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Synthesis of diphenylmethane from formalin and benzene in a biphasic system with 12-tungstophosphoric acid

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Heteropoly acids such as $H_3PW_{12}O_{40}$ are exceptionally active catalysts in the synthesis of diphenylmethane from benzene and formalin (aqueous formaldehyde) in a biphasic system and can be recycled simply by drying the aqueous phase at room temperature.

Diphenylmethane ($PhCH_2Ph$) is an important intermediate in spices, pharmaceutics and other fine chemicals[1] and its alkylated compounds can be used as insulators in place of PCB.[2] $PhCH_2Ph$ has commercially been synthesized by the Friedel–Crafts reaction with benzyl chloride and benzene, using aluminium-amalgam, $AlCl_3$, or $ZnCl_2$ as catalyst.[3] However, both the materials and the catalysts are environmentally unfriendly. Moreover, harmless solid acids like HY zeolite,[4] H-ZSM-5,[5] and sulfated ZrO_2[6] were reported to be of insufficient activity.

Synthesis of $PhCH_2Ph$ by condensation of benzene with formalin [eqn. (1)] is very attractive, since the direct use

$$2C_6H_6 + \text{HCHO (in water)} \rightarrow PhCH_2Ph + H_2O \qquad (1)$$

of formalin is economical and the only by-product of the reaction is water. There are several reports describing reactions between aromatic compounds and paraformaldehyde (water-free oligomers of HCHO) catalysed by liquid acids,[7] solid acids like HY zeolite,[8] and SiO_2-composites of polymer resins.[9] However, when formalin was used instead of paraformaldehyde, no reaction occurred under the same conditions,[7,9] due to serious inhibition by water. There is no report detailing a catalyst effective for the reaction of benzene with formalin. In this communication, we report that $H_3PW_{12}O_{40}$ is unusually active and recyclable for this reaction in a biphasic system. Similar biphasic catalytic systems have been reported for cyclotrimerization of propionaldehyde catalysed by heteropoly acid[10] and for nitration of benzene by lanthanide triflates.[11]

The reaction was performed at 433 K in a stainless steel autoclave (*ca.* 100 cm^3, TAIATSU TECHNO, Japan) with 40 cm^3 of benzene (450 mmol), 6.72 cm^3 of formalin (Wako Chem. Co., HCHO 90 mmol, H_2O 222 mmol, methanol (as stabilizer) 18.2 mmol), and the catalyst (2.3–16.6 mol% with respect to HCHO). The vapor phase was analyzed with a TCD gas chromatograph (Shimadzu, GC-8A) with an active carbon column. Each liquid phase was analyzed with an FID gas chromatograph (Shimadzu, GC-14B) with a 15 m capillary column of cross-linked 5% PhMe siloxane (HP-5, USA) for the aromatic compounds and a Porapak P column for methyl formate and methanol. The TCD-GC with an APS-201 (Flusin T) column was also used for HCHO, HCOOH, and H_2O. All liquid acids (except for *para*-toluenesulfonic acid) were exclusively present in the aqueous phase. When the reaction solution was cooled to room temperature after the reaction (2 h), the solution consisted of two phases, a benzene phase (the upper) and an aqueous phase (the lower), and a phase boundary was apparent.

As Table 1 shows, the conversions of HCHO reached over 93 mol% with $H_3PW_{12}O_{40}$ and $Sc(CF_3SO_3)_3$. It should be emphasized that only $H_3PW_{12}O_{40}$ gave an appreciable amount of $PhCH_2Ph$ (the yield was 35.3% under these conditions), which accumulated in the benzene phase. In addition, dibenzylbenzene ($(PhCH_2)_2C_6H_4$), methyl benzyl ether ($PhCH_2OMe$), and methyl formate (HCOOMe) were detected in the benzene phase, and formic acid, methanol, and excess HCHO in the aqueous phase. For the formation of $PhCH_2Ph$, the following steps are considered:[8] $H_2{}^+COH$ is generated from HCHO and the proton attacks the benzene ring to form, initially, benzyl alcohol. Benzyl alcohol can be transformed to the benzyl cation *via* protonation and dehydration. $PhCH_2Ph$ is produced by the attack of the benzyl cation on the benzene ring. With $H_3PW_{12}O_{40}$ as catalyst, two competitive reactions of HCHO proceeded: (i) attack of the benzyl cation on benzene to form $PhCH_2Ph$ and (ii) dimerization of HCHO to HCOOMe (Tichenko reaction).

On the other hand, $Sc(CF_3SO_3)_3$ efficiently catalysed dimerization of HCHO to HCOOMe, but was inactive for the formation of $PhCH_2Ph$. *para*-Toluenesulfonic acid (PTS) was also active for the dimerization of HCHO, but less active than $H_3PW_{12}O_{40}$ for $PhCH_2Ph$ formation. Mineral acids like H_2SO_4, H_3PO_4, and HNO_3 showed no activity for the formation of $PhCH_2Ph$ and CF_3COOH was also inactive for this reaction. It was confirmed that HCOOMe did not react with benzene under these conditions with any of these catalysts.

A series of other heteropoly acids were examined as catalysts for the synthesis of $PhCH_2Ph$ from benzene and formalin (Table 2). All these heteropoly acids showed activities: $H_4SiW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ were effective, but $H_6P_2W_{18}O_{62}$ and H_4Si-

Table 1 Conversion and selectivity of diphenylmethane synthesis from benzene and formalin with various liquid acids

Catalyst	(mmol)	Conversion[a] (mol%)	Yield[b] (mol%)	Selectivity[a] (mol%) CO	HCOOMe	MeOH	HCOOH	$PhCH_2Ph$	$(PhCH_2)_2CH_2$	$PhCH_2OMe$	MB[c] (%)
$H_3PW_{12}O_{40}$	(4.2)	93.2	35.3	3.3	35.1	5.4	5.3	38.7	11.4	0.8	97.0
$Sc(CF_3SO_3)_3$	(2.1)	95.1	0.0	0.2	83.0	12.3	4.6	0.0	0.0	0.0	100.0
PTS[d]	(12.6)	82.2	4.1	4.2	71.8	7.2	6.3	5.9	1.5	3.0	79.8
HNO_3	(12.6)	24.4	0.0	10.0	90.0	0.0	0.0	0.0	0.0	0.0	100.0
H_3PO_4	(4.2)	18.7	0.0	0.2	68.8	12.0	19.0	0.0	0.0	0.0	100.0
H_2SO_4	(6.3)	33.7	0.0	0.6	92.0	4.0	4.0	0.0	0.0	0.0	101.0

Reaction conditions: benzene 40 cm^3 (450 mmol), formalin 6.72 cm^3 (HCHO 90 mmol, H_2O 222 mmol, methanol 18.2 mmol), 160 °C for 2 h. [a] On the basis of HCHO. [b] $PhCH_2Ph$ (on the basis of HCHO) [c] Mass balance; 100 × (total amount of products and remaining HCHO)/(the initial amount of HCHO) [d] *para*-Toluenesulfonic acid.

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Table 2 Conversion and selectivity of diphenylmethane synthesis from benzene and formalin with heteropoly acids

Catalyst	(mmol)	Conversion (mol%)	Yield (mol%)	Selectivity[a] (mol%)		TON[b]
				HCOOMe	$PhCH_2Ph$	
$H_3PW_{12}O_{40}$	(4.2)	93.2	35.3	34.3	37.9 (79.9)	7.1
$H_4SiW_{12}O_{40}$	(4.2)	92.8	25.4	43.6	27.4 (79.7)	5.1
$H_3PMo_{12}O_{40}$	(4.2)	93.5	23.4	54.8	25.1 (71.1)	4.7
$H_6P_2W_{18}O_{62}$	(2.1)	72.4	9.2	68.8	12.7 (76.1)	2.8
$H_4SiMo_{12}O_{40}$	(4.2)	92.0	3.6	77.1	3.9 (33.9)	0.7

Reaction conditions were the same as given in the footnotes of Table 1. [a] On the basis of HCHO. The figures in parentheses are the selectivities for $PhCH_2Ph$ among the aromatic compounds ($PhCH_2Ph$ + $(PhCH_2)_2CH_2$ + $PhCH_2OMe$). [b] Turnover number defined as (mol of $PhCH_2Ph$)/(mol of catalyst).

Table 3 Recycled $H_3PW_{12}O_{40}$[a]

Run	Conversion (%)	Total yield of aromatics[b] (mmol)	Selectivity (mol%)[c]	
			$PhCH_2Ph$	TON[d]
1	83.5	31.4	79.1	4.5
2	74.7	23.8 (75.6%)	76.2	2.9
3	72.2	21.1 (68.4%)	73.4	2.4
4	64.1	17.8 (56.7%)	70.6	1.7
5	63.1	17.6 (56.1%)	66.7	1.6

Reaction conditions: benzene 40 cm^3 (450 mmol), formalin 6.72 cm^3 (HCHO 90 mmol, H_2O 222 mmol, methanol 18.2 mmol), $H_3PW_{12}O_{40}$ 4.2 mmol, 160 °C, and 30 min. [a] Between the runs, the aqueous phase of $H_3PW_{12}O_{40}$ was dried in the ambient atmosphere. The recovered solid $H_3PW_{12}O_{40}$ was reused without any treatment. [b] Total yield of $PhCH_2Ph$, $(PhCH_2)_2CH_2$ and $PhCH_2OMe$. The figures in parentheses are the percentage yield relative to that of the first run. [c] Selectivity for $PhCH_2Ph$ among the aromatic products on the basis of HCHO. [d] Turnover number defined as (mol of $PhCH_2Ph$)/(mol of catalyst).

$Mo_{12}O_{40}$ were less efficient. With $H_3PW_{12}O_{40}$ as catalyst, when the ratio of HCHO/benzene was reduced from 1:5 to 1:10, keeping the amount of benzene (450 mmol) the same, the yield of $PhCH_2Ph$ became higher (42%) with 43% selectivity and 97% conversion. However, the amount of $PhCH_2Ph$ produced was still higher at 1:5 ratio.

IR spectroscopy showed that, while the Keggin structure of $SiMo_{12}O_{40}^{4-}$ decomposed to some extent after the reaction, the structures of the other polyanions were retained. The pH values of the aqueous phases of these heteropoly acids (pH = 0.10, 0.58, 0.61, 0.79, and 0.96 for $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, $H_6P_2W_{18}O_{62}$, and $H_4SiMo_{12}O_{40}$, respectively) were close to those of $Sc(CF_3SO_3)_3$ (pH = 0.90), H_3PO_4 (pH = 1.25), HNO_3 (pH = 0.65), and H_2SO_4 (pH = 0.19). Thus the exceptionally high activities of the heteropoly acids are due to not only the strong acidity of the solution, but also the soft basicity of the heteropoly anion, which has been proposed by Izumi *et al.*[12] The cationic intermediates are probably stabilized by the heteropoly anions.

The results of five successive reactions are summarized in Table 3, where used $H_3PW_{12}O_{40}$ was recovered simply by drying the aqueous solution at room temperature. The recovered $H_3PW_{12}O_{40}$ was found to be active in the repeated runs, although the conversion of HCHO and yield of aromatics decreased somewhat. As shown in Table 3, the conversion and the total yield of aromatics reached plateaus after the fourth run. These changes in the conversion, yield, and selectivity are due to the remaining carbonaceous species on the heteropoly acid. Elemental analysis showed that the amount of carbon on the used $H_3PW_{12}O_{40}$ was 2.1%, which corresponds to 0.4 molecules of $PhCH_2Ph$ per heteropoly anion at the fifth run. IR spectroscopy of $H_3PW_{12}O_{40}$ revealed that the Keggin structure was completely retained after repeating the reaction five times.

In conclusion, $H_3PW_{12}O_{40}$ is a highly active and recyclable catalyst for use in the synthesis of diphenylmethane from benzene and formalin in a biphasic system. This is a novel example for direct use of formalin in clean organic synthesis with solid acid.

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