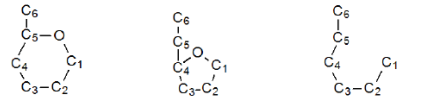
V. An Organization for Carbohydrates That Undergo Radical Cyclization

It is useful in organizing radical cyclization reactions to divide them into groups that have common features. One method for doing this places radicals of similar structure together. Where carbohydrates are concerned, such a plan can be based on the location of the radical center and the multiple bond. A radical center can exist on an atom that is part of the molecular framework (Figure 1) or part of a substituent group. The same possibilities exist for the multiple bond. Cyclization reactions of carbohydrates then naturally divide into the four basic types shown in Figure 2. (A short-hand terminology describing these four types has been proposed[45] and is included in Figure 2.) This division provides the basis for constructing Tables 1-4. In addition to these four tables, two smaller ones are included in recognition of the importance of radical cyclization reactions in the synthesis of nucleosides (Table 5) and carbon-linked disaccharides (Table 6.)



The framework in a typical sugar has one of the three structural types shown above. (A hexose is used as an example.) A framework radical is one centered on a numbered carbon atom, and a framework multiple bond is one involving at least one of these atoms.

Figure 1. Possible carbohydrate frameworks

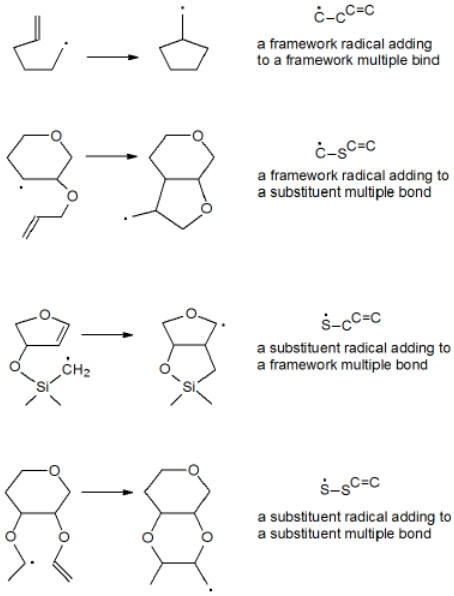


Figure 2. Possible types of cyclization reaction for carbohydrate derivatives

Table 1. Framework Radical Reacting With a Framework Multiple Bond

radical forming substituent	type of multiple bond	number of atoms in the new ring	references
I	$-CH=CHCH_2O-$	5	164, 182
I	$CH_2=CHCH(-)-O-$	5	54, 55
I	$CH_2=CHCH(-)-O-$	6	168
I	$CH_2=CHCH(-)-O-$	7	61, 168
I	$-CH=CHCH(-)-O-$	5	49
I	$-CH=CHCO_2R$	5	60, 64, 68, 69, 85, 92, 164
I	$-CH=CHCO_2Et$	6	91, 92
I	$-CH=CHCO_2Me$	7	61
I	$HC\equiv CCH(-)-O-$	5	171, 172, 185
I	$HC\equiv CCH(-)-O-$	6	186
I	$HC\equiv CCH(-)-O-$	7	61
I	$C_6H_5C\equiv CCH(-)-O-$	6	171, 174
I	$C_6H_5C\equiv CCH(-)-O-$	7	61
I	$Me_2SiC\equiv CC(-)-O-$	5	172
I	$-C\equiv CCO_2Me$	5	172
Br	$-C(-)=CHCO_2R$	5	62, 66, 67, 69, 70, 84, 91, 93
Br	$-CH=CHCO_2Me$	5	87, 89
Br	$-CH(-)-CH=CH-C(-N-)CO$	5	166
MeSC(=S)O–	$CH_2=CHCH_2-$	5	208, 210
MeSC(=S)O–	$CH_2=CCH(-)-O-$	6	22
MeSC(=S)O–	$CH_2=CHCH=CH-$	5	207
MeSC(=S)O–	$-CH=CH-O-$	5	210

Table 1. Framework Radical Reacting With a Framework Multiple Bond (Continued)

radical forming substituent	type of multiple bond	number of atoms in the new ring	references
MeSC(=S)O–	–CH=CHCO$_2$Me	5	210
C$_6$H$_5$OC(=S)O–	CH$_2$=CCH–O–	5	22, 201
C$_6$H$_5$OC(=S)O–	CH$_2$=CCH–O–	6	22, 201
C$_6$H$_5$OC(=S)O–	HC≡CCH–O–	5	178, 181
C$_6$H$_5$OC(=S)O–	HC≡CCH–O–	6	179, 180, 219
C$_6$H$_5$OC(=S)O–	C$_6$H$_5$C≡CCH–	6	175, 176
ImC(=S)O–	CH$_2$=CHCH–O–	5	51, 160, 213
ImC(=S)O–	–OCH=CH–	5	51, 160, 213
ImC(=S)O–	HC≡CCH–O–	5	181
	–CH=CHCO$_2$Me	5	57, 63, 65, 83
	–CH=CHCO$_2$R	5	70, 89
	–CH=CHCO$_2$Me	6	88
	HC≡CCH$_2$–	5	202
	–CH=CCO$_2$*t*-Bu	6	86
	–CH=CHCH=CH$_2$	5	207
C$_6$H$_5$S–	CH$_2$=CHCH–O–	5	158
C$_6$H$_5$S–	CH$_2$=CHCH$_2$–	6	158

Table 1. Framework Radical Reacting With a Framework Multiple Bond (Continued)

radical forming substituent	type of multiple bond	number of atoms in the new ring	references
C$_6$H$_5$S–	–C≡CCH–O–	5	158
MeOC$_6$H$_4$Te–	–CH=CHCO$_2$Et	5	77
H$_2$C=C–	–CH=CHCO$_2$R	5	75, 76
HC≡C–	–CH=CHCH–O–	6	166
HC≡C–	CH$_2$=CHCO–	6	22
HC≡C–	CH$_2$=CHCH–O–	6	196, 201
HC≡C–	–CH=CHCO$_2$Me	7	61

Table 2. Framework Radical Reacting With a Substituent Multiple Bond

radical forming substituent	type of multiple bond	number of atoms in the new ring	references
I	$CH_2{=}C(\mathrm{CH}){-}O{-}$	5	5, 136, 144, 189
I	$CH_2{=}C(\mathrm{CH}){-}O{-}$	6	206
I	$CH_2{=}CHCH_2O{-}$	6	5, 152
I	$CH_2{=}CHCH_2{-}$	6	204
I	$Me_3SiCH{=}C(\mathrm{CH}){-}O{-}$	5	189
I	$CH_2{=}C(\mathrm{SiO})$	5	114
I	$(CH_3)_3CCH{=}CHCH_2O{-}$	5	9
I	$C_6H_5CH{=}CHCH_2O{-}$	5	9, 144, 169, 170
I	$-CH{=}CHCO_2Et$	4	27
I	$-CH{=}CHCO_2Et$	5	91
I	$-CH{=}CHCO_2Et$	6	60, 91
I	$-CH{=}CHCO_2Et$	5 + 6	82
I	$-CH{=}CHCO_2-$	5	112
I	$-CH{=}CHC(=O)NH-$	6	96, 97, 99, 100
I	$-CH{=}CHC(\mathrm{CH}){=}CHC(=O)NH-$	5	107
I	$HC{\equiv}CCH_2O{-}$	5	5, 152
I	$C_6H_5C{\equiv}CCH_2{-}$	6	152
I	$Me_3SiC{\equiv}C(\mathrm{CH}){-}O{-}$	5	177, 189
I	$-C{\equiv}CCH_2O{-}$	5	152
Br	$CH_2{=}CHCH_2O{-}$	5	143, 144, 145, 149
Br	$CH_2{=}CHCH_2{-}$	6	203, 206, 209
Br	$CH_2{=}CHC(Me)_2O{-}$	5	148
Br	$CH_2{=}C(\mathrm{SiO})$	5 + 6	123

Table 2. Framework Radical Reacting With a Substituent Multiple Bond (Continued)

radical forming substituent	type of multiple bond	number of atoms in the new ring	references
Br	$-CH=\underset{\displaystyle CO_2-}{\overset{|}{C}}H-$	5	143
Br	$-CH=CHCO_2Et$	5	27
Br	$-CH=CHCO_2R$	6	27, 203
Br	$-CH=CHCO_2Et$	7	27
Br	$-\underset{\displaystyle CHCO_2Me}{\overset{|}{C}}=CH-$	5	84
Br	$HC\equiv CCH_2O-$	5	143, 148, 151
Br	$HC\equiv CCH_2-$	6	143, 151
Br	$-C\equiv CCH_2O-$	5	143
Br	$-C\equiv CCHO$	5	109
Br	$-CH=\underset{\displaystyle CHC(=O)NH-}{\overset{|}{C}}-CH=CH-$	5	102-106, 108
Br	$-CH=\underset{\displaystyle CC(=O)NH-}{\overset{|}{C}}-CH=$	6	99
C_6H_5Se	$CH_2=\underset{\displaystyle SiO-}{\overset{|}{C}}H-$	5 + 6	11, 12, 113-116
C_6H_5Se	$CH_2=\underset{\displaystyle SiO-}{\overset{|}{C}}H-$	5	115, 116, 119
C_6H_5Se	$CH_2=\underset{\displaystyle SiO-}{\overset{|}{C}}H-$	6	13, 28, 118
C_6H_5Se	$CH_2=\underset{\displaystyle SiO-}{\overset{|}{C}}H-$	8	36
C_6H_5Se	$CH_2=CHCH_2\underset{\displaystyle SiO-}{\overset{|}{C}}H-$	7	24, 28, 29
C_6H_5Se	$CH_2=CHCH_2\underset{\displaystyle SiO-}{\overset{|}{C}}H-$	9	36
C_6H_5Se	$CH_2=\underset{\displaystyle CH-O-}{\overset{|}{C}}H-$	5	161
C_6H_5Se	$CH_2=CHCH_2O-$	6	140, 157
C_6H_5Se	$-\underset{\displaystyle CHCH_2O-}{\overset{|}{C}}=$	5	139, 140
C_6H_5Se	$CH_2=CHCH_2O-$	5	58, 134, 135, 138, 139, 146, 157
C_6H_5Se	$-\underset{\displaystyle CHCH_2NH-}{\overset{|}{C}}=$	5	10

Table 2. Framework Radical Reacting With a Substituent Multiple Bond (Continued)

radical forming substituent	type of multiple bond	number of atoms in the new ring	references
C_6H_5Se	$CH_2{=}CHCH_2NH-$	5	10, 167
C_6H_5Se	$-CH{=}CHCO_2-$	6	140
C_6H_5Se	$-CH{=}CHC(=O)N-$	6	95
C_6H_5Se	$Me_3SiC{\equiv}C\overset{\vert}{S}i-$	5	121
C_6H_5Se	$Me_3SiC{\equiv}CCH_2O-$	5	134
C_6H_5Se	$HC{\equiv}CCH_2O-$	5	58, 134, 135, 138, 139, 146, 157
C_6H_5Se	$RC{\equiv}CCH_2O-$	7	173
$CH_3SC(=O)O$	$CH_2{=}CHCH_2O-$	5	141, 142
$CH_3SC(=O)O$	$CH_2{=}CH\overset{\vert}{C}H-O-$	5	165
$CH_3SC(=O)O$	$HC{\equiv}CCH_2O-$	5	149, 150, 154, 155
$C_6H_5OC(=S)O$	$CH_2{=}CHCH_2O-$	5	157
$C_6H_5OC(=S)O$	$CH_2{=}CH\overset{\vert}{C}{=}N-$	6	220
ImC(=S)O	$-CH{=}CHCO_2-$	5	72, 73, 74
$ArSO_2$	$CH_2{=}CH\overset{\vert}{S}iO-$	5	117
$C_6H_5SO_2$	$CH_2{=}CHCH_2O-$	5	137
$ArSO_2$	$RC{\equiv}C\overset{\vert}{S}iO-$	5	117
$C{\equiv}CH$	$-OCH{=}CHCO_2Et$	5	199
$C{\equiv}CH$	$-OCH{=}CHCO_2Et$	6	199
$C{\equiv}CH$	$-OCH{=}CHCO_2Et$	7	199
$C{\equiv}CH$	$-OCH{=}CHCO_2Et$	8	199
NO_2	$HC{\equiv}CCH_2O-$	5	153
C(=O)H	$-CH{=}C\overset{\vert}{C}C(=O)NH-$	6	101

Table 3. Substituent Radical Reacting With a Framework Multiple Bond

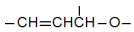
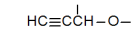
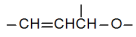
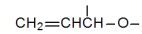
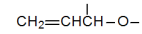
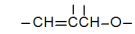
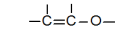
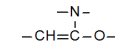
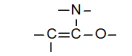
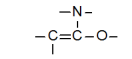
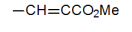
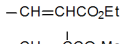
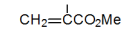
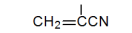
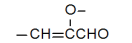
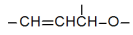
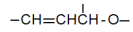
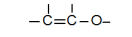
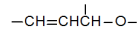
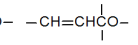
radical forming substituent	type of multiple bond	number of atoms in the new ring	references
I		5	21, 6, 7,109, 159
I		6	6, 7
I		5	185
Br		5	21, 81, 109,124-127, 129,132, 159, 163
Br		6 + 7	184
Br		8	37
Br		6	130
Br		5	124, 133, 183, 211, 212, 214, 218
Br		6	23
Br		5 + 6	23, 215, 217
Br		5	23, 216
Br		5	71
Br		6	7
Br		9	94
Br		9	94
Br		5	109
Cl		5	152, 162
–C≡CH		5	21, 190-193, 195
–C≡CH		5	192, 214
–CH_2C≡CH		5	195
$C_6H_5C(=S)O$–		5	221

Table 4. Substituent Radical Reacting With a Substituent Multiple Bond

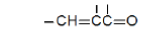
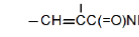
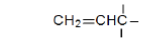
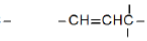
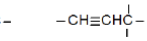
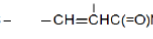
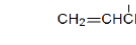
radical forming substituent	type of multiple bond	number of atoms in the new ring	references
I		5	110, 111
I	CH_2=CH–	5	111
I		5	98
I	–CH=CHCO_2–	10	44
Br	CH_2=CHCH_2O–	11	45
Br		6	111, 205
Br	HC≡CCH_2O–	5	156
HC≡C–	CH_2=CHCH_2O–	5 + 6	194
HC≡C–		5	197, 198
HC≡C–		5	197
HC≡C–	$(CH_3)_2$C=CHCH_2O–	5 + 6	194
HC≡C–		6	200
	CH_2=CH	6	147

Table 5. Nucleoside Synthesis

radical forming substituent	type of multiple bond	number of atoms in the new ring	references
Br	–CH=CHCO_2Et	5	80
C_6H_5Se	–CH=CHCO_2Me	5	50
$C_6H_5OC(=S)O$	–CH=CHCO_2Et	5	79

Table 6. Carbon-Linked Saccharides

radical forming substituent	type of multiple bond	number of atoms in the new ring	references
I	$-CH=C(I)CH-O-$	5	9
I	$CH_2=C(I)CO-$	8	33
I	$CF_2=C(I)CO-$	8	31
C_6H_5Se	$CH_2=C(SeC_6H_5)CH-O-$	7	30
C_6H_5Se	$CH_2=C(SeC_6H_5)CH-O-$	8	31, 32, 35, 38, 43
C_6H_5Se	$CH_2=C(SeC_6H_5)CH-O-$	9	38-41, 43, 46
C_6H_5Se	$CH_2=C(SeC_6H_5)CH-O-$	11	38
C_6H_5Se	$CH_2=C(SeC_6H_5)CO-$	8	33, 34
$C_6H_5SO_2$	$CH_2=C(SO_2C_6H_5)CH-O-$	9	42
$C_6H_4NSO_2$	$-SiC(SO_2C_6H_4N)\equiv CCH-O-$	5	117