

ORGANOTINS AS ETHERIFICATION CATALYSTS. III. ETHERIFICATIONS AND HYDRO-HYDROXY-ELIMINATIONS PROMOTED BY BUTYLTIN TRICHLORIDE

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SUMMARY

Butyltin trichloride, as a catalyst precursor, promotes the following processes: (i) etherification of 2,3-unsaturated alcohols, (ii) etherification of functional diols, (iii) cyclization of 2,5-hexanedione, and (iv) dehydration of cyclic diols. Many examples are reported.

INTRODUCTION

As it is already known, dehydration of alcohols can be accomplished in several ways, by using concentrated acids, H_2SO_4 and H_3PO_4 , metallic oxides (e.g., Al_2O_3 , Cr_2O_3 , TiO_2 , WO_3), metallic salts, sulfides, zeolites *etc.*¹

Recently, organotin halides have been successfully employed for the catalytic conversion of diols to cyclic ethers^{2,3}, as well as of unsaturated alcohols to open-chain ethers³. Butyltin trichloride is particularly active in such processes. Furthermore, it can be conveniently used for the preparation of cyclic acetals from aldehydes and diols, under mild conditions and over short reaction times⁴. Butyltin trichloride acts both as an acid catalyst and as a dehydrating agent, with the advantage over tin (IV) chloride and other organotin trichlorides of being less readily hydrolyzed. Therefore, it can be manipulated without any special precaution and can be used in processes involving the removal of water under acid-catalyzed conditions.

In the present paper, we report a study on the following processes mediated by butyltin trichloride: (i) etherification of 2,3-unsaturated alcohols, (ii) etherification of functional diols, (iii) cyclization of 2,5-hexanedione, and (iv) dehydration of cyclic diols.

RESULTS AND DISCUSSION

(i) Etherification of some 2,3-unsaturated alcohols

The following groups of alcohols have been examined: (1) *n*-, *sec*-, and *t*-alkanols (e.g., ethanol, 1- and 2-butanol, 2-methyl-2-propanol, *etc.*), (2) cyclic alcohols (e.g., cyclo-pentanol and -hexanol, tetrahydropyran-2-methanol), and (3) 2,3-unsaturated alcohols. Alcohols of groups 1 and 2 do not react in the presence of the butyltin trichloride.

From group 3, carbinols of the type $\text{CH}_2=\text{CH}-\text{CH}(\text{OH})-\text{R}$ do not show any reaction, while 3-alkyl-allyl carbinols of the type $\text{R}-\text{CH}=\text{CH}-\text{CH}(\text{OH})-\text{R}'$ (R = alkyl group and R' = H or alkyl group) can be dehydrated to give linear ethers.

Data dealing with the etherification of (*E/Z*)-2-buten-1-ol ($E/Z = 84/16$), (*E*)-3-penten-2-ol, and 3-methyl-2-buten-1-ol promoted by butyltin trichloride, as the catalyst precursor ($\text{ROH} / \text{BuSnCl}_3 = 25.5$), are given in table 1. Good conversion yields (from 85 to 90%) are obtained from the three examined 3-alkyl-allyl carbinols (entries 1-3), while no reaction is encountered for 3-buten-2-ol (entry 4), an unsubstituted allyl carbinol.

Etherifications take place at a reasonable rate in the temperature range 80-140°C, and reaction are more facile with the *sec*-carbinol than the *n*-carbinol (compare entry 2 with 1), and still more readily when carbon-3 of the allyl group is dialkylated as in the case of 3-methyl-2-buten-1-ol. (entry 3).

The efficiency of butyltin trichloride in promoting the catalytic conversion of these alcohols to ethers is very high when compared to that of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ⁵. Hydroxy-allylic rearrangements⁵ occur under these conditions, as shown from the recovered carbinol (about 10-15%) consisting of a mixture of the starting carbinol and its isomer arising from an hydroxy-1,3-sigmatropic shift⁶. As a result of the alcohol isomerization, the dehydration processes provide mixtures of isomeric ethers.

A mixture of five isomers is obtained in the case of (*E/Z*)-2-buten-1-ol (entry 1): the isomeric ratio (*E,E*)/(*Z,Z*) between ethers 1 and 2 is 82/18, which is the same as the geometrical ratio $E/Z = 84/16$ of the starting carbinol. Here, as well as in the other two cases (entry 2 and 3) the isomeric distribution of the ethers isomers is governed by statistical factors. The ratios of ethers bearing unrearranged allylic residues to ethers bearing rearranged allylic residues are about 75/25, 90/10, and 80/20 for 2-buten-1-ol, 3-penten-2-ol, and 3-methyl-2-buten-1-ol respectively.

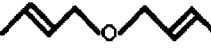
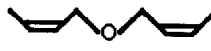
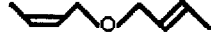





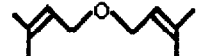
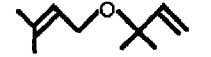

Symmetrical and unsymmetrical diallyl ethers are very important materials for the selective Claisen rearrangements in the synthesis of unsaturated carbonyl compounds⁷ and acyclic terpenes⁸. Recently, synthesis of citral from diprenyl ether⁸ (9) and of lavandulol^{9,10} from both diprenyl and isopentenyl prenyl (10) ethers has been reported.

(ii) Conversion of diols, triols and 2,5-hexanedione to cyclic ethers

Table 2 shows the results obtained for four diols, (*Z*)-2-butene-1,4-diol, (entries 5-7), 2-hydroxyethyl ether (entry 8), 1,10-undecadiene-4,8-diol (entry 9), and (*Z*)-1,2-cyclohexanedimethanol (entry 10), two triols, 1,2,4-butanetriol (entry 11) and 1,2,6-hexanetriol (entries 12, 13), and 2,5-hexanedione (entry 14).

The dehydration of (*Z*)-2-butene-1,4-diol leads to a mixture of 2,5-dihydrofuran and crotonaldehyde in which the cyclic compound is the major component. The yields of both products are lowered on increasing the R ratio (compare entries 5-7), so that the best conditions are reached with $R = 20$, where the conversion yield for the cyclic

Table 1 - Catalytic etherification of some 2, 3-unsaturated alcohols

Entry	ROH ^a g (mol)	Temp. oil bath °C	Time ^b h	g (%) ^c	Recovered mixture	
					Ether	
					no.	(%) ^d
1	<i>(E/Z)</i> CH ₃ CH=CHCH ₂ OH ^e 21.1 (0.293)	140	32	15.8 (85)	1 <i>(E,E)</i>  (52.0)	
					2 <i>(Z,Z)</i>  (11.5)	
					3 <i>(E,Z)</i>  (21.5)	
					4 <i>(syn)</i>  } (15.0)	
					5 <i>(anti)</i>  }	
2	<i>(E)</i> CH ₃ CH=CHCH(OH)CH ₃ 21.1 (0.245)	85	3	16.4 (87)	6 <i>(E,E)</i>  (88.0) ^f	
					7 <i>(Z,Z)</i>  } (12.0)	
					8 <i>(E,Z)</i>  }	
3	(CH ₃) ₂ C=CHCH ₂ OH 16.96 (0.197)	145	1.5	13.7 (90)	9  (75.0)	
					10  (16.0)	
					11  (<9.0)	
4	CH ₂ =CHCH(OH)CH ₃ 20.2 (0.280)	115	3	no reaction		

^a R = ROH/BuSnCl₃ molar ratio = 25.5. ^b This is the time between the mixing of the reactants and the quenching. ^c Converted alcohol percent. ^d Isomeric composition. ^e *E/Z* = 84/16. ^f isomeric ratio = 64/36.

Table 2 - Catalytic conversion of diols, triols and 2,5-hexanedione to cyclic ethers



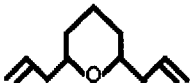
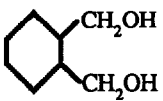

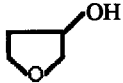
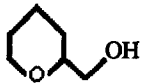

Entry	P ^a	Reactant	R ^b	Temp. oil bath °C	Temp. ^c range °C	Time ^d h	Recovered		Ether		
		g (mol)					Product g (%) ^e	no.	g		
5	II	$\begin{array}{c} \text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2 \\ \qquad \qquad \\ \text{OH} \qquad \qquad \text{OH} \end{array}$									
		27 (0.30) ^f 134 (1.52) ^g	20	165	88-90	4.7	94	(88)	12	63 ^h	
6	I	50.3 (0.607)	30	150	85-88	2.0	25	(58)	12	22 ⁱ	
7	I	50.3 (0.607)	40	150	83-87	2.1	21	(49)	12	18.5 ^j	
8	I	$\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2 \\ \qquad \qquad \qquad \\ \text{OH} \qquad \qquad \qquad \text{OH} \end{array}$									
		28 (0.264)	20	225	85-90	4.0	14.5	(62)	13	14.5	
9	I	$\begin{array}{c} \text{CH}_2-\text{CH}=\text{CH}_2 \qquad \text{CH}_2-\text{CH}=\text{CH}_2 \\ \qquad \qquad \qquad \\ \text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH} \\ \qquad \qquad \qquad \\ \text{OH} \qquad \qquad \qquad \text{OH} \end{array}$									
		12 (0.078)	20	220	90-95	1.0	7	(65)	14	7.0	
10	I										
		30 (0.208)	20	180	95-98	0.7	24	(92)	15	24	
11	II	$\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{CH}-\text{CH}_2 \\ \qquad \qquad \qquad \\ \text{OH} \qquad \qquad \text{OH} \qquad \text{OH} \end{array}$									
		25.5 (0.240) ^f 51.0 (0.480) ^g	20	170	97-100	3.5	39	(92)	16	39	

Table 2 (continued)

12	I	$\begin{array}{c} \text{CH}_2-(\text{CH}_2)_3-\text{CH}-\text{CH}_2 \\ \qquad \qquad \qquad \\ \text{OH} \qquad \qquad \text{OH} \qquad \text{OH} \end{array}$								
		28 (0.208)	20	210	100-145	0.7	15.7	(65)	17	15.7
13	I	28 (0.208)	40	230	105-135	3	16.8	(70)	17	16.8
14	I	$\begin{array}{c} \text{CH}_3-\text{C}-\text{CH}_2-\text{CH}_2-\text{C}-\text{CH}_3 \\ \qquad \qquad \\ \text{O} \qquad \qquad \text{O} \end{array}$								
		23.6 (0.207)	20	155	80-85	2.3	16.4	(81)	18	16.4

^a P = Procedure. ^b R = Reactant/BuSnCl₃. ^c The quoted figures represent the distillation temperature ranges of the ether-water mixture. ^d Reaction time. ^e Conversion %. ^f Initial amount of reactant. ^g Total amount of reactant.

^h The cyclic ether is recovered together with crotonaldehyde (21 g). ⁱ The amount of crotonaldehyde is 3 g. ^j The amount of crotonaldehyde is 2.5 g.

compound is about 88%. This must be compared with previously adopted procedures: e.g. the catalytic cyclodehydration of (*Z*)-2-butene-1, 4-diol with iodine¹¹ and TPP-*t*-BuHCl¹² yields 2, 5-dihydrofuran 31% and 61% respectively.

1,4-Dioxane (13) has been recently prepared from ethylene glycol in the presence of a catalytic amount of Nafion-H¹³ and from diethylene glycol in the presence of Al-Montmorillonite¹⁴ with 50% and 75% yields respectively. The new compound 2,6-diallyltetrahydropyran (14) in the isomeric ratio 50/50 has been synthesized from 1,10-undecadiene-4,8-diol prepared *via allylstannation* as previously reported¹⁵. (*Z*)-1,2-Cyclohexanedimethanol is converted to (*Z*)-hexahydrophthalan (15) in high yield (92%); this should be compared with yields obtained using dimethylsulphoxide¹⁶ (159-161°C, 14h), 66%; H₂SO₄¹¹, 24%; TPP-*t*-BuHCl¹², 99%; DTPP-CH₂Cl₂¹⁷, 76%; and DTPP-Toluene¹⁸, 95%.


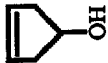
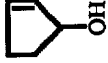









Several procedures have been employed to prepare 3-hydroxy-tetrahydrofuran (HO-THF) (16) and 3-hydroxymethyl-tetrahydropyran (HOM-THP) (17): the cyclodehydration process to form HO-THF has been performed using *p*-toluenesulfonic acid^{19,20} with yields in the 81-88% range; both HO-THF and HOM-THP have been made by pyrolysis of the triol carbonate esters²¹ (88 and 48% respectively). In addition, HO-THF can be prepared (81% yield) by hydrogenation over Ni Raney (ethanol, 60°C, 30 atm) of formildihydrofuran²².

2, 5-Dimethylfuran (18) can be easily prepared from acetylacetone (see entry 14) in high yield (81%). This is an example of cyclodehydration through an intramolecular addition of an alcohol to a ketone, *via* reaction of its enol form. It is our opinion that other 1, 4- and 1, 5-diketones can be converted to furans and pyrans using butyltin trichloride instead of mineral acids as previously reported²³.

(iii) Dehydrations of alicyclic diols.

The results for the hydro-hydroxy-elimination of three alicyclic diols are listed in table 3; 1,3-cyclopentanediol,

Table 3 - Hydro-hydroxy eliminations mediated by BuSnCl_3

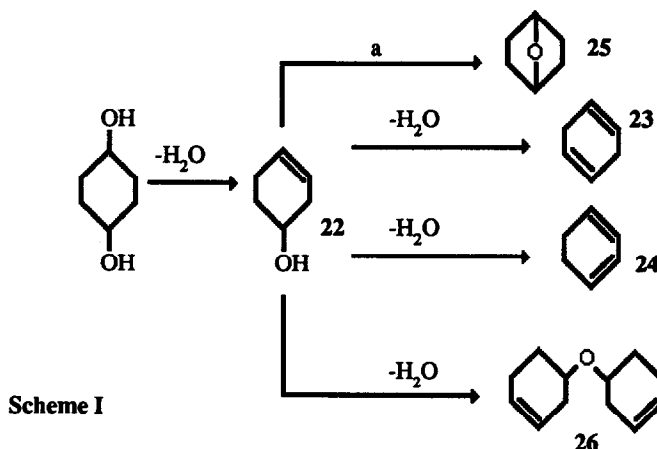
Entry	Reactant g	R ^a (mol)	Temp. oil bath °C	Temp. ^b range °C	h	Time ^c Recovered mixture g	Recovered (%) ^d	Products		
								compd. no.	(g)	
15		(0.147)	20	215-235	95-115	1	10	(87)		
									19 (6)	20 (1.2)
16		(0.5)	20	210-220	98-105 ^e 120-125 ^f	1	46	(96)		
									22 (24)	23 (10)
17		(0.5)	40	200-220	91-96 ^e 125-130 ^f	6	43	(80)		
									22 (17)	23 (9.5)
18		(0.250)	20	180-215	97-100	0.7	27	(86)		
									27 (17)	28 (8)

^a R = Reactant/ BuSnCl_3 . ^b The quoted figures represent the temperature ranges of the distilled products. ^c Reaction time. ^d Conversion percent. ^e Temperature range of the low-boiling distilled products. ^f Temperature range of the high-boiling distilled products.

1,4-cyclohexanediol, and 1,2-cyclooctanediol (entries 15-18) give rise to mixtures of products. The diol conversions are in the range 80-96%. The product distributions depend on the Diol/BuSnCl₃ ratio (compare entries 16 and 17).

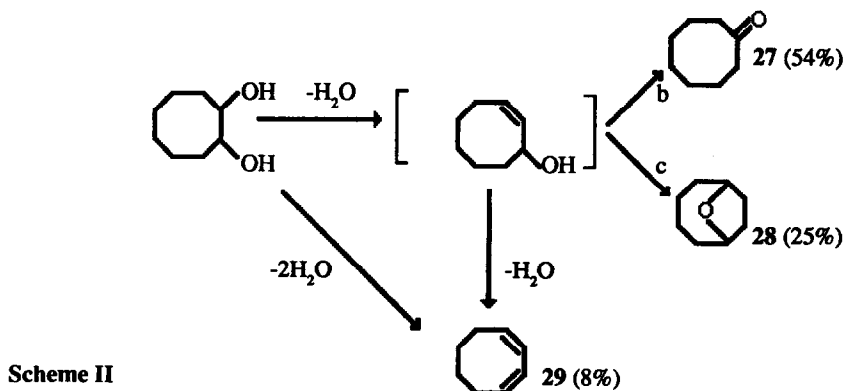
Many studies have been reported on the dehydration of 1,4-cyclohexanediol; products, using catalysts such as sulphuric acid^{24,25} and Al₂O₃²⁶, include 22, 23, 24, and 25 (see scheme I). 1,4-Epoxycyclohexane (25) is formed in high yield by passing a solution of the cyclic diol over activated alumina²⁷, and is the major component, with cyclohexenol and other high-boiling products, when it is dehydrated in the absence of solvent²⁶. In the present study (see entries 16 and 17) the major product is 3-cyclohexene-1-ol (22), in 49% and 35% yields.

Dicyclohex-3-enyl ether (26) is also formed when the amount of BuSnCl₃ is reduced (see, entry 17). Its formation implies the etherification of 3-cyclohexene-1-ol (22) (see Scheme I).



Dehydration of the other two cyclic compounds 1,3-cyclopentanediol and 1,2-cyclooctanediol seems to follow the above scheme: the first step is the formation of cycloalkenols *via* 2-hydroxyhydroxyelimination.

From 1,3-cyclopentanediol (entry 15) two cycloalkenols are obtained: 3-cyclopenten-1-ol (19, 48% yield) and 2-cyclopenten-1-ol (20, 10% yield). Complete dehydration to dicyclopentadiene (21, 30% yield) also results. 2-Cyclooctene-1-ol (see, Scheme II) can be considered to be the first product obtained from the reaction of 1,2-cyclooctanediol and butyltin trichloride. Following this hypothesis, 2-cyclooctene-1-ol may give rise *via* intramolecular rearrangement to cyclooctanone (27, 54% yield) and 1,4-epoxycyclooctane (28, 25% yield). A small amount (8%) of diol is converted to 1,3-cyclo-octadiene (29).



It is interesting to note that in two cases (entry 16 and 17) dehydration processes take place together with intramolecular rearrangements as shown by step *a* of scheme I and steps *b* and *c* of scheme II. An alternative way to explain the formation of compounds 27 and 28 may be advanced. They can arise from cyclooctene oxide^{29,30} as the intermediate instead of the 2-cyclooctene-1-ol.

It is our opinion that the examples reported here well emphasize the potential of BuSnCl_3 . Other organotin compounds previously used³, show a good activity in these as in others processes which are under investigation.

EXPERIMENTAL

Commercial butyltin trichloride was distilled before use. Commercial reagents available from Aldrich-Chemie, were generally used without any purification.

The products were characterized by their IR, ^1H , and ^{13}C NMR spectra recorded on a Perkin-Elmer Model 599B spectrophotometer and a Jeol FX90Q FT NMR spectrometer, respectively. The physical-chemical data of the majority of the recovered compounds were compared with those reported in the literature. The composition of the recovered products was determined either by GLC analysis using a Sigma-3B Perkin-Elmer apparatus equipped with a flame-ionization detector or by ^{13}C NMR spectroscopy. In this case ^{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 decoupling³¹.

Conversion of 2, 3-unsaturated alcohols to linear ethers

The following general procedure was adopted for the runs listed in table 1 (entries 1-4). A mixture of the appropriate carbinol (about 20 g, 0.2-0.3 mol) and butyltin trichloride in the molar ratio 20, was allowed to react with stirring. The progress of the reaction was monitored by GLC from the decrease in the carbinol. The reaction was quenched when the amount of the unreacted carbinol was about 10-15%. After hydrolysis with aqueous Na_2CO_3 (2M), the products were extracted with ethyl ether. Subsequent distillation gave mixtures of ethers alone with unconverted carbinol.

General procedures for the conversion of diol and triols to cyclic ethers

Procedure I

A mixture of the diol and butyltin trichloride at a given ratio $R = \text{Diol}/\text{BuSnCl}_3$ was heated at an appropriate temperature with stirring and the volatile products were directly distilled out. In some cases cyclic ethers distilled together with water (entries 6-9, 12-14) in other cases only water was transferred (entry 9 and 10). Separation of the pure products was made in the former cases by work-up of the distilled material, in the latter cases by work-up of the flask residue, using conventional methods.

Procedure II

A mixture of the alcohol (initially *ca.* 25g) and BuSnCl_3 was heated and the volatiles were distilled out. Additional alcohol (*ca.* 75-100g) was added to the reaction flask at such a rate to maintain the volume of the reaction mixture at *ca.* 30 ml. Ethers were separated from water and purified by distillation over molecular sieves.

Procedures for the dehydration of cyclic diols

1, 3-Cyclopentanediol (entry 15) - A mixture of 1,3-cyclopentanediol (15g) and butyltin trichloride (1.98g) was heated at about 230°C for 1 h. The collected volatile products together with water were treated with ether. After separation of water, work-up of the organic layer gave a mixture of compounds (10g) formed by 3-cyclopenten-1-ol (6g), 2-cyclopenten-1-ol (1.2g), and dicyclopentadiene (2.8g), being 87% the diol conversion.

(E/Z) 1,4-cyclohexanediol, (Z>75%) (entry 16 and 17) - Two runs were performed using the same amount (58g) of 1,4-cyclohexanediol and different amounts of butyltin trichloride, 7.0 and 3.5g for entry 16 and 17 respectively. The apparatus used is the same as that described in procedure I. The mixture, was heated with stirring at about 210°C. A first fraction of low boiling compounds was collected around 100°C and a second fraction of high boiling compounds was collected at 120-125°C. The combined fractions were treated as above to give a mixture of the following compounds: 3-cyclohexene-1-ol (24g), cyclohexa-1,4-diene (10g), cyclohexa-1,3-diene (6g), and 7-oxabicyclo [2,2,1] heptane (4g), being 96% the diol conversion (see, entry 16). In the other run (see, entry 17) the yields of the above compounds are 17, 9.5, 6, and 6g, respectively. In addition dicyclohex-3-enyl ether (3.5g) was recovered. The diol conversion in such a case is 80%.

(E)-1,2-Cyclooctanediol (entry 18) - Freshly distilled (E)-1,2-cyclooctanediol (36.1g) and butyltin trichloride were heated at about 210°C. Water (4.5ml) was distilled out at 97-100°C during 40 minutes. Work-up of the residue was made as above to give the following mixture of compounds: cyclooctanone (17g), 9-oxabicyclo [4,2,1] nonane (8g), and cycloocta-1,3-diene (2g). The calculated diol conversion in such a case is 86%.

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