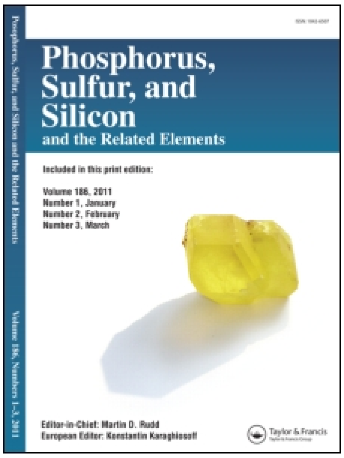

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REDOX TELOMERIZATION OF DIETHYL ALLYL AND VINYLPHOSPHONATES WITH HALO COMPOUNDS AS TELOGENS

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Using copper salts as catalyst, we have telomerized diethyl allyl- and vinylphosphonate monomers with several different halo compounds as telogens. There is a linear relationship between log yield (telogen reactivity) and the σ^* Taft constant of the R group in $RCCl_3$ as telogen. Using this relation, we have determined the values of the σ^* constant for some other halo compounds and have established a classification of these telogens. We have likewise determined the structure of telomers formed with copper and iron salts as initiators for both monomers.

INTRODUCTION

In the preceding paper[1,2] we reported the utilization of the redox telomerization of diethyl vinyl- and allylphosphonate monomers with CCl_4 as telogen. The results obtained are representative for halo telogens in general.

In this paper we have measured the reactivities of several different halogenated compounds as telogens and we have established a linear relationship between log (telogen reactivity) and the σ^* Taft constant of the R group in $RCCl_3$ with the same monomers. In this study we have used the chloro, bromo and functional compounds as telogens and the structure of telomers obtained has been identified by means of infrared, nmr and mass spectra.

RESULTS AND DISCUSSION

Reactivity of Halo Compounds as Telogens

In principle, reaction rates can be correlated by summing the contributions of all structural and reaction parameters that have an effect on the free energy of activation. The classical example of linear free energy equation is the Hammett equation[3]

$$\log (k/ko) = \sigma\rho$$

This relation was developed to correlate reaction rates and equilibria for substituted aromatic compounds, where ρ reflects the sensitivity of the reaction to polar and resonance substitution effects, as represented quantitatively by the substitutent constant σ. The Taft equation[4] is a linear free energy relation similar in form to the Hammett equation, but was developed for aliphatic compounds:

$$\log (k/ko) = \sigma^* \rho^*$$

In radical chemistry, the Taft equation has been used to correlate the rate of $CCl_3^{\bullet}$ addition to substituted olefins.[5,6,7]

In this study, with diethyl vinyl- and allylphosphonate monomers, we have chosen copper salts as catalysts, which leads to monoaddition compounds.[1,2] The taxogen/telogen ratio used here is equal to one, a value which promotes the transfer reaction. In this case, the yield of the reaction measures the reactivity of telogen and, taking for granted that the telomerization reaction is first order,[8] we obtain the following equation:

$$\log \text{yield} = \log (k/ko) = \sigma^* \rho^*$$

We have established, in redox telomerization of vinyl- and allylphosphonates, that CH_2Cl_2 and CH_3Cl do not lead to monoaddition compounds under the conditions used here and a CCl_3 group is necessary in the telogen.

Using, as telogen, compounds having the $RCCl_3$ structure, we have studied the variation of log (yield) versus σ^* of Taft illustrated Figure 1.

The linear correlation coefficient between log (yield) and σ^* is equal to 0.98, confirming the linear function log (yield) $= f(\sigma^*)$.

The following relations have been established with the diethyl vinyl- and allylphosphonates:

$$\log (\text{yield}) = 0.24\ \sigma^* + 1.18 \text{ (with vinyl monomer)}$$
$$\log (\text{yield}) = 0.20\ \sigma^* + 1.08 \text{ (with allyl monomer)}$$

The reactivity of telogens is not influenced by the allyl or vinyl group of monomers studied here and the classification of R groups in $RCCl_3$ is unchanged. However, we notice a slight difference of the angular coefficient between both monomers. The comparison of angular coefficients (0.24 and 0.28) with the one observed by Anthoine[7] in the case of butadiene (0.13) shows that the telomerization of diethyl vinyl- or allylphosphonates is more sensitive to the presence of a polar group than

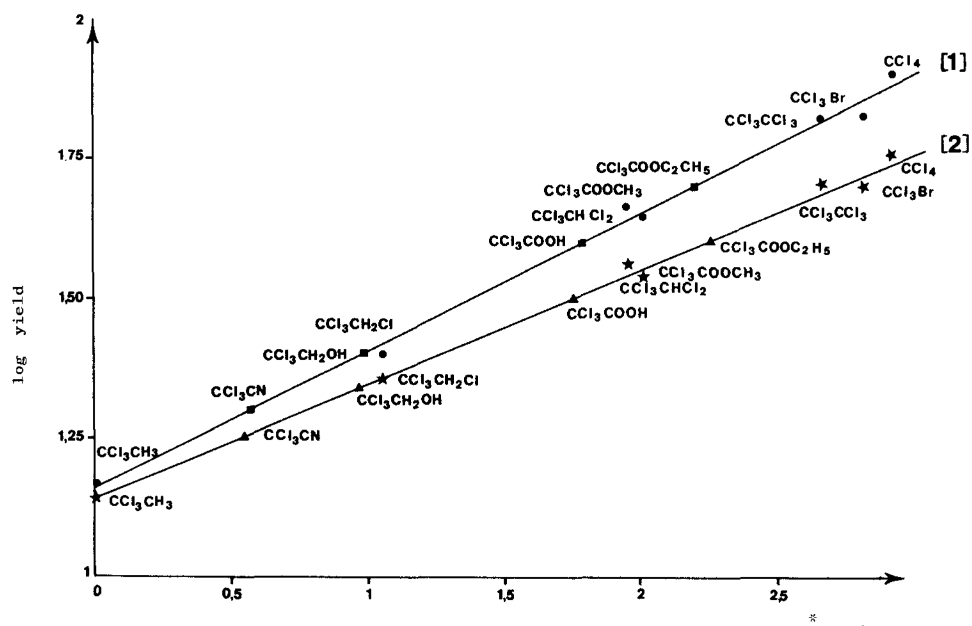

FIGURE 1 The reactivity of Telogens ($RCCl_3$) in redox telomerization of diethyl vinyl- and allylphosphonates: [1] diethyl vinylphosphonate; [2] diethyl allyphosphonate.

that of butadiene, but it is similar to the telomerization of styrene[6] (0.29). We notice, likewise, that the value of the steric-hindrance coefficient is identical with that of styrene and butadiene because in all cases the same telogens have been used. Under the same conditions we have determined, by this relation, σ^* values of various telogens containing a CCl_3 group with these phosphorus monomers (see Table I). We noticed a good correlation of values between both monomers. Similar results were observed by Anthoine[7] with butadiene in the case of $CCl_3COOC_2H_5$, confirming our results.

These results permit us to classify the substituents R of telogens $RCCl_3$ in respect to their aptitude to promote the transfer:

$$CH_3 < CN < CH_2OH < CH_2Cl < COOH < CH_2Cl_2 < COOCH_3 < COOC_2H_5 < CCl_3 < Br < Cl$$

Telomer Structures

Telogens containing only chlorine as halo substituent undergo chain transfer either by chlorine or hydrogen abstraction depending on the most stable telomer radical that can be formed. In redox telomerization it is well established that the homolytic rupture of telogens ($RCCl_3$) leads to fragments $Cl^\bullet$ and $RCCl_2^\bullet$.[8]

The structures of telomers obtained here were identified by means of ir, nmr and mass spectra; they are summarized in the Table II. With telogens studied here, we observe the formation of monoaddition compounds in all cases of telomerization by copper salts as catalysts. With iron salts the results are similar to those obtained with CCl_4 as telogen and we notice a mixture of mono- and diadduct with diethyl vinylphosphonate and only monoaddition compounds with diethyl allylphosphonate. We observe that the yields are dependent on the nature of the telogen.

The telogen has no influence on the structure of the telomers and the direction of addition is predictable. $Cl^\bullet$ is linked to the most substituted carbon and the $^\bullet CCl_2R$ residue to the least substituted one.

The stereoselectivity is caused by steric hindrance resulting from the overall dimensions of R in the vinyl or allyl monomers. In addition we have established in all

TABLE I

The reactivity of Telogens and σ^* Taft constant of R groups in $RCCl_3$ as telogen

	monomer **1**[b]		monomer **2**[b]				
Telogen[a]	yield	log (yield)	yield	log (yield)	σ^*	σ^* calc with **1**	σ^* calc with **2**
CCl_3CH_3	15	1.18	12	1.08	0		
CCl_3CHCl_2	48	1.68	37	1.57	1.94		
CCl_3CH_2Cl	25	1.40	23	1.36	1.05		
CCl_3CCl_3	68	1.83	50	1.70	2.65		
CCl_3Br	70	1.85	50	1.70	2.8		
CCl_3COOCH_3	45	1.65	35	1.54	2.0		
$CCl_3COOC_2H_5$	50	1.70	40	1.60		2.19	2.25
CCl_3CN	20	1.30	18	1.25		0.57	0.54
CCl_3CH_2OH	25	1.40	22	1.34		0.93	0.91
CCl_3COOH	40	1.60	32	1.50		1.78	1.75
CCl_4	80	1.90	57	1.75	2.9		

[a] Amount 10 mmol.
[b] Amount 10 mmol. Initiator $CuCl_2 \cdot 2H_2O$: 1 mmol. Solvent: 10 ml acetonitrile. Temperature 130°C. Reaction time 18 hrs.

TABLE II

Redox telomerization of diethyl vinyl- and allylphosphonates by different halo compounds as telogens with $FeCl_3$/benzoin

Telogen (10 mmol)	monomer **1** (10 mmol) yield (%)	n = 1 (%)	n = 2 (%)	monomer **2** (10 mmol) yield (%)	n = 1 (%)	n = 2 (%)	Telomer structure
CCl_3H	75	95	5	70	100		$Cl[H(R)C—CH_2]_nCCl_2H$
CCl_3CH_3	25	85	15	20	100		$Cl[H(R)C—CH_2]_nCCl_2CH_3$
CCl_3CHCl_2	52	90	10	40	100		$Cl[H(R)C—CH_2]_nCCl_2CHCl_2$
CCl_3CH_2Cl	30	95	5	25	100		$Cl[H(R)C—CH_2]_nCCl_2CH_2Cl$
CCl_3CCl_3	70	82	18	55	100		$Cl[H(R)C—CH_2]_nCCl_2CCl_3$
CCl_3Br	80	78	22	60	100		$Br[H(R)C—CH_2]_nCCl_3$
CCl_3COOCH_3	52	95	5	40	100		$Cl[H(R)C—CH_2]_nCCl_2COOCH_3$
$CCl_3COOC_2H_5$	55	97	3	42	100		$Cl[H(R)C—CH_2]_nCCl_2COOC_2H_5$
CCl_3CN	20	100		24	100		$Cl[H(R)C—CH_2]_nCCl_2CN$
CCl_3CH_2OH	20	100		30	100		$Cl[H(R)C—CH_2]_nCCl_2CH_2OH$
CCl_3COOH	47	100		50	100		$Cl[H(R)C—CH_2]_nCCl_2COOH$
CCl_4	85	75	25	80	100		$Cl[H(R)C—CH_2]_nCCl_3$

R = $(O)P(OC_2H_5)_2$ monomer **1**. $CH_2(O)P(OC_2H_5)_2$ monomer **2**. $FeCl_3$/Benzoin: 1/1 mmol. Solvent 10 ml acetonitrile. Temperature 130°C with $CuCl_2$ as initiator we observe the same structure but in all cases n = 1.

cases studied here that Cl comes from CCl_3 except with CCl_3Br. With this telogen two possible radicals are likely to be formed ($CCl_3^{\bullet}/Br^{\bullet}$ and $CCl_2Br^{\bullet}/Cl^{\bullet}$). We observe, in redox telomerization, the homolytic rupture into $CCl_3^{\bullet}/Br^{\bullet}$. Similar results are obtained with isobutene[9] whereas cationic telomerization leads to the fragments $CCl_2Br^{\bullet}/Cl^{\bullet}$.[10]

It is interesting to note that the functional telogens give compounds with a structure similar to those obtained with alkyl chlorides. However we observe that only monoaddition compounds are formed with these telogens and that the initiator has no influence on the distribution of telomers. Similar results were observed with isoprene and these telogens.[11]

EXPERIMENTAL

The experimental techniques (materials and telomerization procedure) used in this study were outlined in the preceding paper.[2]

The operating conditions for the experiments are reported in the tables.

Telomers of diethyl vinylphosphonate with CCl_3H as telogen

n = 1 b.p. 105°C (at 0.01 mbar) (Found: C, 29.7; H, 5.1; Cl, 37.4; P, 11.0 $C_7H_{14}Cl_3PO_3$ requires C, 29.7; H, 4.9; Cl, 37.5; P, 10.9%). γ_{max} 795 (CCl_2H), 540 (CCl) cm^{-1}. M.s. showed the molecular ion (M^+, 282) and fragment ions at 247 (M-Cl), 199 (M-CCl_2H).

n = 2 b.p. 119°C (at 0.01 mbar) (Found: C, 34.9; H, 6.1; Cl, 23.7; P, 13.8 $C_{13}H_{27}Cl_3P_2O_6$ requires C, 34.9; H, 6.0; Cl, 23.8; P, 13.9%). γ_{max} 810 (CCl_2H), 540 (CCl) cm^{-1}. M.s. showed the molecular ion (M^+, 446) and fragment ion at 411 (M-Cl), 363 (M-CCl_2H).

With CCl_3CH_3 as telogen

n = 1 b.p. 126°C (at 0.01 mbar) (Found: C, 32.4; H, 5.4; Cl, 37.3; P, 104 $C_8H_{16}Cl_3PO_3$ requires C, 32.3;

H, 5.4; Cl, 35.8: P, 10.4%). γ_{max} 840 (CCl_2CH_3), 540 (CCl) cm^{-1}. M.s. showed the molecular ion (M^+, 296) and fragment ions at 281 ($M-CH_3$), 199 ($M-CCl_2CH_3$), 261 (M-Cl).

$n = 2$ b.p. 140°C (at 0.01 mbar) (Found: C, 36.5; H, 6.3; Cl, 23.0; P, 13.5 $C_{14}H_{29}Cl_3P_2O_6$ requires C, 36.4; H, 6.3; Cl, 23.0; P, 13.4%) γ_{max} 840 (CCl_2CH_3), 545 (CCl) cm^{-1}. M.s. showed the molecular ion (M^+, 460) and fragment ions at 445 ($M-CH_3$), 363 ($M-CCl_2CH_3$), 425 (M-Cl).

With CCl_3CHCl_2 as telogen

$n = 1$ b.p. 137°C (at 0.01 mbar) (Found: C, 26.4; H, 3.9; Cl, 48.4; P, 8.4 $C_8H_{14}Cl_5PO_3$ requires C, 26.2; H, 3.8; Cl 48.4; P, 8.4%) γ_{max} 820 (CCl_2H), 545 (CCl) cm^{-1}. M.s. showed the molecular ion (M^+, 364) and fragment ions at 281 ($M-CHCl_2$), 199 ($M-CCl_2CHCl_2$), 329 (M-Cl).

$n = 2$ b.p. 148°C (at 0.01 mbar) (Found: C, 31.8; H, 5.1; Cl, 33.4; P, 11.6 $C_{14}H_{27}Cl_5P_2O_6$ C, 31.7; H, 5.1; Cl, 33.4; P, 11.6 $C_{14}H_{27}Cl_5P_2O_6$ C, 31.7; H, 5.1; Cl, 33.4; P, 11.7%) γ_{max} 825 (CCl_2H), 545 (CCl) cm^{-1}. M.s. showed the molecular ion ((M^+, 528) and fragment ions at 445 ($M-CHCl_2$), 363 ($M-CCl_2CHCl_2$), 493 (M-Cl).

With CCl_3CH_2Cl

$n = 1$ b.p. 140°C (at 0.01 mbar) (Found: C, 29.0; H, 4.6; Cl, 42.7; P, 9.3 $C_8H_{15}Cl_4PO_3$ C, 28.9; H, 4.5; Cl, 42.7; P, 9.3%) γ_{max} 545 (CCl) cm^{-1}. M.s. showed the molecular ion (M^+, 330) and fragment ions at 295 (M-Cl), 281 ($M-CH_2Cl$), 199 ($M-CCl_2CH_2Cl$).

$n = 2$ b.p. 151°C (at 0.01 mbar) (Found: C, 34.0; H, 5.7; Cl, 28.5; P, 12.4 $C_{14}H_{28}Cl_4P_2O_6$ C, 33.9; H, 5.6; Cl 28.6; P, 12.5%) γ_{max} 545 (CCl) cm^{-1}. M.s. showed the molecular ion (M^+, 494) and fragment ions at 459 (M-Cl), 445 ($M-CH_2Cl$), 363 ($M-CCl_2CH_2Cl$).

With CCl_3CCl_3 as telogen

$n = 1$ b.p. 148°C (at 0.01 mbar) (Found : C, 24.0; H, 3.3; Cl, 52.9; P, 7.8 $C_8H_{13}Cl_6PO_3$ requires C, 24.0; H, 3.2; Cl, 53.1; P, 7.7%) γ_{max} 545 (CCl), 740 (CCl_3) cm^{-1}. M.s. showed the molecular ion (M^+, 398) and fragment ions at 363 (M-Cl), 281 ($M-CCl_3$), 199 ($M-CCl_2CCl_3$).

$n = 2$ b.p. 157°C (at 0.01 mbar) (Found: C, 29.9; H, 4.6; Cl, 37.6; P, 10.9 $C_{14}H_{26}Cl_6P_2O_6$ requires C, 29.8; H, 4.6; Cl, 37.7; P, 11.0%) γ_{max} 545 (CCl), 745 (CCl_3) cm^{-1}. M.s. showed the molecular ion (M^+, 562) and fragment ions at 527 (M-Cl), 445 ($M-CCl_3$), 363 ($M-CCl_2CCl_3$).

With CCl_3Br as telogen

$n = 1$ b.p. 142°C (at 0.01 mbar) (Found: C, 23.3; H, 3.6; Cl, 29.3; Br, 22.1; P, 8.6 $C_7H_{13}Cl_3BrPO_3$ requires C, 23.2; H, 3.6; Cl, 29.4; Br, 22.1; P, 8.6%) γ_{max} 605 (CBr) 730 (CCl_3) cm^{-1}. M.s. showed the molecular ion (M^+, 360) and fragment ions at 281 (M-Br), 243 ($M-CCl_3$).

$n = 2$ b.p. 151°C (at 0.01 mbar) (Found: C, 29.7; H, 5.0; Cl, 20.2; Br, 15.2; P, 11.7 $C_{13}H_{26}Cl_3BrP_2O_6$ requires C, 29.7; H, 5.0; Cl, 20.2; Br 15.2; P, 11.8%) γ_{max} CO5 (CBr), 730 (CCl_3) cm^{-1}. M.s. showed the molecular ion (M^+, 524) and fragment ions at 445 (M-Br) 407 ($M-CCl_3$).

With CCl_3COOCH_3 as telogen

$n = 1$ b.p. 145°C (at 0.01 mbar) (Found: C, 31.7; H, 4.7; Cl, 31.1; P, 9.0 $C_9H_{16}Cl_3PO_5$ requires C, 31.7; H, 4.7; Cl, 31.1; P, 9.1%) γ_{max} 540 (CCl), 1725 ($COOCH_3$), 820 (CCl_2) cm^{-1}. M.s. showed the molecular ion (M^+, 340) and fragment ions at 305 (M-Cl), 325 ($M-CH_3$), 281 ($M-COOCH_3$), 199 ($M-CCl_2COOCH_3$).

$n = 2$ b.p. 157°C (at 0.01 mbar) (Found: C, 35.7; H, 5.8; Cl, 21.0; P, 12.1 $C_{15}H_{29}Cl_3P_2O_8$ requires C, 35.6; H, 5.7; Cl, 21.0; P, 12.2%) γ_{max} 540 (CCl), 1725 ($COOCH_3$), 820 (CCl_2) cm^{-1}. M.s. showed the molecular ion (M^+, 504) and fragment ions at 469 (M-Cl), 489 ($M-CH_3$), 445 ($M-COOCH_3$), 363 ($M-CCl_2COOCH_3$).

With $CCl_3COOC_2H_5$ as telogen

$n = 1$ b.p. 149°C (at 0.01 mbar) (Found: C, 33.8; H, 5.1; Cl, 29.9; P, 8.7 $C_{10}H_{18}Cl_3PO_5$ requires C, 33.8; H, 5.1; Cl, 29.9; P, 8.8%) γ_{max} 540 (CCl), 1745 ($COOC_2H_5$) 820 (CCl_2) cm^{-1}. M.s. showed the molecular ion (M^+, 354) and fragment ions at 319 (M-Cl), 325 (M-C_2H_5), 281 (M-$COOC_2H_5$) 199 (M-$CCl_2COOC_2H_5$).

$n = 2$ b.p. 157°C (at 0.01 mbar) (Found: C, 37.1; H, 6.0; Cl, 20.4); P, 11.9 $C_{16}H_{31}Cl_3P_2O_8$ requires C, 37.0; H, 6.0; Cl, 20.5; P, 11.9%) γ_{max} 540 (CCl), 1745 ($COOC_2H_5$) 820 (CCl_2) cm^{-1}. M.s. showed the molecular ion (M^+, 518) and fragment ions at 483 (M-Cl), 489 (M-C_2H_5), 445 (M-$COOC_2H_5$) 363 (M-$CCl_2COOC_2H_5$).

With CCl_3CN as telogen

$n = 1$ b.p. 143°C (at 0.01 mbar) (Found: C, 31.2; H, 4.2; Cl, 31.1; H, 4.2; Cl; 34.5 P, 10.1; N, 4.6%) γ_{max} 545 (CCl), 2250 (CN), 825 (CCl_2) cm^{-1}. M.s. showed the molecular ion (M^+, 307) and fragment ions at 272 (M-Cl 281 (M-CN), 199 (M-CCl_2CN).

With CCl_3CH_2OH as telogen

$n = 1$ b.p. 149°C (at 0.01 mbar) (Found: C, 30.7; H, 5.2; Cl, 33.9; P, 9.9 $C_8H_{16}Cl_3PO_4$ requires C, 30.7; H, 5.1; Cl, 34.0; P, 9.9%) γ_{max} 545 (CCl) 1035 (CH_2OH) cm^{-1}. M.s. showed the molecular ion (M^+, 312) and fragment ions at 277 (M-Cl), 281 (M-CH_2OH), 199 (M-CCl_2CH_2OH).

With CCl_3COOH as telogen

$n = 1$ b.p. 152°C (at 0.01 mbar) (Found: C, 29.4; H, 4.3; Cl, 32.4; P, 9.4 $C_8H_{14}Cl_3PO_5$ requires C, 29.3; H, 4.3; Cl, 32.4; P, 9.4%) γ_{max} 545 (CCl), 1770 (COOH) cm^{-1}. M.s. showed the molecular ion (M^+, 326) and fragment ions at 291 (M-Cl), 281 (M-COOH), 199 (CCl_2COOH).

With CCl_4 as telogen

$n = 1$ b.p. 128°C (at 0.01 mbar) (Found: C, 26.6; H, 4.1; Cl, 44.8; P, 9.8; $C_7H_{13}Cl_4O_3P$ requires C, 26.5; H, 4.1; Cl, 44.6; P, 9.7%). γ_{max} 740 (CCl_3), 545 (CCl) cm^{-1}. M.s. showed the molecular ion (M^+, 316) and fragment ions at 281 (M-Cl), 199 (M-CCl_3).

$n = 2$ b.p. 139°C (at 0.01 mbar) (Found: C, 32.5; H, 5.5; Cl, 29.3; P, 12.8 $C_{13}H_{26}Cl_4O_6P_2$ requires C, 32.4; H, 5.4; Cl, 29.4; P, 12.8%) γ_{max} 740 (CCl_3), 545 (CCl) cm^{-1}. M.s. showed the molecular ion (M^+, 480) and fragment ions at 281 (M-Cl), 363 (M-CCl_3).

Telomers of diethyl allylphosphonate with CCl_3H as telogen

$n = 1$ b.p. 97°C (at 0.01 mbar) (Found: C, 32.4; H, 5.4; Cl, 35.7; P, 10.5 $C_8H_{16}Cl_3PO_3$ requires C, 32.3; H, 5.4; Cl, 35.8; P, 10.4%) γ_{max} 795 (CCl_2H), 540 (CCl) cm^{-1}. M.s. showed the molecular ion (M^+, 296) and fragment ions at 261 (M-Cl), 213 (M-CCl_2H).

With CCl_3CH_3 as telogen

$n = 1$ b.p. 104 (at 0.01 mbar) (Found: C, 34.8; H, 5.8; Cl, 34.1; P, 9.9 $C_8H_{18}Cl_3PO_3$ requires C, 34.7; H, 5.8; Cl, 34.2; P, 10.0%) γ_{max} 840 (CCl_2CH_3), 540 (CCl) cm^{-1}. M.s. showed the molecular ion (M^+, 310) and fragment ions at 275 (M-Cl), 295 (M-CH_3), 213 (M-CCl_2CH_3).

With CCl_3CHCl_2

$n = 1$ b.p. 123°C (at 0.01 mbar) (Found: C, 28.5; H, 4.3; Cl, 46.6; P, 8.2 $C_9H_{16}Cl_5PO_3$ requires C, 28.4; H, 4.2; Cl, 46.6; P, 8.1%) γ_{max} 820 (CCl_2H), 545 (CCl) cm^{-1}. M.s. showed the molecular ion (M^+, 378) and fragment ions at (343 (M-Cl), 295 (M-$CHCl_2$), 213 (M-CCl_2CHCl_2).

With CCl_3CH_2Cl as telogen

$n = 1$ b.p. 130°C (at 0.01 mbar) (Found: C, 31.2; H, 4.9; Cl, 40.0; P, 9.0 $C_9H_{17}Cl_4PO_3$ requires C, 31.3; H, 4.9; Cl, 41.0; P, 8.9%) γ_{max} 545 (CCl) cm^{-1}. M.s. showed the molecular ion (M^+, 344) and fragment ions at 309 (M-Cl), 295 (M-CH_2Cl), 213 (M-CCl_2CH_2Cl).

With CCl_3CCl_3 as telogen

$n = 1$ b.p. 139°C (at 0.01 mbar) (Found: C, 26.1; H, 3.7; Cl, 51.3; P, 7.5 $C_9H_{15}Cl_6PO_3$ requires C, 26.1; H, 3.6; Cl, 51.3; P, 7.5%) γ_{max} 545 (CCl), 740 (CCl_3) cm^{-1}. M.s. showed the molecular ion (M^+, 412) and fragment ions at 377 (M-Cl), 295 (M-CCl_3), 213 (M-CCl_2CCl_3).

With CCl_3Br as telogen

$n = 1$ b.p. 143°C (at 0.01 mbar) (Found: C, 25.6; H, 4.0; Cl, 28.2; Br, 21.3; P, 8.2 $C_8H_{15}Cl_3BrPO_3$ requires C, 25.5; H, 4.0; Cl, 28.3; Br, 21.2; P, 8.2%) γ_{max} 605 (CBr), 730 (CCl_3) cm^{-1}. M.s. showed the molecular ion (M^+, 374) and fragment ions at 295 (M-Br), 257 (M-CCl_3).

With CCl_3COOCH_3 as telogen

$n = 1$ b.p. 141°C (at 0.01 mbar) (Found: C, 33.8; H, 5.1; Cl, 30.0; P, 8.6 $C_{10}H_{18}Cl_3PO_5$ requires C, 33.8; H, 5.1; Cl, 30.0; P, 8.7%) γ_{max} 540 (CCl), 1725 ($COOCH_3$), 820 (CCl_2) cm^{-1}. M.s. showed the molecular ion (M^+, 354) and fragment ions at 319 (M-Cl), 339 (M-CH_3), 295 (M-$COOCH_3$) 213 (M CCl_2COOCH_3).

With $CCl_3COOC_2H_5$ as telogen

$n = 1$ b.p. 146°C (at 0.01 mbar) (Found: C, 35.8; H, 5.6; Cl, 28.7; P, 8.3 $C_{11}H_{20}Cl_3PO_5$ requires C, 35.8; H, 5.4; Cl, 28.8; P, 8.4%) γ_{max} 540 (CCl), 1745 (COC_2H_5), 820 (CCl_2) cm^{-1}. M.s. showed the molecular ion (M^+, 368) and fragment ions at 333 (M-Cl), 339 (M-C_2H_5), 295 (M-$COOC_2H_5$), 213 (M-$CCl_2COOC_2H_5$).

With CCl_3CN as telogen

$n = 1$ b.p. 139°C (at 0.01 mbar) (Found: C, 93.5; H, 4.7; Cl, 32.9; P, 9.5; N. 4.4 $C_9H_{15}Cl_3PO_3N$ requires C, 33.5; H, 4.6; Cl, 33.0; P, 9.6; N, 4.4%) γ_{max} 545 (CCl), 2250 (CN), 825 (CCl_2) cm^{-1}. M.s. showed the molecular ion (M^+, 321) and fragment ions at 286 (M-Cl), 295 (M-CN), 213 (M-CCl_2CN).

With CCl_3CH_2OH as telogen

$n = 1$ b.p. 142°C (at 0.01 mbar) (Found: C, 33.1; H, 5.4; Cl, 32.4; P, 9.5 $C_9H_{18}Cl_3PO_4$ requires C, 33.0; H, 5.5; Cl, 32.5; P, 9.5%) γ_{max} 545 (CCl), 1035 (CH_2OH) cm^{-1}. M.s. showed the molecular ion (M^+, 326) and fragment ions at 291 (M-Cl), 295 (M-CH_2OH), 213 (M-CCl_2CH_2OH).

With CCl_3COOH as telogen

$n = 1$ b.p. 157°C (at 0.01 mbar) (Found: C, 32.0; H, 4.7; Cl, 31.2; P, 9.0 $C_9H_{16}Cl_3PO_5$ requires C, 32.0; H, 4.7; Cl, 31.1; P, 9.1%) γ_{max} 545 (CCl), 1770 (COOH) cm^{-1}. M.s. showed the molecular ion (M^+, 340) and fragment ions at 305 (M-Cl), 295 (M-COOH), 213 (M-CCl_2COOH).

With CCl_4 as telogen

$n = 1$ b.p. 120°C (at 0.01 mbar) (Found: C, 29.0; H, 4.6; Cl, 42.7; P, 9.3 $C_8H_{15}Cl_4O_3P$ requires C, 29.0; H, 4.5; Cl, 42.7; P, 9.3%) γ_{max} 730 (CCl_3), 540 (CCl) cm^{-1}. M.s. showed the molecular ion (M^+, 330) and fragment ions at 295 (M-Cl), 213 (M-CCl_3).

The NMR spectra are similar of those obtained in the preceding paper.[2]

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