Synthesis of Chlorinated Telechelic Oligomers. 2. Telomerization of Allyl Acetate with Functional Telogens

B. Améduri and B. Boutevin*

Ecole Nationale Supérieure de Chimie de Montpellier, URA D 11930, 8 Rue Ecole Normale, 34053 Montpellier Cedex, France

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ABSTRACT: The redox telomerization of allyl acetate with functional telogens with a trichloromethyl end group, catalyzed by a ruthenium complex, led to telechelic telomers. The series of reactivity of these telogens about such a taxogen was proposed. We noticed it was essential to use an activated telogen which exhibits an electroattractive group in the α position about the CCl_3 end group to obtain the expected telechelic product in satisfactory yields. The diacetates were changed into diols in excellent yields. The obtained products were characterized by both ^1H and ^{13}C NMR.

Introduction

Telechelic oligomers are very interesting intermediates for many applications[1-4]—binders for propergols, prepolymers for paints, chain extenders, etc.—and usually they lead to well-defined structured polymers (e.g., polyurethanes) when they are monodispersed. Even if several authors[5-7] could prepare such intermediates, but in difficult and long synthesis, others[8,9] succeeded in obtaining diols simply by radical telomerizations of undecylenic derivatives with dithiols.

Furthermore, Harell[5] and Boutevin[9] showed that the monodispersity of such telechelics improved the mechanical properties of polymers. Several publications mention that there are different ways to prepare telechelic oligomers, and the redox telomerization[10-26] seems to be quite adequate.

Moreover, almost no papers[20] about chlorinated diols have been published: previous works mention the obtaining of such halogenated products by double monoaddition of chlorinated functional telogens onto a nonconjugated diene.[20]

Another interesting method in synthesizing telechelic monodispersed oligomers concerns the redox telomerization of a functional taxogen with a functional telogen[10,21-24] (Table I).

We notice that both allyl acetate and allyl alcohol were used by few authors. Even if Dongala[15] mentioned the redox telomerization of both taxogens led to low molecular weight telomers, it is crucial to obtain selectively the monoadduct compound which is telechelic; thus, we used dichlorotris(triphenylphosphine)ruthenium [$RuCl_2(PPh_3)_3$] as catalyst because we showed in previous work[20] it gave better yields in a "clean" reaction and in milder conditions. Furthermore, allyl acetate is twice more reactive than allyl alcohol,[10] and the hydrolysis of a diacetate into a diol is quantitative.

In this paper, we are focusing on the obtaining of telechelic chlorinated monodispersed oligomers prepared from the redox telomerization of allyl acetate with functional telogens with a trichloromethylated end group in the presence of the ruthenium complex.

Discussion

Among the results mentioned in the literature (Table I), we notice that the redox telomerization gave better yields, and still most yields were poor and none of the used telogens exhibited an acetate end group. We thought it would be interesting to use a transfer agent that allowed us to obtain diacetates in good yields, which are easily changed into diols.

(I) Telomerization of Allyl Acetate with Functional Telogens That Exhibit a Trichloromethylated End Group. (A) Synthesis of the Telogens. First we performed the preparation of the telogens: these either were commercially available (Cl_3CCO_2Me) or were prepared by acetylation or telomerization of allyl acetate with different compounds.

(1) The direct addition of acetyl chloride onto 2,2,2-trichloroethanol led quantitatively to 2,2,2-trichloroethyl acetate at room temperature; the scale up of such monoacetate gave the same yield as that obtained on the research scale (where Ac means $COCH_3$):

$$Cl_3CCH_2OH + ClAc \xrightarrow[RT]{} \underset{1}{Cl_3CCH_2OAc}$$

Such a product was characterized by both ^1H and ^{13}C NMR[24] as detailed under Experimental Section.

(2) Synthesis of Novel Functional Telogens by Telomerization of Allyl Acetate with Different $Cl_3C\sim G$ Compounds, with G = OAc, OH, CO_2CH_3. (a) By Radical Telomerization. Belbachir[27] studied the radical telomerization of methyl undecylenate onto chloroform, and he obtained the monoadduct in 24 h at 65 °C with an initial [initiator]/[monomer] molar ratio of about 10%. We carried out the radical addition of allyl acetate with chloroform in almost the same conditions, given in Table II, as follows:

$$H_2C{=}CHCH_2OCOCH_3 + HCCl_3 \longrightarrow$$

$$\underset{2}{Cl_3C(CH_2)_3OCOCH_3} + \underset{3}{Cl_3C(CH_2CH(CH_2))_2H} + \underset{4}{Cl_3C(CH_2CH(CH_2))_3H}$$

(with OAc on each CH$_2$)

We notice a synergism of action of both initiators AIBN and di-*tert*-butyl peroxide since we obtained 75% at 120 °C. Furthermore, the yields in diadduct and triadduct are rather high even for a large excess of telogen, e.g., R_0 = [telogen]/[taxogen] initial molar ratio of 10. Such a phenomenon, which might be strange, is rather normal with reference to the radical telomerization of allyl acetate with methyl trichloroacetate and methyl dichloroacetate carried out by Bertrais et al.[22] (Table I). These authors determined the transfer constants of 1.35 and 0.27,

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Table I
Telomerization of Taxogens with Telogens Leading to Telechelic 1:1 Adducts

taxogen	telogen	exptl conditions	yield, %	ref
allyl acetate	$HP(O)(OEt)_2$	radical telom (Bz_2O_2, 120 °C, 4 h)	50	22
	$HCCl_2CO_2CH_3$	as above	50	22
	$Cl_3CCO_2CH_3$	as above	50	22
	$Cl_3CCO_2CH_3$	redox telom, $FeCl_3$/benzoin (15 h, 140 °C)	60	21
allyl alcohol	$Cl_3CCO_2CH_3$	as above	30	21
	$Cl_3CCH_2CHClCO_2CH_3$	as above	20	21
	$Cl_3CCH_2CHClCN$	as above	0	21
	$Cl_3CCH_2CHClCH_2Cl$	as above	0	21
	$Cl_3CCH_2CHClCH_2OH$	as above	8	21
methyl acrylate	$Cl_3CCH_2CHClCO_2CH_3$	as above	30	21
	$Cl_3CCH_2CHClCN$	as above	0	21
	$Cl_3CCH_2CHClCH_2Cl$	as above	20	21
	$Cl_3CCH_2CHClCH_2OH$	as above	10	21
acrylonitrile	$Cl_3CCH_2CHClCO_2CH_3$	as above	25	21
	$Cl_3CCH_2CHClCN$	as above	0	21
	$Cl_3CCH_2CHClCH_2OH$	as above	10	21
allyl chloride	$Cl_3CCH_2CHClCO_2CH_3$	as above	25	21
	$Cl_3CCH_2CHClCN$	as above	0	21
	$Cl_3CCH_2CHClCH_2Cl$	as above	20	21
methyl methacrylate	$Cl_3CCO_2CH_2CH_3$	10 h, Carius tubes, 80 °C	62	32
methyl vinyl ketone	$Cl_3CCO_2CH_2CH_3$	as above	64	32

Table II
Telomerization of Allyl Acetate with Chloroform (12 h at 120 °C) in the Presence of Different Initiators with the Corresponding Initial C_0 (=[Initiator]/[Monomer]) and R_0 (=[Chloroform]/[Monomer]) Molar Ratio[a]

R_0	initiator	T, °C	C_0, 10^{-2}	overall yield, %	% $n=1$	% $n=2$	% $n=3$
10	AIBN	120	6	23	46	42	12
10	di-*tert*-butyl peroxide [$(tBuO)_2$]	120	3	55	30	42	28
10	AIBN/$(tBuO)_2$	120	3/5	75	44	40	16

[a] The yields of the first three adducts are listed.

respectively, and they showed that for a molar ratio of R_0 = 1.0 $\overline{DP}_n \sim 3.5$ when the dichloroacetic ester was used.

Both the monoadduct and the diadduct were characterized by ^1H and ^{13}C NMR.

Besides the singlet at 2.0×10^{-6} corresponding to the methyl group of the acetate function, the ^1H NMR spectrum of the monoadduct exhibits complex systems AA′BB′X_2 (the X, AA′, and BB′ parts appear at 4.10×10^{-6}, 2.05×10^{-6}, and 2.70×10^{-6}, respectively, because we compared such a spectrum to that of the fluorinated siliconated ether, $(C_2H_5O)_3Si(CH_2)_3O(CH_2)_2C_6F_{13}$, prepared in our laboratory,[28] since we know that CCl_3 and $OCOCH_3$ are more electroattractive than $Si(OEt)_3$ and $O(CH_2)_2C_6F_{13}$, respectively.

$(C_2H_5O)_3SiCH_2CH_2CH_2OCH_2CH_2C_6F_{13}$

δ 0.63 1.67 3.40

$Cl_3CH_2CH_2CH_2OCOCH_3$

δ 2.70 2.05 4.10

We scaled up the radical telomerization of allyl acetate with chloroform with the mixture of both initiators in a Pfaudler vessel (4.5 L), and we obtained the same yield (Table II) as that obtained on the research scale.

(b) By Redox Telomerization. (b.1) Redox Telomerization of Allyl Acetate with α,ω-Bistrichloromethylated End Group Telogens.

$$Cl_3C\sim\sim CCl_3 + H_2C{=}CHCH_2OAc \rightarrow Cl_3C\sim\sim CCl_2CH_2CHClCH_2OAc$$

It is essential that the telomerization be redox catalyzed (with copper or iron salts or the ruthenium complex) since it favors the monoadduct compound.[25,26] These reactions were focused on a series of three di-CCl_3 telogens: 1,1,1,3,3,3-hexachloropropane, hexachloroacetone, and 1,1,1,3,3,3-hexachloro-2,2-difluoropropane.

(b.1.1) Synthesis of Di-CCl_3 Telogens. Telomerization of vinylidene chloride (VDC) was performed with carbon tetrachloride.

The telomerization of VDC with CCl_4 leads directly to the di-CCl_3 telogens (Table III). When such a reaction was initiated by peroxides, high molecular weight telomers were obtained, whereas redox telomerization—except with potassium ferrocyanide or potassium ferricyanide—gave higher adducts in better yields. Furthermore, it is essential, in the case of copper salts, to perform the reaction at a temperature higher than that of the threshold of thermal initiation ($T \geq 120$ °C). These catalysts give the highest yields with a very good selectivity of monoaddition. However, no telomerization was catalyzed by dichlorotris(triphenylphosphine)ruthenium(II) which seems to exhibit very interesting catalytic properties (good yields, milder conditions of use, excellent monoselectivity[13,20,24,30,31]); in this case, we noticed the selective formation of the two first adducts, but the reaction catalyzed by copper salts gave better yields (Table III). Furthermore, we did not observe any synergic effect of both catalysts.

Also, when we used a 2-fold excess or more of VDC about CCl_4, in the presence of $RuCl_2(PPh_3)_3$, we obtained selectively the monoadduct at 30% only, whereas Belbachir[27] obtained 50% using copper salts under the same conditions.

We also performed the telomerization of VDC by changing the catalyst concentration to study both the $\overline{DP}_n$ and the yield. As for Maubert,[32] who investigated the telomerization of methyl acrylate with CCl_4, we showed (Table IV) that the lower the catalyst concentration, the

Table III
Telomerization of Vinylidene Chloride with CCl_4 in the Presence of Different Catalysts or Initiators

R_0	catalyst or initiator	C_0	T, °C	t, h	solvent	obtained isomer	$\overline{DB}_n$	yield	ref
2	$FeCl_2$	0.02	90	15	n-butylamine	$Cl_3CCH_2CCl_3$	1.0	3	37
2	$FeCl_2$	0.02	90	15	2-propanol	$Cl_3C(CH_2CCl_2)_nCl$	3.0–3.5	5	38
2	$CuCl_2$	0.02	90	14	2-propanol	none		0	38
2	$CuCl_2$	0.02	126	15	CH_3CN	$Cl_3CCH_2CCl_3$	1.00	77	39
5	Bz_2O_2	0.02	110	14	none	$Cl_3C(CH_2CCl_2)_nCl$	100	10	27
2	$FeCl_3$/benzoin	0.02/0.02	110	14	CH_3CN	as above	10	10	27
2	$FeCl_36H_2O$/benzoin	as above	110	14	CH_3CN	as above	10	10	27
2	$Fe(CN)_6K_3$/benzoin	as above	110	14	CH_3CN	as above	100	5	27
2	$Fe(CN)_3K_4$/benzoin	as above	110	14	CH_3CN	as above	100	5	27
2	CuCl	0.01	120	14	CH_3CN	as above	1.07	75	27
2	$CuCl_2$	0.01	120	14	CH_3CN	as above	1.09	75	27
2	$CuCl_2{\cdot}4H_2O$	0.01	120	14	CH_3CN	as above	1.11	75	27
2	Cu (ethyl acetonate)	0.01	120	14	CH_3CN	as above	1.30	75	27
2	CuCN	0.01	120	14	CH_3CN	as above	1.34	75	27
1	$RuCl_2(PPh_3)_3$	10^{-3}	120	22	PhH	as above	1.30	37	24
1	$RuCl_2(PPh_3)_3$	10^{-3}	120	22	MeCN	as above	1.25	14	24
1	Cu^+/Cu^{2+}	10^{-2}	120	22	MeCN	as above	1.20	74	24
1	$Cu^+/Cu^{2+}/RuCl_2(PPh_3)_3$	$10^{-2}/5 \times 10^{-3}$	120	22	MeCN	as above	1.12	65	24

Table IV
Influence of the C_0 (=Initial [Catalyst]/[Monomer]) Molar Ratio on the Yield and the Distribution of Adducts for the Telomerization of Vinylidene Chloride with CCl_4 Catalyzed by Copper Salts

C_0	yield, %	% $n = 1$	% $n = 2$	% $n = 3$	% $n \geq 4$
10^{-2}	75	88	11	1	0
10^{-3}	39	52	29	13	6
10^{-4}	6	15	20	18	47
10^{-5}	2	0	2	5	93

Table V
Telomerization of Allyl Acetate with 1,1,1,3,3,3-Hexachloropropane in the Presence of Different Catalysts and under Different Experimental Conditions (*Atmospheric Pressure), t = 24 h, Yields Calculated from GC Analysis

R_0	catalyst	C_0	t, h	T, °C	monoadduct yield, %	diadduct yield, %
0.50*	$FeCl_3$/benzoin	0.030/0.025	14	80	0	0
0.40	$RuCl_2(PPh_3)_3$	0.018	15	100	45	5
0.38	$FeCl_3$/benzoin	0.021/0.020	13	120	53	0
0.38	CuCl	0.031	18	120	15	0
0.38	$CuCl_2$	0.024	24	120	18	0
0.38	$RuCl_2(PPh_3)_3$	0.022	24	120	58	10
0.20	$RuCl_2(PPh_3)_3$	0.020	24	120	55	14

higher the $\overline{DP}_n$ and the lower the yield.

We scaled up the telomerization of VDC with CCl_4 in a Pfaudler vessel (4.5 L) in the presence of CuCl and obtained 75% yield.

(b.1.2) Telomerization of Allyl Acetate with $Cl_3C\sim\sim CCl_3$. (b.1.2.1) With $Cl_3CCH_2CCl_3$. When $Cl_3CCH_2CCl_3$ was used, several experiments were carried out by using different catalysts (Table V). We notice that even with a high monomer amount, the monoadduct was favored and that the ruthenium complex gave the best yields.

(b.1.2.2) With $Cl_3CCH_2CCl_2CH_2CCl_3$. Under these optimal conditions the monoaddition of allyl acetate with 1,1,1,3,3,5,5,5-octachloropentane [using $RuCl_2(PPh_3)_3$; $C_0 = 10^{-2}$, T = 120 °C, and t = 24 h] led to about 25% monoadduct.

(b.1.2.3) With $Cl_3CCOCCl_3$ and $Cl_3CCF_2CCl_3$. In the same way we prepared monoacetates from hexachloroacetone and 1,1,1,3,3,3-hexachloro-2,2-difluoropropane, and we noticed that the ruthenium complex gave the best monoadduct yield when a greater telogen amount was used, compared to previous investigations performed in our laboratory (Table VI).

(b.1.2.4) With CCl_4. Stark[36] mentioned that CCl_4 exhibits a high transfer constant in redox telomerization and such telogen is interesting since its behavior is similar to that of di-CCl_3 telogens

$$CCl_4 + H_2C{=}CHCH_2OAc \rightarrow Cl_3CCH_2CHClCH_2OAc$$

yielding a telomer which can be used as telogen for further telomerizations. We notice that the above reaction led to the best results (with better yields) for experiments carried out at atmospheric pressure in milder conditions, when they were catalyzed by the ruthenium complex.

(b.2) Redox Telomerization of VDC with $Cl_3C\sim\sim G$, where G = OAc, OH, or CO_2CH_3. New telomers/telogens may be prepared from $Cl_3C\sim\sim G$ compounds by addition of vinylidene chloride. Thus, such an obtained telogen exhibits the properties of higher chlorine contents and more longer chain length product. The expected scheme in

$$Cl_3C\sim\sim G + H_2C{=}CCl_2 \xrightarrow{\text{cat.}} Cl_3CCH_2CCl_2\sim\sim G$$

The results are listed in Table VII.

We notice that the $FeCl_3$/benzoin system, which gave interesting previous results,[24,27] did not lead to any product. Furthermore, the ruthenium complex led to poor yields with, yet, an excellent selectivity of monoaddition. Regarding the copper salts, the higher the temperature (up to 140 °C), the higher the yield and the better the selectivity.

$Cl_3C(CH_2)_3OAc$ did not react to yield the expected telomer. This may be because the C–Cl cleavage is not possible due to a lack of activation of CCl_3: the electronegative acetate group is too far away to direct the cleavage. Thus, we tried other more activated telogens: Cl_3CCH_2OAc, $Cl_3CCH_2CHClCH_2OAc$, $Cl_3CCH_2CCl_2CO_2CH_3$, and $Cl_3CCO_2CH_3$.

Table VII shows that the activating group must be located in the α position about CCl_3 to obtain the expected telomer in satisfactory yields.

An unusual cleavage occurs for the $Cl_3CCH_2CCl_2CO_2CH_3$ telogen where the electronegative ester group activates more CCl_2 in α about it than CCl_3, which is too far. Thus, it is not surprising to obtain $Cl_3CCH_2C(Cl,CO_2CH_3)CH_2CCl_3$ instead of $Cl_3CCH_2CCl_2CH_2CCl_2CO_2Me$.

(B) Synthesis of Diacetates. We studied the telomerization of allyl acetate onto the telogens prepared

Table VI
Telomerization of Allyl Acetate with 1,1,1,3,3,3-Hexachloro-2,2-difluoropropane under Different Conditions (Experimental, Nature of Catalyst, Etc.)

R_0	catalyst	C_0, 10^{-2}	t, h	T, °C	monoadduct yield, %	diadduct yield, %	ref
0.8	$CuCl_2$	1.0	48	95	63	17	10
0.8	$CuCl_2$	1.0	24	125	64	0	10
0.4	$CuCl_2$	1.0	48	125	48	32	10
1.6	Cu^+/Cu^{2+}	3.0	24	120	50	5	
0.5	Cu^+/Cu^{2+}	1.6	22	125	51	15	
1.2	$RuCl_2(PPh_3)_3$	0.8	24	115	55	5	
0.4	$FeCl_3$/benzoin	1.0/1.0	24	80	52	0	10
0.4	$FeCl_3$/benzoin	1.0/1.0	24	125	52	27	10

Table VII
Telomerization of Vinylidene Chloride with $Cl_3C\sim G$ Telogens in the Presence of Different Initiators or Catalysts

telogen	R_0	catalyst or initiator	C_0, 10^{-2}	t, h	T, °C	overall yield, %	monoadduct yield, %
$Cl_3C(CH_2)_3OAc$	1.6	Cu^+/Cu^{2+}	1.5	36	140	0	0
	1.6	$RuCl_2(PPh_3)_3$	0.8	20	125	0	0
	1.1	$FeCl_3$/benzoin	1.0/1.0	20	110	0	0
$Cl_3CCH_2CHClCH_2OAc$	5.0	AIBN	5.0	4	80	0	0
	4.6	$(tBuO)_2$	6.6	5	120	0	0
	1.1	AIBN/$(tBuO)_2$	3.5/5.0	5	120	0	0
	1.6	Cu^+/Cu^{2+}	1.0	14	120	0	0
	1.6	$RuCl_2(PPh_3)_3$	0.5	14	115	5	100
	1.4	$FeCl_3$/benzoin	2.0/1.5	20	120	0	0
Cl_3CCH_2OAc	1.6	Cu^+/Cu^{2+}	2.0	30	140	5	100
	1.6	$RuCl_2(PPh_3)_3$	1.0	36	120	10	100
	1.6	$RuCl_2(PPh_3)_3$	1.0	18	130	9	100
	1.6	$FeCl_3$/benzoin	1.5/1.5	20	120	0	0
$Cl_3CCO_2CH_3$	1.6	Cu^+/Cu^{2+}	1.0	20	110	46	72
	1.6	Cu^+/Cu^{2+}	1.0	18	120	58	78
	1.6	Cu^+/Cu^{2+}	1.0	22	130	73	80
	1.6	$RuCl_2(PPh_3)_3$	0.3	11	120	5	100
	1.6	$RuCl_2(PPh_3)_3$	0.6	21	130	8	100
	1.6	$FeCl_3$/benzoin	1.6/1.5	21	110	0	0

Table VIII
Telomerization of Allyl Acetate with Functional Telogens That Exhibit a CCl_3 End Group

telogen	R_0	catalyst or initiator	C_0, 10^{-2}	t, h	T, °C	yield, %	remarks
$Cl_3C(CH_2)_3OAc$	1.2	Cu^+/Cu^{2+}	2.5	24	130	0	
	1.1	$RuCl_2(PPh_3)_3$	1.0	48	120	0	
$Cl_3CCH_2CCl_2CH_2CHClCH_2OAc$	1.5	Cu^+/Cu^{2+}	2.0	24	130	10	
	1.2	$RuCl_2(PPh_3)_3$	0.9	20	110	19	
	1.4	$FeCl_3$/benzoin	1.8/1.8	24	130	5	
$Cl_3CCH_2CCl_2CO_2CH_3$	1.6	Cu^+/Cu^{2+}	1.2	24	125	23	compd B obtained only as above
	1.7	$RuCl_2(PPh_3)_3$	0.6	24	125	35	compd B obtained only as above
$Cl_3CCH_2CHClCH_2OAc$	1.5	Cu^+/Cu^{2+}	1.3	36	120	15	
	1.6	$RuCl_2(PPh_3)_3$	0.5	40	115	45	
Cl_3CCH_2OAc	1.5	Cu^+/Cu^{2+}	1.3	24	125	24	
	1.7	$RuCl_2(PPh_3)_3$	0.4	19	100	56	
	1.5	$FeCl_3$/benzoin	1.2/1.2	24	125	15	
$Cl_3CCOCCl_2CH_2CHClCH_2OAc$	1.5	Cu^+/Cu^{2+}	1.1	26	125	26	
	1.2	$RuCl_2(PPh_3)_3$	1.4	21	115	58	
$Cl_3CCF_2CCl_2CH_2CHClCH_2OAc$	1.4	Cu^+/Cu^{2+}	1.5	24	130	32	
	1.3	$RuCl_2(PPh_3)_3$	1.3	21	115	63	
$Cl_3CCO_2CH_3$	1.5	Cu^+/Cu^{2+}	1.5	24	130	55	
	1.3	$RuCl_2(PPh_3)_3$	0.4	15	105	70	

previously to yield novel diacetates as in the scheme

$$CH_3COOCH_2CH{=}CH_2 + Cl_3C\sim OCOCH_3 \rightarrow CH_3CO_2CH_2CHClCH_2CCl_2\sim OCOCH_3$$

It is essential to perform such a reaction in the selective 1:1 addition; thus, the redox telomerization[25,26,36] will be more adequate. The different telogens used, the conditions of reaction, and the results are listed in Table VIII.

Moreover, the $CCl_2CH_2CHClCH_2OCOCH_3$ group will be observed on each telomer and will be characterized by both ^1H and ^{13}C NMR as given in Table IX.

We notice the interesting AA'XBB' system which gives special multiplet in ^1H NMR and also the absence of the signal of the CCl_3 (90–100 × 10^{-6}) in ^{13}C NMR.

(1) With $Cl_3C(CH_2)_3OAc$ as Telogen. The telomerization of allyl acetate with $Cl_3C(CH_2)_3OAc$ did not lead to any telomer. As for the telomerization of VDC, this telogen does not react because of a lack of activation of the CCl_3 end group. Thus, we decided to increase that activation by using electronegative groups closer to it.

Table IX
^{1}H NMR and ^{13}C NMR Data for $CCl_2CH_2CHClCH_2OCOCH_3$

^{1}H NMR Data
$CCl_2CH^A{}_2CH^BClCH^C{}_2OCOCH^D{}_3$

	hydrogen			
	A	B	C	D
δ	2.9	4.6	4.5	2.0
intensity	2	1	2	3
multiplicity	AA′ multiplet doubled quartet	X multiplet	BB′ multiplet	singlet
	J_{AX} = 7.2 Hz		J_{BX} = 4.5 Hz	
	J_{AX} = 3.5 Hz		J_{BX} = 5.5 Hz	
	$J_{AA'}$ = 15.9 Hz		$J_{BB'}$ = 11.0 Hz	

^{13}C NMR Data
$C^ACl_2C^BH_2C^CHClC^DH_2OC^EOC^FH_3$

	carbon					
	A	B	C	D	E	F
δ	80–90	48–53	53–59	66–68	170	20–21

(2) With $Cl_3CCH_2CCl_2CH_2CHClCH_2OCOCH_3$. The telomerization of allyl acetate with this telogen was carried out in the presence of several catalysts—copper or iron salts and ruthenium complex—and this latter led to the best yields (about 20%) of the telechelic compound $AcOCH_2CHClCH_2CCl_2CH_2CCl_2CH_2CHClCH_2OAc$ (Table VIII). Such a poor yield is not surprising since the central methylene group reduces the electronic effects of the CCl_3 group.

The separation and purification of the diacetate was performed by column chromatography.

(3) With $Cl_3CCH_2CCl_2CO_2CH_3$. A and B compounds were expected to be obtained:

$Cl_3CCH_2CCl_2CO_2CH_3$ → $AcOCH_2CHClCH_2CCl_2CH_2CCl_2CO_2Me$ A

+

$H_2C{=}CHCH_2OAc$ → $CCl_3CH_2CCl(CO_2Me)CH_2CHClCH_2OAc$ B

Usually, the CCl_3 end group is cleaved in redox telomerization but the obtaining of the telomer resulting from the telomerization of allyl acetate with such a telogen occurred by a cleavage of the C–Cl bond of the CCl_2 group as for the telomerization of VDC with such a telogen. This is shown on the ^{13}C NMR spectrum (Figure 1), where we still observe the presence of the signal of the CCl_3 group (at 90–100 × 10^{-6}) and the absence of that of the CCl_2 one (which usually appears in the 80–90 × 10^{-6} range).

Because of another asymmetric carbon linked to the CO_2CH_3 group, such a telomer is composed of two isomers threo and erythro, and we are not surprised to observe on the ^{13}C NMR spectrum all the peaks doubled.

Furthermore, such a clue was confirmed by the doublet of the methylene group in the α position about the CCl_3 one in B (Figure 2) because of the presence of the asymmetric carbon, whereas the ^{1}H NMR spectrum of the A product would have exhibited a singlet only.

The ruthenium complex gave yields better (35%) than that obtained in the presence of copper salts (23%).

(4) With $Cl_3CCH_2CHClCH_2OAc$. This reaction was carried out by Dongala et al.,[11] who obtained about 10% with copper salts ($AcOCH_2CHClCH_2CCl_2CH_2CHClCH_2OAc$). Our investigation, catalyzed by the ruthenium complex, led to about 45%.

In this case, too, the separation and purification of the diacetate were performed by column chromatography.

(5) With Cl_3CCH_2OAc. The telomerization of allyl acetate with 2,2,2-trichloroethyl acetate was mainly performed at 100 °C at atmospheric pressure in the presence of the ruthenium complex and led to about 50–60% telomer (diacetate) after distillation. Such an experiment was scaled up (see Experimental Section) and gave similar results.

However, no telomer was obtained under the same conditions with copper salts, and in the presence of iron salts the yields were low (15–25%).

The ^{1}H NMR spectrum (Figure 3) shows the singlet of the telogen.

The multiplicity sequence (*J* mod) ^{13}C NMR spectrum (Figure 4) exhibits the expected peaks (absence of the CCl_3 group about appearance of the CCl_2 at 86.5 × 10^{-6} and two different chemical shifts for the carbonyl groups of both acetate functions because of different environments).

(6) With $Cl_3CRCCl_2CH_2CHClCH_2OAc$, where R = CO or CF_2. The telomerizations of allyl acetate with such telogens were carried out in Carius tubes by using different catalysts. Similar yields were obtained for both copper salts and ruthenium complex, but the iron salt did not show improvement. However, the fluorinated telomer was obtained in higher yields than those of the ketonated one.

It is interesting to note that, instead of performing stepwise telomerizations, bistelomerizations of allyl acetate onto α,ωbistrichloromethylated end groups were also carried out:

$Cl_3CRCCl_2CH_2CHClCH_2OAc$ C

$Cl_3CRCCl_3 + 2H_2C{=}CHCH_2OAc$ → $R(CCl_2CH_2CHClCH_2OAc)_2$ D

Table X lists the different di-CCl_3 telogens used, the experimental conditions, and the yields in diacetates. We notice that the telogens had to be activated and that the copper in higher concentrations and the longer reaction times in Carius tubes led to satisfactory yields of telechelic products.

(7) With $Cl_3CCO_2CH_3$. This telogen is more activated than the previous ones and therefore gave the best results of the series. Dongala[11] studied such reactant catalyzed by copper salt (yield = 50%).

The addition of this compound onto allyl acetate was carried out in the presence of ruthenium at atmospheric pressure and yielded 70% telechelic product after distillation.

(II) Chemical Change. It is well-known that the acetate end group is easily hydrolyzable. Hugon[10] performed such a reaction by using $AlLiH_4$. However, it is necessary to control this reaction carefully since the reduction of CHCl into CH_2 may occur.

Recently, quantitative hydrolysis of multiacetate was successful.[34] We performed that reaction using KCN in catalytic quantities in methanol as we did previously.[20,24]

We carried out the hydrolysis of $AcOCH_2CCl_2CH_2CHClCH_2OAc$, $AcOCH_2CHClCH_2CCl_2CH_2CHClCH_2OAc$, and $AcOCH_2CHClCH_2CCl_2RCCl_2CH_2CHClCH_2OAc$, where R represents C=O or CF_2 groups, and we obtained quantitatively the diols.

On the expected ^{1}H NMR spectra we notice the absence of the signal at 2 × 10^{-6} and the presence of a broad signal corresponding to the HO group. Thus, the methylene in α of the OH group is less shifted to high fields. In the same way, the ^{13}C NMR spectra reveal the absence of both the methyl group (δ = 20 × 10^{-6}) and the carbonyl group (δ = 169 × 10^{-6}) of the acetate function, and the

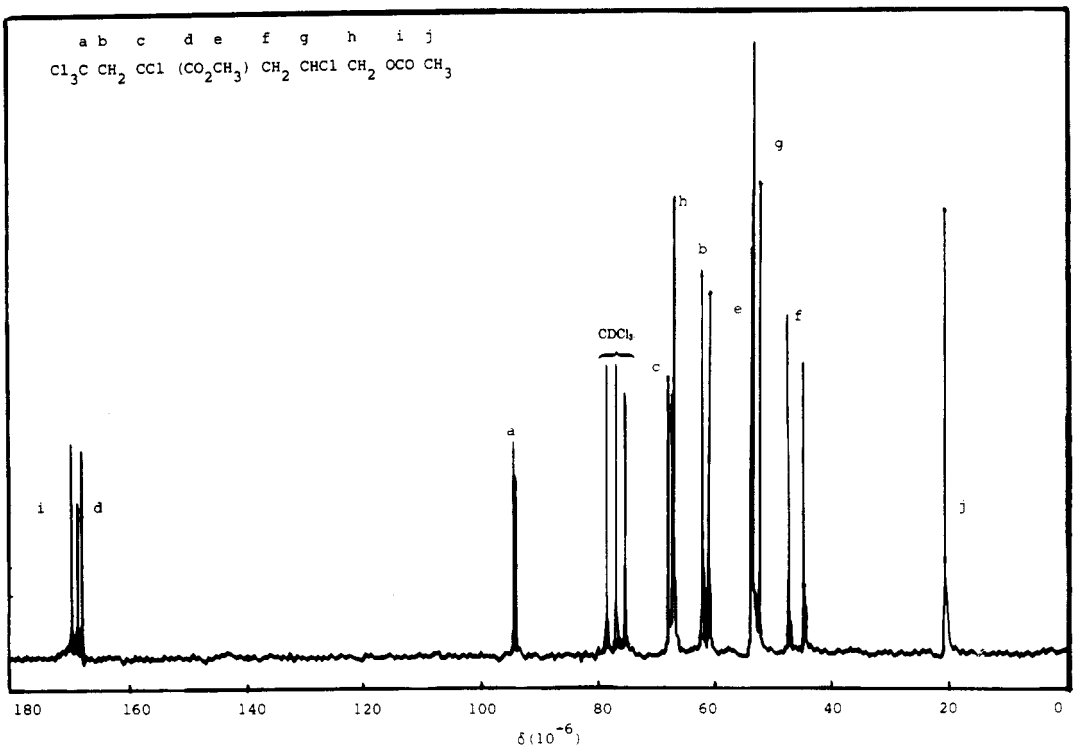

Figure 1. ^{13}C NMR spectrum of $Cl_3CCH_2CCl(CO_2CH_3)CH_2CHClCH_2OCOCH_3$.

signal of the methylene group in α of the OH is shifted toward the low fields.

Conclusion

First, we prepared novel functional telogens that exhibit a trichloromethylated end group from catalyzed telomerization of vinylidene chloride or allyl acetate with $Cl_3C\sim G$ or di-CCl_3 end groups. Then the redox catalysis, carried out with dichlorotris(triphenylphosphine)ruthenium, of allyl acetate with functional telogens allowed us to prepare chlorinated monodispersed telechelic oligomers with different molecular weights. Such a catalyst is very interesting for the 1:1 monoaddition and does not cause dehydrochlorination. However, it is essential to use an activated telogen, especially those in which an electronegative group is located in the α or β position about the trichloromethylated end group to obtain satisfactory yields. We propose the following series from the least reactive to the most reactive:

$$Cl_3C(CH_2)_3OAc < Cl_3CCH_2CCl_2CH_2CHClCH_2OAc \ll Cl_3CCH_2CHClCH_2OAc < Cl_3CH_2OAc < Cl_3CCOCCl_2CH_2CHClCH_2OAc < Cl_3CCF_2CCl_2CH_2CHClCH_2OAc < Cl_3CCO_2CH_3$$

Moreover, the diacetates have been quantitatively hydrolyzed into diols, and such hydroxylic telomers can be used in the synthesis of chlorinated polymers.

Experimental Section

Because of the low boiling point of vinylidene chloride (bp 30–32 °C/760 mmHg), we carried out these telomerizations in Carius tubes. However, the different reactions using allyl acetate (supplied by Aldrich) were performed either in Carius tubes (CT) or at atmospheric pressure (bp 100 °C/760 mmHg) in a two-necked round-bottom flask equipped with a condenser and a device for the introduction of nitrogen.

The reactions were carried out in acetonitrile when copper or iron salts were used, whereas benzene, chlorobenzene, or no solvent was required for reactions that needed the ruthenium complex.

All the experimental procedures have been described in previous work[20]—as has been the preparation of the ruthenium complex[35]—as well as the control of the reactions by gas chromatography, GPC analyses, and the characterization by ^1H and ^{13}C NMR.

(I) Preparation of Telogens. (A) Synthesis of 2,2,2-Trichloroethyl Acetate. The reaction was carried out in a 5-L three-necked round-bottom flask, cooled by an icy water bath, where 10.7 mol of acetyl chloride was added dropwise onto 10.4 mol of stirred 2,2,2-trichloroethanol. After addition, the reaction was left stirred for 3 h and the gross was distilled. A colorless liquid was obtained in an excellent yield (over 95%): bp 68–70 °C/20 mmHg; IR (CCl_4, cm^{-1}) 1670 FF, 1590 f, 1575 f, 1420 F, 795 FF, 765 FF, 670 FF; ^1H NMR ($CDCl_3$, 10^{-6}) 2.15 (s, 3 H), 4.75 (s, 2 H); ^{13}C NMR ($CDCl_3$, 10^{-6}) 20.14, 73.64, 94.82, 168.51. Anal. Calcd for $C_4H_5Cl_3O_2$ (FW = 191.5) (found): Cl, 55.63 (56.46).

(B) Synthesis of 4,4,4-Trichlorobutyl Acetate. In a Pfaudler vessel, 2.0 mol of allyl acetate, 4.20 mol of $CHCl_3$ in the presence of 0.064 mol of AIBN, and 0.070 mol of di-*tert*-butyl peroxide were stirred for 15 h at 120 °C. The distillation of the gross led to two liquid fractions.

(1) 214 g of colorless $Cl_3C(CH_2)_3OCOCH_3$: bp 78–82 °C/2.3 mmHg); IR (CCl_4, cm^{-1}) 2900 F, 1730 FF, 1230 FF, 1050 F, 700 m, 600 F; ^1H NMR ($CDCl_3$, 10^{-6}) 2.00 (s, 3 H), 2.05 (m, 2 H), 2.70 (m, 2 H), 4.10 (t, 2 H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 10^{-6}) 20.3, 26.5, 51.5, 62.0, 99.1, 169.9. Anal. Calcd for $C_6H_9Cl_3O_2$ (FW = 219.5) (found): C, 32.80 (33.89); H, 4.10 (4.97); Cl, 48.52 (48.58).

(2) 50 g of a yellow liquid [$Cl_3CCH_2CH(CH_2OCOCH_3)(CH_2)_3OCOCH_3$]: bp 145–152 °C/2 mmHg; ^1H NMR ($CDCl_3$, 10^{-6}) 1.8 (m, 3 H), 2.0 (m, 6 H), 2.8 (m, 2 H); ^{13}C NMR ($CDCl_3$, 10^{-6}) 20.0, 25.1, 28.1, 35.4, 54.4, 63.3, 65.0, 98.8, 172.7. Anal. Calcd for $C_{11}H_{17}Cl_3O_4$ (FW = 319.5) (found): C, 41.32 (40.71); H, 5.33 (6.29); Cl, 33.33 (32.84).

(C) Telomers of Vinylidene Chloride (VDC). (1) With CCl_4 as Telogen. A mixture composed of 6.36 mol (616.9 g) of VDC, 6.34 mol (973.1 g) of CCl_4, 0.18 mol (6.3 g) of cuprous chloride, and 10.57 mol (434.0 g) of acetonitrile was stirred in a Pfaudler vessel at 132 °C for 7 h. After acidic treatment, the volatile reactants were evaporated. The distillation led to several liquids.

(1) 870 g of colorless $Cl_3CCH_2CCl_3$: bp 38–40 °C/8 × 10^{-3} mmHg; ^1H NMR (CCl_4, 10^{-6}) 4.14 (s) (confirmed Belbachir's work[27]); ^{13}C NMR ($CDCl_3$, 10^{-6}) 70.31, 92.56. Anal. Calcd for $C_3H_2Cl_6$ (FW = 251.2) (found): C, 14.34 (15.62); Cl, 84.86 (84.05).

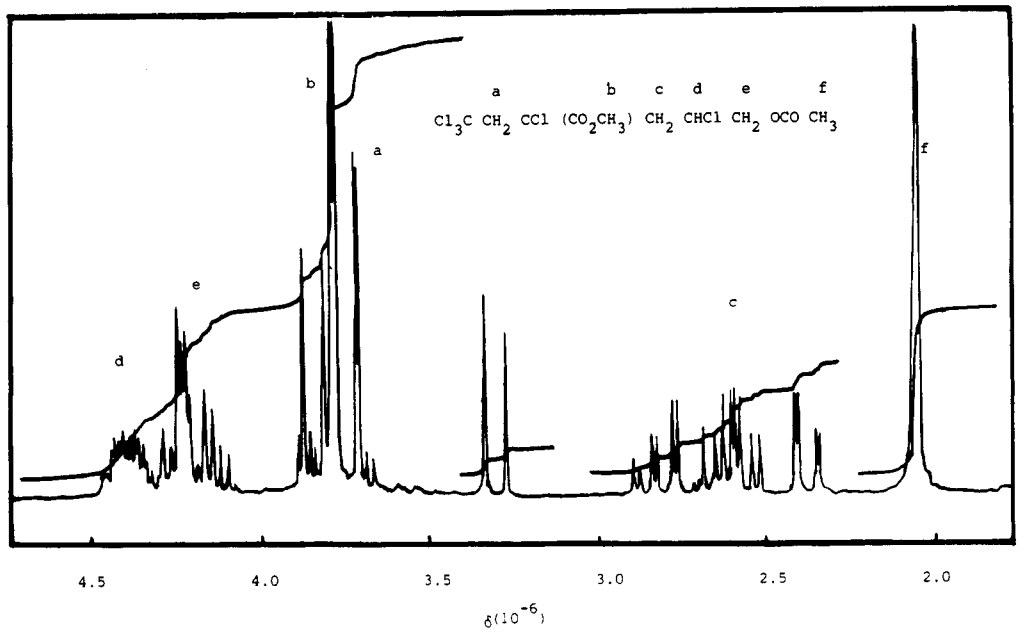

Figure 2. ^{1}H NMR spectrum of $Cl_3CCH_2CCl(CO_2CH_3)CH_2CHClCH_2OCOCH_3$.

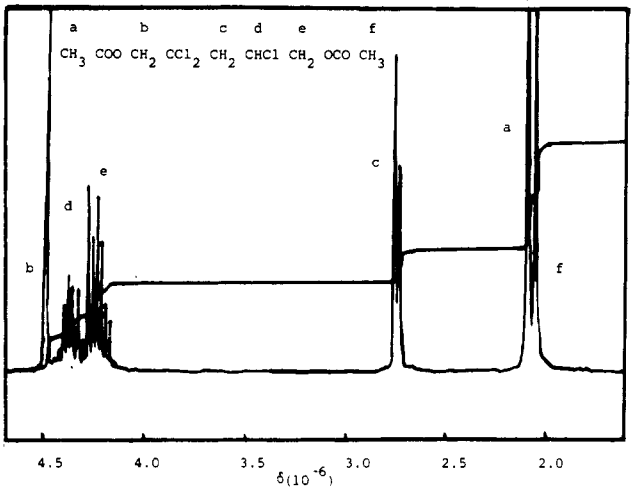

Figure 3. ^{1}H NMR spectrum of $CH_3CO_2CH_2CCl_2CH_2CHClCH_2OCOCH_3$.

(2) 220 g of yellow $Cl_3CCH_2CCl_2CH_2CCl_3$: bp 98–100 °C/8 × 10^{-3} mmHg; ^{1}H NMR (CCl_4, 10^{-6}) 4.04 (s) (as Belbachir[27]); ^{13}C NMR ($CDCl_3$, 10^{-6}) 65.61, 81.82, 93.56. Anal. Calcd for $C_5H_4Cl_8$ (FW = 347.1) (found): C, 13.83 (14.59); Cl, 81.64 (80.92).

(2) With $Cl_3CCO_2CH_3$. In a medium CT we reacted 82.2 g (0.85 mol) of VDC, 236.8 g (1.33 mol) of $Cl_3CCO_2CH_3$, 1.41 g of an equimolar $CuCl/CuCl_2$ mixture, and 22.6 g of acetonitrile for 22 h at 120 °C. After cooling, the telomers were distilled.

(1) Colorless liquid $Cl_3CCH_2CCl_2CO_2CH_3$: bp 58–60 °C/0.15 mmHg; IR (CCl_4, cm^{-1}) 1770 FF, 1740 FF, 1450 F, 1310 FF, 1250 FF, 1200 FF, 1100 F, 1000 F; ^{1}H NMR (CCl_4, 10^{-6}) 3.92 (s, 3 H), 4.06 (s, 2 H) (as Belbachir[27]); ^{13}C NMR ($CDCl_3$, 10^{-6}) 54.75, 63.26, 78.82, 92.96, 164.68. Anal. Calcd for $C_5H_5Cl_5O_2$ (FW = 274.5) (found): C, 21.86 (20.42); H, 1.82 (2.09); Cl, 64.66 (64.02).

(2) Yellow viscous liquid, blend of two isomers which contain two base units of VDC: bp 104–107 °C/0.04 mmHg; ^{1}H NMR (CCl_4, 10^{-6}) 3.86 (s, 1 H), 3.90 (s, 2 H), 3.93 (s, 3 H), 3.95 (s, 2 H); ^{13}C NMR ($CDCl_3$, 10^{-6}) 54.10, 54.80, 57.53, 60.48, 65.50, 66.76, 80.13, 82.32, 93.34, 94.16, 165.34, 167.91. Anal. Calcd for $C_7H_7Cl_7O_2$ (FW = 371.5) (found): C, 22.61 (21.86); H, 1.88 (2.35); Cl, 66.89 (66.05).

(3) With $Cl_3CCH_2CCl_2CO_2CH_3$. We introduced in a CT 2.24 g of VDC, 10.04 g of telogen, 0.056 g of an equimolar $CuCl/CuCl_2$ mixture, and 8.7 g of acetonitrile. The mixture was stirred for 13 h at 120 °C, and after distillation of the unreacted telogen, we distilled the telomer $(Cl_3CCH_2)_2CClCO_2CH_3$: bp 105 °C/0.08 mmHg (white crystals mp 84 °C); ^{1}H NMR ($CDCl_3$, 10^{-6}) AB system at 3.80 (J_1 = 15 Hz), 3.87 (s, 3 H); ^{13}C ($CDCl_3$, 10^{-6}) 54.14, 60.59, 65.56, 94.21, 168.12. Anal. Calcd for $C_7H_7Cl_7O_2$ (FW = 371.5) (found): C, 22.61 (21.9); H, 1.90 (1.54); Cl, 66.90 (66.71).

(4) With $CCl_3CH_2CHClCH_2OAc$. Such a telogen was prepared by telomerization of allyl acetate with CCl_4 (see Discussion). In a CT saturated with nitrogen, we introduced 0.050 mol (4.90 g) of VDC, 0.054 mol (13.8 g) of $Cl_3CCH_2CHClCH_2OAc$, 3.24 × 10^{-4} mol (0.31 g) of $RuCl_2(PPh_3)_3$, and 13.0 g of benzene. After reaction (19 h at 115 °C), the gross was evaporated and injected in GC/SM. The spectrum showed a peak, the retention time of which (R_T = 11.3–11.6 min) is greater than that of the telogen (R_T = 7.3–7.6 min). Furthermore, the peak m/z = 117 explained the CCl_3 end group.

(5) With Cl_3CCH_2OAc. We introduced in the CT 0.15 mol (15.0 g) of vinylidene chloride, 0.06 mol (12.1 g) of telogen, 1.6 × 10^{-3} mol (1.5 g) of $RuCl_2(PPh_3)_3$, and 13.7 g of benzene. The reaction lasted 19 h at 115 °C. The GC spectrum showed that by the peak corresponding to the unreacted telogen (R_T = 2.2–3.0 min) another one appeared corresponding to that of $Cl_3CCH_2CCl_2CH_2OCOCH_3$.

(6) Telomerization of VDC with $Cl_3C(CH_2)_3OCOCH_3$. The CT was filled with a mixture composed of 0.066 mol (6.2 g) of VDC, 0.072 mol (5.8 g) of telogen, 6.8 × 10^{-4} mol (0.11 g) of $FeCl_3$, 6.3 × 101^{-4} mol (0.13 g) of benzoin, and 9.5 g of acetonitrile. The reaction lasted 20 h at 110 °C. After evaporation of volatile products, the GC analysis did not exhibit any peak besides that of the unreacted telogen.

(D) Other Novel Telogens Obtained from Monoaddition of Allyl Acetate with CCl_4 or $Cl_3C{\sim}CCl_3$. (1) With CCl_4 as Telogen. The experimental protocol is detailed under Discussion.

2,4,4,4-Tetrachlorobutyl acetate: bp 70–72 °C/0.38 mmHg; IR (CCl_4, cm^{-1}) 2960 m, 1670 FF, 1590 f, 1575 f, 1420 F, 1240 F, 1020 F, 795 FF, 670 FF; ^{1}H NMR ($CDCl_3$, 10^{-6}) AA′ system at 3.2 (2 H, $J_{AA'}$ = 15.9 Hz, J_{AX} = 4.5 Hz, $J_{A'A}$ = 5.5 Hz), BB′ system at 4.2 (2 H, J_{BX} = 4.5 Hz, J_{BX} = 5.5 Hz, $J_{BB'}$ = 11.0 Hz), complex signal at 4.3 (1 H); ^{13}C NMR ($CDCl_3$, 10^{-6}) 20.3, 53.2, 58.4, 66.2, 96.2, 169.6. Anal. Calcd for $C_6H_8Cl_4O_2$ (FW = 254) (found): C, 28.35 (27.00); H, 3.15 (2.92); Cl, 55.91 (56.68).

(2) With $Cl_3CCH_2CCl_3$ as Telogen. A mixture composed of 2.07 mol (207 g) of allyl acetate, 3.30 mol (832 g) of 1,1,1,3,3,3-hexachloropropane, and 8.0 × 10^{-3} (7.9 g) of $RuCl_2(PPh_3)_3$ was stirred in a Pfaudler vessel (4.5 L) for 16 h at 110 °C. After precipitation of the catalyst into hexane, we distilled the gross. A yellow liquid was obtained.

2,4,4,6,6,6-Hexachlorohexyl acetate: bp 60–65 °C/8 × 10^{-5} mmHg; yield 38%; ^{1}H NMR ($CDCl_3$, 10^{-6}) 2.1 (s, 3 H), 3.2 (m, 2 H, AB part of ABX system; J_{AX} = 7.3 Hz, J_{BX} = 3.8 Hz, and J_{AB} = 15.9 Hz), 4.0 (s, 2 H), 4.5 (m, 2 H), 4.8 (m, 1 H, X part of

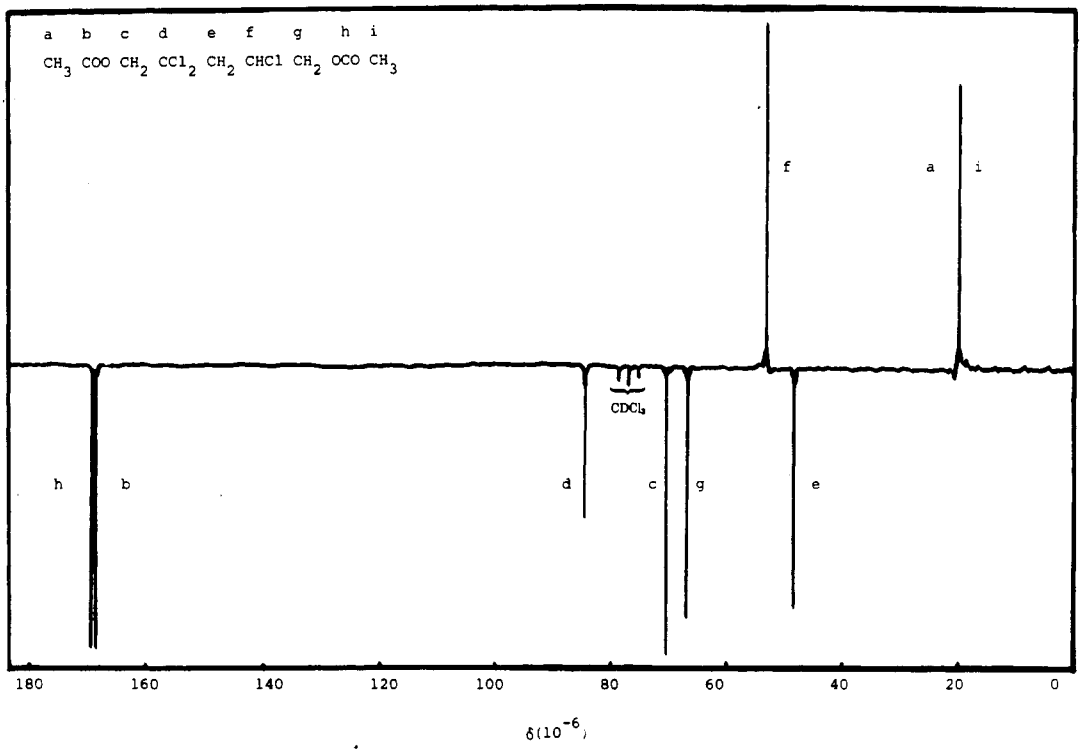

Figure 4. 80-MHz multiplicity ^{13}C NMR spectrum of $CH_3CO_2CH_2CCl_2CH_2CHClCH_2OCOCH_3$.

Table X
Bistelomerization of Allyl Acetate with Di-CCl_3 Telogens

telogen	R_0	catalyst	C_0, 10^{-2}	t, h	T, °C	monoadduct yield, %	diadduct yield, %	ref
$Cl_3CCH_2CCl_3$	0.4	Cu^+/Cu^{2+}	3.0	24	120	17	0	
	0.4	$RuCl_2(PPh_3)_3$	1.5	30	110	58	0	
	0.5	$FeCl_3$/benzoin	3.0/3.0	24	80	0	0	
$Cl_3CCH_2CCl_2CH_2CCl_3$	0.4	Cu^+/Cu^{2+}	2.1	32	120	16	0	
	0.4	$RuCl_2(PPh_3)_3$	0.8	32	120	28	0	
$Cl_3CCOCCl_3$	0.4	Cu^+/Cu^{2+}	2.5	30	120	10	50	
	0.4	$RuCl_2(PPh_3)_3$	1.0	30	120	35	10	
$Cl_3CCF_2CCl_3$	0.4	Cu^+/Cu^{2+}	1.0	312	95	16	66	10
	0.4	$RuCl_2(PPh_3)_3$	0.4	18	120	75	10	13
	0.4	$FeCl_3$/benzoin	1.0/1.0	24	125	52	27	10
$Cl_3C(CF_2CFCl)_2CF_2CCl_3$	0.4	Cu^+/Cu^{2+}	9.5	52	130	0	95	
	0.4	$RuCl_2(PPh_3)_3$	0.4	140	135	50	28	13
$Cl_3C(CF_2CFCl)_3CF_2CCl_3$	0.4	Cu^+/Cu^{2+}	8.0	52	130	0	90	

ABX system); ^{13}C NMR ($CDCl_3$, 10^{-6}) 20.52, 51.69, 53.55, 66.54, 66.92, 85.81, 93.29, 169.98. Anal. Calcd for $C_8H_{10}O_2Cl_6$ (FW = 350) (found): C, 27.33 (28.21); H, 2.86 (3.54); Cl, 60.68 (59.46).

(3) Hexachloroacetone as Telogen. In a three-necked round-bottom flask equipped with a condenser and a nitrogen flow, a mixture composed of 0.192 mol (50.3 g) of telogen, 0.125 mol (12.5 g) of allyl acetate, and 0.7×10^{-3} mol (0.65 g) of ruthenium complex was stirred at 115 °C for 20 h. After precipitation of the catalyst and distillation of the unreacted telogen, we obtained a pale yellow liquid.

2,4,4,6,6,6-Hexachloro-5-oxohexyl acetate: bp 60–65 °C/8×10^{-5} mmHg; ^1H NMR ($CDCl_3$, 10^{-6}) 2.1 (s, 3 H), AB part of ABX system at 3.0 (2 H, J_{AX} = 7.4 Hz, J_{BX} = 3.2 Hz, and J_{AB} = 15.6 Hz), 4.2 (m, 2 H), 4.3 (m, 1 H; X part); ^{13}C NMR ($CDCl_3$, 10^{-6}) 20.47, 50.44, 52.89, 66.54, 81.11, 91.49, 169.87, 180.08. Anal. Calcd for $C_8H_8O_3Cl_6$ (FW = 365.0) (found): C, 26.30 (27.81); Cl, 58.34 (57.62).

(4) $Cl_3CCF_2CCl_3$ as Telogen. In a three-necked round-bottom flask, we stirred, as previously, a mixture of 0.165 mol of $Cl_3CCF_2CCl_3$, 0.115 mol of allyl acetate, and 0.6×10^{-3} mol of $RuCl_2(PPh_3)_3$ at 110 °C for 19 h. After elimination of the unreacted compounds, we distilled the expected telomer.

2,4,4,6,6,6-Hexachloro-5,5-difluorohexyl acetate: bp 100–105 °C/8×10^{-4} mmHg; ^1H NMR ($CDCl_3$, 10^{-6}) 2.05 (s, 3 H) 2.85 (m, 2 H, AA' system), 4.50 (m, 2 H, BB' system), 4.60 (m, 1 H, X part) (similar to Hugon[10]); ^{13}C NMR ($CDCl_3$, 10^{-6}) 20.3, 47.7, 58.1, 66.8, 85.9, 87.4, 88.9, 92.7, 94.6, 96.5, 100.9, 114.5, 128.0 (J = 268.3 Hz), 169.8. Anal. Calcd for $C_8H_8O_2F_2Cl_6$ (FW = 387.0) (found): C, 24.80 (25.21); Cl, 55.04 (55.79); F, 9.83 (8.24).

(II) Synthesis of the Diacetates from Telomerization of Allyl Acetate with Functional Telogens. (A) With $Cl_3C(CH_2)_3OAc$. Even in CT under strong conditions (T = 120 °C, t = 48 h) the mixture of 0.068 mol of $Cl_3C(CH_2)_3OAc$, 0.065 mol of allyl acetate, and 0.006 mol of ruthenium complex did not show any interesting peak in either GC or GPC analyses.

(B) With $Cl_3CCH_2CCl_2CH_2CHClCH_2OCOCH_3$. This reaction was carried out for 20 h at 110 °C in CT by using 0.057 mol of telogen, 0.048 mol of allyl acetate, 0.007 mol of $RuCl_2(PPh_3)_3$, and about 10 mL of benzene. After distillation of the excess of telogen, the residue was chromatographed over a silica column using a diethyl ether/petroleum ether blend (10:90) as eluent with an increasing gradient of polarity. The diacetate is an orange oil.

2,4,4,6,6,8-Hexachloro-1,9-diacetoxynonane: ^1H NMR ($CDCl_3$, 10^{-6}) 2.1 (s, 3 H), 3.0 (m, 2 H), 3.8 (s, 2 H), 4.5 (m, 2 H), 4.8 (m, 1 H); ^{13}C NMR ($CDCl_3$, 10^{-6}) 20.50, 51.58, 53.60, 61.23, 66.84, 85.00, 169.87. Anal. Calcd for $C_{13}H_{18}Cl_6O_4$ (FW = 451) (found): C, 34.59 (34.12); H, 3.99 (3.69); Cl, 47.23 (48.24).

(C) With $Cl_3CCH_2CCl_2CO_2Me$. We introduced in the CT 0.068 mol (6.8 g) of allyl acetate, 0.114 mol (31.4 g) of telogen, 3.85×10^{-4} mol of the ruthenium complex, and 4.0 g of benzene. After precipitation of the catalyst into hexane, we distilled the telogen and chromatographed the residue by a petroleum ether/diethyl ether blend (90:10).

4-Methyl ester 2,4,6,6,6-pentachlorohexyl acetate: ^1H NMR (Figure 2, $CDCl_3$, 10^{-6}) 2.0 (s, 3 H), AB part of an ABX system at 2.6 (J_{AB} = 14.8 Hz, J_{AX} = 6.3 Hz, J_{BX} = 2.0 Hz), 3.8 (m, 2 H), 4.3 (m, 2 H), 4.4 (m, 1 H); ^{13}C NMR (Figure 1, $CDCl_3$, 10^{-6}) 20.20, 44.43, 47.05, 52.40, 53.49, 53.77, 60.59, 61.63, 66.90, 67.20, 67.69, 94.00, 94.21, 167.85, 168.61, 169.54, 169.65. Anal. Calcd for $C_{10}H_{13}Cl_5O_4$ (FW = 374.5) (found): C, 32.04 (32.21); H, 3.47 (3.05); Cl, 47.40 (47.52).

(D) With 2,4,4,4-Tetrachlorobutyl Acetate. This reaction was carried out in a 3-L three-necked round-bottom flask for 40 h at 115 °C by using 5.0 mol of telogen, 3.1 mol of allyl acetate, and 1.6×10^{-2} mol of $RuCl_2(PPh_3)_3$. After reaction, 760 g of unreacted telogen was distilled and the residue was flash chromatographed, yielding an orange liquid diacetate (yield 39%).

2,4,4,6-Tetrachloro-1,7-diacetoxyheptane: ^1H NMR ($CDCl_3$, 10^{-6}) 2.0 (s, 3 H), 2.6–2.9 (m, 2 H, AA'XBB' system $J_{AA'}$ = 16.0 Hz, J_{AX} = 4.0 Hz, $J_{A'X}$ = 10.0 Hz), 3.5–4.2 (m, 1 H, X part of AA'X system); ^{13}C NMR ($CDCl_3$, 10^{-6}) 20.6, 52.7, 53.7, 67.0, 89.2, 170.2. Anal. Calcd for $C_{11}H_{16}Cl_4O_4$ (FW = 354) (found): C, 37.05 (37.29); H, 4.18 (4.52); Cl, 40.92 (40.11).

(E) With Cl_3CCH_2OAc. In a Pfaudler vessel (4.5 L) we reacted 4.6 mol of allyl acetate and 7.8 mol of telogen in the presence of 1.7×10^{-2} mol of the ruthenium complex for 19 h at 100 °C. After precipitation of the catalyst and distillation of the unreacted Cl_3CCH_2OAc, we distilled the expected diacetate [bp 110–112 °C/0.15 mmHg (colorless liquid)] which decomposed from 135 °C.

2,2,4-Trichloro-1,5-diacetoxypentane: IR (CCl_4, cm^{-1}) 2950 m, 1750 FF, 1430 m, 1380 F, 1220 FF, 1050 F, 730 m, 600 m; ^1H NMR (Figure 3, $CDCl_3$, 10^{-6}) 2.05 (s, 3 H), 3.05 (m, 2 H, AB part of ABX system J_{AX} = 3.6 Hz, J_{BX} = 7.6 Hz, J_{AB} = 15.4 Hz), 3.90 (s, 3 H), 4.20 (m, 2 H), 4.40 (m, 1 H, X part); ^{13}C NMR (Figure 4, $CDCl_3$, 10^{-6}) 20.06, 48.34, 53.19, 66.52, 70.22, 86.51, 168.71, 169.45. Anal. Calcd for $C_9H_{13}Cl_3O_4$ (FW = 291.5) (found): C, 37.05 (36.78); 4.46 (4.56); Cl, 36.54 (36.44).

(F) With $Cl_3CCOCCl_2CH_2CHClCH_2OAc$. We carried out this reaction in CT with 0.058 mol of telogen, 0.048 mol of allyl acetate, and 0.007 mol of $RuCl_2(PPh_3)_3$ for 21 h at 115 °C. The gross was chromatographed by a petroleum ether/diethyl ether blend (90:10). We obtained an orange oil.

2,4,4,6,6,8-Hexachloro-5-oxo-1,9-diacetoxynonane: ^1H NMR ($CDCl_3$, 10^{-6}) 2.1 (s, 3 H), 3.1 (m, 2 H), 4.3 (m, 2 H), 4.4 (m, 1 H); ^{13}C NMR ($CDCl_3$, 10^{-6}) 20.6, 50.2, 53.0, 66.9, 82.3, 170.1, 180.3. Anal. Calcd for $C_{13}H_{16}O_5Cl_6$ (FW = 465) (found): C, 32.92 (33.55); H, 3.12 (3.44); Cl 46.22 (45.81).

(G) With $Cl_3CCF_2CCl_2CH_2CHClCH_2OAc$. We used almost the same conditions and amounts as previously. We distilled the excess of monoacetate, and the residue was flash chromatographed.[13]

5,5-Difluoro-2,4,4,6,6,8-hexachloro-1,9-diacetoxynonane: ^1H NMR ($CDCl_3$, 10^{-6}) 2.0 (s, 3 H), 2.9 (m, 2 H, AA' system), 4.5 (m, 2 H, BB' system), 4.6 (m, 1 H, X part); ^{13}C NMR ($CDCl_3$, 10^{-6}) 20.20, 47.87, 52.73, 66.59, 85.97, 87.56, 89.08 (J = 1.56 Hz), 102.29, 115.61, 128.99 (J = 268.90 Hz), 169.91. Anal. Calcd for $C_{13}H_{16}O_4Cl_6F_2$ (FW = 487) (found): C, 32.85 (32.20); H, 3.47 (3.29); Cl, 43.12 (43.74); F, 7.39 (7.80).

(H) With $Cl_3CCO_2CH_3$. In a two-necked round-bottom flask equipped with a condenser and a device for a nitrogen flow, a mixture composed of 0.247 mol of methyl trichloroacetate, 0.190 mol of allyl acetate, and 8.29×10^{-4} mol of $RuCl_2(PPh_3)_3$ was stirred for 15 h at 100–105 °C. After precipitation of the catalyst in hexane, we distilled the telomer (colorless liquid).

Methyl 2,2,4-trichloro-5-acetoxypentanoate: bp 83–85 °C/0.05 mmHg; 70% yield after distillation; IR ($CHCl_3$, cm^{-1}) 3000 m, 2650 m, 1750 FF, 1420 F, 1350 F, 1220 FF, 1150 F, 840 m (confirms ref 11); ^1H NMR ($CDCl_3$, 10^{-6}) 2.0 (s, 3 H), 3.0 (m, 2 H, AB part from ABX system, J_{AX} = 7 Hz, J_{AB} = 14 Hz, and J_{BX} = 4 Hz), 3.9 (s, 3 H), 4.3 (m, 3 H); ^{13}C NMR ($CDCl_3$, 10^{-6}) 19.87, 49.85, 53.44, 53.99, 66.10, 81.55, 164.90, 169.27. Anal. Calcd for $C_8H_{11}O_4Cl_3$ (FW = 277.5) (found): C, 34.59 (33.82); H, 3.96 (4.09); Cl, 38.38 (37.74).

(3) Synthesis of Diols. The diols were obtained by carrying out at room temperature for 5 h the hydrolysis of n mol of diacetate with 0.1n mol of KCN in methanol (30 mL for 5×10^{-4} mol of KCN). Then the mixture was filtered over a silica bed and the solvent evaporated.

2,4,4,6,6,8-Hexachloro-1,9-dihydroxynonane: ^1H NMR ($CDCl_3$, 10^{-6}) 3.0 (m, 2 H, AB part of ABX system, J_{AX} = 2.4 Hz, J_{BX} = 6.9 Hz, J_{AB} = 15.6 Hz), 3.5 (s, 1 H) shifted with dilution, 3.8 (s, 2 H), 4.5 (m, 2 H), 4.8 (m, 1 H, X part); ^{13}C NMR ($CDCl_3$, 10^{-6}) 50.42, 54.21, 62.35, 66.99, 85.84. Anal. Calcd for $C_9H_{14}O_2Cl_6$ (FW = 367) (found): C, 29.43 (29.01); H, 3.81 (3.72); Cl, 58.04 (58.71).

2,4,4,6-Tetrachloro-1,7-dihydroxyheptane: The purification occurred by column chromatography [we used a petroleum ether/diethyl ester blend (90:10)], and we obtained a turbid milky viscous liquid (T_g = −54.8 ± 0.2 °C); IR (CCl_4, cm^{-1}) 3600 F, 3500–3100 (broad band) FF, 2960 m, 1050 F, 700 m, 590 F; ^1H NMR ($CDCl_3$, 10^{-6}) 2.90 (d, 2 H), 2.85 (m, 2 H, AB part of ABX system, J_{AX} = 2.3 Hz, J_{BX} = 7.0 Hz, J_{AB} = 15.6 Hz), 3.20 (s, 1 H) shifted with dilution, 4.30 (m, 1 H, X part); ^{13}C NMR ($CDCl_3$, 10^{-6}) 48.35, 57.42, 66.75, 85.72. Anal. Calcd for $C_7H_{12}O_2Cl_4$ (FW = 270) (found): C, 31.85 (31.11); H, 4.54 (4.44); Cl, 51.88 (52.59).

2,2,4-Trichloro-1,5-dihydroxypentane: This diol crystallizes in $CHCl_3$ in a white powder: mp 65–67 °C ($CHCl_3$); IR (KBr, cm^{-1}) 3570 F, 3360 F, 1070 F, 960 f, 600 f; ^1H NMR (CD_3OD, 10^{-6}) 2.5 (s, 1 H), 2.8 (d, 1 H), 3.0 (s, 1 H) shifted with dilution, 3.8 (s, 2 H), 4.4 (m, 1 H); ^{13}C NMR (CD_3CN, 10^{-6}) 47.78, 58.91, 66.55, 71.85, 92.43. Anal. Calcd for $C_5H_9Cl_3O_2$ (FW = 207.5) (found): C, 28.95 (29.16); H, 4.35 (4.33); Cl, 51.32 (49.98).

2,4,4,6,6,8-Hexachloro-5-oxo-1,9-dihydroxynonane: ^1H NMR ($CDCl_3$, 10^{-6}) 2.70 (s, 1 H) shifted with dilution, 2.85 (m, 2 H, ABX system, AB part J_{AX} = 2.3 Hz, J_{BX} = 6.9 Hz, J_{AB} = 15.7 Hz), 2.95 (d, 2 H), 4.30 (m, 1 H, X part); ^{13}C NMR ($CDCl_3$, 10^{-6}) 48.29, 56.92, 66.39, 82.58, 180.43. Anal. Calcd for $C_9H_{12}O_3Cl_6$ (FW = 381) (found): C, 28.11 (28.35); H, 2.98 (3.15); Cl, 56.12 (55.91).

2,4,4,6,6,8-Hexachloro-5,5-difluoro-1,9-dihydroxynonane: white crystals mp 95–98 °C (H_2O); ^1H NMR ($CDCl_3$, 10^{-6}) 2.85 (m, 2 H, ABX system, AB part J_{AX} = 2.4 Hz, J_{BX} = 6.9 Hz, J_{AB} = 15.6 Hz), 2.95 (d, 2 H), 3.10 (s, 1 H) shifted with dilution, 4.35 (m, 1 H, X part); ^{13}C NMR ($CDCl_3$, 10^{-6}) 49.06, 57.09, 66.11, 85.42, 87.11, 88.64, 99.92, 114.35, 127.89 (J = 268.2 Hz). Anal. Calcd for $C_9H_{12}O_2Cl_6F_2$ (FW = 403) (found): C, 26.54 (26.80); H, 2.79 (2.98); Cl, 53.21 (52.85); F, 9.81 (9.43).

Methyl 2,2,4-trichloro-5-hydroxypentanoate: IR ($CHCl_3$, cm^{-1}) 3600 F, 3400 FF, 2980 F, 1750 FF, 1250 F, 1100–1000 FF; ^1H NMR ($CDCl_3$, 10^{-6}) 2.95 (m, 2 H, AB part of ABX system), 3.50 (s, 1 H) shifted with dilution, 3.65 (d, 2 H, J = 5.3 Hz), 3.80 (s, 3 H), 4.15 (m, 1 H, X part); ^{13}C NMR ($CDCl_3$, 10^{-6}) 48.85, 54.31, 57.92, 65.94, 82.10, 165.67. Anal. Calcd for $C_6H_9Cl_3O_3$ (FW = 235.5) (found): C, 30.60 (31.40); H, 38.20 (37.90); Cl, 45.21 (44.72).

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Registry No. VDC·CCl_4 (telomer), 87079-44-5; VDC·$Cl_3CCO_2CH_3$ (telomer), 132775-24-7; VDC·$Cl_3CCH_2CCl_2CO_2CH_3$ (telomer), 132802-04-1; VDC·$Cl_3CCH_2CHClCH_2OAc$ (telomer), 132775-25-8; VDC·Cl_3CCH_2OAc (telomer), 132775-26-9; VDC·$Cl_3C(CH_2)_3OAc$ (telomer), 132775-27-0; H_2C=$CHCH_2$OAc·CCl_4 (telomer), 28376-51-4; H_2C=$CHCH_2OAc$·$Cl_3C(CH_2)_3$OAc (telomer), 132775-28-1; H_2C=$CHCH_2OAc$·HCl_3 (telomer), 132775-30-5; H_2C=$CHCH_2OAc$·$Cl_3C(CF_2CFCl)_2CF_2CCl_3$ (telomer), 132775-31-6; H_2C=$CHCH_2OAc$·$Cl_3C(CF_2CFCl)_3CF_2CCl_3$ (telomer), 132775-32-7; H_2C=$CHCH_2OAc$·$Cl_3CCH_2CCl_2CH_2CCl_3$ (telomer), 132775-29-2; $AcOCH_2CCl_3$, 625-24-1; AcCl, 75-36-5; $HOCH_2CCl_3$, 115-20-8; $AcO(CH_2)_3CCl_3$, 132775-16-7; H_2C=$CHCH_2OAc$, 591-87-7; $CHCl_3$, 67-66-3; *t*-$Bu(O)_2$Bu-*t*, 110-05-4; $Cl_3CCH_2CH(CH_2OAc)(CH_2)_3OAc$, 100054-07-7; $AcOCH_2CHCl(CH_2CCl_2)_2Cl$, 88544-03-0; $AcOCH_2CHClCH_2CCl_2COCCl_3$, 132775-17-8; $AcOCH_2CHCl(CH_2CCl_2)_2CH_2CHClCH_2OAc$, 132775-18-9; $AcOCH_2CHClCH_2C(CH_3)(Cl)CH_2CCl_3$, 132775-19-0; $AcOCH_2CHClCH_2CCl_2CH_2CHClCH_2OAc$, 132775-20-3; $AcOCH_2CCl_2CH_2CHClCH_2OAc$, 132775-21-4; $AcOCH_2CHClCH_2CCl_2COCCl_2CH_2CHClCH_2OAc$, 132854-61-6; $AcOCH_2CHClCH_2CCl_2CF_2CCl_2CH_2CHClCH_2OAc$, 77304-42-8; $MeOCOCCl_2CH_2CHClCH_2OAc$, 67047-82-9; $HOCH_2CHCl(CH_2CCl_2)_2CH_2CHClCH_2OH$, 132775-22-5; $HOCH_2CHClCH_2CCl_2CH_2CHClCH_2OH$, 34909-89-2; $HOCH_2CCl_2CH_2CHClCH_2OH$, 67001-93-8; $CO(CCl_2CH_2CHClCH_2OH)_2$, 132775-23-6; $CF_2(CCl_2CH_2CHClCH_2OH)_2$, 77304-50-8; $MeOCOCCl_2CH_2CHClCH_2OH$, 67001-87-0; $AcOCH_2CHClCH_2CCl_2CF_2CCl_3$, 77304-41-7.