Tetrahedron Vol. 45, No. 4, pp. 1187 to 1196, 1989
Printed in Great Britain.

0040-4020/89 \$3.00+.00

ORGANOTINS AS ETHERIFICATION CATALYSTS. II. CATALYTIC CONVERSION OF ALCOHOLS TO OPEN-CHAIN AND CYCLIC ETHERS BY ORGANOTIN TRICHLORIDES

Giuseppe TAGLIAVINI*, Daniele MARTON and Donatella FURLANI

DIPARTIMENTO DI CHIMICA INORGANICA, METALLORGANICA E ANALITICA
UNIVERSITA' DI PADOVA
Via Marzolo, 1 - I 35131-PADOVA (Italia)

(*Received in Japan* 16 *August* 1988)

SUMMARY

1,5-Heptadien-4-ol and various 1,4- and 1,5-glycols are catalytically converted to open-chain and cyclic ethers respectively in the presence of butyltin trichloride. The dehydration of alcohols is mediated by formation of organoalkoxytin dihalides $BuSn(OR)Cl_2$. A mechanism for the formation of these ethers is proposed.
The catalytic activity of other organotins together with $SnCl_4$ has been examined for the conversion of 1,5-pentanediol to THP; the scale of the catalytic efficiency is:

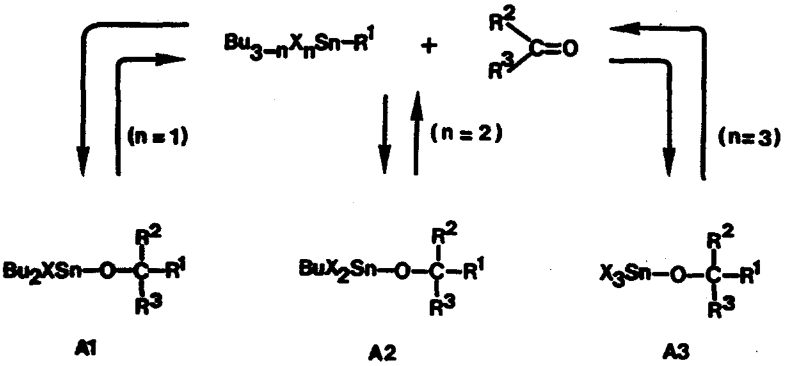
$$MeSnCl_3 \geq PhSnCl_3 > SnCl_4 > BuSnCl_3 > Me_2SnCl_2 > Bu_2SnCl_2 >> [Bu_2SnCl]_2O.$$

INTRODUCTION

Organotin compounds are coming to play a significant role as catalysts and reagents for the synthesis of organic compounds [1-4]. Particularly, many organotin alkoxides $R_3Sn\text{-}OR'$ have been prepared in the past and employed for synthetic purposes [3,4]. However, there is not information available about the related organoalkoxytin halides $R_{3-n}(R'O)SnX_n$ (n = 1,2, and 3; X = halogen), except for $Bu_2(MeO)SnCl$[5] which takes part in addition reactions with unsaturated organic substrates[6].

In our previous papers, we have shown how useful and versatile reagents are the organoalkoxytin halides arising from *allylstannation* of carbonyl compounds and allyltin halides[7]. Allylstannation, as depicted in Scheme 1, implies the formation of the new organoalkoxytin halides A1, A2, and A3. Since the electrophilicity of the tin

SCHEME 1 - *Allylstannation*



R^1 = allyl, crotyl, 1-methylallyl, cyclohex-2-enyl, cynnamyl;
R^2 = H or organic group; R^3 = organic group; X = Cl, Br

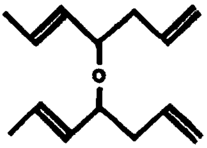
centre is increased due to the halogen atoms bonded to the metal, these organoalkoxytin halides behave differently from their parent compounds R$_3$Sn-OR'[3,5,6,8-10]. As a matter of fact the alkoxy-halides A1, A2, and A3 give rise to many reactions: (i), hydrolysis leads to homoallyl-,2-methylhomoallyl-, cinnamyl-, cyclohex-2-enyl-, 1-allenyl-, and 2-acetylenyl-carbinols[11-19]; (ii), esters of 1-alken-4-yl carboxylic acids can be prepared by reaction of adducts A1 with acyl chlorides[20]; (iii) 4-chloro-2,6-dialkyl-,4-bromo-2,6-dialkyl-, (*E*/*Z*)-4-chloro-2,6-dialkyl-3-methyl-tetrahydropyrans are the products of the thermal breakdown of the adducts formed by insertion of a further molecule of aldehyde into the Sn-O bond of the organoalkoxytin di- and tri-halides A2 and A3[21-24]; (iv), 9-chloro-2,6-diethyl-*cis* -oxabicyclo |3.3.1|-nonane arises from the thermal rearrangement of the adduct BuCl$_2$Sn-O-CH(C$_2$H$_5$)-O-CH(C$_2$H$_5$)- , which is thought to be the insertion product of two molecules of propanal into the tin-cyclohex-2-enyl bond of BuCl$_2$Sn- [25]; (v), formation of alkenyl- and alkynyl-N-alkyl carbamates is based on the selective insertion of aldehydes with respect to EtNCO into the alkenyl- and alkynyl-tin bonds[26]; (vi), synthesis of new open-chain ethers from 4-*n*-butyl-dichlorostannoxy-, 3-methyl-4-*n*-butyldichlorostannoxy-hepta-1,5-diene, and 4-n-butyldichlorostannoxy-nona-1,5-diene, that is, from organoalkoxytin dihalides of type A2[27].

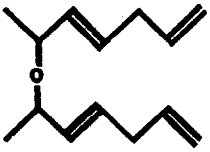
The ability of organoalkoxytin di- and tri-halides to form C-O-C bonds[21-25,27], prompted us to indagate about the possibility of catalytic etherification processes mediated by organotin substrates. A previous note has already been published[28] about the catalytic dehydration of 1,4-butane- and 1,5-pentane-diol to form tetrahydrofuran (THF) and tetrahydropyran (THP) respectively, under the mediation of butyltin trichloride. In the present paper, we report an extensive study about etherification processes which can be mediated by various organotin species for the formation of either open-chain or cyclic ethers. The paper also represents a part of our research programme dealing with systems in which organoalkoxytin halides can be involved.

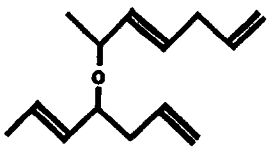
RESULTS AND DISCUSSION

Formation of open-chain ethers from alcohols in the presence of butyltin trichloride as catalyst precursor

Data dealing with the etherification of 1,5-heptadien-4-ol promoted by butyltin trichloride as catalyst precursor are given in Table 1. Etherification takes place at room temperature (see entry 1): after three days, about 75% of the carbinol is converted into a mixture of the following open-chain isomeric ethers:


E1


E2


E3

These ethers have the same constitution as those previously prepared[27] by means of *allylstannation* of the crotonaldehyde with allyl-*n* -butyltin dichloride, and here likewise, each constitutional isomer E1, E2, and E3 consists of two configurational isomers. The unreacted recovered carbinol C (see Table 1) represents a mixture of the initial carbinol with its isomer 1,4-heptadien-6-ol, which probably arises from an hydroxy-allylic rearrangement[29]. The same results are also obtained in the other runs performed at 80°C (see entries 2-4) and at 85°C (see entry 5). Comparison of the results dealing with entries 2-4 shows that the reaction time increases on increasing the R = ROH/BuSnCl$_3$, molar ratios, *i.e.* on decreasing the amount of the catalyst precursor. With the minimum used amount of BuSnCl$_3$ (see entry 5), the carbinol conversion rate is about 7 g.h^{-1} at 85°C.

Taking into account for our previous findings and speculations[27] about the thermal intermolecular breakdown of alkoxides of type CH$_3$-CH=CH-CH(OSnBuCl$_2$)-CH$_2$-CH=CH$_2$ (A2)', and CH$_3$-CH(OSnBuCl$_2$)-CH=CH-CH$_2$-CH=CH$_2$ (A2)'' to give ethers E1, E2, and E3, we propose Scheme 2 in order to explain the present homogeneous etherification catalytic process.

We point out that only ether E1 has already been prepared[3] in very low yields by dehydration of the

Table 1 - *Catalytic etherification of 1,5-heptadien-4-ol by BuSnCl$_3$*

Entry	ROH mol (g)	BuSnCl$_3$ mol (g)	R, molar ratio[a]	Temp. oil bath °C	Reaction time[b]	Recovered mixture				
						g	Composition (%)[c]			
							C	E1	E2	E3
1	0.0384 (4.3)	0.0060 (1.693)	6.4	20	3 d	4.00	22	41	22	15
2	0.0384 (4.3)	0.0060 (1.693)	6.4	80	20 min	4.05	24	42	26	8
3	0.0384 (4.3)	0.0030 (0.846)	12.8	80	90 min	4.05	25	44	22	9
4	0.0384 (4.3)	0.0015 (0.423)	25.6	80	150 min	4.10	36	39	19	6
5	0.1921 (21.51)	0.0075 (2.115)	25.6	85	160 min	15.60	12	51	26	11

[a] R = ROH/BuSnCl$_3$ molar ratio under the reaction conditions

[b] This is the time between the mixing of the reactants and the quenching

[c] C: unreacted carbinol; E1, E2, and E3: recovered constitutional ethers (see above)

unsaturated carbinol by means of sulphuric and phosphoric acid. However, a control of the reaction of the carbinol CH_3-CH=CH-CH(OH)-CH_2-CH=CH_2 with sulphuric acid yields a mixture of ethers E1, E2, and E3, as that found by using BuSnCl$_3$.

Also the carbinols R-CH=CH-CH(OH)-CHR′-CH=CH_2 (R = H and R′ = CH_3, and R = C_3H_7 and R′ = H) in the presence of BuSnCl$_3$ are catalytically converted into mixtures of isomeric ethers as those arising from thermal allylstannation processes[27].

SCHEME 2 - *A possible mechanism of the etherification of 1,5-heptadien-4-ol promoted by BuSnCl$_3$ as catalyst precursor, through the intermediate formation of organoalkoxytin dihalides (A2)′ and (A2)″*

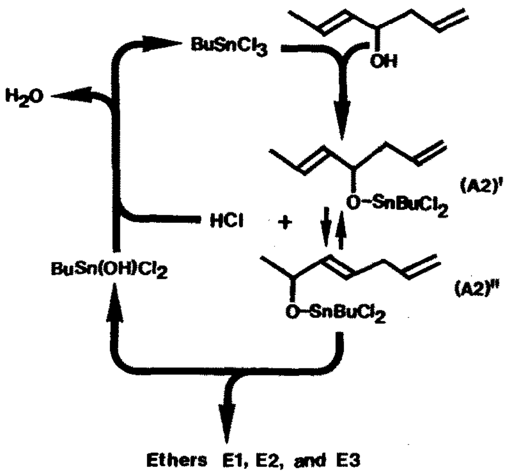
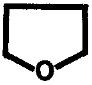
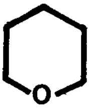
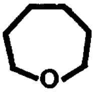
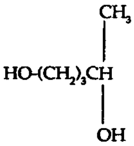
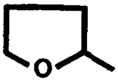
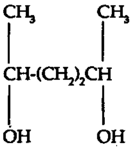
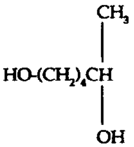
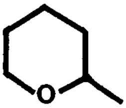
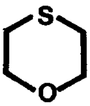


Table 2 - *Catalytic conversion of diols to cyclic ethers by $BuSnCl_3$ in the molar ratio $R = Diol/BuSnCl_3 = 20$ - Procedure I*

Entry	Diol		$BuSnCl_3$		Temp. oil bath °C	Cyclic ether	Yield g (%)	Reaction time, h	Diol[a] conversion rate, $g.h^{-1}$
	g	(mmol)	g	(mmol)					
6	$HO\text{-}(CH_2)_4OH$ 14.4	(200)	2.80	10	150-190		10.9 (94)	0.62	21.8
7	$HO\text{-}(CH_2)_5OH$ 10.4	(100)	1.40	5	150-210		9.8 (98)	0.40	25.5
8	$HO\text{-}(CH_2)_6OH$ 11.0	(93.1)	1.31	4.60	200-230		3.8 (40)	1.33	—
9	 $HO\text{-}(CH_2)_3CH(CH_3)OH$ 4.9	(47)	0.66	2.35	170-180		3.9 (96)	0.24	19.6
10	 $CH_3CH(OH)\text{-}(CH_2)_2CH(OH)CH_3$ 9.0	(76)	1.10	3.80	150-200		7.5[b] (98)	0.25	35.3
11	 $HO\text{-}(CH_2)_4CH(CH_3)OH$ 4.5	(38.1)	0.537	1.90	195-210		3.6 (94)	0.56	7.5
12	$HO\text{-}(CH_2)_2S\text{-}(CH_2)_2OH$ 12.22	(99.84)	1.41	4.99	180-200		4.3 (42)	0.16	—

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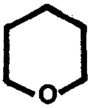
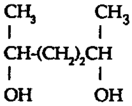
[a] Calculated diol conversion rate: (Grams of Diol x Yield %)/Reaction time (h)

[b] A mixture of two isomers in the ratio about 50/50

Table 3 - *Catalytic conversion of diols to cyclic ethers by $BuSnCl_3$ in the molar ratio $R = Diol/BuSnCl_3 = 20$ - Procedure II*

Entry	Diol, g Initial amount (Total amount)	$BuSnCl_3$ g	Temp. oil bath °C	Temp.[a] range °C	Cyclic ether g (yield %)	Reaction time, h	Diol conversion rate, $g.h^{-1}$	Diol feeding rate, $g.h^{-1}$
13	$HO\text{-}(CH_2)_5OH$ 23 (115)	3.150	205-210	92-98	 93 (98)	4.7	24.5	25.0
14	 $CH_3CH(OH)(CH_2)_2CH(OH)CH_3$ 24.2 (144.2)	2.864	160-165	81-83	 121.5[b] (100)	4.3	33.5	34.0

[a] The quoted figures represent the distillation temperature ranges of the ether-water mixture

[b] A mixture of two isomers in the ratio about 50/50

Table 4 - *Catalytic conversion of 1,4-butanediol to THF on varying the $R = Diol/BuSnCl_3$ molar ratio at 165°C - Procedure II*

Entry	Diol, g Initial amount (Total amount)	$BuSnCl_3$	R[a] molar ratio	Temp.[b] range °C	THF g (yield %)	Reaction time, h	Diol conversion rate, $g.h^{-1}$ (mol. h^{-1})	Diol feeding rate, $g.h^{-1}$
15	25.4 (101.6)	0.805	100	80-84	91.2 (99)	9	11.2 (0.124)	12.2
16	25.4 (152.4)	3.220	24.8	82-84	119 (97)	6	19.8 (0.220)	20.0
17	25.4 (152.4)	8.130	9.8	82-85	120 (97)	4.18	28.7 (0.318)	28.0
18	20.4 (101.7)	12.750	5.0	83-85	90.3 (98)	3.10	29.1 (0.322)	28.0

[a] $R = Diol/BuSnCl_3$ molar ratio under the reaction conditions

[b] The quoted figures represent the distillation temperature of the ether-water mixture

Table 5 - *Catalytic activity of various organotins in the conversion of 1,5-pentanediol to THP at the molar ratio R = Diol/Cat = 20*
Procedure I

Entry	Diol g (mol)	Catalyst g (mol)	Temp. oil bath °C	Temp.[a] °C	Reaction time, h	THP g (yield %)	Diol conversion rate, g.h^{-1}
19	14.22 (0.1365)	MeSnCl$_3$ 1.64 (0.00683)	200-215	95-115	0.28	11.80 (~100)	41.6
20	13.98 (0.1340)	PhSnCl$_3$ 2.03 (0.00670)	180-205	80-94	0.33	10.95 (95)	40.2
21	16.52 (0.1586)	SnCl$_4$ 2.06 (0.00793)	174-190	74-92	0.55	12.70 (93)	30.7
22	20.00 (0.1920)	BuSnCl$_3$ 2.82 (0.01000)	190-210	74-90	0.75	16.20 (98)	26.1
23	16.17 (0.1550)	Me$_2$SnCl$_2$ 1.70 (0.00760)	235-245	90-118	1.00	6.98 (52)	8.4
24	10.60 (0.1092)	Bu$_2$SnCl$_2$ 1.55 (0.0051)	215-220	61-70	2.50	1.50 (17)	0.6
25	12.81 (0.1230)	[Bu$_2$SnCl]$_2$O 1.70 (0.00307)	220-230	-	-	-	-

[a] Distillation temperature range of the THP-H$_2$O mixture

Formation of cyclic ethers from diols in the presence of BuSnCl$_3$ as catalyst precursor

Following *procedure I*, seven diols have been submitted to the dehydration process in the presence of BuSnCl$_3$. Data arising from the performed runs are collected in Table 2. The R = Diol/BuSnCl$_3$ molar ratio has been kept constant in all runs (R = 20), in order to compare the reactivity of the involved diols. As one can see, the values of the reaction temperature at which the diol conversion takes place is roughly in the range of 180-200°C. Thus, the diol conversion rate figures as quoted in the last column of Table 2 can be related to the efficiency of the dehydration process, at least for the runs in which the yields are in the range 94-98% (see entries 6, 7, 9, 10, and 11). Among these diols, the highest conversion value is found for 2,5-hexanediol (35.3 g.h^{-1}) and the lowest for 1,5-hexanediol (7.5 g.h^{-1}).

As expected, five and six carbon atoms rings are easily formed: a low conversion rate is found in the run concerning the formation of the oxepane (see entry 8), and also in the case of 2,2'-thiodiethanol (see entry 12).

Data collected in Table 3 have been obtained following *procedure II*: only two diols have been examined. In both cases, yields are very high: 98% and about 100% for the dehydration of 1,5-pentanediol and 2,5-hexanediol respectively.

The diol conversion rates (25 and 34 g.h^{-1}, respectively) are very similar to those found according to *procedure I* (compare, entry 13 with entry 7 and entry 14 with entry 9). Runs of Table 3 prove the catalytic efficiency of BuSnCl$_3$, whose activity remains unchanged after about 5 h.

Table 4 lists the data about the catalytic conversion of 1,4-butanediol to THF at 165°C on varying the R = Diol/$BuSnCl_3$ ratio. All runs are characterized by very high yields (from 97 to 99%), and the diol conversion rates appear to increase in an inverse exponential way with R, as it might be expected for a homogeneous catalytic process.

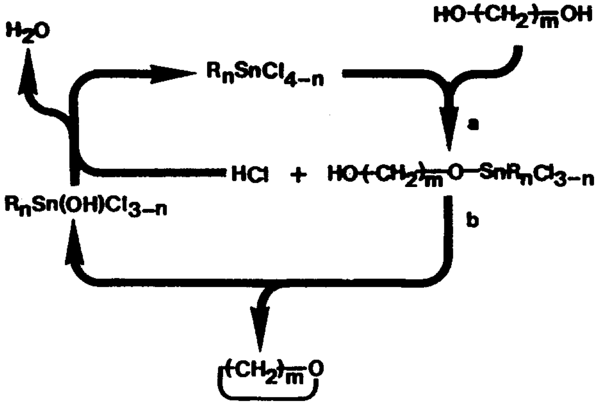
Also in these cases, the catalytic precursor $BuSnCl_3$ shows a very high efficiency since the conversion rate remains at a constant value after 9 h (see entry 15 of Table 4).

Catalytic activity of some organotins in the conversion of 1,5-pentanediol to THP

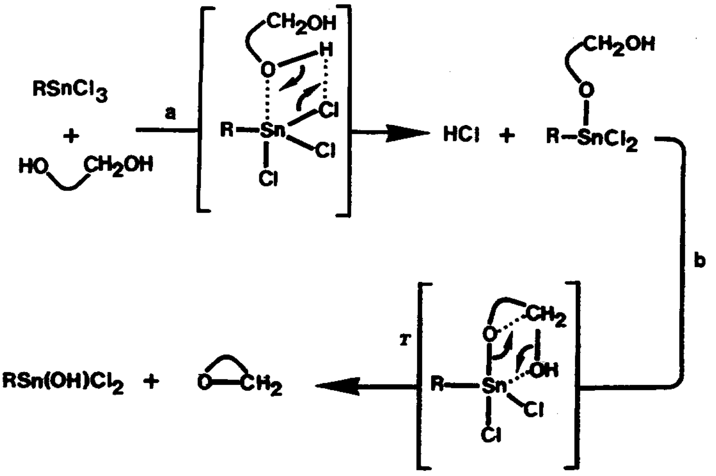
Table 5 lists the data about the dehydration of 1,5-pentanediol to form THP in the presence of various organotin compounds. The molar ratio R = Diol/Cat (Cat = catalyst) has been mantained constant at the value of 20 in all cases and the work-up has been made following *procedure I*. As one can see the catalytic efficiency is shown by the sole organotins of the type R_nSnCl_{4-n} with n = 0,1, and 2, and the order of activity is as follows:

$$MeSnCl_3 \geq PhSnCl_3 > SnCl_4 > BuSnCl_3 > Me_2SnCl_2 > Bu_2SnCl_2 >> [Bu_2SnCl]_2O.$$

SCHEME 3 - *A possible mechanism for cyclic ethers formation from diols (m = 4, 5, and 6) with R_nSnCl_{4-n} compounds (R = Me, Bu, and Ph; n = 0, 1, and 2) as catalyst precursors, through the intermediate formation of alkoxytin halides of type A1, A2, and A3.*



SCHEME 4



A very poor activity is found for Bu_2SnCl_2, for which the diol conversion rate is found to be 0,6 $g.h^{-1}$ with respect to those of $SnCl_4$ and $RSnCl_3$ compounds the values of which are in the range 26.1-41.6 $g.h^{-1}$. However, Me_2SnCl_2 is more active than Bu_2SnCl_2, while $[Bu_2SnCl]_2O$ is completely unactive.

On the light of these findings, organoalkoxytin halides seem likely to be intermediates in the etherification process. Scheme 3 furnishes a possible mechanism for the cyclic ethers formation.

A possible mechanism for step *a* concerning the formation of the organoalkoxytin halides A2 and step *b* dealing with the formation of cyclic ethers and $RSn(OH)Cl_2$ species from the rearrangement of A2, is shown in Scheme 4.

The proposed step *a* is based upon one of the numerous procedures for the preparation of the parent organotin alkoxydes R_3Sn-OR'[31]. The activated complex *T*, as pictured in Scheme 4, may offer an idea of how the tin centre can mediate this process of cyclization.

General comments

The potentiality and the versatility of organoalkoxytin halides as intermediates for synthetic purposes appear to be quite high. The thermal[21-25,27] and the catalytic reactions are specific for this class of compounds, which behave differently with respect to their parent compounds R_3Sn-OR'[4-6]. It is noted that the reactions depend on the number of halogen atoms linked to the tin centre. As a matter of fact, in the present case only the intermediates having two (A2) or three (A3) halogens bonded to the tin atom are operating (see Scheme 3), and this is in line with our previous findings about allylstannation[7,11-22] (*e.g.*, compare the catalytic production of the open-chain ethers E1, E2, and E3, with their preparation *via* thermal breakdown of organoalkoxytin halides prepared *in situ via allylstannation*[27]).

The reported data represent the first results about etherification processes mediated by organotins having acidic properties. Usually, other Lewis acids have being employed[32] and elevated temperatures (~250°C) in excess of mineral acids have being required for such etherification processes[33-36]. The number of papers published on the subject so far is so large that their quotation for a comparison with the present results would be cumbersome. We only recall a recent report[37], in which the conversion rate of 1,4-butanediol to form THF is 10 $g.h^{-1}$ in the presence of *Nafion-H*[38], being the ratio Diol/Cat = 50 g/2.5 g = 20; in the present case (see entry 15 of Table 4) the conversion rate of the same diol is 12.2 $g.h^{-1}$ with a ratio Diol/Cat = 25.4 g/0.805 g = 31.5.

Work is now in progress in order to: (i), isolate some of these organoalkoxytin halides, (ii), test other reactions where these compounds can be involved, and (iii), improve the efficiency of these processes.

EXPERIMENTAL

Commercial samples of organotins were distilled before use. Commercial diols available from Aldrich-Chemie, were used without any purification. The products were characterized by their IR, 1-H, and 13-C NMR spectra, recorded on a Perkin-Elmer Model 599B spectrophotometer and a Jeol FX90Q FT NMR spectrometer, respectively. The isomeric composition of the products mixtures were determined by 13-C NMR spectroscopy and GLC analysis using a Sigma-3B Perkin-Elmer apparatus equipped with a flame-ionization detector. 13-C NMR spectra were recorded using sufficiently long pulse intervals to avoid saturation of the nuclear spins (at least 25 s), and the nuclear Overhauser effect (NOE) was suppressed by gated decoupling[39].

Conversion of 1,5-heptadien-4-ol to ethers by butyltin trichloride

Runs listed in Table 1 were carried out in a three necked flask equipped with a separatory funnel and condenser. Mixtures of carbinol (4.3 g, 38.4 mmol) and butyltin trichloride in molar ratios 25.6, 12.8, and 6.4 were allowed to react under stirring. The progress of the reactions was then monitored by GLC looking at the decrease of the chromatographic peak of the carbinol. Then the system was hydrolyzed with 20 ml of a 2M aqueous of Na_2CO_3 and the products extracted with Et_2O. Subsequent distillation gave mixtures of ethers together with unconverted carbinol.

General procedures for the catalytic conversion of diols to cyclic ethers

Procedure I

A 50 ml round-bottomed reaction flask containing the diol and the catalyst precursor was equipped with a Claisen head and receiver. The reaction mixture was heated at an appropriate temperature in a oil bath with stirring. Cyclic ethers distilled together with water as they were formed. The catalyst was practically unchanged at the end of the reaction.

Procedure II

A 50 ml three-necked round-bottomed flask (reactor) containing commercial diol (20-25 ml) and butyltin trichloride as catalyst precursor (or other organotins), was equipped with a separatory funnel containing a large amount of diol (3-6 times of the amount into the flask-reactor), a Claisen head and a graduate receiver properly suited to measure the amount of water distilled over the time together the cyclic ether. The reaction mixture was heated at an appropriate temperature in a oil bath with stirring. A continuous feeding of diol from the separatory funnel into the reaction flask was performed in order to maintain the same initial volume of diol (20-25 ml). In such a way, the conversion of the total amount of diols was over in different times. A part from THF (soluble in water) the other ethers were separated from the water layer and dried. Their purity was checked by conventional methods.

ACNOWLEDGEMENT

We thank Ministero della Pubblica Istruzione (MPI, Roma) for financial support.

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