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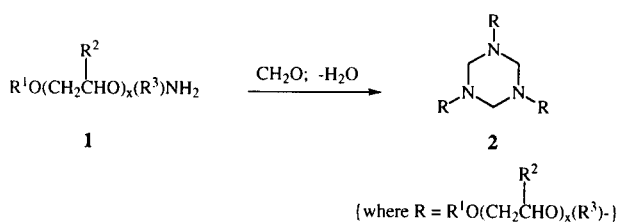
Received October 8, 1999

Unhindered polyalkoxylated primary amines, upon treatment with an equimolar equivalent of formaldehyde, cyclized quantitatively to afford perhydro-1,3,5-*s*-triazines. This series of derivatives, based upon primary amine terminated poly(propylene and butylene oxides), possessed a molecular weight range of 1,900-5,800. Structure confirmation was accomplished by gel permeation chromatography and 2D nmr spectroscopy methods.

*J. Heterocyclic Chem.*, **37**, 1157 (2000).

Substituted perhydro-1,3,5-*s*-triazines **2** have shown utility as corrosion inhibitors [1], biocides [2], crosslinking agents for the manufacture of polyurethanes [3], stabilizers for natural rubber latex foam [4], and scavengers for the removal of sulfide gases from petroleum fuels [5]. Previous synthetic reports involved the condensation of formaldehyde with low molecular weight amines to afford the corresponding perhydrotriazine molecules in 22-90% conversion [6]. Normal aliphatic amines (*i.e.* methyl through butyl) typically cyclized in the range of 70-80% [4]. In some instances, unsaturation [7] or heteroatoms [8] were present in the starting amines. Unknown are accounts that describe the reaction of higher molecular weight amines **1**, derived from polyalkoxylated initiators.

We now report a general synthesis of high molecular weight perhydrotriazines *via* the simple and quantitative conversion of unhindered polyether-containing primary amines [9]. Alcohol and alkylphenol initiators were alkoxylated with propylene or butylene oxides to obtain several backbone types of different molecular weights [10]. Conversion of these polyetherols to starting polyetheramines **1b-f** was accomplished in a two step cyanoethylation/catalytic hydrogenation sequence as previously described [11]. Perhydrotriazine cyclizations were run by charging an equimolar equivalent of polyetheramine and paraformaldehyde in toluene solvent, followed by azeotropic water removal at 120-130 °C for three hours.



For entries 1-8 of Table 1, the conversion to perhydrotriazine was at least 99% based upon 500 MHz <sup>1</sup>H nmr.

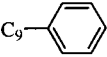
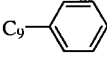
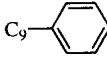
Complete disappearance of the starting amine's triplet resonance from the alpha carbon methylene protons, and the emergence upfield of a new product triplet was observed for entries 1-8. Gel permeation chromatography (GPC) of the reaction products confirmed a three-fold molecular weight increase for all symmetrical examples due to the desired ring formation. Number average molecular weight ( $\bar{M}_n$ ) data reported in Table 1 are in agreement with the theoretical product values [10b]. Calibration of the GPC method was accomplished relative to a polystyrene standard. Electrospray ionization mass spectrometry (ESI-MS) analysis of perhydrotriazine **2a** displayed a sodiated molecular ion [M + Na]<sup>+</sup> at m/z 830.8 [12].

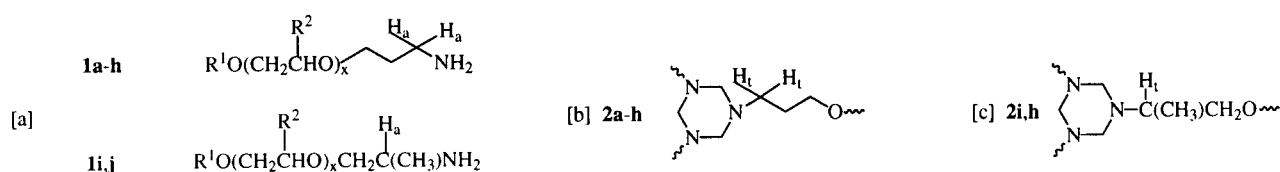
Adding steric bulk near the starting amine group in the form of an alpha methyl substituent (Entries 9,10; Table 1) lowered the perhydrotriazine conversion to 55-60%. In these experiments, the remainder of the product mixture consisted of the corresponding uncyclized aldimine.

Pulsed-Field-Gradient (PFG) heteronuclear single quantum correlation (HSQC) [13] and heteronuclear multiple bond correlation (HMBC) [14] 2D nmr methods were used to characterize perhydrotriazine **2d** structural fragment **f1** in Figure 1. Overlaid HMBC and HSQC spectra have also been displayed as gray and black contour peaks, respectively. These were expanded to four different carbon chemical shift ( $\delta_C$ ) ranges, while keeping the proton chemical shift ( $\delta_H$ ) range constant. Four  $\delta_C$  regions represent the three carbons (a-c) of the propoxyl amine groups and the perhydrotriazine ring methylenes (d).

Assignments in the HMBC spectra have been illustrated schematically with through-bond connectivity arrows for structural fragment **f1**, while the one-bond HSQC cross-peaks were identified directly in the 2D spectra. Propoxyl amine <sup>1</sup>H and <sup>13</sup>C resonances were assigned by starting with the HSQC methylene cross-peak at  $\delta_C$ ,  $\delta_H$  = 67.7, 3.53 ppm, which was assigned to **f1C4H4**. A methylene carbon assigned to **f1C4H4** correlated (cross-peaks b and c) long-range to two protons at  $\delta_H$  2.48 and 1.70 ppm, assigned to **f1H2** and **f1H3**. These methylene protons correlated one-bond to carbons at  $\delta_C$  50.0 and 28.6 ppm, which were assigned

Table 1  
Perhydrotriazine Cyclization of Polyetheramines with Formaldehyde

Entry	Starting Polyetheramine 1				Data for Perhydrotriazine 2			
	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	x	δH <sub>a</sub> (ppm) [a]	δH <sub>t</sub> (ppm) [b,c]	M̄ <sub>n</sub> [d]	Polydispersity (M <sub>w</sub> /M <sub>n</sub> )
1	C <sub>13</sub>	–	(CH <sub>2</sub> ) <sub>3</sub>	0	2.78	2.48	846	1.06
			<b>1a</b>				<b>2a</b>	
2	<i>n</i> -C <sub>14-16</sub>	CH <sub>3</sub>	(CH <sub>2</sub> ) <sub>3</sub>	10	2.85	2.47	1,880	1.36
			<b>1b</b>				<b>2b</b>	
3		CH <sub>3</sub>	(CH <sub>2</sub> ) <sub>3</sub>	14	2.79	2.50	3,360	1.17
			<b>1c</b>				<b>2c</b>	
4	<i>n</i> -C <sub>12-15</sub>	CH <sub>3</sub>	(CH <sub>2</sub> ) <sub>3</sub>	24	2.80	2.47	5,710	1.28
			<b>1d</b>				<b>2d</b>	
5	C <sub>13</sub>	CH <sub>2</sub> CH <sub>3</sub>	(CH <sub>2</sub> ) <sub>3</sub>	20	2.79	2.47	5,380	1.19
			<b>1e</b>				<b>2e</b>	
6		CH <sub>3</sub>	(CH <sub>2</sub> ) <sub>3</sub>	24	2.78	2.46	5,810	1.20
			<b>1f</b>				<b>2f</b>	
7		33.3 mole% <b>1a</b> + 66.7 mole% <b>1d</b>			2.78	2.47	4,420	1.11
			<b>1g</b>				<b>2g</b>	
8		50 mole% <b>1d</b> + 50 mole% <b>1e</b>			2.79	2.47	5,550	1.15
			<b>1h</b>				<b>2h</b>	
9	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>2</sub> CH(CH <sub>3</sub> )	10	3.11	2.59	3,170	1.22
			<b>1i</b>				<b>2i</b>	
10		CH <sub>3</sub>	CH <sub>2</sub> CH(CH <sub>3</sub> )	11	3.13	2.61	3,300	1.13
			<b>1j</b>				<b>2j</b>	



[d] Waters instruments: 515 pump, WISP autosampler, and 410 RI detector; Polymer Labs Pligel column.

to cross-peaks **f1C2H2**, **f1C3H3**. Corroborating evidence was the long-range correlations (cross-peaks d and e) from **f1C2** to **f1H4** and **f1H3**, and (cross-peaks f and g) from **f1C3** to **f1H4** and **f1H2**.

Assignment of the <sup>1</sup>H and <sup>13</sup>C resonances of the perhydrotriazine ring methylene was deduced from the long-range correlation (cross-peak a) of the carbon at δC 75.1 ppm to **f1H2** methylene protons at δH 2.48 ppm. Lone oxygenated carbon **f1C4** is the only one that can be within

three bonds of **f1H2**. Therefore, the only possible assignment of cross-peak a is a three-bond correlation of the formaldehyde-derived methylene carbon to methylene protons, **f1H2**, of the propoxyl amine group.

In conclusion, we have demonstrated an unexpected, very high yield synthesis of high molecular weight polyalkoxylated symmetrical perhydrotriazines. These new molecules are under investigation as fuel intake deposit control additives.

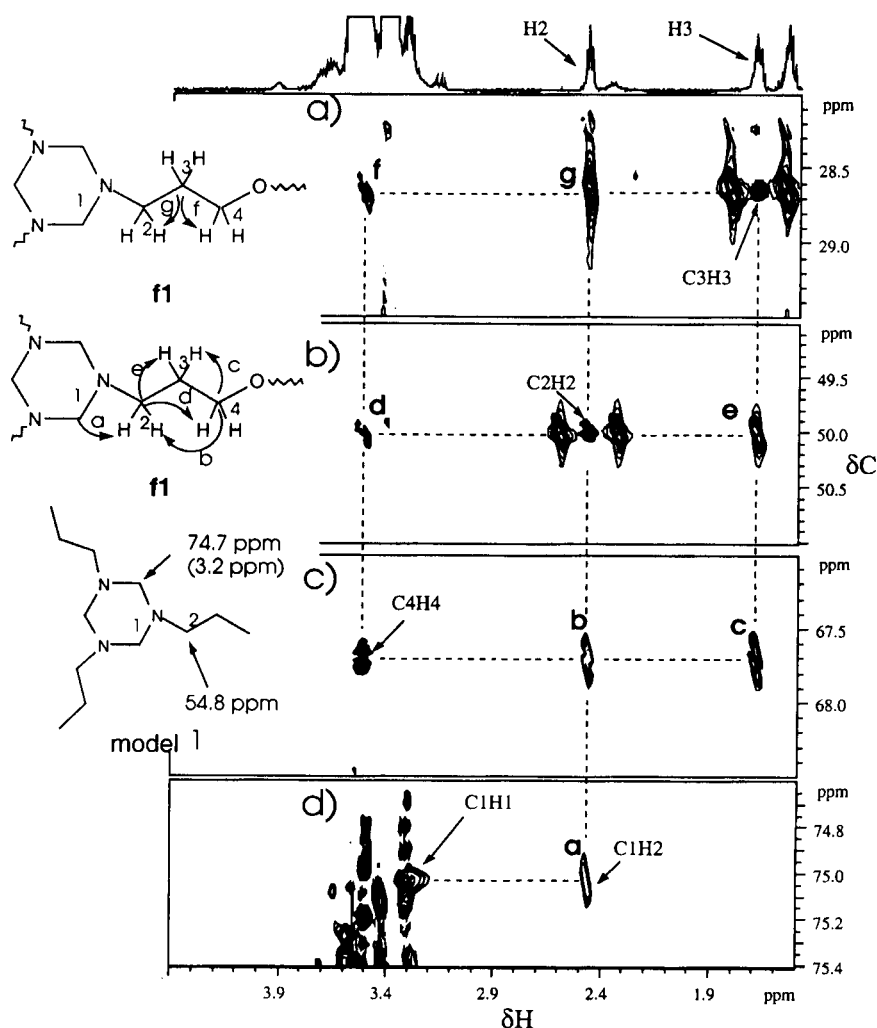


Figure 1. Overlaid HMBC (Gray) and HSQC (Black) spectra for perhydrotriazine **2d**.

## EXPERIMENTAL

Table 2  
Assignments of Structural Fragment (**f1**) [a]

<b>f1</b>	$\delta C$ (ppm)	$\delta H$ (ppm)
1	75.1	3.3
2	50.0	2.48
3	28.6	1.70
4	67.7	3.53

[a] Table 2 lists the assigned  $\delta H$  and  $\delta C$  values of **f1**. Model 1 provides known  $\delta C$  and  $\delta H$  values for perhydro-1,3,5-tris(*n*-propyl)triazine.

The nmr experiments were performed on a Bruker AMX-II 500 MHz spectrometer equipped with a 10 amp Accustar gradient amplifier and GRASP II™ version probe containing actively shielded gradients. Samples were prepared in 5mm tubes to approximately 10 wt. % solution using deuteriochloroform. The probe temperature was controlled using a FTS Air-Jet cooler that provided -20 °C nitrogen to the probe inlet. Nitrogen gas was heated to a final probe temperature of 32 °C using a Bruker B-VT 2000 variable temp controller unit. All sequences used a sinusoidal or square gradient of 1 ms with a gradient strength ranging between 5-30 G cm<sup>-1</sup> and 0.1 ms recovery delay.

Acquisition of the HMBC spectrum was at 500.13 MHz using gradient strengths of 50%(G1), 30.1%(G2), and 40%(G3) of a maximum gradient strength of 60 G cm<sup>-1</sup>. Also employed were a 254 ms acquisition time, 1 s relaxation delay, and spectral

widths of 5050 Hz in **f2** and 12500 Hz in **f1**. Pulses consisted of a 8.15  $\mu\text{s}$   $^1\text{H}$  90°, 10.5  $\mu\text{s}$   $^{13}\text{C}$  90°, with a 50 ms ( $\Delta$ ) long-range coupling delay. This sequence did not include a refocusing delay prior to acquisition and, therefore, was not  $^{13}\text{C}$  decoupled in the **f2** domain. A final 2D matrix of 2048 data points in **f2** and 2048  $t_1$  increments in **f1** (linear predicted out to 4096 points) with 40 scans per  $t_1$  increment was obtained.

The phase-sensitive HSQC spectrum was obtained at 500.13 MHz using TPPI [15], square gradients of 1 ms duration, and gradient strengths of 50%(G1), 12.5%(G2), 50%(G1), and -12.5%(G2) of maximum gradient strength. It used a 202 ms acquisition time, 1 s relaxation delay, spectral widths of 5050 Hz in **f2** and 12500 Hz in **f1**, a 8.1  $\mu\text{s}$   $^1\text{H}$  90°, 10.5  $\mu\text{s}$   $^{13}\text{C}$  90°. Garp decoupling power was at 3676 Hz and the data were processed according to the method of States, *et. al.* [16] using Bruker's echo-antiecho transformation parameter. A 2D matrix was obtained of 4096 data points in **f2** (zero filled to 8192 points), and 2048  $t_1$  increments in **f1** (linear predicted out to 4096 points) with 64 scans per  $t_1$  increment.

All spectra were processed with a  $\pi/2$  squared sine weighting function in both dimensions. The **f1** dimension was extended to twice its original size using a linear prediction with 64 coefficients.

ESI-MS of perhydrotriazine **2a** was run on a Bruker Apex II 47e FTMS instrument.

Acknowledgments.

We thank Diane Vrobel for her nmr spectroscopy assistance and David Aaserud for mass spectra efforts.

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- [10a] Typical polydispersities (*i.e.*,  $\bar{M}_w/\bar{M}_n$ ) of the starting polyetherols ranged from 1.10 to 1.20 as measured by gel permeation chromatography.  $\bar{M}_w$  refers to weight average molecular weight, and  $\bar{M}_n$  to number average molecular weight; [b] For a discussion of  $\bar{M}_w$ ,  $\bar{M}_n$ , and polydispersity definitions and calculations see: P. E. Slade, in *Techniques and Methods of Polymer Evaluation, Volume 4: Polymer Molecular Weights Pt 1*, Marcel Dekker, Inc., New York, 1975, pp 2-7.
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