

### C3 Cyclopolymerization. III.\* Preparation of $\alpha,\omega$ -Bis(*p*-vinylphenyl)-alkanes and 1,3-Bis(4-vinylnaphthyl)propane

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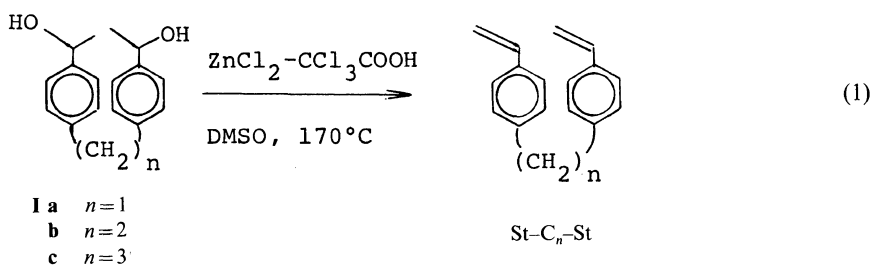
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**ABSTRACT:** Dehydration of  $\alpha$ -phenethyl alcohols was carried out in DMSO at 170°C by a mixed catalyst of zinc chloride and trichloroacetic acid. By this reaction,  $\alpha,\omega$ -bis(*p*-vinylphenyl)alkanes and 1,3-bis(4-vinylnaphthyl)propane were prepared in a good yield of 52 to 88%.

**KEY WORDS** Preparation of Monomer / Styrene Derivatives /  
Vinylnaphthalene Derivatives / Zinc Chloride-Trichloroacetic Acid /  
Dehydration / Dimethyl Sulfoxide /

In the series of papers, we have reported the cyclopolymerization of 1,3-bis(*p*-vinylphenyl)propane (St-C<sub>3</sub>-St).<sup>1</sup> However, it was difficult to prepare the monomer as planned, since there were no very good methods for the preparation

of the monomer and related compounds in high yield (*vide infra*). Moreover, distyryl compounds such as title compounds are useful as crosslinking agents so that the good preparative method is of general interest.



Recently we carried out the acid-catalyzed dehydration (eq 1) of  $\alpha$ -phenethyl alcohol derivatives in dimethyl sulfoxide (DMSO). In this paper, we report on the method for this dehydration and compare it with other reported methods. This method seems applicable to the preparation of multistyryl-group-containing compounds as well as

styrene derivatives.

#### EXPERIMENTAL

##### General

No correction was made for melting points. NMR spectra were taken by a Varian T-60A NMR spectrometer in CDCl<sub>3</sub>, using TMS as the internal standard. IR spectra were recorded on a Hitachi 215 grating IR spectrophotometer. DMSO and other

\* Part II: J. Nishimura, M. Mimura, N. Nakazawa, and S. Yamashita, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 2071 (1980).

**Table I.** Physical properties of St-C<sub>n</sub>-St and VN-C<sub>3</sub>-VN

Compound	Yield	mp	IR (ν C=C)	NMR (τ)		
	%	°C	cm <sup>-1</sup>	-CH <sub>2</sub> -	Vinyl (ABX)	Aromatic (AB)
St-C <sub>1</sub> -St	52	35—36 (32) <sup>a</sup>	1626 992, 906	6.10 (s)	4.79	2.85
					4.30	2.65
					3.27	
St-C <sub>2</sub> -St	68	98.2—98.9 (95.5—97.5) <sup>a</sup>	1628 995, 912, 904	7.05 (s)	4.77	2.83
					4.30	2.65
					3.25	
St-C <sub>3</sub> -St	87	51 (50.0—51.5) <sup>a</sup>	1630 996, 912, 904	8.35 (quin) <sup>b</sup>	4.88	2.97
				7.43 (t) <sup>b</sup>	4.40	2.75
					3.38	
St-C <sub>4</sub> -St	88	60.0—61.1 (60.5—61.8) <sup>a</sup>	1627 992, 902, 887	8.55 (quin) <sup>b</sup>	4.88	2.91
				7.43 (t) <sup>b</sup>	4.38	2.75
					3.38	
St-C <sub>5</sub> -St	73	33.0—34.0	1630 992, 912, 900	8.00—9.00 (m) <sup>b</sup>	4.92	3.00
				7.47 (t)	4.42	2.82
					3.40	
VN-C <sub>3</sub> -VN <sup>c</sup>	54	106.0—107.0	1627 989, 910, 900	7.74 (quin) <sup>b</sup>	4.57	2.33—2.83 (m) <sup>d</sup>
				6.78 (t) <sup>b</sup>	4.27	1.72—2.18 (m) <sup>d</sup>
					2.33—2.83	

<sup>a</sup> Reference 2.<sup>b</sup> Broad.<sup>c</sup> Reference 3.<sup>d</sup> Non-AB-type.

reagents were of the highest commercially available grade, and used in most cases without further purification.

#### Preparation of St-C<sub>3</sub>-St (General Procedure)

1,3-Bis[*p*-(1-hydroxyethyl)phenyl]propane (**Ic**, 5.0 g, 0.018 mol) and anhydrous zinc chloride (0.50 g, 0.0037 mol) were dissolved in 10 ml of DMSO and heated for 5 min at 170°C. Into this mixture, trichloroacetic acid (0.50 g, 0.0031 mol) was added carefully. Soon, a vigorous reaction occurred. The mixture was further heated at 170°C for 15 to 17 min. When a trace amount of insoluble material appeared in the system, the mixture was poured into 100 ml of water. The product was extracted twice by 100 ml of petroleum ether. The extract was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, condensed by evaporation, and then purified by column chromatography, using 20 g of basic alumina and 500 ml of petroleum ether as eluent. Following evaporation of the eluent, St-C<sub>3</sub>-St was obtained in an 87% yield (3.8 g) as a white crystalline compound. Once recrystallized from ethanol, it

showed a mp of 51°C (lit.<sup>1</sup> mp 50.0 to 51.5°C).

In Table I are summarized several monomers prepared by this dehydration, along with their physical properties.

#### Pyrolysis of $\alpha$ -Phenethyl Alcohol over Alumina

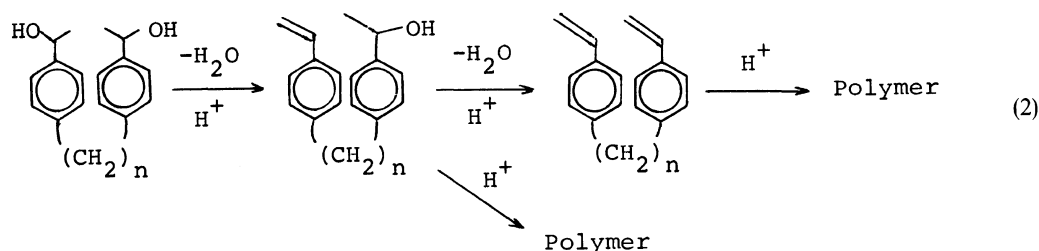
Into a Pyrex glass tube ( $\phi$  26 mm  $\times$  500 mm) equipped with a dropping funnel at the top and a two necked flask at the bottom, granular alumina ( $\phi$  4 to 6 mm, provided by Nakarai Chemicals, Ltd.) was packed by the length of 280 mm. The packed tube was placed within a vertically held tubular electric furnace with a heating part of 340 mm. The system was evacuated at 1 to 3 mmHg and heated at 380 to 400°C. The flask at the bottom was chilled in a dry ice-methanol bath. From the funnel, 50 ml of dioxane solution of  $\alpha$ -phenethyl alcohol (40 gl<sup>-1</sup>) was added over a period of 30 min. The pyrolysis products obtained were warmed to room temperature on standing and then the dioxane was evaporated. The residue was dissolved in petroleum ether and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. By passing the petroleum ether solution through a short basic-

alumina-packed column, polymeric materials were removed and then it was analyzed by GLC with SE-30 packed glass column (2 m) at 170 or 200°C. Each component was isolated by preparative GLC and assigned by NMR and a comparison with the retention time of authentic samples.

## RESULTS AND DISCUSSION

Dehydration of  $\alpha$ -phenethyl alcohol derivatives over potassium hydrogen sulfate near 200°C is the standard preparative method of styrene deriv-

atives.<sup>4</sup> However, this method is limited to the preparation of distillable and monofunctional styrenes, since products must usually be distilled out as soon as produced. Otherwise, cationic polymerization occurs rapidly. In fact, multistyryl compounds, such as  $\alpha,\omega$ -bis(*p*-vinylphenyl)alkanes (St-C<sub>*n*</sub>-St) and 1,3-bis(4-vinylnaphthyl)propane (VN-C<sub>3</sub>-VN) can hardly be prepared by this method even in a low yield. The second dehydration, as shown in eq 2, must compete with rapid cationic polymerization; normally the former may be much slower than the latter.



**Table II.** Products from the pyrolysis of  $\alpha$ -phenethyl alcohol and its derivatives over alumina at 380 to 400°C

Alcohol	g l <sup>-1</sup> in dioxane	Relative yield/% <sup>a</sup>			
		St-C <sub><i>n</i></sub> -St	II	III	
$\alpha$ -Phenethyl alcohol	Without dioxane	100 <sup>b</sup>		0 <sup>c</sup>	
	40	85 <sup>b</sup>		15 <sup>c</sup>	
<b>Ia</b> and <b>Ic</b> <sup>d</sup>	38	<i>n</i> = 1	74	18	8
		<i>n</i> = 3	74	20	6
<b>Ib</b> and <b>Ic</b> <sup>d</sup>	41	<i>n</i> = 2	72	17	11
		<i>n</i> = 3	74	19	7

<sup>a</sup> From the peak ratio on the chromatograph.

<sup>b</sup> For styrene.

<sup>c</sup> For ethylbenzene.

<sup>d</sup> Equimolar mixture.

The dehydration route of  $\alpha$ -phenethyl alcohol derivatives to styrene derivatives, however, has several advantages: simple, selective, and sufficient preparation of appropriate alcohols *via* regioselective acylation of aromatics, simple purification of starting materials, etc. Hence, the reaction should be improved to some extent.

Wiley and Mayberry<sup>2</sup> reported the vapor phase

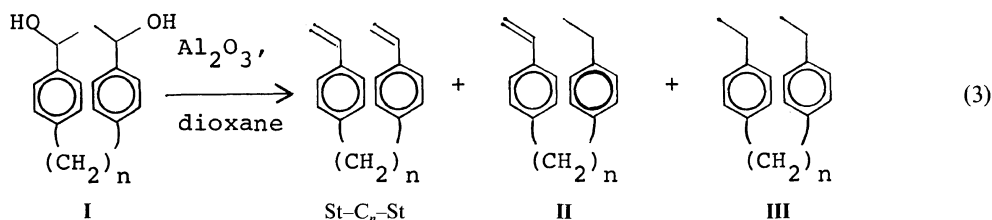
acid-catalyzed dehydration of  $\alpha$ -phenethyl alcohol derivatives over alumina, using dioxane as the carrier. They prepared St-C<sub>*n*</sub>-St and related compounds in moderate yields of 17 to 47%. The lowest yield was recorded for the preparation of St-C<sub>3</sub>-St; this is the most interesting monomer for cyclopolymerization.<sup>1</sup> We tried to carry out the reaction for the preparation of St-C<sub>3</sub>-St many times, but could

not exceed even the reported yield of 17%.

In Table II are summarized the results of gas chromatographic analysis of dehydration products of  $\alpha$ -phenethyl alcohol and its derivatives over alumina. The dehydration of liquid alcohol, as in the case of  $\alpha$ -phenethyl alcohol without dioxane as solvent, went well, giving styrene but no byproducts of molecular weight similar to the olefin. When dioxane was used as the diluent, however, ethylbenzene or the hydrogenated byproduct was obtained in significant yield. The cationic intermediate from  $\alpha$ -phenethyl alcohol may perhaps abstract hydride from dioxane or its pyrolysis products.

Since alcohols (**Ia**, **b**, **c**) are solid and insoluble in

toluene etc., it is necessary to use dioxane as the solvent. In order to keep conditions the same, at least to two alcohols, the dioxane solution of a pair of alcohols was examined in the dehydration process over alumina. All alcohols gave the hydrogenated products, **II** and **III**, as well as St-C<sub>n</sub>-St. The ratios of these three products were almost the same for all three alcohols investigated. The formation of a considerable amount of byproducts, similar to the desired olefin, made isolation of the olefin difficult. In fact, VN-C<sub>3</sub>-VN prepared by this method was accompanied by hydrogenated products which could not be removed by recrystallization and column chromatography.<sup>3</sup>



**Table III.** Preparation of St-C<sub>3</sub>-St by acid-catalyzed dehydration in DMSO<sup>a</sup>

Catalyst	mmol	Yield
		%
—	—	0 <sup>b</sup>
AlCl <sub>3</sub> <sup>c</sup>	0.5	0.3
AlCl <sub>3</sub> <sup>c</sup>	0.1	0.2
SnCl <sub>4</sub> <sup>c</sup>	0.5	17.9
TiCl <sub>4</sub> <sup>c</sup>	0.5	2.0
ZnCl <sub>2</sub>	0.5	13.5
ZnBr <sub>2</sub>	0.5	8.6
BF <sub>3</sub> OEt <sub>2</sub>	0.5	34.7
HCl	0.5	22.1
CHCl <sub>2</sub> COOH	0.5	0.5
CCl <sub>3</sub> COOH	0.5	3.0
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> H·H <sub>2</sub> O	0.5	47.2
KHSO <sub>4</sub>	0.5	48.6
ZnCl <sub>2</sub> /CCl <sub>3</sub> COOH	0.5/0.5	52.9
ZnCl <sub>2</sub> /CHCl <sub>2</sub> COOH	0.5/0.5	15.1
BF <sub>3</sub> OEt <sub>2</sub> /CCl <sub>3</sub> COOH	0.5/0.5	47.0

<sup>a</sup> Reaction conditions: **Ic**, 5 mmol; DMSO, 2 ml; temp, 170°C; time, 12 min.

<sup>b</sup> Reaction time, 420 min.

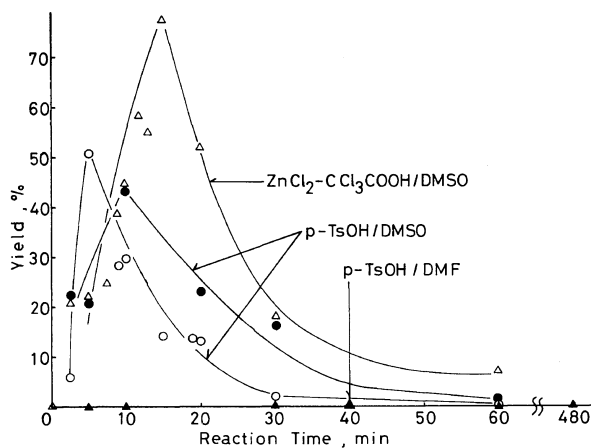
<sup>c</sup> These catalysts gave polymeric material after heating for 12 min.

Traynelis *et al.*<sup>5</sup> reported the dehydration of  $\alpha$ -phenethyl alcohol by prolonged heating in DMSO in the presence of a radical inhibitor. Styrene was obtained in 39% yield after heating for 16 hr at 160°C. We tried the method for preparing St-C<sub>3</sub>-St. The yield was from 0 to 41% after heating for 7 hr or more. Reproducibility was poor. There was even the further problem that purification of the appropriate alcohol and DMSO completely inhibited the reaction. It is considered that traces of acids contained in the starting materials and DMSO may act perhaps as catalysts.

Various Lewis acids and Brønsted acids were combined with DMSO for the dehydration of 1,3-bis[*p*-(1-hydroxyethyl)phenyl]propane (**Ic**). The reaction mixtures were treated by the same standard procedure for yield comparison. The results are summarized in Table III. Only potassium hydrogen sulfate and *p*-toluenesulfonic acid gave by itself the monomer in moderate yield.

Using *p*-toluenesulfonic acid, dehydration was investigated in order to elucidate how St-C<sub>3</sub>-St was produced and consumed mainly by polymerization. The results are illustrated in Figure 1. The yield of St-C<sub>3</sub>-St became maximum in *ca.* 5 min and then sharply decreased ("point-type").<sup>6</sup> After heating for

Preparation of  $\alpha,\omega$ -Bis(*p*-vinylphenyl)alkanes



**Figure 1.** Preparation of St-C<sub>3</sub>-St. Reaction conditions: **Ic**, 5 mmol; (△), ZnCl<sub>2</sub> (0.5 mmol)-CCl<sub>3</sub>COOH (0.5 mmol), DMSO (10 ml); (○), *p*-TsOH (0.5 mmol), DMSO (2 ml); (●), *p*-TsOH (0.5 mmol), DMSO (10 ml); (▲), *p*-TsOH (0.5 mol), DMF (2 ml).

30 min, a large amount of insoluble polymer appeared with an isolated trace of St-C<sub>3</sub>-St. The consumption of St-C<sub>3</sub>-St clearly decreased on diluting the reaction mixture with DMSO, but the maximum yield was not satisfactory (see Figure 1). Since neither the Lewis acids nor Brønsted acids investigated made the reaction efficient by itself, a search was made for mixed catalysts. Among the mixed catalysts studied, the catalyst made from zinc chloride and trichloroacetic acid (1:1 mole ratio) gave excellent performance in the dehydration process, in view of the considerably rapid formation of St-C<sub>3</sub>-St and its relatively slow consumption in the system (rather "plateau-type"). A typical example is shown in Figure 1. Using this catalyst, several St-C<sub>*n*</sub>-St and VN-C<sub>3</sub>-VN were prepared in respectable yield and are listed in Table I.

*N,N*-Dimethylformamide (DMF), a more basic solvent than DMSO, did not work as shown in Figure 1, but DMSO seemed not only to work as a retardant for the cationic polymerization, but also to participate in the dehydration itself directly. Further research is still necessary for further

clarification.

The dehydration method by the mixed catalyst reported here provides a rather easy, convenient, laboratory preparation for various styrene derivatives, especially multistyryl and related compounds.

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