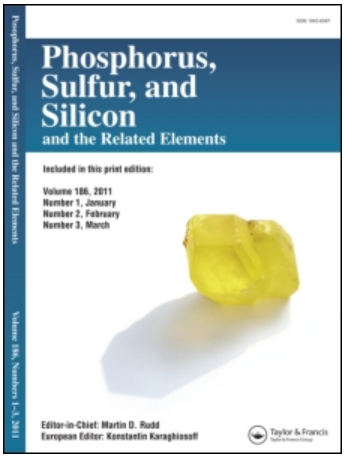

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REDOX TELOMERIZATION OF DIETHYL ALLYL AND VINYLPHOSPHONATES WITH CARBON TETRACHLORIDE AS TELOGEN

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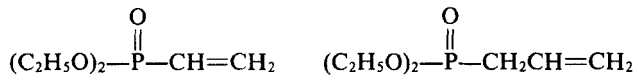
The addition of carbon tetrachloride to diethyl allyl- and vinylphosphonates giving good yields of the 1:1 addition products has been studied using transition metal salts with redox systems. This redox system offers several advantages when compared with ordinary initiation techniques. The preparation and characterization of several new addition adducts is reported. Particularly the influence of reaction parameters (initiator, solvent, temperature and taxogen/telogen ratio) on the nature, yields and structure of the resulting telomers have been studied.

INTRODUCTION

Telomerization is defined as the process of reacting, under polymerization conditions, a molecule (YZ) which is called a telogen, with more than one unit of polymerizable compound having ethylenic unsaturation (A) called a taxogen to form products called telomers having the formula Y $(A)_n$ Z.[1]

Many allyl and vinyl compounds containing phosphorus have been polymerized and copolymerized.[2,3] However, very little has been published on telomerization of allyl and vinyl monomers containing phosphorus.[4–6]

The purpose of the present work is to describe diethyl vinylphosphonate (**1**), and diethyl allylphosphonate (**2**), in relation to redox telomerization and the use of carbon tetrachloride as telogen with the two phosphorus-containing monomers.



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2

The influence of reaction parameters on the nature, yields and the structure of the resulting telomers was studied.

RESULTS AND DISCUSSION

Influence of the Initiator

A wide variety of initiators have been used for redox telomerization of diethyl allyl- and vinylphosphonates with carbon tetrachloride[7] and we have completed these re-

TABLE I

Results of the redox telomerization of diethyl allyl- and vinylphosphonates **1** and **2** in acetonitrile. Influence of the initiator nature

Monomer[a]	Initiation[b]	Yield %	Percentage of telomer with $n=1$	$n=2$	$n=3$	$n=4$	$n=5$
1	$CuCl_2 \cdot 2H_2O$	80	100				
	$CuSO_4 \cdot 5H_2O$	78	100				
	$FeCl_3$/benzoin	85	75	25			
	$FeCl_3 \cdot 6H_2O$/benzoin	75	100				
	$NH_4Fe(SO_4)_2 \cdot 12H_2O$	40	40	30	10	10	10
	$NiSO_4 \cdot 7H_2O$/benzoin	60	30	34	16	12	8
	$CoSO_4 \cdot 7H_2O$/benzoin	35	60	35	5		
	$SbCl_5$/benzoin	20	70	25	5		
	$ZnSO_4 \cdot 7H_2O$/benzoin	0					
	$SnCl_4$/benzoin	0					
	$SnCl_2$/benzoin	0					
2	$CuCl_2 \cdot 2H_2O$	57	100				
	$CuSO_4 \cdot 5H_2O$	50	100				
	$FeCl_3$/benzoin	80	100				
	$NH_4Fe(SO_4)_2 \cdot 12H_2O$	25	50	37	13		
	$NiSO_4 \cdot 7H_2O$/benzoin	45	50	30	10	5	5
	$CoSO_4 \cdot 7H_2O$/benzoin	28	68	12	7	8	5
	$SbCl_5$/benzoin	15	80	10	5	5	
	$ZnCO_4 \cdot 7H_2O$/benzoin	0					
	$SnCl_4$/benzoin	0					
	$SnCl_2$/benzoin"	0					
	$FeCl_3 \cdot 6H_2O$/benzoin	70	100				

[a] Amount: 10 mmol.
[b] Amount: 1 mmol.
Solvent: 10 ml. Temperature: 130°C. Telogen CCl_4: 10 mmol. Reaction time: 18 hrs.

sults (see Table I). We observe that the product distribution depends on initiator type:

—Cooper salts give only the monoadduct and the kind of anion does not have much effect

—Iron salts lead to a mixture of mono and diadduct with compound **1** and only to a monoadduct compound with monomer **2**.

—Degrees of telomerization varying between 1 and 5, depending on the kind of anion, are observed with nickel, cobalt and antimony salts.

The other initiators do not lead to telomers under the same conditions.

We have observed that anhydrous salts give compounds having a higher degree of telomerization than those obtained with hydrous salts. Similar results were obtained by Onishchenko and Englin[8] with other monomers. We observe, when using $FeCl_3$, a high percentage of diadduct when the initiator concentration decreases (see Table II). However there is no difference of initiation rate contrary to results obtained by Englin.[8]

Influence of the Solvent

The effects of solvent in redox telomerization have been extensively reviewed by Englin,[9] Freidlina[10] and Rigal.[11] The effects of solvent polarity on telomerizations

TABLE II

Redox telomerization of diethyl vinylphosphonate influence of the initiator concentration

Initiator[a] Concentration mmol	Yield %	Percentage of telomer with $n = 1$	$n = 2$
10	83	100	
1	85	75	25
0.8	87	70	30
0.5	80	60	40
0.2	80	55	45
0.1	85	45	55
0.05	80	42	58

[a] Initiator: $FeCl_3$/benzoin 1/1.

Solvent: acetonitrile 10 ml. Temperature: 130°C. Telogen: CCl_4 10 mmol. Reaction time: 18 hrs. Monomer: 10 mmol.

are expected to be similar to those encountered in polymerization. It has been shown that the rate of reaction may be profoundly affected by changing the solvent. The rate of reaction increases with the dielectric constant of the medium and the degree of polymerization increases with the donor effect of solvents. With diethyl allyl- and vinylphosphonates, studied here, the solvent does not play an important role (see Table III) except hydroxylic solvents and particularly secondary alcohols which lower the average degree of telomerization. The solvent quantity has no effect on the telomerization reaction but the absence of solvent (bulk telomerization) increases the percentage of high molecular weight product.

Influence of the Temperature

Series of experiments with monomers **1** and **2** containing phosphorus and carbon tetrachloride as telogen (see Table IV) show that the degrees of telomerization are

TABLE III

Redox telomerization of diethyl vinylphosphonate. Influence of solvent

Solvent ml	Yield %	Percentage of telomer with $n = 1$	$n = 2$
MeCN (20)	84	72	28
MeCN (15)	87	75	25
MeCN (10)	85	75	25
MeCN (5)	83	78	22
C_6H_6 (10)	75	72	28
hexane (10)	80	74	26
toluene (10)	78	77	23
MeOH (10)	70	65	35
tBuOH (10)	75	85	15
iPrOH (10)	70	90	10
—	75	50	50

Monomer: 10 mmol. Initiator: $FeCl_3$/Benzoin 1 mmol./1 mmol. Telegen: CCl_4 10 mmol. Temperature: 130°C. Reaction time: 18 hrs.

TABLE IV

Redox telomerization of diethyl allyl- and vinylphosphonates. Influence of the temperature

Monomer 10 mmol Initiator 1 mmol	Temperature °C	1 Yield %	1 $n=1$	1 $n=2$	2 Yield %	2 $n=1$
$FeCl_3$/Benzoin	90	20	78	22	10	100
	105	40	75	25	25	100
	120	70	76	24	60	100
	130	85	75	25	80	100
	140	87	72	28	80	100
$CuCl_2$, $2H_2O$	90	2	100		0	100
	105	40	100		20	100
	120	60	100		50	100
	130	90	100		85	100
	140	85	100		85	100

Telogen: CCl_4 10 mmol. Solvent: acetonitrile 10 ml. Reaction time: 18 hrs.

insensitive to temperature. However the yield varies with the temperature. We have observed that the initiation temperature is lowered with the iron salts. Similar results have been observed with isoprene in redox telomerization.[12]

Influence of the Taxogen/Telogen Ratio

The product distribution in most cases of telomerization depends on the taxogen/telogen ratio (r). In the case of monomers containing phosphorus studied here, an initial value of r equal to two leads only to the mono-adduct compound and the degree of telomerization increases with r with $FeCl_3 \cdot 6H_2O$ as catalyst (see Table V). However we notice that the polydispersity increases with r; therefore the selectivity decreases when r increases.

Structure of the Telomers

The structures of the resulting telomers were identified by their IR, NMR and mass spectra. There are different possibilities for telogen addition to the monomer. In

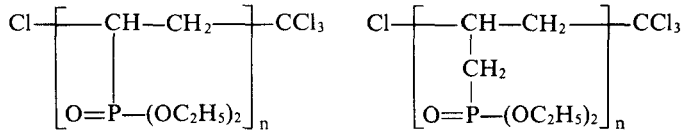
TABLE V

Redox telomerization of diethyl allyl- and vinylphosphonate. Influence of the taxogen/telogen ratio (r)

Monomer 10 mmol. r	1 Yield %	1 $n=1$	1 $n=2$	2 Yield %	2 $n=1$	2 $n=2$
0.2	72	100		65	100	
0.5	70	100		67	100	
1	75	100		70	100	
1.5	80	100		70	100	
2	77	100		70	100	
2.5	70	85	15	68	90	10
5	72	75	25	65	80	20
10	65	60	40	55	75	25

Initiator: $FeCl_3 \cdot 6H_2O$/benzoin 1 mmol/1 mmol. Solvent: acetonitrile 10 ml. Temperature: 130°C. Reaction time: 18 hrs.

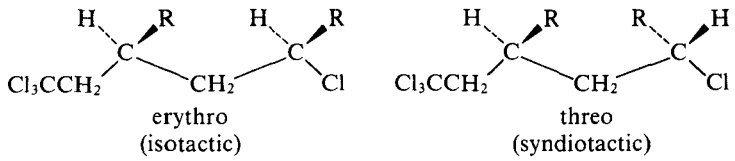
redox telemerization, rupture of telogen CCl_4 leads to fragments $Cl^{\cdot}$ and $CCl_3^{\cdot}$,[11] which may add to the α or β carbon atom of the olefins. The preferential formation of the reaction products is likely to result from the steric requirements; similar results have been obtained with isobutene as monomer.[13] The analysis of the telomers by NMR (see Figure 1 and 2) leads to structures **1a** and **2a**.



1a **2a**

Thus, redox telomerization of the monomer **1** and **2** with CCl_4 leads to selective structures in which Cl is linked to the most substituted carbon atom and the CCl_3 residue to the least substituted one.

Telomerization of unsymmetrical vinyl or allyl monomers containing phosphorus with carbon tetrachloride gives a product having one asymmetric carbon per monomer unit in the telomer. A study on the diadduct compounds by NMR shows the preference for syndiotactic chain growth of vinyl or allyl monomers. The steric interactions have significant impact on stereoisomer formation.



erythro (isotactic) threo (syndiotactic)

R = $(O)P—(OC_2H_5)_2$ or $CH_2(O)P—(OC_2H_5)_2$

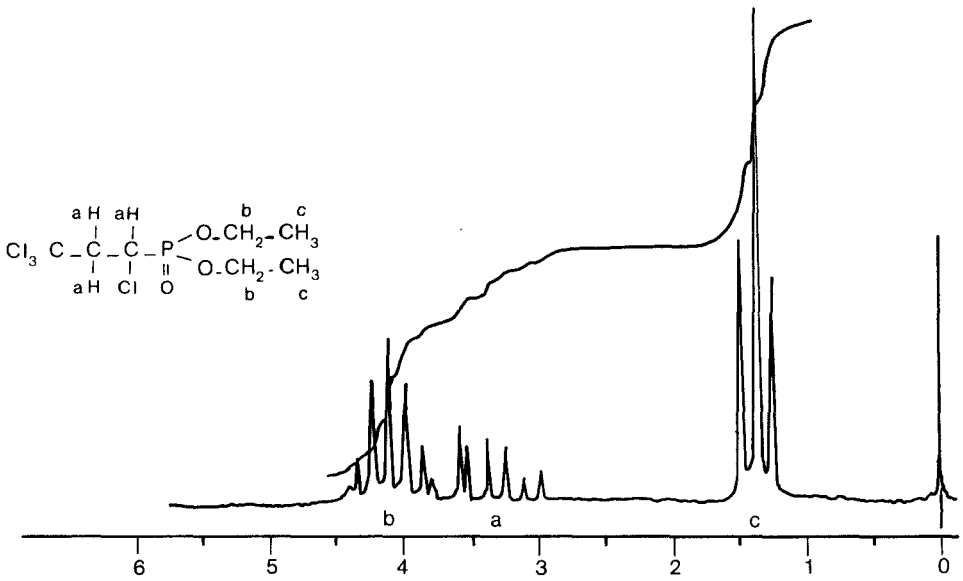


FIGURE 1 1 H NMR spectrum of $n = 1$ telomer of diethyl vinylphosphonate with CCl_4 as telogen.

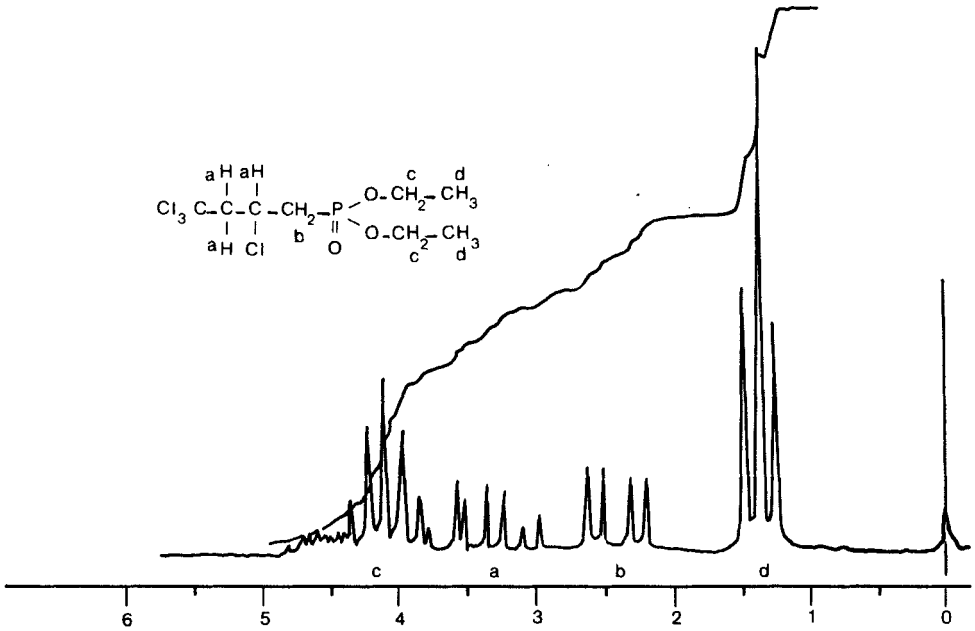


FIGURE 2 1 H NMR spectrum of $n = 1$ telomer of diethyl allylphosphonate with CCl_4 as telogen.

CONCLUSION

The present work emphasizes the versatility of redox telomerization and shows several advantages compared with other initiation techniques.

We notice selectivity of the structure in the cases studied here and we have observed that the product distribution depends on initiator type, but the solvent and the temperature do not play an important role with the two monomers.

EXPERIMENTAL

The elemental analysis and spectral data of all the compounds were performed by personnel in this laboratory. Infrared spectra were obtained on Perkin Elmer 720 spectrophotometer. Nmr spectra were measured with a Varian A 60 spectrometer using tetramethylsilane as internal standard and carbon tetrachloride as solvent. Mass spectra were obtained with a Varian IVB spectrometer at 70 eV.

General Procedure

The monomer, the telogen, the solvent and the initiator were weighed in a Carius tube. The monomer mixture was out gassed in the usual way and the reaction tube was sealed under vacuum. The reaction tube was stirred in a thermostat maintained at 130 ± 1°C during 18 hrs. After the end of reaction the solution was filtered, the solvent was evaporated off and the telomers were distileted under vacuum (for details see Table I).

Telomers of Diethyl Vinylphosphonate with CCl_4 (1a)

$n = 1$ 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} 710–750 (CCl_3), 520–600 (CCl) cm^{-1}. N.m.r. δ1.39 t (6H, CH_3), 4.26 q (4

H, O-CH_2) 3.60–4.05 m (H, PHCl-CH_2). 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%). I.r. and n.m.r. were similar to n = 1 M.s. showed the molecular ion (M^+, 480) and fragment ions at 281 (M-Cl), 363 (M-CCl_3).

n = 3 b.p. 154°C (at 0.01 mbar) (Found: C, 35.4; H, 6.2; Cl, 21.9; P, 14.3 $C_{19}H_{39}Cl_4O_9P_3$ requires C, 35.3; H, 6.0; Cl, 21.9; P, 14.4%). I.r. and n.m.r. were similar to n = 1. M.s. showed the molecular ion (M^+, 644) and fragment ions at 603 (M-Cl), 527 (M-CCl_3).

n = 4 b.p. 165°C (at 0.01 mbar) (Found: C, 37.2; H, 6.5; Cl, 17.5; P, 15.2 $C_{25}H_{52}Cl_4O_{12}P_4$ requires C, 37.1; H, 6.4; Cl, 17.5; P, 15.3%) I.r. and n.m.r. were similar to n = 1. M-s. showed the molecular ion (M^+, 808) and fragment ions at 773 (M-Cl), 691 (M-CCl_3).

n = 5 b.p. 180°C (at 0.01 mbar) (Found: C, 38.3; H, 6.7; Cl, 14.5; P, 15.8 $C_{31}H_{65}Cl_4O_{15}P_5$ requires C, 38.2; H, 6.7; Cl, 14.6; P, 15.9%) I.r. and n.m.r. were similar to n = 1 M-s. showed the molecular ion (M^+, 972) and fragment ions at 935 (M-Cl), 855 (M-CCl_3).

Telomers of Diethyl Allylphosphonate with CCl_4 (**2a**)

n = 1 b.p. 120°C (at 0.01 mbar) Found: C, 29.0; H, 4.6; Cl, 42.7; P, 9.03 $C_8H_{15}Cl_4O_3P$ requires C, 29.0; H, 4.5; Cl, 42.7; P, 9.3%). γ_{max} 710–750 (CCl_3), 520–600 (CCl) cm^{-1}. N.m.r. δ1.38 t (6H, CH_3), 2.38 d (2H, PCH_2), 4.12 q (4H, OCH_2), 3.0–3.7 m (3H, PHCl-CH_2). M-s. showed the molecular ion (M^+, 330) and fragment ions at 295 (M-Cl), 213 (M-CCl_3).

n = 2 b.p. 132°C (at 0.01 mbar) (Found: C, 35.4; H, 5.9; Cl, 27.8; P, 12.1 $C_{15}H_{30}Cl_4O_6P_2$ requires C, 35.3; H, 5.9; Cl, 27.8; P, 12.1%). I.r. and n.m.r. were similar to n = 1. M-s. showed the molecular ion (M^+, 508) and fragment ions at 473 (M-CL), 391 (M-CCl_3).

n = 3 b.p. 146°C (at 0.01 mbar) (Found: C, 38.5; H, 6.6; Cl, 20.5; P, 13.4 $C_{22}H_{45}Cl_4O_9P_3$ requires C, 38.4; H, 6.5; Cl, 20.6; P, 13.5%). I.r. and n.m.r. were similar to n = 1. M-s. showed the molecular ion (M^+, 686) and fragment ions at 651 (M-Cl), 569 (M-CCl_3).

n = 4 b.p. 158°C (at 0.01 mbar) (Found: C, 40.2; H, 7.0; Cl, 16.3; P, 14.2 $C_{29}H_{60}Cl_4O_{12}P_4$ requires C, 40.2; H, 6.9; Cl, 16.4; P, 14.3%). I.r. and n.m.r. were similar to n = 1. M-s. showed the molecular ion (M^+, 864) and fragment ions at 829 (M-Cl) 747 (M-CCl_3).

n = 5 b.p. 172°C (at 0.01 mbar) (Found: C, 41.4; H, 7.2; Cl, 13.5; P, 14.8 $C_{36}H_{75}Cl_4O_{15}P_5$ requires C, 41.4; H, 7.2; Cl, 13.6; P, 14.8%). I.r. and n.m.r. were similar to n = 1. m-s. showed the molecular ion (M^+, 1042) and fragment ions at 1007 (M-Cl), 925 M-CCl_3).

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