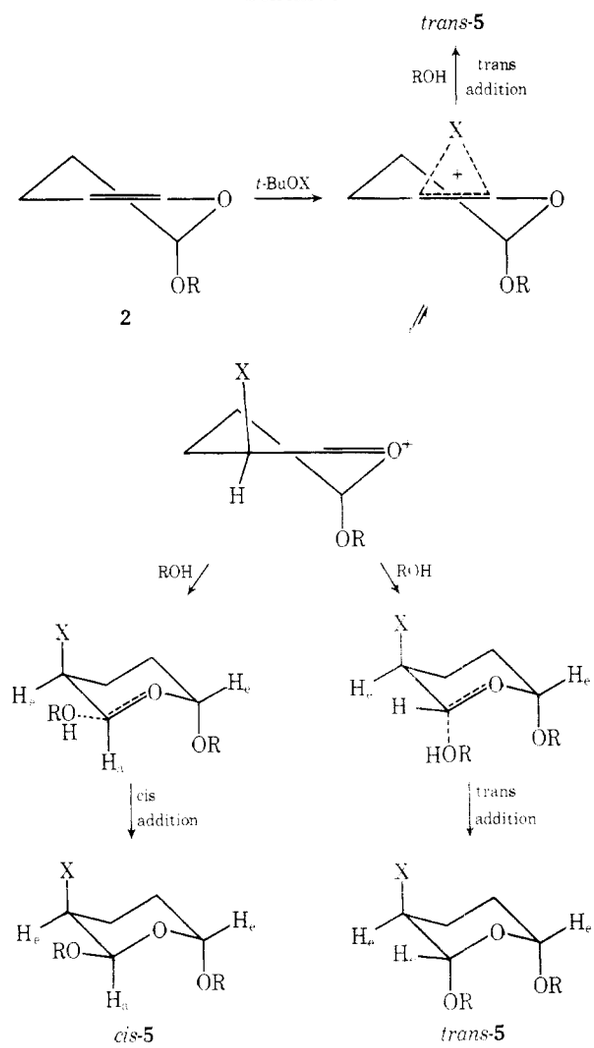
Dihydropyran	Hypohalite/solvent	Product	Isolated yield,[a] %
 **2a**	*t*-BuOCl/MeOH[b]	 **5a**	61
 **2a**	*t*-BuOBr/MeOH[c]	 **5b**	63
 **2b**	*t*-BuOCl/EtOH[b]	 **5c**	76
 **2b**	*t*-BuOBr/EtOH[c]	 **5d**	74

[a] Isolated by column chromatography. [b] Reaction conditions are described in the Experimental Section for **5a**. [c] Reaction conditions are described in the Experimental Section for **5b**.

chlorite and slightly less (ca. 40:60) with *tert*-butyl hypobromite. The starting 2-alkoxy-3,4-dihydro-2*H*-pyrans (**2a** and **2b**, as well as **3a** and **3b**), as has been previously reported,[13] exist predominantly (greater than 90%, NMR analysis) in the conformation where the C-2 anomeric proton is equatorial (alkoxy group is axial). This stereochemistry about the original anomeric center, as indicated by 100-MHz NMR spectroscopy, was preserved in the products (now C-6 in *cis*- and *trans*-**5**). The signal for the anomeric C-6 proton in each diastereomer was a superficial triplet ($J_{ea} \approx J_{ee}$ = 3.0–4.0 Hz) as expected for an equatorial proton at this position. The stereochemistry about the newly developed anomeric center at C-2, however, was clearly two diastereomers with the two different proton signals as doublets with small coupling constants (5.7–7.0 Hz) indicating an axial proton in one and equatorial proton in the other coupled to the adjacent equatorial (J_{ae} and J_{ee}) proton at C-3. These results are depicted in Scheme I.

The presence of the bulky axial alkoxy group at C-2 would result in a preferential trans addition of the halogen to the dihydropyran **2**. Subsequent addition of alcohol to the intermediate oxocarbonium ion would be affected by the axial alkoxy group as well. Trans-diaxial addition creates a rather serious 1,3 interaction between alkoxy groups thus making the

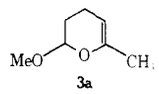
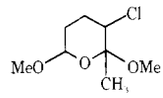
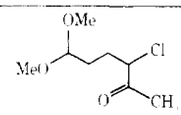
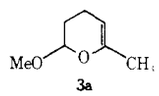
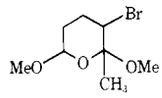
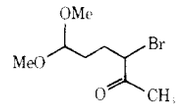
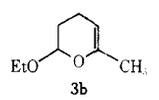
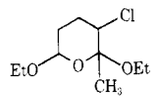
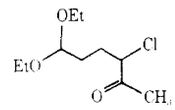
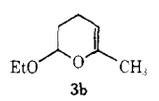
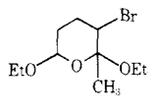
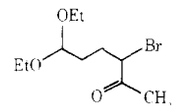
Scheme I



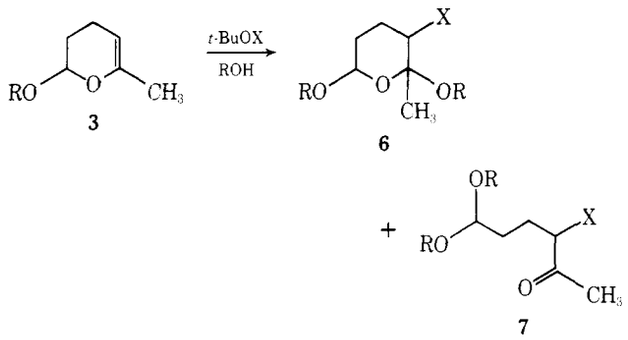
cis-equatorial addition much more competitive. With *tert*-butyl hypobromite some trans product would arise from the intermediate bromonium ion.

In contrast to these results with 3,4-dihydro-2*H*-pyran (**1**) and its 2-alkoxy derivatives **2a** and **2b**, addition of the *tert*-butyl hypohalites in alcohol to the 2-alkoxy-6-methyl-3,4-dihydro-2*H*-pyrans **3a** and **3b** yielded mixtures of products **6a–d** and **7a–d** that are derived from 1,2- and 1,4-addition, respectively (see Table III). The 1,2-addition products **6a–d** were mixtures of cis and trans isomers. The ratio and the

Table III. *tert*-Butyl Hypohalite Addition to 2-Alkoxy-6-methyl-3,4-dihydro-2*H*-pyrans

Dihydropyran	Hypohalite/solvent	Products: 1,2-Addition (yield)[a]	Products: 1,4-Addition (yield)[a]
 **3a**	*t*-BuOCl/MeOH[b]	 **6a** (39%)	 **7a** (40%)
 **3a**	*t*-BuOBr/MeOH[c]	 **6b** (62%)	 **7b** (21%)
 **3b**	*t*-BuOCl/EtOH[b]	 **6c** (36%)	 **7c** (53%)
 **3b**	*t*-BuOBr/EtOH[c]	 **6d** (47%)	 **7d** (39%)

[a] Isolated by column chromatography. [b] Reaction conditions are described in the Experimental Section for the addition of *tert*-butyl hypochlorite to 2-methoxy-6-methyl-3,4-dihydro-2*H*-pyran (**3a**). [c] Reaction conditions are described in the Experimental Section for the addition of *tert*-butyl hypobromite to 2-methoxy-6-methyl-3,4-dihydro-2*H*-pyran (**3a**).



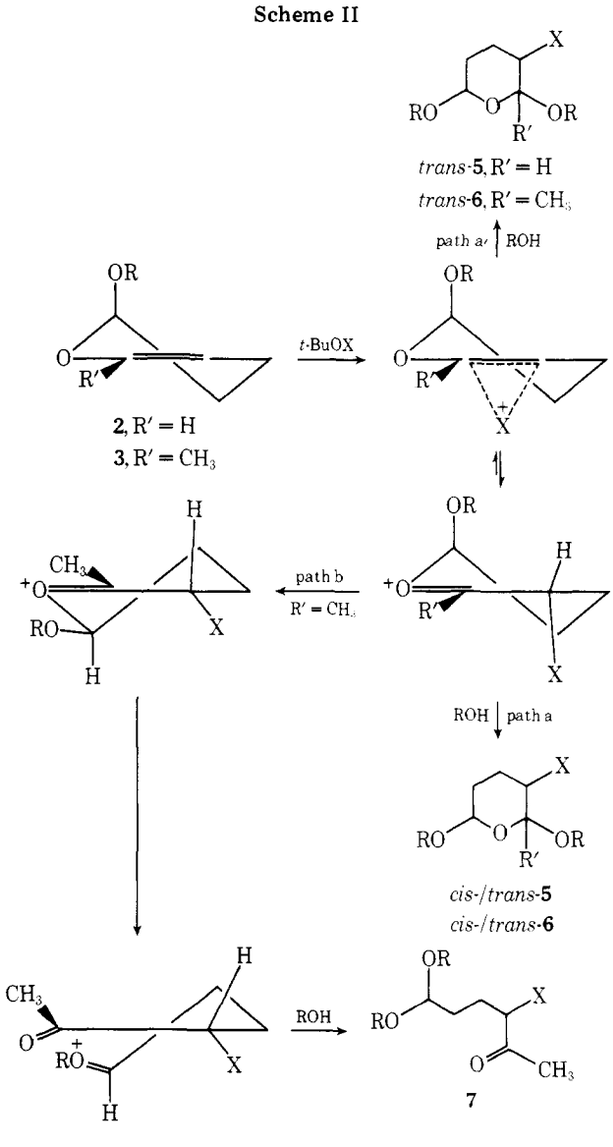
stereochemistry of the products were similar to those obtained with the 2-alkoxy-3,4-dihydro-2*H*-pyrans (**2a** and **2b**). That is, the stereochemistry about the original anomeric center was preserved and the cis and trans isomers are diastereomers at the new anomeric center.

The ratio of the 1,2- vs. 1,4-addition products in the reaction of *tert*-butyl hypochlorite with dihydropyrans **3a** and **3b** was found not to be significantly affected by the temperature of the reaction. For example, with **3a** the ratio of 1,2- to 1,4-addition was ca. 50:50 for −50, −15, and 20 °C. For **3b**, this ratio was the same at the low temperature and ca. 40:60 at −15 and 20 °C. At temperatures below −15 °C competing side products derived from free-radical reactions[5d,9d] became important. One such product that was characterized was the allylic chlorinated product 2-alkoxy-6-chloromethyl-3,4-dihydro-2*H*-pyran (**8**).[14]

The addition of *tert*-butyl hypobromite to these pyrans **3a** and **3b**, however, had to be performed at −60 °C to prevent serious competition from free-radical reactions. Even the use of free-radical inhibitors or exclusion of light did not effectively suppress these reactions. The ratio of 1,2- vs. 1,4-additions at this temperature was ca. 75:25 for **3a** and 60:40 for **3b**.

We interpret these results and the differences between the addition of *tert*-butyl hypohalites to 2-alkoxy-3,4-dihydro-2*H*-pyrans (**2a** and **2b**) and 2-alkoxy-6-methyl-3,4-dihydro-2*H*-pyrans (**3a** and **3b**) in the following manner (see Scheme II). As was discussed earlier, the presence of the bulky axial

Scheme II



alkoxy group at the anomeric carbon would result in the preferential formation of the trans halonium ion and subsequently the oxocarbonium ion. When X is chlorine, path a, via the oxocarbonium ion, would dominate as the route to cis and trans 1,2-addition products. When X is bromine, path a', via the bromonium ion intermediate, would become competitive yielding trans 1,2-addition products. However, when R' is a group that can stabilize the oxocarbonium ion intermediate, such as methyl, a new course (path b) becomes important. This stabilization evidently allows time for the conformational change that enables participation (synchronous assistance)[15] of the 2-alkoxy group that ultimately yields the 1,4-addition product **7**.

Although the sine qua non for the formation of the 1,4-addition product from these dihydropyran systems is the presence of the 6-methyl group, it is the unique synergistic effect of the 6-alkyl group coupled with the 2-alkoxy group that diverts the normal course of the addition reaction.

Experimental Section[16]

General Comments. The 2-alkoxy-3,4-dihydro-2*H*-pyrans (**2a, 2b**) and the 2-alkoxy-6-methyl-3,4-dihydro-2*H*-pyrans (**3a, 3b**) were prepared by a method previously described.[17] Pyran **1** and **2b** are available from Aldrich Chemical Co. The *tert*-butyl hypochlorite and *tert*-butyl hypobromite were prepared,[5a,c] dried over $CaCl_2$, and stored in the dark below 0 °C until use. All solvents were reagent grade. All reactions were performed in dry glassware under a static nitrogen atmosphere. The reaction temperature was monitored with an internal thermometer. Gas chromatography (GLC) analyses were performed on 120 × 0.4 cm (i.d.) glass columns packed with 5% Carbowax 20M supported on 60–80 mesh Chromosorb W (AW, DMCS). Distillations were accomplished with short-path or Kügelrohr apparatus; all boiling points are uncorrected. Column chromatography was performed on 60–100 mesh Floridin magnesium silicate (Florisil) columns by eluting with petroleum ether and petroleum ether–Et_2O. The assigned structure of each product (or mixture) was consistent with the spectral data and composition analysis (±0.4% for C, H, X). The latter (**4a–k, 5a–d, 6a–d, 7a–d**) were submitted to the Editor. Significant data on all new compounds are included in the Experimental Section. A representative selection of experiments is described to illustrate these reactions.

3-Chloro-2-*n*-butoxytetrahydropyran (4e). To a stirred and cooled (−50 °C) solution of 3,4-dihydro-2*H*-pyran (**1**, 2.91 g, 34.6 mmol) in 1-butanol (35 ml) was slowly added (ca. 10 min) 3.80 g (35.0 mmol) of *tert*-butyl hypochlorite, during which time the exothermic reaction caused the temperature to rise to −40 °C. After 5 min the cooling bath (dry ice–ethanol) was removed and the reaction mixture allowed to warm to 0 °C and then partitioned between ice–water and petroleum ether. The organic layer was separated, washed with water (four times) and brine, and then dried ($MgSO_4$). Removal of solvent in vacuo afforded 6.37 g of a pale yellow oil. Analysis (GLC) of the oil indicated a 15:85 mixture of cis and trans isomers of **4e** that after distillation (bp 103–108 °C, 14 mm) and column chromatography afforded 4.51 g (66%) of **4e** as a colorless oil: bp 106–108 °C (14 mm); IR (film) 2970, 2940, 2880, 1460, 1440, 1200, 1135, 1095, 1070, 1030, 870, 730 cm^{-1}; NMR (100 MHz, CCl_4) δ 4.62 (0.17 H, d, J = 3.2 Hz, equatorial anomeric proton, cis isomer), 4.46 (0.83 H, d, J = 3.5 Hz, equatorial anomeric proton, trans isomer), 4.02–3.25 (5 H, m), 2.45–1.20 (8 H, complex m), 0.93 (3 H, perturbed t, J = 7.0 Hz); mass spectrum *m/e* (rel intensity) 194 (M^+, 4), 192 (M^+, 13), 138 (3), 136 (8), 121 (13), 119 (31), 92 (12), 90 (40), 83 (15), 64 (9), 62 (32), 57 (57), 55 (100), 41 (71), 29 (76).

3-Bromo-2-*n*-butoxytetrahydropyran (4f). To a stirred and cooled (−50 °C) solution of 3,4-dihydro-2*H*-pyran (**1**, 316 mg, 3.76 mmol) and dihydroquinone (1–2 mg, free-radical inhibitor) in 1-butanol (7 ml) was slowly added (ca. 10 min) 688 mg (4.50 mmol) of *tert*-butyl hypobromite, during which time the exothermic reaction caused the temperature to rise to −40 °C. After 5 min, the cooling bath (dry ice–ethanol) was removed and the reaction mixture allowed to warm to 0 °C. Normal workup, as described above for **4e**, afforded a pale orange oil. Analysis (GLC) of the orange oil indicated a 10:90 mixture of cis and trans isomers of **4f** that after column chromatography afforded 715 mg (77%) of **4f** as a colorless oil: IR (film) 2970, 2940, 2880, 1460, 1440, 1200, 1130, 1090, 1070, 1025, 870, 730 cm^{-1}; NMR (100 MHz, CCl_4) δ 4.60 (0.10 H, d, J = 3.1 Hz, equatorial anomeric proton, cis isomer), 4.49 (0.90 H, d, J = 3.6 Hz, equatorial anomeric proton, trans isomer), 4.07–3.25 (5 H, complex m), 2.55–2.15 (1 H, m), 2.15–1.70 (2 H, m), 1.70–1.20 (5 H, m), 0.93 (3 H, perturbed t, J = 7.0 Hz); mass spectrum *m/e* (rel intensity) 238 (M^+, 29), 236 (M^+, 30), 182 (5), 180 (5), 165 (48), 163 (49), 136 (65), 134 (67), 108 (26), 106 (26), 83 (16), 73 (17), 57 (57), 55 (100), 41 (33), 29 (34).

3-Chloro-2-acetoxytetrahydropyran (4j). To a stirred and cooled (10 °C) solution of 3,4-dihydro-2*H*-pyran (**1**, 3.36 g, 40.0 mmol) in glacial acetic acid (35 ml) was slowly added (ca. 10 min) 4.44 g (40.9 mmol) of *tert*-butyl hypochlorite, during which time the exothermic reaction caused the temperature to rise to 20 °C. After 10 min the reaction mixture was worked up, as described above for **4e**, and afforded 6.59 g of a pale yellow oil. Analysis (GLC) of the oil indicated a 32:68 mixture of cis and trans isomers of **4j** that after distillation afforded 5.95 g (85%) of **4j** as a colorless oil: bp 126–128 °C (18 mm); IR (film) 2970, 2900, 2870, 1755, 1440, 1230, 1140, 1120, 1070, 1040, 1020, 950, 870, 770, 740 cm^{-1}; NMR (100 MHz, CCl_4) δ 5.98 (0.32 H, d, J = 3.2 Hz, equatorial anomeric proton, cis isomer), 5.63 (0.68 H, d, J = 4.9 Hz, equatorial anomeric proton, trans isomer), 4.13–3.48 (3 H, m), 2.50–1.30 (4 H, m), on which is superimposed two singlets at 2.09 (0.96 H, s, cis isomer) and 2.05 (2.04 H, s, trans isomer); mass spectrum *m/e* (rel intensity) 180 (M^+, 1), 178 (M^+, 5), 138 (4), 136 (18), 121 (10), 119 (44), 92 (8), 90 (25), 83 (22), 64 (10), 62 (33), 55 (100), 43 (53), 41 (75), 39 (65), 29 (32), 27 (46).

3-Chloro-2,6-dimethoxytetrahydropyran (5a). To a stirred and cooled (−55 °C) solution of 2-methoxy-3,4-dihydro-2*H*-pyran (**2a**, 1.25 g, 11.0 mmol) in methanol (30 ml) was slowly added (ca. 5 min) 1.30 g (12.0 mmol) of *tert*-butyl hypochlorite, during which time the exothermic reaction caused the temperature to rise to −50 °C. After 5 min the cooling bath (dry ice–2-propanol) was removed and the reaction mixture allowed to warm to 0 °C. Normal workup, as described above for **4e**, afforded 1.30 g of a yellow oil. Analysis (GLC) of the oil indicated one major peak, which on subsequent NMR analysis suggested ca. 50:50 mixture of diastereomers of **5a**, that after column chromatography afforded 1.21 g (61%) of **5a** as a pale yellow oil: IR (film) 2980, 2950, 2850, 1450, 1390, 1220, 1200, 1160, 1120, 1060, 1010, 940, 910, 790 cm^{-1}; NMR (100 MHz, CCl_4) δ 4.71 (0.5 H, t, J = 3.5 Hz, equatorial anomeric proton at C-6), 4.56 (0.5 H, d, J = 6.0 Hz, anomeric proton at C-2), 4.48 (0.5 H, t, J = 3.5 Hz, equatorial anomeric proton at C-6), 4.33 (0.5 H, d, J = 5.7 Hz, anomeric proton at C-2), 3.83–3.50 (1 H, m), 3.46 (1.5 H, s), 3.43 (1.5 H, s), 3.41 (1.5 H, s), 3.39 (1.5 H, s), 2.42–1.45 (4 H, m); mass spectrum *m/e* (rel intensity) 181 (1), 179 (2), 151 (4), 149 (12), 122 (6), 120 (18), 107 (4), 105 (11), 94 (14), 92 (39), 75 (15), 71 (24), 58 (100), 43 (11), 41 (15).

3-Bromo-2,6-dimethoxytetrahydropyran (5b). To a stirred and cooled (−60 °C) solution of 2-methoxy-3,4-dihydro-2*H*-pyran (**2a**, 660 mg, 5.79 mmol) in methanol (15 ml) was slowly added (ca. 5 min) 1.07 g (7.0 mmol) of *tert*-butyl hypobromite, during which time the exothermic reaction caused the temperature to rise to −55 °C. After 5 min the cooling bath (dry ice–2-propanol) was removed and the reaction mixture allowed to warm to 0 °C. Normal workup, as described above for **4e**, afforded 1.23 g of a yellow oil. Analysis (GLC) of the oil indicated one major peak, which on subsequent NMR analysis indicated ca. 40:60 mixture of diastereomers of **5b**, that after column chromatography afforded 1.00 g (76%) of **5b** as a pale yellow oil: IR (film) 2970, 2935, 2910, 2820, 1440, 1375, 1225, 1170, 1120, 1050, 1010, 950, 730 cm^{-1}; NMR (60 MHz, CCl_4) δ 4.79–4.36 (2 H, overlapping triplets and doublets, equatorial anomeric protons at C-6 and anomeric protons at C-2), 3.94–3.61 (1 H, m), 3.46 (1.2 H, s), 3.42 (1.8 H, s), 3.40 (1.8 H, s), 3.37 (1.2 H, s). 2.42–1.15 (4 H, m); mass spectrum *m/e* (rel intensity) 225 (1), 223 (1), 195 (15), 193 (15), 166 (30), 164 (32), 151 (10), 149 (10), 138 (22), 136 (22), 118 (10), 113 (7), 85 (40), 71 (26), 58 (100), 45 (11), 43 (13), 41 (15).

Reaction of 2-Methoxy-6-methyl-3,4-dihydro-2*H*-pyran (3a) with *tert*-Butyl Hypochlorite. To a stirred solution (20 °C) of 2-methoxy-6-methyl-3,4-dihydro-2*H*-pyran (**3a**, 5.78 g, 45.2 mmol) in methanol (57 ml) was slowly added (ca. 20 min) 5.00 g (47.0 mmol) of *tert*-butyl hypochlorite, during which time the exothermic reaction caused the temperature to rise to 25 °C. After 10 min the reaction mixture was worked up, as described above for **4e**, and afforded 8.11 g of a yellow oil. Analysis (GLC) of the oil indicated a 49:51 mixture of 1,2-addition product **6a** and 1,4-addition product **7a**. Careful column chromatography afforded 3.42 g (39%) of **6a** (NMR analysis indicated ca. 33:67 mixture of diastereomers that are partially resolved by GLC) as a pale yellow oil and 3.56 g (40%) of **7a** as a colorless, viscous oil.

3-Chloro-2,6-dimethoxy-2-methyltetrahydropyran (6a). IR (film) 2970, 2920, 2810, 1450, 1380, 1220, 1210, 1185, 1115, 1065, 1015, 990, 980, 960, 900, 865, 810 cm^{-1}; NMR (100 MHz, CCl_4) δ 4.56 (1 H, t, J = 3.8 Hz, equatorial anomeric proton), 4.00–3.85 (1 H, m, two overlapping triplets, J = ca. 4 Hz), 3.41 (3 H, s), 3.30 (1 H, s), 3.28 (2

H, s), 2.72–2.30 (1 H, m), 2.30–1.50 (3 H, complex m), 1.41 (1 H, s), 1.36 (2 H, s); mass spectrum *m/e* (rel intensity) 195 (0.25), 193 (0.75), 181 (0.5), 179 (1.5), 165 (2.7), 163 (8), 127 (2.6), 122 (1.7), 121 (2.5), 120 (6), 119 (7), 108 (8), 106 (25), 91 (12), 71 (41), 58 (100), 43 (31), 41 (14).

3-Chloro-6,6-dimethoxy-2-hexanone (7a). IR (film) 2950, 2840, 1722, 1440, 1390, 1360, 1125, 1070, 915 cm^{-1}; NMR (100 MHz, CCl_4) δ two overlapping triplets at 4.38 (1 H, t, J = 5.5 Hz) and 4.17 (1 H, t, J = 7.3 Hz), 3.24 (6 H, s), 2.24 (3 H, s), 2.00–1.55 (4 H, complex m); mass spectrum *m/e* (rel intensity) 195 (0.1), 193 (0.3), 165 (2), 163 (6), 127 (4), 85 (2), 75 (100), 71 (86), 58 (48), 47 (13), 43 (49), 41 (18), 31 (12).

Reaction of 2-Methoxy-6-methyl-3,4-dihydro-2*H*-pyran (3a) with *tert*-Butyl Hypobromite. To a stirred and cooled (−60 °C) solution of 2-methoxy-6-methyl-3,4-dihydro-2*H*-pyran (**3a**, 358 mg, 2.80 mmol) in methanol (8 ml) was slowly added (ca. 5 min) 536 mg (3.40 mmol) of *tert*-butyl hypobromite, during which time the exothermic reaction caused the temperature to rise to −55 °C. After 5 min the cooling bath (dry ice–2-propanol) was removed and the reaction mixture allowed to warm to 0 °C. Normal workup, as described above for **4e**, afforded 647 mg of a yellow oil. Analysis (GLC) of the oil indicated a 76:24 mixture of 1,2-addition product **6b** and 1,4-addition product **7b**. Careful column chromatography afforded 418 mg (62%) of **6b** (NMR analysis indicated ca. 40:60 mixture of diastereomers) as a pale yellow oil and 138 mg (21%) of **7b** as a colorless, viscous oil.

3-Bromo-2,6-dimethoxy-2-methyltetrahydropyran (6b). IR (film) 2970, 2925, 2810, 1440, 1370, 1210, 1165, 1100, 1055, 1010, 970, 955, 890, 860 cm^{-1}; NMR (60 MHz, CCl_4) δ 4.55 (1 H, t, J = 4 Hz, equatorial anomeric proton), 4.15–3.88 (1 H, m, two overlapping triplets), 3.40 (3 H, s), 3.30 (1.2 H, s), 3.29 (1.8 H, s), 2.84–2.20 (1 H, complex m), 2.20–1.54 (3 H, complex m), 1.46 (1.2 H, s), 1.44 (1.8 H, s); mass spectrum *m/e* (rel intensity) 239 (1), 237 (1), 209 (5), 207 (5), 180 (2), 178 (2), 166 (5), 165 (2), 164 (5), 163 (2), 152 (6), 150 (6), 99 (11), 85 (11), 71 (30), 58 (100), 43 (22).

3-Bromo-6,6-dimethoxy-2-hexanone (7b). IR (film) 2935, 2825, 1715, 1435, 1355, 1120, 1060 cm^{-1}; NMR (100 MHz, CCl_4) δ two overlapping triplets centered at 4.34 (1 H, t, J = 6 Hz) and 4.32 (1 H, t, J = 7 Hz), 3.26 (6 H, s), 2.31 (3 H, s), 2.22–1.82 (2 H, m), 1.82–1.50 (2 H, m); mass spectrum *m/e* (rel intensity) 209 (14), 207 (18), 166 (3), 164 (3), 127 (73), 95 (11), 84 (16), 75 (100), 71 (73), 58 (36), 43 (68), 32 (73), 31 (100).

3-Chloro-2-methoxytetrahydropyran (4a). Bp 73–75 °C (14 mm); NMR (100 MHz, CCl_4) δ 4.52 (0.15 H, d, J = 3.0 Hz, equatorial anomeric proton, cis isomer), 4.38 (0.85 H, d, J = 3.2 Hz, equatorial anomeric proton, trans isomer), 3.93–3.39 (3 H, m), 3.40 (0.45 H, s, cis isomer), 3.36 (2.55 H, s, trans isomer), 2.40–1.05 (4 H, m); mass spectrum *m/e* (rel intensity) 152 (M^+, 2), 150 (M^+, 5), 124 (3), 122 (10), 121 (6), 119 (26), 92 (24), 90 (50), 87 (24), 75 (12), 64 (30), 62 (91), 61 (91), 55 (100), 41 (18), 39 (17).

3-Chloro-2-ethoxytetrahydropyran (4b). Bp 120–122 °C (17 mm); NMR (100 MHz, CCl_4) δ 4.61 (0.15 H, d, J = 3.2 Hz, equatorial anomeric proton, cis isomer), 4.45 (0.85 H, d, J = 3.5 Hz, equatorial anomeric proton, trans isomer), 3.93–3.58 (3 H, m), 3.58–3.28 (2 H, m), 2.49–2.08 (1 H, m), 2.08–1.58 (2 H, m), 1.58–1.09 (1 H, m), two overlapping triplets at 1.25 (0.45 H, t, J = 7.1 Hz, cis isomer) and 1.20 (2.55 H, t, J = 7.1 Hz, trans isomer); mass spectrum *m/e* (rel intensity) 166 (M^+, 2), 164 (M^+, 7), 138 (1), 136 (4), 121 (6), 119 (24), 101 (14), 92 (8), 90 (26), 83 (13), 75 (58), 64 (16), 62 (53), 57 (18), 55 (100), 47 (55), 41 (36), 39 (35), 29 (51), 27 (66).

3-Chloro-2-*n*-propoxytetrahydropyran (4c). Bp 113–115 °C (30 mm); NMR (100 MHz, CCl_4) δ 4.58 (0.15 H, d, J = 3.0 Hz, equatorial anomeric proton, cis isomer), 4.42 (0.85 H, d, J = 3.4 Hz, equatorial anomeric proton, trans isomer), 3.95–3.19 (5 H, complex m), 2.45–1.20 (4 H, complex m) on which is superimposed a hextet at 1.59 (2 H, hextet, J = 7.1 Hz), and two overlapping triplets at 0.98 (0.45 H, t, J = 7.1 Hz) and 0.94 (2.55 H, t, J = 7.1 Hz); mass spectrum *m/e* (rel intensity) 180 (M^+, 21) 178 (M^+, 60), 152 (2), 150 (7), 138 (5), 136 (15), 121 (32), 119 (95), 92 (26), 90 (75), 89 (45), 83 (15), 64 (14), 62 (41), 55 (100), 43 (67), 41 (17).

3-Chloro-2-isopropoxytetrahydropyran (4d). Bp 94–95 °C (20 mm); NMR (100 MHz, CCl_4) δ 4.71 (0.15 H, d, J = 3.5 Hz, equatorial anomeric proton, cis isomer), 4.52 (0.85 H, d, J = 3.7 Hz, equatorial anomeric proton, trans isomer), 4.02–3.60 (3 H, m), 3.58–3.27 (1 H, m), 2.47–2.05 (1 H, m), 2.05–1.59 (2 H, m), 1.59–1.25 (1 H, m), two anisochronous methyl signals at 1.18 (3 H, d, J = 6.2 Hz) and 1.12 (3 H, d, J = 6.2 Hz); mass spectrum *m/e* (rel intensity) 134 (2), 132 (7), 121 (6), 119 (18), 100 (7), 83 (7), 64 (2), 62 (7), 55 (23), 43 (100), 31 (17), 29 (14).

3-Chloro-2-*sec*-butoxytetrahydropyran (4g). Bp 125–127 °C (30 mm); NMR (100 MHz, CCl_4) δ doublets centered at 4.86 and 4.69 (0.1 H, d, J = ca. 3 Hz, equatorial anomeric protons, two cis diastereomers), doublets centered at 4.49 and 4.46 (0.9 H, d, J = 3.6 Hz, equatorial anomeric protons, two trans diastereomers), 3.95–3.30 (4 H, m), 2.45–2.05 (1 H, m), 2.05–1.65 (2 H, m), 1.65–1.25 (3 H, m), two sets of overlapping doublets centered at 1.20 and 1.18 (0.3 H, J = ca. 7 and 6 Hz, two cis diastereomers) and 1.16 and 1.09 (2.7 H, d, J = 6.0 and 6.5 Hz, two trans diastereomers), and at least two overlapping triplets centered at 0.92 and 0.89 (3 H, J = 7.0 Hz); mass spectrum *m/e* (rel intensity) 194 (M^+, 3), 192 (M^+, 10), 179 (0.5), 177 (1.5), 165 (1), 163 (4), 138 (17), 136 (46), 121 (27), 119 (100), 92 (28), 90 (80), 83 (14), 64 (9), 62 (26), 57 (66), 55 (90), 41 (40), 29 (43).

3-Chloro-2-*tert*-butoxytetrahydropyran (4h). Bp 118–122 °C (10 mm); NMR (100 MHz, CCl_4) δ 4.89 (0.15 H, d, J = 3.3 Hz, equatorial anomeric proton, cis isomer), 4.60 (0.85 H, d, J = 4.3 Hz, equatorial anomeric proton, trans isomer), 4.00–3.25 (3 H, m), 2.46–2.06 (1 H, m), 2.06–1.60 (2 H, m), 1.60–1.30 (1 H, m), 1.24 (1.35 H, s, cis isomer), 1.22 (7.65 H, s, trans isomer); mass spectrum *m/e* (rel intensity) 194 (M^+, 0.2), 192 (M^+, 0.8), 179 (0.5), 177 (2), 139 (2), 137 (6), 121 (7), 119 (23), 92 (2), 90 (6), 83 (11), 57 (100), 55 (17), 41 (13).

3-Chloro-2-benzyloxytetrahydropyran (4i). Bp 120–123 °C (1 mm); NMR (100 MHz, CCl_4) δ 7.24 (5 H, apparent s), two overlapping AB systems of the anisochronous benzylic protons centered at 4.70 (0.33 H, d, J = 12.2 Hz) and 4.46 (0.33 H, d, J = 12.2 Hz) for the cis isomer and at 4.68 (0.67 H, d, J = 12.2 Hz) and 4.42 (0.67 H, d, J = 12.2 Hz) for the trans isomer that are superimposed on the equatorial anomeric protons centered at 4.69 (0.33 H, d, J = 3.2 Hz, cis isomer) and 4.53 (0.67 H, d, J = 3.4 Hz, trans isomer), 3.95–3.61 (2 H, m), 3.61–3.30 (1 H, m), 2.48–1.20 (4 H, m); mass spectrum *m/e* (rel intensity) 228 (M^+, 0.4), 226 (M^+, 1.2), 190 (3), 144 (12), 91 (100), 77 (4), 65 (12), 55 (10), 41 (6), 39 (13).

3-Chloro-2-propionoxytetrahydropyran (4k). Bp 126–130 °C (14 mm); IR (film) 1752 cm^{-1}; NMR (100 MHz, CCl_4) δ 6.00 (0.45 H, d, J = 3.0 Hz, equatorial anomeric proton, cis isomer), 5.63 (0.55 H, d, J = 4.9 Hz, equatorial anomeric proton, trans isomer), 4.08–3.43 (3 H, complex m), two overlapping quartets at 2.38 (0.9 H, q, J = 7.3 Hz) and 2.33 (1.1 H, q, J = 7.3 Hz), 2.20–1.40 (4 H, m), two overlapping triplets at 1.18 (1.35 H, t, J = 7.3 Hz, cis isomer) and 1.14 (1.65 H, t, J = 7.3 Hz, trans isomer); mass spectrum *m/e* (rel intensity) 121 (11), 119 (32), 100 (4), 83 (6), 77 (4), 57 (100), 55 (22), 43 (4), 41 (7), 39 (8), 29 (32), 28 (43), 27 (14).

3-Chloro-2,6-diethoxytetrahydropyran (5c). NMR (100 MHz, CCl_4) δ 4.80 (0.6 H, t, J = 3.8 Hz, equatorial anomeric proton at C-6), 4.64 (0.6 H, d, J = 7.0 Hz, anomeric proton at C-2), 4.54 (0.4 H, t, J = ca. 3 Hz, equatorial anomeric proton at C-6), 4.38 (0.4 H, d, J = 6.2 Hz, anomeric proton at C-2), 4.02–3.32 (5 H, complex m), 2.50–1.90 (2 H, m), 1.90–1.40 (2 H, m), two overlapping triplets at 1.21 (4.8 H, t, J = 7.0 Hz) and 1.17 (1.2 H, t, J = 7.1 Hz); mass spectrum *m/e* (rel intensity) 209 (0.3), 207 (1), 165 (3), 163 (9), 137 (2), 136 (2), 135 (6), 134 (7), 108 (8), 106 (26), 99 (8), 93 (2), 91 (8), 85 (8), 80 (5), 78 (15), 72 (100), 57 (17), 47 (13), 45 (8), 44 (50), 43 (23), 41 (16), 29 (28).

3-Bromo-2,6-diethoxytetrahydropyran (5d). NMR (60 MHz, CCl_4) δ two overlapping triplets at 4.85 (0.9 H, t, J = 3.2 Hz, equatorial anomeric proton at C-6) and 4.75 (0.1 H, t, J = ca. 4 Hz, equatorial anomeric proton at C-6) on which is superimposed a doublet at 4.75 (0.9 H, d, J = 6.6 Hz, anomeric proton at C-2), 4.44 (0.1 H, d, J = 6.6 Hz, anomeric proton at C-2), 4.20–3.14 (5 H, complex m), 2.44–2.00 (2 H, m), 1.95–1.52 (2 H, m), two overlapping triplets at 1.25 (0.3 H, t, J = 7.0 Hz) and 1.22 (5.7 H, t, J = 7.2 Hz); mass spectrum *m/e* (rel intensity) 253 (1), 251 (1), 209 (5), 207 (7), 180 (14), 178 (15), 152 (6), 150 (6), 124 (5), 122 (4), 99 (20), 85 (5), 72 (100), 57 (9), 44 (27), 43 (10), 41 (11), 29 (15).

3-Chloro-2,6-diethoxy-2-methyltetrahydropyran (6c). NMR (100 MHz, CCl_4) δ 4.65 (0.5 H, t, J = 3.0 Hz, equatorial anomeric proton), 4.56 (0.5 H, t, J = 3.2 Hz, equatorial anomeric proton), 4.03–3.20 (5 H, m) that includes a quartet at 3.53 (q, J = 7.0 Hz), 2.50–2.22 (1 H, m), 2.22–1.43 (3 H, m), 1.40 (3 H, s), two overlapping triplets at 1.18 (3 H, t, J = 7.0 Hz) and 1.16 (3 H, t, J = 7.0 Hz); mass spectrum *m/e* (rel intensity) 223 (1), 221 (3), 179 (8), 177 (24), 150 (2), 148 (8), 136 (6), 134 (18), 122 (19), 120 (54), 92 (21), 85 (32), 72 (100), 57 (16), 45 (27), 44 (64), 42 (17), 29 (21), 27 (13).

3-Chloro-6,6-diethoxy-2-hexanone (7c). IR (film) 1725 cm^{-1}; NMR (100 MHz, CCl_4) δ 4.42 (1 H, t, J = 4.7 Hz), 4.17 (1 H, q, J = 7.7 and 5.9 Hz), 3.53 (4 H, q, J = 7.0 Hz), 2.26 (3 H, s), 2.02–1.37 (4 H, m), 1.15 (6 H, t, J = 7.0 Hz); mass spectrum *m/e* (rel intensity) 179 (9), 177 (27), 103 (100), 85 (82), 75 (46), 72 (33), 57 (33), 47 (73), 44 (33), 43 (90), 29 (45), 27 (23).

3-Bromo-2,6-diethoxy-2-methyltetrahydropyran (6d). NMR (60 MHz, CCl_4) δ two overlapping triplets at 4.64 (0.6 H, t, J = ca. 5 Hz) and 4.59 (0.4 H, t, J = ca. 4 Hz), 4.20–3.10 (5 H, complex m) that

includes a quartet at 3.58 (q, J = 7 Hz), 2.75–2.20 (1 H, m), 2.20–1.57 (3 H, m), 1.48 (1.2 H, s), 1.46 (1.8 H, s), 1.19 (6 H, t, J = 7 Hz); mass spectrum m/e (rel intensity) 267 (1), 265 (1), 253 (1), 251 (1), 223 (12), 221 (12), 180 (10), 178 (10), 166 (10), 164 (8), 141 (15), 113 (12), 85 (26), 72 (100), 57 (18), 43 (49), 29 (16).

3-Bromo-6,6-diethoxy-2-hexanone (7d). IR (film) 1718 cm^{-1}; NMR (60 MHz, CCl_4) δ two overlapping triplets at 4.38 (1 H, t, J = 5 Hz) and 4.32 (1 H, t, J = 7 Hz), 3.88–3.08 (4 H, m), 2.30 (3 H, s), 2.24–1.38 (4 H, complex m), 1.18 (6 H, t, J = 7 Hz); mass spectrum m/e (rel intensity) 268 (M^+, 1), 266 (M^+, 1), 223 (30), 221 (32), 180 (3), 178 (3), 166 (2), 164 (2), 151 (3), 149 (3), 113 (11), 103 (100), 85 (58), 75 (28), 72 (28), 57 (17), 47 (26), 43 (47), 29 (12).

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Registry No.—**1**, 110-87-2; **2a**, 4454-05-1; **2b**, 103-75-3; **3a**, 28194-35-6; **3b**, 52438-71-8; *cis*-**4a**, 6559-29-1; *trans*-**4a**, 6559-30-4; *cis*-**4b**, 6559-31-5; *trans*-**4b**, 6559-32-6; *cis*-**4c**, 61092-36-2; *trans*-**4c**, 61092-37-3; *cis*-**4d**, 61092-38-4; *trans*-**4d**, 61092-39-5; *cis*-**4e**, 61092-40-8; *trans*-**4e**, 61092-41-9; *cis*-**4f**, 55162-86-2; *trans*-**4f**, 61092-42-0; *cis*-(*R**)-**4g**, 61092-43-1; *cis*-(*S**)-**4g**, 61092-44-2; *trans*-(*R**)-**4g**, 61092-45-3; *trans*-(*S**)-**4g**, 61092-46-4; *cis*-**4h**, 61092-47-5; *trans*-**4h**, 61092-48-6; *cis*-**4i**, 61092-49-7; *trans*-**4i**, 61092-50-0; *cis*-**4j**, 14750-43-7; *trans*-**4j**, 14750-42-6; *cis*-**4k**, 61092-51-1; *trans*-**4k**, 61092-52-2; *cis*-**5a**, 61092-53-3; *trans*-**5a**, 61092-54-4; *cis*-**5b**, 38017-14-0; *trans*-**5b**, 61092-55-5; *cis*-**5c**, 61092-56-6; *trans*-**5c**, 61092-57-7; *cis*-**5d**, 61092-58-8; *trans*-**5d**, 61092-59-9; *cis*-**6a**, 61092-60-2; *trans*-**6a**, 61092-61-3; *cis*-**6b**, 61092-62-4; *trans*-**6b**, 61092-63-5; *cis*-**6c**, 61092-64-6; *trans*-**6c**, 61092-65-7; *cis*-**6d**, 61092-66-8; *trans*-**6d**, 61092-67-9; **7a**, 61092-68-0; **7b**, 61092-69-1; **7c**, 61092-70-4; **7d**, 61092-71-5; **8c**, 61092-72-6; *t*-BuOCl, 507-40-4; *t*-BuOBr, 1611-82-1; 2-chloro-1,1-dibutoxyethane, 17437-27-3; butyl vinyl ether, 111-34-2.

References and Notes

(1) Part 5 in the series "The Chemistry of 2-Alkoxy-3,4-dihydro-2*H*-pyrans". For part 4 see A. J. Duggan and S. S. Hall, *J. Org. Chem.*, **40**, 2238 (1975).

(2) Taken in part from the Ph.D. Thesis of A.J.D. that was submitted to the Graduate School, Rutgers University, Oct 1974.

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(4) (a) Unpublished observations in our laboratory, S. S. Hall, A. J. Duggan, and M. Mackaravitz, on the relative reactivity of tetracyanoethylene with pyrans **2** and **3**; (b) A competitive rate study, using *tert*-butyl hypochlorite in methanol, designed to measure the effect of substituents on the reactivity of the 3,4-dihydro-2*H*-pyran ring system will be published.

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(11) Since many of the corresponding bromine derivatives of Table I have been prepared with *N*-bromophthalimide in hydroxylic solvents [E. M. Gaydou, *Tetrahedron Lett.*, 4055 (1972)] only a few reactions using *tert*-butyl hypobromite were pursued.

(12) 2-Chloro-1,1-di-*n*-butoxyethane from *n*-butyl vinyl ether and *tert*-butyl hypochlorite in 1-butanol at −15 °C as a colorless oil after distillation (90% yield): bp 120 °C (15 mm); NMR (100 MHz, CCl_4) δ 4.49 (1 H, t, J = 5.6 Hz), 3.48 (4 H, q, J = 6.3 Hz) on which is superimposed a doublet at 3.38 (2 H, d, J = 5.6 Hz), 2.46–1.18 (8 H, m), 0.92 (6 H, perturbed t, J = ca. 7 Hz); mass spectrum m/e (rel intensity) 159 (4), 137 (3), 136 (3), 135 (10), 134 (9), 103 (9), 80 (6), 78 (18), 57 (100), 56 (38), 43 (19), 41 (65), 29 (55).

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(14) 2-Ethoxy-6-chloromethyl-3,4-dihydro-2*H*-pyran (**8c**): IR (film) 1655 cm^{-1}; NMR (100 MHz, CCl_4) δ 4.97–4.86 (1 H, m), 4.54 (1 H, t, J = 3.3 Hz), 4.46 (2 H, s), 3.80 (1 H, d of q, J = 9.8 and 7.3 Hz), 3.46 (1 H, d of q, J = 9.8 and 7.3), 2.55–2.13 (2 H, m), 2.04–1.50 (2 H, m), 1.16 (3 H, t, J = 7.3 Hz); mass spectrum m/e (rel intensity) 178 (M^+, 3), 176 (M^+, 9), 141 (30), 140 (30), 133 (7), 131 (21), 95 (47), 85 (70), 72 (100), 57 (92), 45 (17), 43 (99), 31 (41), 29 (64), 27 (35).

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