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The synthesis of cyclotriveratrylene using heteropolyacids ($H_{3+x}PMo_{12-x}V_xO_{40}$) as recyclable heterogeneous catalysts

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The synthesis of cyclotriveratrylene (CV) using formaldehyde (37%) in the presence of heteropolyacids, $H_{3+x}PMo_{12-x}V_xO_{40}$ (x = 1–3) was studied in different solvents. In all cases the heteropolyacid with $x = 3$ gave the highest yield using ethanol as solvent. The effects of the catalyst and the solvent on the reaction were studied.

Key words: cyclotriveratrylene (CV), formaldehyde, heteropolyacid, catalyst.

1. INTRODUCTION

The facile condensation reaction between formaldehyde and phenols or their derivatives provides a major route to obtain rigid macrocycles used in supramolecular chemistry. Calixarenes, the best-known class of phenol-derived macrocycles, are prepared in this way, as are spherands and their relatives. Cyclotriveratrylene (CV), however, is an excellent exemplar of the ‘molecular basket’ type of ligands and has been known for the best part of a century. Many derivatives have been prepared and some exhibit useful inclusion properties such as that in Figure 1.

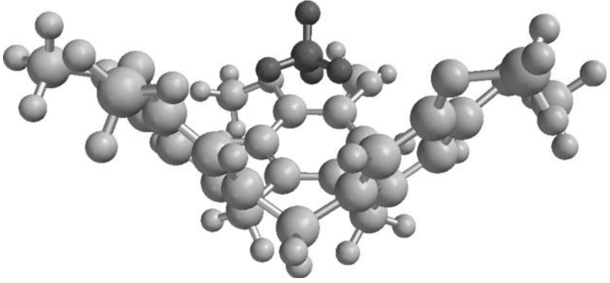

Fig. 1. Structure of a cyclotriveratrylene inclusion complex.

The synthesis included here is based on that reported by Robinson. In her paper the structure of the colourless crystalline precipitate resulting from the condensation of veratrole with formaldehyde in sulphuric acid was given a dimeric, rather than trimeric, configuration. At the time the product was believed to be 2,3,6,7-tetramethoxy-9,10-dihydroxyanthracene; however, as this was determined by the percentage of carbon and hydrogen in the compound, it is an understandable error as the composition would be the same for any higher homologue. The procedure is a result of much trial and error together with careful observation: as will be seen from the literature surrounding acid-catalysed reactions between aldehydes and phenols (or their derivatives such as resorcinol, pyrogallol and veratrole), yields are highly variable [1-6]. The structure of cyclotriveratrylene (CV) is (10,15-dihydro-2,3,7,8,12,13-hexamethoxy-5*H*-tribenzo[a,d,g]cyclononene).

The application of heteropolyacids, HPAs, as catalytic materials is growing continuously in the catalytic field. These compounds possess unique properties such as: well-defined structure, Brønsted acidity, possibility to modify their acid–base and redox properties by changing their chemical composition (substituted HPAs), ability to accept and

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release electrons, high proton mobility, being environmentally benign and presenting fewer disposal problems [7]. Because of their stronger acidity, they generally exhibit higher catalytic activity than conventional catalysts such as mineral acids, ion exchange resins, mixed oxides, zeolites, etc [8].

2. EXPERIMENTAL

Chemicals and apparatus

All compounds were purchased from Merck Company and all of the catalysts were prepared in accordance with the literature data [9-12]. The Wells–Dawson, $H_6[P_2W_{18}O_{62}]$ was prepared as described elsewhere [13] from an aqueous solution of α/β $K_6P_2W_{18}O_{62}.{}_{10}H_2O$ salt, which was treated with ether and concentrated (37%) HCl solution. All products were identified and their physical and spectroscopic data were compared with those of authentic samples. Melting points were measured using Barnstead Electro thermal. IR spectra were recorded on Bruker 4000–400 cm^{-1}. ^1H NMR spectra were recorded on a FT-NMR Bruker 90 MHz. The yields are based on GC/mass analysis using Agilent 6890 GC system Hp-5 capillary 30m×530μm×1.5μm nominal.

General preparation of cyclotriveratrylene (CTV)

Add cold 1,2-dimethoxybenzene (10 mL, 78.5 mmol) to heteropolyacid (0.04 mmol) in a 150 mL round-bottomed flask and stir vigorously. Add dropwise aqueous formaldehyde (12.5 mL, 37 %) and then add the indicated solvent (75 mL) using a syringe at indicated times, again with vigorous stirring. The syringe needle should be pushed through a septum that has a second needle inserted to release the pressure. Again, it is vital that stirring is vigorous otherwise the formaldehyde will fail to mix properly. By the end of the addition, about 45 min, the reaction mixture becomes a paste. Leave the paste for indicated times, then add indicated solvent (75 mL), stir and warm the mixture briefly with a heat gun to break up any large solid lumps. The progress of the reaction was monitored by TLC using petroleum ether:ethyl acetate as eluent. After completion, the reaction mixture was cooled to room temperature. Then the mixture was filtered, washed with ethanol (3×50 mL) and with diethyl ether (50 mL), then the solid residue was isolated and dissolved in dichloromethane. The catalyst was filtered off and the solvent was evaporated from the reaction mixture. The solid product was purified by recrystallization from aqueous dichloromethane. The crude product was obtained in quantitative yield as off-white powder. The yields were determined by GC-MS.

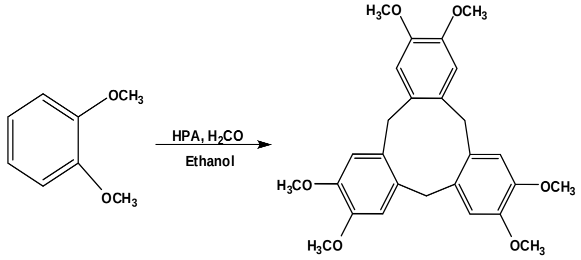
m.p.: 225–228 ^oC; IR (ν, cm^{-1}): 1518, 1269, 1094; ^1H NMR (δ, ppm; $CDCl_3$),: 6.7 (s, 6 H, ArH), 4.9, 3.5 (dd, 6 H, CH_2), 3.7 (s, 18 H, CH_3).

Reusability of the catalyst

The catalyst was recovered after the reaction and was reused in these reactions. Several subsequent recoveries had only slightly decreased the catalytic activity, pointing to the stability and retention capability of this polyanion. At the end of the reaction, the catalyst was filtered, washed with diethyl ether, dried at 130 ^oC for 1 h, and reused in another run. The recycled catalyst was used in three consecutive runs without appreciable loss in catalytic activity.

3. RESULTS AND DISCUSSION

Synthesis of cyclotriveratrylene (CV) with formaldehyde (37%) in different solvents was explored using vanadium (V)-substituted polyoxomolybdates, $H_{3+x}PMo_{12-x}V_xO_{40}$ (x = 1–3) and Wells-Dawson, $H_6[P_2W_{18}O_{62}]$, (Scheme 1). Heteropolyacids with x = 1–3 catalyze the synthesis of cyclotriveratrylene leading to a major product depending on the solvent of the reaction. In a systematic study in the presence of all catalysts, the reaction was examined with different solvents and then in the solvent of choice. In the latter, the effects of the reaction time were studied. Recrystallization often results in the formation of a fine white solid.



Scheme 1. Synthesis of cyclotriveratrylene

Effect of the solvent

The synthesis of cyclotriveratrylene (CV) at reflux temperature was carried out using various common solvents such as carbon tetrachloride, dichloromethane, and chloroform. The results are shown in Table 1. With all catalysts, the highest yield of cyclotriveratrylene and the shortest time required for completion of the reaction was obtained with ethanol as solvent. The highest yield of 98% for cyclotriveratrylene in ethanol indicates the influence of the solvent on the reaction yield (Table 1).

Table 1. Catalytic synthesis of cyclotriveratrylene with formaldehyde (37%) in the presence of different solvents and catalysts

Entry	Solvent	Catalyst	Temperatur(°C)	Time (h)	Yield (%)[a]
1	CCl_4	$H_4[PMo_{11}VO_{40}]$	RT	5	70
2	CH_2Cl_2	$H_4[PMo_{11}VO_{40}]$	RT	4.5	75
3	$CHCl_3$	$H_4[PMo_{11}VO_{40}]$	RT	3	81
4	Ethanol	$H_4[PMo_{11}VO_{40}]$	RT	2	94
5	Ethanol	$H_5[PMo_{10}V_2O_{40}]$	RT	1.5	95.5
6	CCl_4	$H_5[PMo_{10}V_2O_{40}]$	RT	4	81.5
7	CH_2Cl_2	$H_5[PMo_{10}V_2O_{40}]$	RT	3.5	85
8	$CHCl_3$	$H_5[PMo_{10}V_2O_{40}]$	RT	3	90
9	Ethanol	$H_6[PMo_9V_3O_{40}]$	RT	1	98
10	CH_2Cl_2	$H_6[PMo_9V_3O_{40}]$	RT	2.5	92
11	$CHCl_3$	$H_6[PMo_9V_3O_{40}]$	RT	2	94
12	CCl_4	$H_6[PMo_9V_3O_{40}]$	RT	3	88.5
13	CCl_4	$H_6[P_2W_{18}O_{62}]$	RT	6	61
14	CH_2Cl_2	$H_6[P_2W_{18}O_{62}]$	RT	5	63
15	$CHCl_3$	$H_6[P_2W_{18}O_{62}]$	RT	4.5	65.5
16	Ethanol	$H_6[P_2W_{18}O_{62}]$	RT	3	90

Effect of the catalyst

The hetropolyacids of the series $H_{3+x}PMo_{12-x}V_xO_{40}$ (x = 1–3) showed good to excellent catalytic behaviour in the synthesis of cyclotriveratrylene in ethanol, carbon tetrachloride, dichloromethane and chloroform. The results are shown in Table 1. $H_6[PMo_9V_3O_{40}]$ catalyzes efficiently the formation of cyclotriveratrylene giving a total yield of 98% in ethanol. The yield with this catalyst was found to decrease from 98% to 88.5% when the solvent was changed from ethanol to carbon tetrachloride (Table 1, entries 9-12). In addition, $H_4[PMo_{11}VO_{40}]$ and $H_5[PMo_{10}V_2O_{40}]$ gave a total yield of 70% and 81.5% in carbon tetrachloride, respectively (entries 1 and 6). In other words, the activities of the $H_{3+x}PMo_{12-x}V_xO_{40}$ (x = 1–3) catalysts in the synthesis of cyclotriveratrylene in carbon tetrachloride, were found to decrease in the following order: $H_6[PMo_9V_3O_{40}]$>$H_5[PMo_{10}V_2O_{40}]$ >$H_4[PMo_{11}VO_{40}]$ >$H_6[P_2W_{18}O_{62}]$. Many properties of the heteropoly compounds in solution depend on the reaction time, the solvent type, the structure of the catalyst, the pH value of the solution, and other factors. The Keggin anion has an assembly of 12 corner-shared octahedral MoO_6 from trimetallic groups $[Mo_3O_{13}]$ around a heteroatom tetrahedron PO_4 [14]. The introduction of vanadium (V) into the Keggin framework of $[PMo_{12}O_{40}]^{3-}$ is beneficial for catalytic reactions [15]. Usually positional isomers coexist when two or more vanadium atoms are incorporated into the Keggin structure (for example 5 and 13 isomers for x=2 and 3, respectively) [16]. Studies on these isomers in catalytic reactions indicated that different isomers displayed different reactivities [17-19]. The efficiency of the catalysts is related to the mol percentage of metal atoms. The Wells–Dawson HPA has 18 tungsten atoms, so the relative efficiency of the systems is: Keggin>Wells–Dawson. Considering the mass catalytic ratio (Mo = 96, V = 51), it is clear that Keggin HPAs are more efficient than others.

4. CONCLUSIONS

Recyclable, eco-friendly, easily prepared and inexpensive vanadium (V)-substituted polyoxomolybdates were used as catalysts for the synthesis of cyclotriveratrylene. Important features of this protocol are: simplicity and versatility of process engineering and environmentally safe disposal. The catalyst can be easily recovered, regenerated and reused without appreciable loss of structure and activity, thus providing economic and environmentally friendly method for preparation of cyclotriveratrylene.

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СИНТЕЗА НА ЦИКЛОВЕРАТРИЛЕН С ПОМОЩТА НА ХЕТЕРО-ПОЛИКИСЕЛИНИ ($H_{3+x}PMO_{12-x}V_xO_{40}$) КАТО РЕЦИКЛИРУЕМИ ХЕТЕРОГЕННИ КАТАЛИЗАТОРИ

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(Резюме)

Изследвана е синтезата на цикловератрилен (CV) от формалдехид (37%) в присиствие на хетеро-поликиселини ($H_{3+x}PMo_{12-x}V_xO_{40}$, x = 1–3) в различни разтворители. Изучен е ефектът на катализатора и на разтворителя върху хода на реакцията. Във всички случаи хетеро-поликиселините с x = 3 дават най-висок добив при етанол като разтворител.