NOTE

The Synthesis of Alkoxymethyl Derivatives of Benzoguanamine

INTRODUCTION

Several reports appear in the patent literature[1-18] and brief communications[5,6,19] describing the reaction of formaldehyde with melamine to give various methylolmelamines. With the exception of hexamethylolmelamine,[6] hexamethoxymethylmelamine,[5,6] trimethylolmelamine,[14] trimethoxymethylmelamine,[15] and triethoxymethylmelamine,[10,16] few other methylolated or alkoxylated derivatives of melamine or benzoguanamine[22] have been described in pure form. The literature usually describes many of these materials as resinous materials. The kinetics of reaction of formaldehyde with melamine has appeared in several reports[23,24] to be pH dependent.

The object of this investigation was to prepare several of the previously unknown pure alkoxymethyl derivatives of benzoguanamine.

RESULTS AND DISCUSSION

The alkoxymethyl derivatives were prepared from the corresponding methylol derivative by using an excess amount of the alcohol in the presence of acid. Methyl and ethyl alcohol yielded solid alkoxymethyl derivatives whereas *n*-propyl and *n*-butyl alcohol yielded liquid products in the benzoguanamine case. The related products in the melamine case have not been isolated in a pure enough state to warrant their inclusion in this communication.

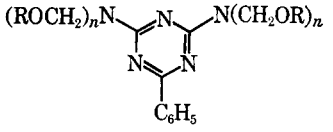
In order to obtain nonpolymeric products mild temperatures (50–70°C) were utilized in the methylolation step and (room temperature) in the alkoxylation procedure. The alkoxymethyl derivatives were isolated by filtration or low temperature concentration under vacuum. Residual salts were removed by precipitation in benzene.

Tetramethoxymethyl benzoguanamine gave an immediate crystalline precipitate after 10 min and appeared to be quite pure. Tetrabenzyloxybenzoguanamine was the only other alkoxylated product that precipitated from its reaction mixture and did not require concentration. The use of benzyl alcohol for alkoxylation requires a rapid filtration; otherwise polymeric products are produced. A crystalline product is obtained from benzoguanamine but undefined products are produced from melamine. The failure of the earlier literature to isolate nonpolymeric products was probably due to their higher reaction temperatures.

The results in Tables I and II show that the melting points of the methylolated derivatives undergo a drastic reduction on alkoxylation. This is expected since hydrogen bonding is reduced. The higher molecular weight alcohols yielded noncrystalline products and are difficult to purify by distillation because of their tendency to polymerize. The melting point reductions are more pronounced in the melamine series since six hydroxymethyl groups are involved compared to four in the benzoguanamine series.

All the compounds reported in Tables I and II polymerize in the presence of acids at room temperature, and even faster at elevated temperatures, to give highly insoluble crosslinked polymers.

TABLE I
Summary of Synthesized Benzoguanamine Compounds



R	n	MP, °C	Calcd., % C	Calcd., % H	Calcd., % N	Found, % C	Found, % H	Found, % N
H	2	130–131	50.80	5.54	22.84	50.72	6.11	22.30
CH_3	2	89–90	56.30	6.88	19.30	56.62	6.78	18.70
C_2H_5	2	48–49	60.10	7.87	16.70	60.97	7.97	16.80
C_3H_7	2	liq.[a]	63.10	8.65	—	62.30	8.44	—
C_4H_9	2	liq.	65.60	9.24	13.20	65.22	9.28	13.70
$C_6H_5CH_2$	2	74–75	73.70	6.16	10.50	74.00	6.22	10.53

[a] Mol. wt. calcd., 475: found, 480 (vapor pressure osmometry).

TABLE II
Infrared Spectra of the Compounds Described in Table I.

Compound R	n	Major infrared bands,[a] μ
Benzoguanamine		
H	2	2.95 (m); 3.40 (w); 6.26 (w); 6.47 (s); 7.20 (s); 9.85 (m); 10.07 (m); 11.50 (w); 12.12 (w); 12.78 (w); 14.25 (w).
CH_3	2	3.40 (m); 6.27 (m); 6.45 (s); 6.55 (s); 6.75 (s); 6.89 (m); 7.22 (s); 7.55 (s); 9.11 (s); 9.36 (m); 9.95 (s); 11.00 (m); 11.50 (s); 11.70 (m); 14.20 (m).
C_2H_5—	2	3.35 (w); 6.09 (s); 6.20 (s); 6.50 (s); 7.24 (m); 7.55 (m); 9.15 (s); 9.53 (m); 9.85 (w); 10.00 (w); 11.22 (w); 11.50 (w); 11.85 (w); 12.90 (m); 14.35 (w).
C_3H_7—	2	3.37 (w); 6.05 (s); 6.17 (s); 6.50 (s); 7.24 (m); 7.55 (s); 9.10 (s); 9.50 (m); 9.95 (w); 12.90 (m); 14.35 (w).
C_4H_9—	2	3.37 (m); 3.46 (m); 6.25 (m); 6.50 (s); 6.73 (m); 6.87 (m); 7.25 (s); 7.55 (m); 9.20 (s); 12.09 (m); 14.22 (m).
$C_6H_5CH_2$—	2	3.30 (w); 3.50 (w); 6.26 (w); 6.45 (s); 6.52 (s); 7.18 (m); 7.25 (m); 9.18 (m); 9.35 (m); 9.75 (m); 13.55 (m); 14.35 (m).

[a] Relative intensities of bands are denoted by: s = strong; m = medium; and w = weak.

EXPERIMENTAL

In order to illustrate the general methods used in the synthesis of the methylol and alkoxymethyl derivatives of benzoguanamine, the preparation of tetramethylolbenzoguanamine and tetramethoxymethylbenzoguanamine are described below.

Tetramethylolbenzoguanamine[22]

To a flask were added 187 g (1.0 mole) of benzoguanamine and 519 ml 37% formaldehyde solution (6.39 moles) at pH 7.9. The mixture was warmed at 71°C for 80 min and then allowed to cool slowly to room temperature. The white solid was filtered, washed with methanol, and dried in a vacuum oven at 35°C to yield 126.8 g, mp 130–131°C and 118 g, mp 128–130°C (total yield 79.5%).

Tetramethoxymethylbenzoguanamine

To a flask were added 27.65 g (0.09 mole) tetramethylolbenzoguanamine, 150 g (5.62 moles) of methanol, and 9 ml concentrated hydrochloric acid. The mixture was stirred and the solution became clear. In a few minutes, a crystalline precipitate formed which was filtered and dried to yield 22.2 g, mp 91–92°C and 0.9 g, mp 88–89°C. Recrystallization of 2 g of the first fraction from methanol yielded a material of mp 89–90°C.

MATERIALS

Benzoguanamine was obtained from Rohm and Haas Company.
Formaldehyde was obtained from Borden, Inc.
The alcohols were obtained from commercial sources and distilled before use.

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