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MONTMORILLONITE, AN EFFICIENT CATALYST FOR THE PREPARATION OF DIALKOXYMETHANES[†]

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Abstract: The reaction of various alcohols with paraformaldehyde in presence of montmorillonite to give dialkoxymethanes (2a-g) in very good yield is described.

Recently there has been considerable attention towards the use of heterogeneous catalysts¹ for organic transformations. Zeolites² and clays^{3,4} are the major contributors in this field. The Bronsted and Lewis acid properties of zeolites and clays have been exploited for several organic transformations.⁵ As a part of our on going research programme on utilization of zeolites and clays for organic synthesis,⁶ we herein report an unprecedented clay catalyzed formation of dialkoxymethanes starting from paraformaldehyde and alcohols.

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Montmorillonite has been used widely as a solid acid catalyst.⁷ It belongs to smectite family of clay and most of the clays belonging to this family are assemblies of tetrahedral layer of silicate units (SiO_4) and octahedral aluminate units (AIO_6) . One octahedral aluminate layer is sandwiched between two tetrahedral silicate layers.^{7c} The resulting three layered sheets are separated by an interlamellar space, some times called the gallery. In nature, isomorphous substitution of Si or Al in both octahedral and tetrahydral layer is very common. As a consequence valencies of the coordinated oxygen are no longer saturated. The negative charge on the sheet is then balanced by cations held in the interlamellar space. The stability is gained by interlamellar water, as a result the sheet may expand to accommodate more water or solvent molecules. We believe that the paraformaldehyde slowly decomposes to formaldehyde in the interlamellar space, where alcohol molecules along with water molecules are already present. Eventually, the formaldehyde formed is trapped by alcohol to generate dialkoxymethane. This reaction failed to give dialkoxymethane when zeolite was used as a catalyst, as paraformaldehyde molecules are unable to enter into the zeolite cavities, where most of the acidic sites are available for the reaction.

The reaction of various alcohols (1a-f, 4 - 6 equivalent) with paraformaldehyde when carried out at reflux temperature of alcohols or at 140 °C (in case of higher boiling alcohols; see Table) in the presence of montmorillonite (20% by mass to that of paraformaldehyde) for 6 - 12 hrs. offered dialkoxymethanes (2a-f) in 70 - 80% isolated yields (Scheme 1). The formation of dialkoxymethanes was confirmed from their spectral data. The results are summarized in Table 1. In case of cyclohexyl alcohol (1d) and benzyl alcohol (1e) the formation of small quantities of dicyclohexyl ether (0.7%) and dibenzyl ether (10%) was detected by glc analysis. Interestingly, no polymerization was observed when propane-1,3-diol was reacted with equivalent

Entry No	Alcohols	Reaction	Reaction	Product	Yield ^a	Reference
		Temp.(⁰C)	time (hrs.)		(%)	
1	1a	refluxed	6	2a	80	8
2	1b	refluxed	12	2 b	72	8
3	1c	refluxed	12	2c	70	9
4	1d	refluxed	6	2d	76	10
5	1e	140	12	2e	71	11
6	1f	140	6	2f	83	10
7	1g	140	6	2g	70	12

Table 1.The preparation of dialkoxymethanes (2a-f) starting from alcohols (1a-f)and paraformaldehyde in presence of montmorillonite.

^a Yield of isolated products after distillation.

$$\begin{array}{rcl} \text{R-OH} & + & (\text{CH}_2\text{O})_n & \xrightarrow[\text{feflux, 140^{\circ}\text{C}}]{\text{reflux, 140^{\circ}\text{C}}} & \text{R-O-CH}_2\text{-O-R} \\ \hline \text{1a-f} & & & & & & \\ \text{1a-f} & & & & & & & \\ \text{R} = & \text{a) ethyl} & & \text{d) cyclohexyl} & & & & & & \\ \text{b) n-butyl} & & & \text{e) benzyl} & & & & & & \\ \text{c) iso-butyl} & & & \text{f) n-octyl} & & & & & & \\ \end{array}$$

Scheme 1

amount of paraformaldehyde at 140 °C. The cyclic 1,3-dioxane (2g) was the only product obtained in 70% yield from this reaction.

Experimental Section

¹H NMR spectra were recorded in CDCl₃ solution on Varian FT80 (80 MHz) or Bruker WH90 (90 MHz) spectrometer. The chemical shifts are reported in ppm downfield from tetramethylsilane. IR spectra were recorded on a Perkin-Elmer Infracord spectrophotometer Model 599-B using sodium chloride optics. All glc analysis were carried out on Hewlet-Packard-5890 equipped with integrator Model No. 3392 using BP-1 capillary column at programmed temperature of 70 - 160 °C (8 °C per minute). All alcohols were distilled prior to use. The clay, montmorillonite K 10 was obtained from Fluka Chemie AG.

General procedure for the preparation of Dialkoxymethane (2a-f)

A mixture of paraformaldehyde (10 g), alcohol (**1a-f**, 4 to 6 equivalent) and montmorillonite (2 g) was refluxed (in case of **1a-d**) or heated at 140 °C (in case of **1e,f**) for 6 to 12 hrs. The reaction mixture was cooled to room temperature and catalyst was removed by filtration. The excess of alcohol was removed by distillation and the residue was distilled under vacuum to get dialkoxymethane (**2b-f**). In case of diethoxymethane (**2a**), the catalyst was removed by filtration and the filtrate was diluted with equal volume of aqueous potassium carbonate solution (5%). The organic layer was separated, dried over anhydrous potassium carbonate and distilled to give diethoxymethane (**2a**).

Diethoxymethane (2a) : Colorless liquid, b.p. 87 - 89 °C (lit.⁸ 89 °C). IR (neat) : 1450, 1390, 840 cm⁻¹; ¹H NMR : 1.16 (t, *J* = 8 Hz, 6H), 3.52 (q, *J* = 8 Hz, 4H), 4.56 (s, 2H).

Di-*n*-butyloxymethane (2b) : Colorless liquid, b.p. 150 °C/70 mm. (lit.⁸ 56 - 60°C/12 mm). IR (neat) : 1450, 1380, 830, 740 cm⁻¹; ¹H NMR : 0.95 (t, *J* = 6 Hz, 6H), 1.00 - 1.84 (m, 8H), 3.51 (t, *J* = 6 Hz, 4H), 4.55 (s, 2H).

Di-*iso*-**butyloxymethane** (**2c**) : Colorless liquid, b.p. 99-100 °C/90 mm. (lit.⁹ 164 °C). IR (neat) : 1465, 1400, 1380, 1060 cm⁻¹; ¹H NMR : 0.88 (d, *J* = 7 Hz, 12H), 1.55 - 2.00 (m, 2H), 3.26 (d, *J* = 7 Hz, 4H), 4.60 (s, 2H).

Dicyclohexyloxymethane (2d) : Colorless liquid, b.p. 148-150 °C/10 mm. (lit.¹⁰ 144 - 145°C/15 mm). IR (neat): 1440, 1360, 930, 890 cm⁻¹; ¹H NMR : 1.00-2.10 (m, 20H), 3.24-3.87 (m, 2H), 4.71 (s, 2H).

Dibenzyloxymethane (2e) : Colorless liquid, b.p. 120-122 °C/0.5 mm. (lit.¹¹ 184-90°C/15 mm). IR (neat): 1460, 1390, 1170, 740 cm⁻¹; ¹H NMR : 4.66 (s, 4H), 4.86 (s, 2H), 7.32 (s, 10H).

Di-*n*-octyloxymethane (2f) : Colorless liquid, b.p. 135-140 °C/3 mm. (lit.¹⁰141 - 143°C/3mm). IR (neat) : 1460, 1380, 725 cm⁻¹; ¹H NMR : 0.90 (t, *J* = 6 Hz, 6H), 1.20 - 1.70 (m, 24H), 3.55 (t, *J* = 6 Hz, 4H), 4.65 (s, 2H).

1,3-Dioxane (**2g**) : A mixture of paraformaldehyde (3 g, 10 mmol), propane-1,3-diol (9.12 g, 12 mmol) and montmorillonite (0.6 g) was heated at 140 °C (bath) for 6 hr. The product, 1,3-dioxane (**2g**, 6.18 g, 70%) was isolated from the reaction mixture by distillation as colorless liquid, b.p. 104-106 °C (lit.¹² 105-106 °C).

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