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Synthesis of Chlorinated Telechelic Oligomers. 1. Telomerization of Nonconjugated Dienes with Functional Telogens

B. Améduri and B. Boutevin*

Ecole Nationale Supérieure de Chimie de Montpellier, URA D 11930, 8 Rue Ecole Normale, 34075 Montpellier, Cédex, France.

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ABSTRACT: The redox telomerization of nonconjugated dienes with functional telogens with a trichloromethyl end group catalyzed with a ruthenium complex led to monoadducts and telechelic oligomers. Such compounds have been characterized by both ^{1}H and ^{13}C NMR. The diacetates have been changed into diols, and the thermal parameters have been studied.

Introduction

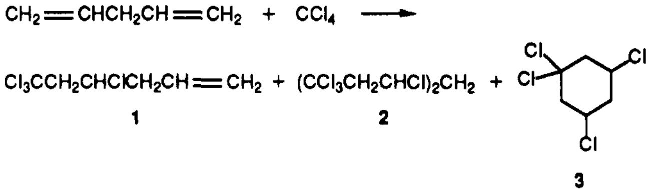
Telechelic oligomers have been shown to be very interesting intermediate reactants for many applications[1-4]—binders for propergols, prepolymers for paints, chain extenders, etc.—and when they are monodispersed they usually lead to well-defined structured polymer. Among them, monodispersed diols are very important products since they can be used as precursors for polymer and especially polyurethanes. It is crucial that such diols must be both telechelic and monodispersed for improving mechanical properties. Bill,[5] Harell,[6] and Eisenbach[7] succeeded in preparing such diols but in difficult organic syntheses in many steps. However, they showed that such diols led to polymer with 10 times higher strain–stress modulus than those with available polydispersed diols.[6] In our laboratory,[8,9] monodispersed telechelic diols have been prepared simply by radical telomerization with dithiol and undecylenic derivatives.

However, it is interesting to notice that no chlorinated *mono*dispersed telechelic diol has been prepared. Halogenated compounds exhibit remarkable properties such as corrosion resistance, film-forming materials for chlorinated products, and thermal resistance, with improvement of the surface state for fluorinated ones. Several publications mention that there are ways to prepare telechelic oligomers[10-17] and telomerization seems to be quite adequate: thus, the monoaddition of a functional telogen with a functional monomer[10-14] leads to a telechelic (previous work developing chlorinated diols has been patented[10]), just like the monoaddition of a functional monomer with bis(trichloromethyl) telogens.[13,15,16] Finally the monoaddition of a functional telogen with a nonconjugated diene is another way of synthesizing such telechelic compounds as several authors have discussed (Table I). All kinds of monomers (vinylic, allylic, styrenic) are used, and the telogens always contain trihalogenated methyl groups. Usually the catalysts used in the above reactions are cuprous or ferric salts, but we can also notice peroxidic initiators.[19,25,27,28] However, no such reaction catalyzed by $RuCl_2(PPh_3)_3$ has been reported, even if this catalyst was more selective in monoaddition reactions.[32-35]

In this paper we are focusing on the synthesis of chlorinated monodispersed telechelic diacetates and diols from the redox telomerization of nonconjugated dienes: 1,5-hexadiene and 1,9-decadiene catalyzed with $RuCl_2(PPh_3)_3$ with 2,2,2-trichloroethyl acetate and 2,4,4,4-tetrachlorobutyl acetate.

Discussion

(1) Modeling. Telomerization of 1,4-Pentadiene with CCl_4. The telomerization of 1,4-pentadiene with CCl_4, catalyzed by $RuCl_2(PPh_3)_3$, may lead to compound 1 resulting from the monoaddition of CCl_4 onto one double bond only, to compound 2 resulting from the addition of CCl_4 onto both double bonds, and to compound 3 resulting from an intramolecular cyclic mechanism of 1, according to the following scheme:



In previous work[17,18] a cyclic side product was already obtained in the telomerization of 1,5-hexadiene with $CCl_3CO_2CH_3$.

In order to compare the reactivity of the ruthenium complex with cuprous or ferric salts, we performed the reaction at 115 °C for 12 h, with C_o = (catalyst)/(diene) = 8.5×10^{-3} and R_o = (telogen)/(diene) = 2.84. The distillation gave the same products as Corallo et al. obtained:[17] 43% of monoadduct **1**; 57% of diadduct **2** without any trace of cyclic compound **3**. When R_o equaled 3.2, the diadduct was obtained quantitatively. The characteristics of the spectrum are the same as those of Corallo's; however, we notice on the ^{13}C NMR spectrum that all the peaks are separated in two, probably because of the presence of diastereoisomers in the blend.

The attribution, by comparison with those of fluorinated ether,[36] is given here ($\delta 10^{-6}$):

$Cl_3C—CH_2—CHCl—CH_2—O—CO—CH_3$
96.3 58.8 53.4 66.5
$Cl_3C—CH_2—CHCl—CH_2—O—CH_2—CH_2—C_6F_{13}$
97.1 58.9 54.6 74.6 63.1 31.9
$Cl_3C—CH_2—CHCl—CH_2—CHCl—CH_2—CCl_3$
96.3 62.1 54.6 47.9

These reactions allowed us to conclude that the $RuCl_2(PPh_3)_3$ complex is more selective than copper or iron salts since no byproducts, such as cyclic compounds, were observed and quantitative yields in diadduct were obtained. Subsequently, we used such a catalyst in this study.

(2) Telomerization of 1,5-Hexadiene and 1,9-Decadiene with Functional Telogens. The telogens used are, respectively, $CCl_3CH_2OCOCH_3$ and 2,4,4,4-tetrachlorobutyl acetate (monoadduct of allyl acetate with CCl_4[37]).

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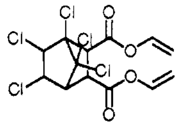
Table I
Reactions of Addition of Telogens onto Nonconjugated Dienes

diene	telogen	exptl conditions	remarks	ref
divinylbenzene	CCl_4	CuCl (90–100 °C)	telechelic (quantitative)	17
	$Cl_3CCO_2CH_3$	CuCl (120 °C)	telechelic (quantitative)	18
	$Cl_3CP(O)Cl_2$		polymerization	20
diallylamine	CCl_4	Cu^+/Cu^{2+}	polymer	17
diallyl ether	CCl_4	radical	polymer and byproducts,	27, 28
		Cu^+/Cu^{2+}	mono- and diadduct	17
	$Cl_3CCO_2CH_3$	CuCl (120 °C)	cyclic compound, mono- and diadduct	18
diallyl thioether	CCl_4	Cu^+/Cu^{2+}	telechelic, byproducts (degradation)	17
triallyl phosphate	CCl_4		low molecular weight telomers	29–31
1,5-hexadiene	CCl_4	Cu^+/Cu^{2+}	quantitative, monoadduct	17
		$HNEt_3$ 120 °C, 20 h	diadduct, cyclic compound	
	$Cl_3CCO_2CH_3$	120 °C, 12 h	90% yield (as previously)	18
	Cl_3CCO_2H	Cu^+/Cu^{2+} (120 °C)	diacid	18
$H_2C{=}CH(CF_2)_2CH{=}CH_2$ (3,3,4,4-tetrafluoro-1,5-hexadiene)	CCl_4	T = 120 °C $(tBuO)_2$ CuCl $CuCl_2{\cdot}2H_2O$ $FeCl_3{\cdot}6H_2O$ $FeCl_3{\cdot}4H_2O$	blend of linear products (monoadduct and telechelic) and cyclic compounds (the amount of which varies vs the initiator or the catalyst quantities)	19
diethylene glycol	CCl_4	CuCl	cross-linked polymer	17
divinyl ether	$Cl_3CP(O)Cl_2$	CuCl	cross-linked polymer	20
diallyl succinate	$Cl_3CP(O)Cl_2$		addition and polymerization	20
allyl methacrylate	CCl_4		diadduct	17
divinyl adipate	CCl_4	CuCl	decomposition of products	17
ethylene glycol dimethacrylate	$Cl_3CCO_2CH_3$	CuCl (120 °C)	difunctional and byproducts	18
tetraethylene glycol dimethacrylate	$Cl_3CCO_2CH_3$	CuCl (120 °C)	difunctional and byproducts	18
	CCl_4	CuCl (120 °C)	difunctional and byproducts	17
	CCl_4	benzoyl peroxide (80 °C, 15 h)	polymer	21
diallyl phthalate	CCl_4	T = 105 °C	monoadduct	22, 23
	CBr_4	T = 105 °C	monoadduct	24
	Cl_3CCCl_3	H_2O_2	monoadduct	25
	$Cl_3CCHClCCl_3$	H_2O_2	monoadduct	25
	Cl_3CCHCl_2	H_2O_2	monoadduct	25
	$Cl_3CP(O)Cl_2$			26, 27

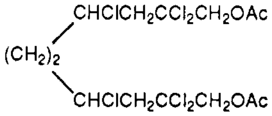
(A) Telomerization of 1,5-Hexadiene with $CCl_3CH_2OCOCH_3$.

$$CH_2{=}CH(CH_2)_2CH{=}CH_2 + CCl_3CH_2OAc \rightarrow 4 + 5$$

with

$H_2C{=}CH(CH_2)_2CHClCH_2CCl_2CH_2OAc$

4



5

$$(CH_2)_2(CHClCH_2CCl_2CH_2OAc)_2$$

It is possible to direct the synthesis toward the formation of telechelic 5 about 4 by varying the initial ratio of R_o to C_o as shown in Table II. The respective quantities of adducts are obtained by GPC (Figure 1). It is interesting to notice that the catalyst concentration directs the reaction toward a higher amount of telechelic. However, an important quantity of catalyst reduces such effect as Derouet showed for the addition of CCl_4 onto butadiene and polybutadiene.[38]

The monoadduct 4 was distilled, and then the residue was chromatographed over silica, which led to the telechelic compound 5.

The characterization of such telomers has been given by NMR. For instance, Figure 2 exhibits the ^1H NMR spectrum of both compounds 4 and 5. First, we notice the disappearance of the signal of double bond in 5 about 4. Then, we observe that the signal of the allylic methylene group in 4 has been shifted toward high fields (0.5×10^{-6}) for diadduct 5. It is worth noting the separation in two parts of the methylene group in the α position about $-CCl_2CH_2OCOCH_3$ due to the presence of both diastereoisomers.

Table II
Influence of C_o and R_o on Obtaining the Monoadduct (M) and the Diadduct (D) for the Telomerization of 1,5-Hexadiene with 2,2,2-Trichloroethyl Acetate[a]

10^3C_o	R_o	% M	% D
8.0	1.6	60	40
4.4	3.2	60	40
8.6	3.2	35	65
26.8	3.2	25	75

[a] C_o = (catalyst)/(diene) molar ratio; R_o = (telogen)/(diene) molar ratio.

The assignment of each group in ^{13}C NMR is given in the following formula ($\delta 10^{-6}$):

$$\begin{array}{cccccccc} CH_2{=} & CH{-} & CH_2{-} & CH_2{-} & CHCl{-} & CH_2{-} & CCl_2{-} & CH_2{-} \\ 115.7 & 136.9 & 38.2 & 29.9 & 56.8 & 52.2 & 87.2 & 70.4 \\ & & & & & & & O{-}CO{-}CH_3 \\ & & & & & & & 168.9 \quad 20.3 \end{array}$$

Most peaks are easily explained, and we discuss the other ones. The chemical shift of the $-CCl_2-$ group appears at 89×10^{-6} for both 4 and 5, whereas we observed the signal of a $-CCl_3$ group at 96×10^{-6}. As the methylene group of the telogen $CCl_3CH_2OCOCH_3$ gives a signal at 73.6×10^{-6},[37] we can easily attribute the signal at 70.4×10^{-6} to the methylene group in the α position to the acetate.

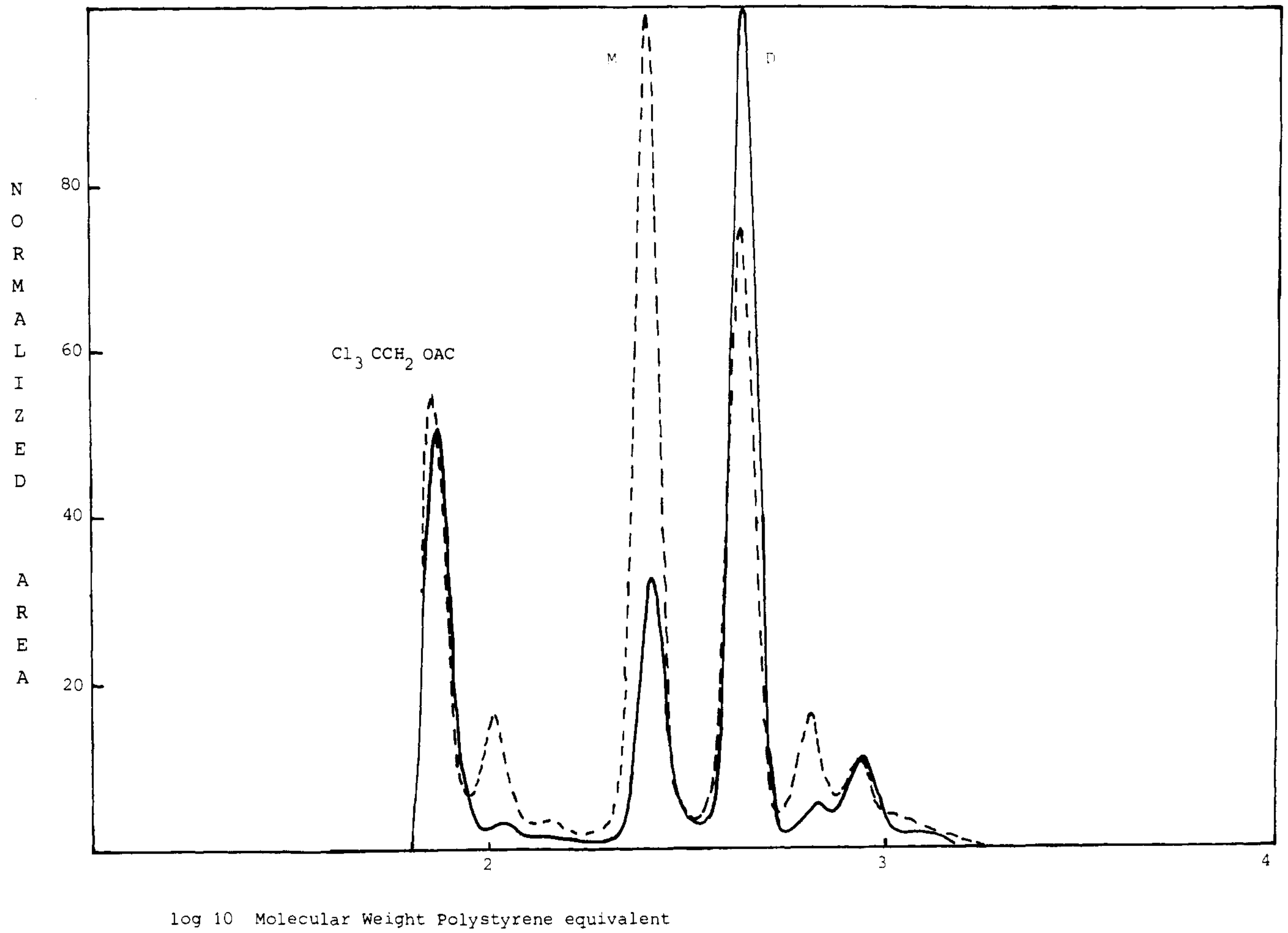
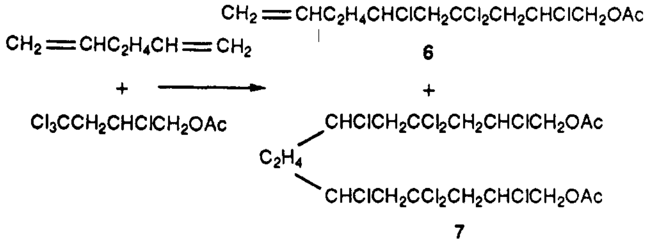


Figure 1. GPC spectra of the products of the telomerization of 1,5-hexadiene with 2,2,2-trichloroethyl acetate catalyzed with $RuCl_2(PPh_3)_3$: R_o = 1.6, dotted line; R_o = 3.2, full line.

But it is more difficult to attribute the peaks at 56 and 52 × 10^{-6}. However, the multiplicity sequence spectrum shows that they correspond to the CHCl group and the methylene group in the α position about CCl_2, respectively. Such interpretation is contrary to that of compound 2 since in this latter case the methylene group is located in the α position to the CCl_3 group, which is more electroattractive than CCl_2 in compound 4 or 5.

(B) Telomerization of 1,5-Hexadiene with $CCl_3CH_2CHClCH_2OCOCH_3$.



$$\begin{array}{ccl} CH_2{=}CHC_2H_4CH{=}CH_2 & & CH_2{=}CHC_2H_4CHClCH_2CCl_2CH_2CHClCH_2OAc \quad \mathbf{6} \\ + & \longrightarrow & + \\ Cl_3CCH_2CHClCH_2OAc & & C_2H_4\begin{cases} CHClCH_2CCl_2CH_2CHClCH_2OAc \\ CHClCH_2CCl_2CH_2CHClCH_2OAc \end{cases} \quad \mathbf{7} \end{array}$$

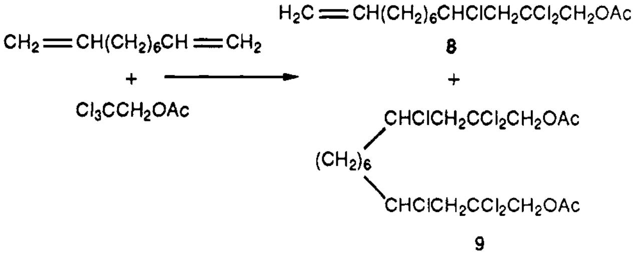
In this case too, we notice that the high R_o ratio favors the formation of diadduct 7: R_o = 1.6, 70% of 6 and 25% of 7; R_o = 3.2, 30% of 6 and 60% of 7.

The separation of 6 and 7 has been performed as in the first case by distillation and chromatography (90:10 petroleum ether/diethyl ether).

The NMR spectra of compounds 6 and 7 represent the superposition of the spectra of compounds 4, 5, and the corresponding telogen. As previously, we observe two peaks separated into two parts, which come from the presence of both diastereoisomers.

The details of the characteristics of the spectra are given in the Experimental Part.

(C) Telomerization of 1,9-Decadiene with $CCl_3CH_2OCOCH_3$. In the literature we have noticed that no article mentions any telomerization of this monomer. It is interesting since on the one hand it does not favor the cyclization and on the other hand it may lead to rather high molecular weight telomers.



$$\begin{array}{ccl} CH_2{=}CH(CH_2)_6CH{=}CH_2 & & H_2C{=}CH(CH_2)_6CHClCH_2CCl_2CH_2OAc \quad \mathbf{8} \\ + & \longrightarrow & + \\ Cl_3CCH_2OAc & & (CH_2)_6\begin{cases} CHClCH_2CCl_2CH_2OAc \\ CHClCH_2CCl_2CH_2OAc \end{cases} \quad \mathbf{9} \end{array}$$

As previously, the reaction has been followed by GPC, but the separation by distillation is impossible due to their high molecular weights. The telechelic oligomer 9 has been isolated by a supercritical fluid. McGrath[39,40] showed that such a technique was suitable for a selective separation of monodispersed oligomers in a mixture. In our case, we chose CO_2 as the supercritical fluid.

The telechelic 9 has been characterized by ^1H NMR. Actually the most interesting difference lies on the appearance of three complex signals in the (1.1–1.9) × 10^{-6} range, which correspond to the central methylene groups. These in α, β, and γ positions about the –CHCl– group give signals at 1.85, 1.45, and 1.15 × 10^{-6}, respectively.

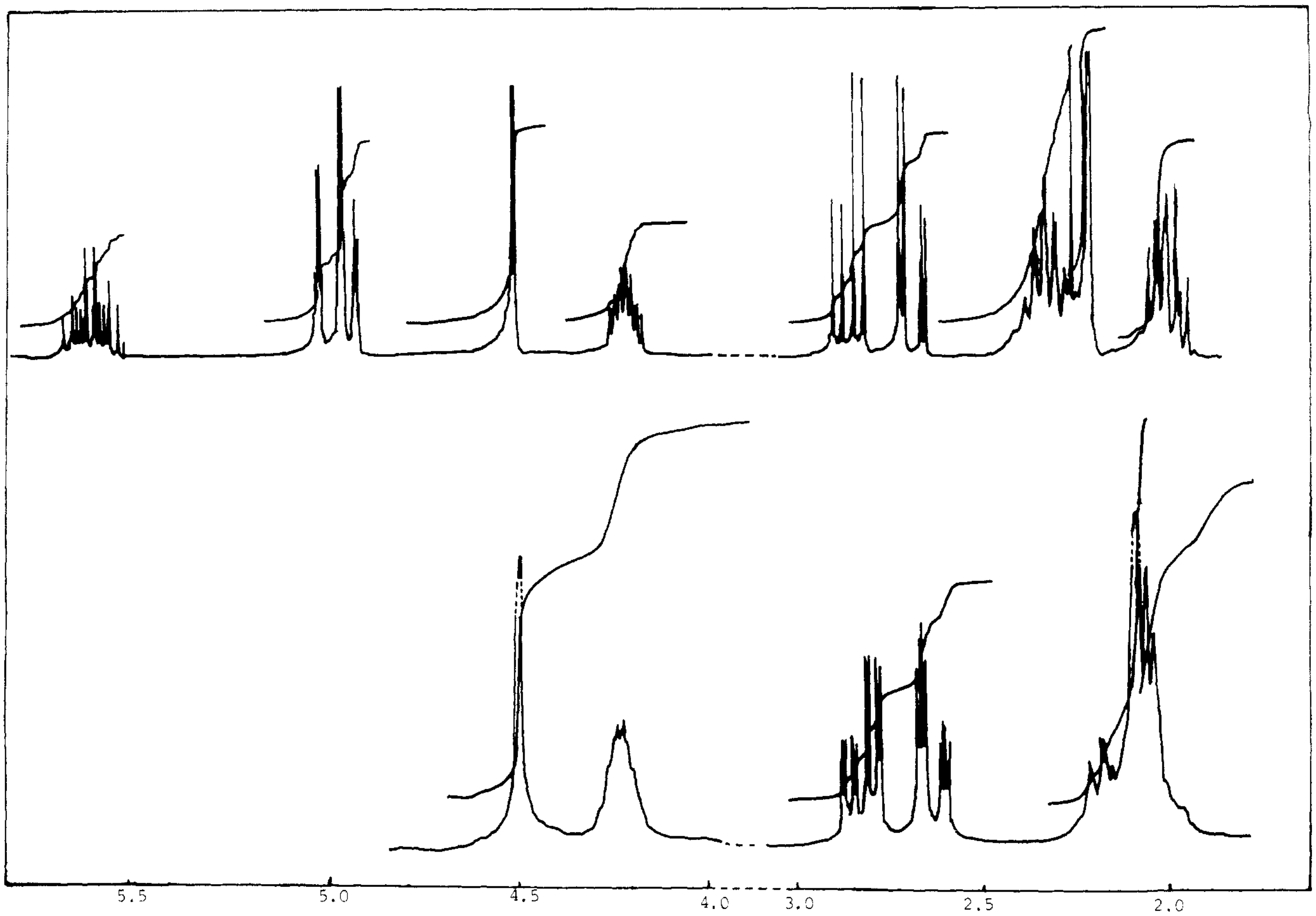


Figure 2. ^{1}H NMR spectra of **4** (top) and **5** (bottom).

In ^{13}C NMR the assignment is given as follows ($\delta 10^{-6}$):

115.82 38.89 24.95 27.88
CH_2=CH—CH_2—CH_2—CH_2—CH_2—CH_2—
136.29 29.24 24.90

55.72 86.31 169.57
CH_2—CHCl—CH_2—CCl_2—CH_2—OCO—CH_3
33.76 52.25 69.58 20.39

(CH_3—CO—O—CH_2—CCl_2—CH_2—CHCl—CH_2—
20.23 168.91 70.25 87.56 52.38 56.64 30.55
CH_2—CH_2)—
28.10 25.13

(D) Telomerization of 1,9-Decadiene with $CCl_3CH_2CHClCH_2OAc$. In this case the telomerization of 1,9-decadiene with $CCl_3CH_2CHClCH_2OAc$ catalyzed with $RuCl_2(PPh_3)_3$ led to the expected monoadduct **10** and difunctional telomer **11**.

CH_2=CH$(CH_2)_6$CHCl$CH_2CCl_2CH_2$CHClCH_2OAc
10
[$(CH_2)_3$CHCl$CH_2CCl_2CH_2$CHClCH_2OAc$]_2$
11

Contrary to the previous case, both products were separated by liquid–liquid extraction with hexane and decane.

The ^{1}H NMR spectra are very complex (two ABX systems) at about 2.8 × 10^{-6} corresponding to both methylene groups in the α position to the CCl_2 group, and it is similar in both spectra.

The ^{13}C NMR confirms our interpretation, and Figure 2 shows the spectra of **10** and **11**. As previously, the attribution of each peak is made by comparison with the model compound. The main difficulty encountered is about C^3 (allylic) and C^8 (α of CHCl group) in compound **10**. Levy[41] mentions that for 1,7-octadiene the allylic carbon and the central methylene groups give signals at 34.3 and 29.0 × 10^{-6}, respectively. This allows us to attribute the signals at 33 and 39 to the allylic methylene and methylene in the α position about the CHCl group, respectively. A confirmation of that attribution is made in the spectrum of diadduct. So, the peak at 39.4 × 10^{-6} should be attributed to the CHCl group.

(3) Chemical Change. The hydrolyses of diacetates into diols were performed by using potassium cyanide in a catalytic amount with methanol at room temperature according to Herzig et al.[42] The method avoids dehydrochlorination of our adducts by a very hard base. All of these chemical reactions were quantitative:

$$CH_3COOR_{Cl}OCOCH_3 \xrightarrow[MeOH]{KCN} HOR_{Cl}OH + 2CH_3CO_2CH_3$$

With diacetates **5** and **11** we obtained diols **5′** and **11′**.

$HOCH_2CCl_2CH_2CHCl(CH_2)_2CHClCH_2CCl_2CH_2OH$
5′
$HOCH_2CHClCH_2CCl_2CH_2CHCl$-
$(CH_2)_6CHClCH_2CCl_2CH_2CHClCH_2OH$
11′

In ^{1}H and ^{13}C NMR we notice the absence of an acetate function (peaks at about 2 × 10^{-6} in the ^{1}H NMR and 170/20 × 10^{-6} in the ^{13}C NMR).

Furthermore, the methylene group in the α position about the hydroxy group is shifted more toward the low fields.

Moreover, it is interesting to notice that **5′** crystallizes (F = 98–100° ($CHCl_3$)) whereas **11′** is a liquid. The crys-

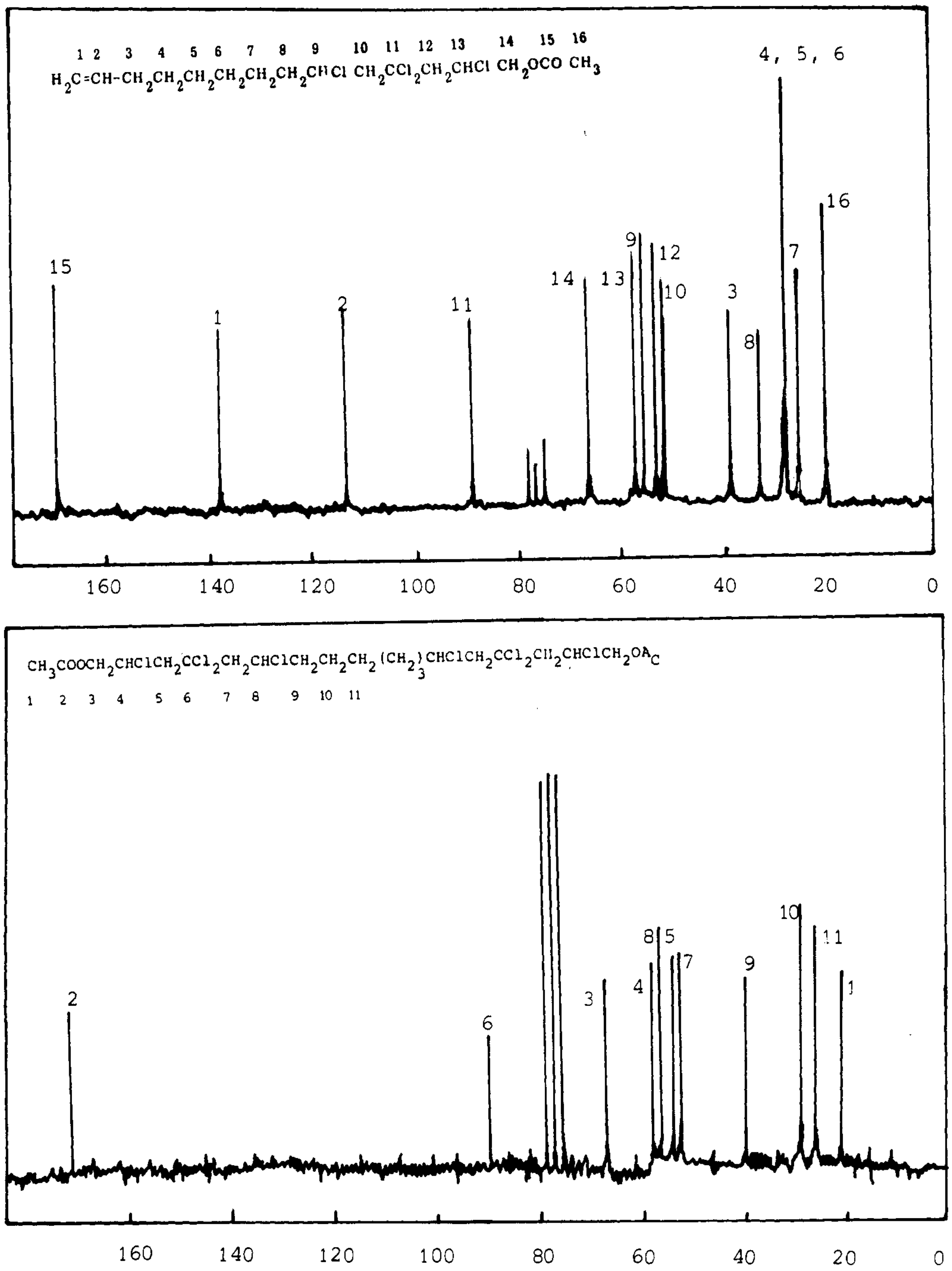


Figure 3. ^{13}C NMR spectra of **10** (top) and **11** (bottom).

talline behavior can be explained by the presence of a high chlorine content in the molecule **5′** just like in $HOCH_2CCl_2CH_2CHClCH_2OH$ (F = 43° ($CHCl_3$)),[37] and yet the hexamethylene group prevents **11′** from crystallizing. Furthermore, DSC characterization shows a change in the T_g. For compound **5′** we found $T_g = -20 \pm 2$ °C whereas for telomer **11′** $T_g = -38 \pm 2$ °C.

Conclusion

The redox catalysis carried out with dichlorotris(triphenylphosphine)ruthenium(II) of a nonconjugated diene (1,4-pentadiene, 1,5-hexadiene, and 1,9-decadiene) with CCl_4, 2,2,2-trichloroethyl acetate, or 2,4,4,4-tetrachlorobutyl acetate allowed us to prepare telechelic oligomers with different molecular weights. Such a catalyst is very interesting for the 1:1 monoaddition and excludes the formation of cyclic compounds.

The influences of both R_0 and C_0 direct the reaction toward the formation of the telechelic product.

Moreover, it is interesting to notice that the heavy telomers have been purified either by supercritical extraction, using carbon dioxide as the supercritical fluid without producing dehydrochlorination products, or by liquid–liquid extraction.

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

Experimental Part

Because of both low boiling points of 1,4-pentadiene (Eb_{760} = 25–26 °C) and 1,5-hexadiene (Eb_{760} = 58–59 °C), we carried out these telomerizations in Carius tubes. However, the different reactions using 1,9-decadiene were performed either in Carius tubes (CT) or at atmospheric pressure (Eb_{760} = 169 °C) in a two-necked round-bottom flask equipped with a condenser and a device for the introduction of nitrogen.

The Carius tubes we used had the following characteristics:

type of CT	small	medium
thickness, mm	2	3
outside diameter, mm	23	40
length, mm	260	310

These tubes were first saturated with nitrogen and then filled with the reactives, under nitrogen, cooled in a liquid nitrogen/acetone mixture ($T \sim -80$ °C), sealed, and placed into the cavity of a block made of aluminum, put in a shaken autoclave equipped with a thermoregulator. The temperature was fixed at 115 °C, and the time of reaction was about 14-20 h. At the end of the reaction the tube was left at room temperature and then cooled with liquid nitrogen and opened.

After the reaction, in the case of the telomerization of 1,4-pentadiene with CCl_4, the solvent and volatile reactants were evaporated and the residue was analyzed by gas chromatography using a Delsi apparatus (Model 330) equipped with an OV1 column (filled up with 3% silicone grease), 1 m long and with an inner diameter of 1/8 in. The nitrogen pressure at the entrance of the column was 0.6 bar, and the detector and injector temperatures were 260 and 255 °C, respectively. The temperature program started from 60 °C and reached 270 °C with a heating rate of 15 °C/min. The GC apparatus was connected to a Hewlett-Packard integrator (Model 3390) or Delsi Enica 10, which automatically calculated the area of each peak on the spectrum.

In the cases of the telomerization of 1,5-hexadiene and 1,9-decadiene with $RCCl_3$ (R = CH_2OAc and $CH_2CHClCH_2OAc$), the gross of these reactions was monitored by GPC usig a Trivector Trilab apparatus equipped with a Knauer HPLC (Model 64) pump. We used THF as eluent (flow 1.5 mL/min at T = 30 °C). The separation was carried out with a set of three Polymer Lab columns; the diameters of the pores were 1000, 500, and 50 Å. The detection has been performed by a Knauer differential refractometer.

The different pure telomers were characterized by ^1H and ^{13}C NMR at room temperature. ^1H NMR spectra were recorded on a Bruker CW 60 apparatus or for a higher resolution on a Bruker WM 360 or Bruker AC 250, by using deuterated chloroform as the solvent and tetramethylsilane as the internal reference. The letters s, d, t, q, and m designate singlet, doublet, triplet, quartet, and multiplet, respectively.

The ^{13}C NMR spectra were performed on a Bruker WP 80 apparatus, and the telomers were generally diluted in $CDCl_3$ (reference).

Dichlorotris(triphenylphosphine)ruthenium(II) was prepared according to Stephenson et al.[43] This catalyst might be oxidized from air and usually turns to a green color;[44] thus, all the reactions using such a catalyst were carried out under nitrogen. We noticed that it was compulsory to take this catalyst off after reaction by precipitation in hexane or diethyl ether before distilling the gross, because this complex might produce secondary reactions such as dehydrochlorination by degradation.

Telomerization of 1,4-Pentadiene with CCl_4. We introduced into the CT a mixture of 0.075 mol of 1,4-pentadiene, 0.19 mol of CCl_4, and 6.3×10^{-4} mol of Ru complex. After 12 h at 115 °C, the gross was distilled.

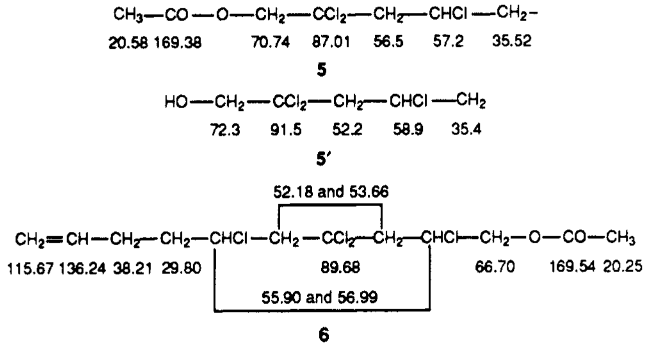
A colorless liquid was isolated ($Eb_{0.15mbar}$ = 38-39 °C) and corresponded to the monoadduct 1. The following pure fraction was also a colorless liquid ($Eb_{0.2mbar}$ = 100-103 °C) and corresponded to the diadduct 2.

Monoadduct 4,6,6,6-Tetrachloro-1-hexene (1). ^1H NMR: same characteristics as Corallo et al.[17] ^{13}C NMR ($CDCl_3$, 10^{-6}): δ 136.72, 115.69, 96.28, 62.51, 54.55, 42.32. Anal. Calcd for $C_6H_8Cl_4$ (M = 222 g) (found): C, 32.35 (32.05); H, 3.12 (3.0); Cl, 63.75 (63.96).

Diadduct 1,1,1,3,5,7,7,7-Octachloroheptane (2). ^1H NMR: same characteristics as Corallo et al.[17] ^{13}C NMR ($CDCl_3$, 10^{-6}): δ 96.29, 96.13, 62.12, 61.63, 54.59, 53.28, 47.87, 47.49. Anal. Calcd for $C_7H_8Cl_8$ (M = 376 g) (found): C, 22.46 (22.34); H, 2.34 (2.13); Cl, 74.97 (75.53).

Telomerization of 1,5-Hexadiene with CCl_3CH_2OAc. In order to eliminate the stabilizer, we treated the diene with a diluted sodium hydroxide solution (10%) followed by washing several times with water.

Chart I



The diene was then stored under molecular sieves (3 Å). We filled up the CT with 0.05 mol of 1,5-hexadiene, 0.16 mol of CCl_3CH_2OAc, and 0.38 g of the Ru complex (case where R_0 = 3.2). After reaction and treatment, the product was characterized by GPC and the monoadduct 4 was then isolated by distillation ($Eb_{0.001bar}$ = 60-65 °C).

Monoadduct 2,2,4-Trichloro-7-octenyl Acetate (4). ^1H NMR (Figure 2; $CDCl_3$, 10^{-6}): δ 2.0 (s, 3 H), 1.9 (m, 2 H), 2.2 (m, 2 H), 2.8 (dq, 2 H, ABX system, AB part), 4.2 (m, 1 H, ABX system, X part), 4.5 (s, 2 H), 5.0-5.9 (m, 3 H). ^{13}C NMR ($CDCl_3$, 10^{-6}): δ 20.27, 29.89, 38.18, 52.18, 56.76, 70.42, 87.19, 115.73, 136.85, 168.85. Anal. Calcd for $C_{10}H_{15}Cl_3O_2$ (M = 273.5 g) (found): C, 44.02 (43.88); H, 5.39 (5.48); Cl, 38.35 (38.94).

The residue was chromatographed over a silica column using a petroleum ether/diethyl ether blend (90:10) as eluent with an increasing gradient of polarity. After evaporation of the solvent, the diacetate crystallized in yellow needles (F = 82-84 °C).

Diadduct 2,2,4,7,9,9-Hexachloro-1,10-diacetoxydecane (5). ^1H NMR ($CDCl_3$, 10^{-6}): δ 1.85-2.15 (m, 2 H), 2.10 (s, 3 H), 4.50 (s, 2 H), 2.75 (8 peaks, 2 H, ABX system, AB part, J_{AX} = 2.3 Hz, J_{BX} = 6.9 Hz, J_{AB} = 15.7 Hz), 4.25 (4 peaks, 1 H, ABX system, X part). ^{13}C NMR ($CDCl_3$, 10^{-6}): Spectral data appear in Chart I. Anal. Calcd for $C_{14}H_{20}Cl_6O_4$ (M = 465 g) (found): C, 36.34 (36.13); H, 4.15 (4.30); Cl, 46.12 (45.81).

Hydrolysis of Diadduct 5. A mixture composed of 0.0043 mol of 5, 0.0004 mol of KCN, and about 30 mL of methanol was stirred for 12 h at room temperature under a nitrogen flow.

After filtration over silica, evaporation of the solvent, and recrystallization in chloroform, we obtained white crystals (F = 98-100 °C; $CHCl_3$).

Diol 2,2,4,7,9,9-Hexachloro-1,10-dihydroxydecane (5′). ^1H NMR (CD_3CN, 10^{-6}): δ 1.9-2.0 (m, 1 H), 2.1-2.3 (m, 1 H, 2.6-2.9 (AB part of ABX system, 2 H), 4.3-4.5 (X part, 1 H), 3.8-4.0 (m, 1 H). ^{13}C NMR (CD_3CN, 10^{-6}): Spectral data appear in Chart I. Anal. Calcd for $C_{10}H_{16}Cl_6O_2$ (M = 381 g) (found): C, 31.82 (31.50); H, 4.02 (4.20); Cl, 55.69 (55.91).

Telomerization of 1,5-Hexadiene with $CCl_3CH_2CHClCH_2OAc$. The Carius tube was filled up with 0.04 mol of 1,5-hexadiene, 0.13 mol of telogen, and 3.2×10^{-4} mol of the ruthenium complex. After 16 h of reaction at 115 °C, the GPC spectrum exhibited three main peaks: excess of telogen and mono- and diadduct.

The monoadduct 6 was distilled ($Eb_{0.05mbar}$ = 129-132 °C).

2,4,4,6-Tetrachloro-9-nonenyl Acetate (6). ^1H NMR ($CDCl_3$, 10^{-6}): δ 1.8-1.9 (m, 2 H), 2.0 (s, 3 H), 2.1-2.3 (m, 2 H), 2.6-2.8 (2 AB parts of ABX systems, 4 H), 4.5 (qd, 2 H), 4.0-4.3 (2X parts), 2 H), 4.9-5.1 (m, 1 H), 5.7-5.9 (m, 2 H). ^{13}C NMR ($CDCl_3$, 10^{-6}): Spectral data appear in Chart I. Anal. Calcd for $C_{12}H_{18}Cl_4O_2$ (M = 336 g) (found): C, 42.72 (42.86); H, 5.59 (5.36); Cl, 42.51 (42.26).

We performed a column chromatography as for 5, and we obtained a yellow liquid, the NMR characteristics of which show that the diacetate was obtained.

2,4,4,6,9,11,11,13-Octachloro-1,14-diacetoxytetradecane (7). ^1H NMR ($CDCl_3$, 10^{-6}): δ 1.8-2.1 (m, 2 H), 2.0 (s, 3 H), 2.6-2.8 (2 AB parts, 4 H), 4.1-4.4 (m, 4 H) ^{13}C NMR ($CDCl_3$, 10^{-6}): δ 20.29, 30.24, 51.62, 52.89, 55.76, 56.91, 67.01, 88.54, 169.60. Anal. Calcd for $C_{18}H_{26}Cl_8O_4$ (M = 590 g) (found): C, 36.48

(36.61); H, 4.62 (4.41); Cl, 47.88 (48.14).

Telomerization of 1,9-Decadiene. (a) Elimination of the Stabilizers. We got rid of the stabilizers from this diene in the same way as we did in the case of 1,5-hexadiene.

(b) Telomerization of 1,9-Decadiene with Cl_3CCH_2OAc. We put in the Carius tube 8.2 g (0.059 mol) of 1,9-decadiene, 17.8 g (0.013 mol) of Cl_3CCH_2OAc, and 0.50 g (5.2×10^{-4} mol) of $RuCl_2(PPh_3)_3$.

After reaction (16 h at 115 °C) the gross was extracted by supercritical extraction with carbon dioxide. The pressure was gradually increased up to 230 bar in order to eliminate all the lower molecular weight compounds (solvent and telogen), and then we collected several fractions.

We recovered in the extraction cell a residue that corresponds to the diacetate **9**.

Monoadduct 2,2,4-Trichloro-11-undecenyl Acetate (8). ^{1}H NMR ($CDCl_3$, 10^{-6}): δ 1.3–1.8 (m, 12 H), 2.0 (s, 3 H), 2.7–2.8 (AB system, J_{AB} = 14.2 Hz, J_{AX} = 4.2 Hz, J_{BX} = 6.8 Hz), 4.0–4.2 (X part, 1 H), 4.5 (s, 2 H), 4.8–5.1 (m, 1 H), 5.6–5.9 (m, 2 H). ^{13}C NMR ($CDCl_3$, 10^{-6}): δ 20.39, 24.95, 27.88, 29.24, 33.76, 38.89, 52.25, 55.72, 69.58, 86.31, 115.82, 136.29, 169.57. Anal. Calcd for $C_{14}H_{23}Cl_3O_2$ (M = 329.5 g) (found): C, 51.28 (50.99); H, 6.81 (6.98); Cl, 32.58 (32.32).

Diadduct 2,2,4,11,13,13-Hexachloro-1,14-diacetoxytetradecane (9). ^{1}H NMR ($CDCl_3$, 10^{-6}): δ 1.5 (m, 2 H), 1.8 (m, 2 H), 2.1 (s, 3 H), 2.8 (AB system, 2 H J_{AX} = 4.4 Hz, J_{BX} = 6.7 Hz, J_{AB} = 14.6 Hz), 4.1 (X part, 1 H), 4.5 (s, 2 H). ^{13}C NMR ($CDCl_3$, 10^{-6}): δ 20.23, 25.13, 28.10, 30.55, 52.38, 56.64, 70.25, 87.36, 168.91. Anal. Calcd for $C_{18}H_{28}Cl_6O_4$ (M = 521 g) (found): C, 41.72 (41.46); H, 5.19 (5.37); Cl, 41.24 (40.88).

(c) Telomerization of 1,9-Decadiene with 2,4,4,4-Tetrachlorobutyl Acetate. The Carius tube was filled with a mixture composed of 33.2 g (0.239 mol) of 1,9-decadiene, 191.8 g (0.754 mol) of 2,4,4,4-tetrachlorobutyl acetate, and 1.85 g (1.9×10^{-3} mol) of $RuCl_2(PPh_3)_3$. The reaction time was 20 h at 115 °C. After opening of the tube, the gross was added dropwise into 7-fold excess of diethyl ether, which was vigorously stirred. After filtration of the catalyst and evaporation of the solvent, we distilled 115.8 g of telogen. The residue was then added dropwise in a hexane solution stirred vigorously and then poured into a separatory funnel. The orange lower phase was extracted twice with decane and led to the telechelic compound whereas the upper phase was mainly composed of the monoadduct product, which was extracted by isooctane (upper phase).

Monoacetate 2,4,4,6-Tetrachloro-13-tetradecenyl Acetate (10). ^{1}H NMR ($CDCl_3$, 10^{-6}): δ 1.1–1.5 (m, 6 H), 1.7 (m, 2 H), 1.9–2.1 (m, 4 H), 2.0 (s, 3 H), 2.7 (AB parts of ABX systems, 4 H), 4.2 (m, 2 H), 4.4 (m, 2 H), 4.6 (m, 2 H), 5.7 (m, 1 H). ^{13}C NMR ($CDCl_3$, 10^{-6}): δ 20.43, 25.76, 28.49, 29.09, 33.46, 39.21, 52.36, 53.80, 55.18, 57.81, 66.84, 89.80, 114.16, 138.58, 169.72. Anal. Calcd for $C_{16}H_{26}Cl_4O_2$ (M = 392 g) (found): C, 48.71 (48.98); H, 6.98 (6.63); Cl, 36.01 (36.22).

Diacetate 2,4,4,6,13,15,15,17-Octachloro-1,18-diacetoxyoctadecane (11). ^{1}H NMR ($CDCl_3$, 10^{-6}): δ 1.3–1.6 (m, 4 H), 1.8 (m, 2 H), 2.1 (s, 3 H), 2.7 (2 AB parts of ABX systems, 4 H), 4.3 (m, 2 H), 4.5 (m, 2 H). ^{13}C NMR ($CDCl_3$, 10^{-6}): δ 20.47, 25.71, 28.44, 39.20, 52.40, 53.66, 56.22, 57.75, 66.98, 89.79, 169.92. Anal. Calcd for $C_{22}H_{34}Cl_8O_4$ (M = 646 g) (found): C, 40.58 (40.87); H, 5.39 (5.26); Cl, 44.18 (43.96).

Hydrolysis of the Diacetate. A total of 1.5 g (0.0023 mol) of diacetate 11, 0.015 g (0.0002 mol) of potassium cyanide, and about 40 mL of methanol were stirred at room temperature for 12 h. After filtration over silica and evaporation of the methanol, we obtained a yellow-orange oil. ^{1}H NMR (DMSO-d_6, 10^{-6}): δ 1.2–1.6 (m, 4 H), 1.7–2.0 (m, 2 H), 2.6–3.2 (2 AB parts of ABX systems, 4 H), 3.6 (CD part of CDY system, 2 H), 4.3 (m, 2 H), 5.4 (shift when diluted, 1 H). ^{13}C NMR (DMSO-d_6, 10^{-6}): δ 25.62, 28.35, 37.69, 38.72, 38.94, 51.93, 55.37, 58.76, 65.80, 91.62. Anal. Calcd for $C_{18}H_{30}Cl_8O_2$ (M = 562 g) (found): C, 38.29 (38.43); H, 5.68 (5.34); Cl, 50.79 (50.53).

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