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Highly Efficient Method for Solvent-Free Synthesis of Diarylmethane and Triarylmethane from Benzylic Alcohols Using P_2O_5/Al_2O_3 or P_2O_5/SiO_2 at Room Temperature

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ABSTRACT

A highly efficient procedure for the synthesis of triarylmethane and diarylmethane *via* benzylation of aromatic hydrocarbons from benzyl alcohols using supported P_2O_5 on SiO_2 and/or Al_2O_3 under solvent-free conditions is described. Excellent yields of triarylmethane and diarylmethane were obtained using P_2O_5-SiO_2 (50 % W/W) and/or P_2O_5-Al_2O_3 (50 % W/W) at room temperature. The reusability of both supported P_2O_5 on SiO_2 and Al_2O_3 were examined. Both supported reagents show favorable activities in first and second runs, however, a decline in reactivity was observed in following attempts. The reaction is scalable to >0.03 mole amounts.

KEYWORDS

Diarylmethane, triarylmethane, aromatic alcohol, P_2O_5, silica gel, alumina.

1. Introduction

Arylmethanes are useful compounds in organic synthesis and industry[1] as they are important structural motifs in protection of functional groups.[2] These motifs are also found in the structure of several biologically active compounds as well as known drugs. Established drugs such as clotrimazole (antifungal), letrozole (anticancer), trimethoprim (antibiotic), papaverine (antispasm), bisacody (laxative) and piritrexim (antifolate) have the arylmethyl residue in their scaffolds.[3] Additionally, these compounds are widely employed in dye technologies and are particularly useful precursors for the preparation of pigments and inks; for example, they are used in the dyeing of ceramics, leather and polyacrylonitrile fibres.[1] Furthermore, arylmethanes are the basic skeleton of several dye reagents and indicators useful in indication of pH, histology, cytology and also fluorescence.[4,5]

Although various procedures have been established for the synthesis of arylmethanes, the most commonly used protocol for accessing diphenylmethane is the Friedel-Crafts benzylation reaction that generally involves the reaction with benzyl halides in the presence of a catalytic amount of a Lewis acid such as $AlCl_3$.[6] The other traditional methods for the synthesis of diarylmethanes include: a combination of Friedel-Crafts acylation and subsequent reduction using $InCl_3$,[7] condensation between one equivalent of formaldehyde and two equivalents of arenes in the presence of concentrated sulphuric acid,[8] Wolf-Kishner as well as Clemmenson reduction of aromatic ketones,[9,10] catalytic condensation of the Grignard reagent with hydrocarbons[11] and more recently, the Suzuki-Miyuara-coupling of benzylic phosphates with arylbronic acids.[12] Other methods for the synthesis of diarylmethanes and their derivatives have also been established.[13–17]

The most commonly known route to access triphenylmethane synthesis is the Friedel and Crafts benzylation reaction which generally is achieved by using benzene/$CHCl_3$/$AlCl_3$ or benzene/CCl_4/$AlCl_3$.[1] Some other methods have also been established for triphenylmethane synthesis.[18]

The established methods for di- and tri-arylmethane synthesis often suffer from many disadvantages and drawbacks such as: long reaction times, less available reagents, tedious work-up as well as cumbersome procedures, the complexity of by-products, the use of toxic solvents and harsh reaction conditions such as strong acidic media which can harm sensitive functional groups in the molecule. Thus, there is still a need to establish mild and convenient procedures to lessen these inefficiencies.

Phosphorus pentoxide (phosphoric anhydride) is a useful reagent which is readily employed in various organic transformations and syntheses; for example, P_2O_5 is widely employed as a dehydration agent for the formation of anhydride from two molecules of an ordinary acid,[19] ketenimines from amides,[19] vinyl ethers from acetals,[19] nitriles from amides,[19] amides from oximes (Beckmann rearrangement),[20] phenolic esters from carboxylic acids [21] and oxidation of alcohols namely the Onodera reaction.[22]

As a part of a programme to find new applications for supported P_2O_5 in organic transformations, we report the efficient synthesis of triaryl as well as diarylmethane *via* supported P_2O_5 on silica and/or alumina (Scheme 1).

2. Results and Discussion

Initially, the effect of P_2O_5, either on its own or in combination form with various supports (alumina and silica gel) on the synthesis of diarylmethane was investigated. The reaction of anisole and *p*-chlorobenzyl alcohol was used as a model compound and the effect of reagents and various supports was studied. The results are given in Table 1.

As the data in Table 1 indicate, P_2O_5 supported on both Al_2O_3

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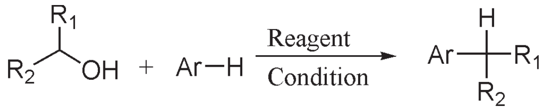


R_1, R_2 =aryl, H

Reagent:P_2O_5-Al_2O_3 (50% W/W) and/or P_2O_5-SiO_2 (50% W/W)

Condition: Solvent Free, r.t.

Scheme 1

and SiO_2 afforded the best yields for the benzylation reaction of anisole at room temperature in the shortest reaction times. Although the use of different amounts of supported P_2O_5, either at room temperature or 40 °C, (Table 1, Entries 1–3) leads to reasonable yields, a technical problem is encountered as the reaction media become pasty during mixing with P_2O_5. This drawback makes the reaction and work-up procedures tedious. Using excessive amounts of P_2O_5 (Table 1, Entries 4 and 5) does not lead to reasonable yields for the same reasons and using supported and unsupported P_2O_5 at 25–60 °C leads to a black mixture (Table 1, Entries 6 and 13). Furthermore, using Al_2O_3 and SiO_2 alone gave no product after 3 h (Table 1, Entries 7–10).

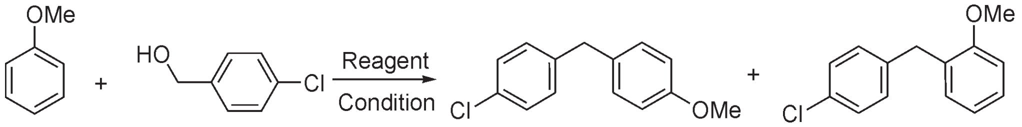
To realize the versatility as well as the generality of this method, the optimized conditions were extended to include more model reactions and the results are depicted in Table 2.

Using P_2O_5-Al_2O_3 and/or P_2O_5-SiO_2 provide excellent yields of diarylmethanes at room temperature (Table 2). Using the above reaction, some arenes are efficiently converted to a mixture of corresponding ortho and para diarylmethanes in the indicated ratios (Table 2, Entries 1–2, 7–14). Phenols and anilines are unable to be converted to diarylmethanes using this method even if the react time is prolonged (Table 2, Entries 15–18). It is rationalized that the presence of hydroxyl and amino moieties on phenol and aniline makes these compounds prone to primarily reaction with P_2O_5 and hence not enough benzyl cation may be generated. Furthermore, the ester or amide of P_2O_5 with phenol and aniline can decrease the negative charge density on both phenol and aniline which may result in their lower tendency to follow an electrophile aromatic substitution reaction.

Similarly, this procedure can be extended to the preparation of triarylmethanes from benzhydrol and various arenes using P_2O_5-Al_2O_3 and/or P_2O_5-SiO_2. Triarylmethanes are successfully prepared in excellent yields using P_2O_5-Al_2O_3 and/or P_2O_5-SiO_2 at room temperature (Table 3, Entries 1–8).

Using P_2O_5-Al_2O_3 and/or P_2O_5-SiO_2 exclusively provides the corresponding triarylmethane from *p*-methyl anisole and/or 1,2-dimethyl benzene with benzhydrol in excellent yields at ambient temperature (Table 3, Entries 1–4); however, when anisole or toluene were employed as substrate, a trace amount of benzhydryl ether is also isolated (<10 %) (Table 3, Entries 5–8). Owing to the bulkiness of the benzhydryl cation the electrophilic substitution for anisole and/or toluene is only achieved at the para position. As the data in Table 3 indicate, all attempts at the synthesis of triarylmethane, chloro- and bromobenzene using both P_2O_5-Al_2O_3 and/or P_2O_5-SiO_2 at room temperature failed. In an attempt to obtain the corresponding triarylmethanes the temperature was increased to 90 °C. However, above 60 °C the benzhydryl ether is formed instead and no triarylmethane is generated even in trace amounts (Table 3, Entries 9–12). The lack of reactivity of chloro and/or bromo benzene to form the benzhydryl cation is explained by the electron-withdrawing effect of chloro and bromo residues on the benzene ring which decreases the negative charge density dispersed over the aryl ring leading to increased stability and hence low reactivity of the benzhydryl cation in comparison to the benzyl cation.

Table 1 Optimization of reagent conditions for synthesis of diarylmethane.



Entry	Reagent	Temp/°C	Condition	Time/min	Colour of mixture	Isolated yield/% (o:p)[d]
1	P_2O_5 (0.3 g)	r.t.	Solvent free	60	Pink	50 (41:59)[a]
2	P_2O_5 (0.3 g)	40	Solvent free	60	Pink	50 (35:65)[a]
3	P_2O_5 (0.5 g)	r.t.	Solvent free	10	Pink	63 (36:64)[a]
4	P_2O_5 (0.6 g)	r.t.	Solvent free	10	Pink	60 (36:64)[b]
5	P_2O_5 (0.8 g)	r.t.	Solvent free	10	Pink	60 (36:64)[b]
6	P_2O_5 (0.5 g)	r.t. to 60	Solvent free	–	Black	–
7	SiO_2	60	Solvent free	180	White	NR[c]
8	SiO_2	90	Solvent free	180	White	NR[c]
9	Al_2O_3	60	Solvent free	180	White	NR[c]
10	Al_2O_3	90	Solvent free	180	White	NR[c]
11	P_2O_5 (0.5 g)-SiO_2 (0.5 g)	r.t.	Solvent free	10	Pink	85 (40:60)
12	P_2O_5 (0.5 g)-Al_2O_3 (0.5 g)	r.t.	Solvent free	11	Pink	82 (37:63)
13	P_2O_5 (0.5 g)-SiO_2 (0.5 g)	r.t. to 60	Solvent free	–	Black	–

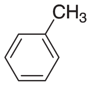
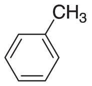
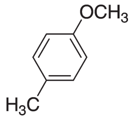
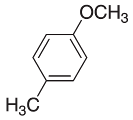
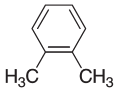
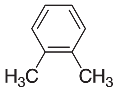
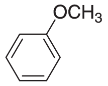
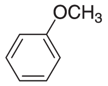
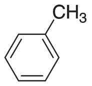
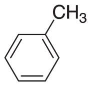
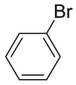
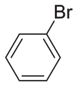
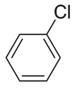
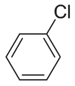
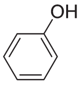
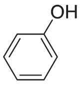
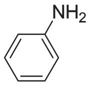
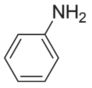
[a] Tedious work-up procedures because of pasty mixture.

[b] Very tedious work-up procedures because of pasty mixture.

[c] No reaction after 180 min.

[d] The ratio of *ortho* and *para* methoxybenzyl-4-chlorobenzene isomers was indicated using GC analysis.

Table 2 Preparation of diarylmethane: *p*-chlorobenzyl alcohol (1 mmol) and arenes (1 mmol) in the presence of P_2O_5-SiO_2 (50 % W/W) and/or P_2O_5-Al_2O_3 (50 % W/W) [a] at room temperature

Entry	Ar-H	Supported	Time/min	Colour of mixture	Isolated yield/% (o:p)[b, Ref.]
1		P_2O_5-SiO_2	14	Pink	85(40:60) [c]
2		P_2O_5-Al_2O_3	15	Pink	82(40:60) [c]
3		P_2O_5-SiO_2	10	Pink	85 [16]
4		P_2O_5-Al_2O_3	11	Pink	82 [16]
5		P_2O_5-SiO_2	20	Pink	83 [16,17]
6		P_2O_5-Al_2O_3	24	Pink	80 [16,17]
7		P_2O_5-SiO_2	10	Pink	85 (40:60) [16]
8		P_2O_5-Al_2O_3	11	Pink	82 (37:63) [16]
9		P_2O_5-SiO_2	15	Pink	84(40:60) [16,17]
10		P_2O_5-Al_2O_3	18	Pink	81(39:61) [16,17]
11		P_2O_5-SiO_2	10	Pink	83(38:62) [16]
12		P_2O_5-Al_2O_3	12	Pink	80(35:65) [16]
13		P_2O_5-SiO_2	10	Yellow	83(43:57) [16]
14		P_2O_5-Al_2O_3	12	Yellow	81(40:60) [16]
15		P_2O_5-SiO_2	180	White	NR [d]
16		P_2O_5-Al_2O_3	180	White	NR [d]
17		P_2O_5-SiO_2	180	White	NR[d]
18		P_2O_5-Al_2O_3	180	White	NR[d]

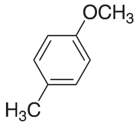
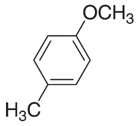
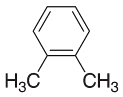
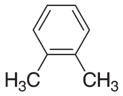
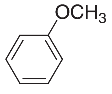
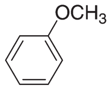
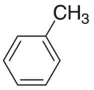
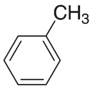
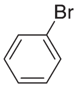
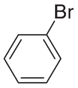
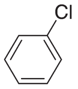
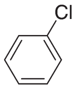
[a] 1 g P_2O_5-Al_2O_3 (50 % W/W) for a mixture consist of aromatic alcohol (1 mmol) and arene (1 mmol) is used.

[b] The ratios of *ortho* and *para* isomers are assigned using GC analysis and all the compounds are characterized by IR and NMR spectroscopy and compared with authentic samples.

[c] Used aromatic alcohol (1 mmol) is benzyl alcohol.

[d] No reaction after 180 min.

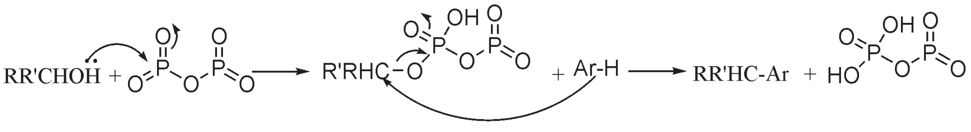
Table 3 Preparation of triarylmethane: benzhydrol (1 mmol) and arenes (1 mmol) in the presence of supported P_2O_5-SiO_2 or P_2O_5-Al_2O_3 (50 % W/W)[a] at room temperature.

Entry	Ar-H	Supported	Time/min	Colour of mixture	Isolated yield/% (o:p) Ref.
1		P_2O_5-SiO_2	7	Orange-brown	86 [23]
2		P_2O_5-Al_2O_3	9	Orange-brown	82 [23]
3		P_2O_5-SiO_2	15	Orange-brown	85 [24]
4		P_2O_5-Al_2O_3	17	Orange-brown	83 [24]
5		P_2O_5-SiO_2	10	Orange-brown	78[b,c](0:100) [23]
6		P_2O_5-Al_2O_3	11	Orange-brown	75[b,c](0:100) [23]
7		P_2O_5-SiO_2	25	Orange-brown	70[b,c](0:100) [24]
8		P_2O_5-Al_2O_3	30	Orange-brown	65[b,c](0:100)[24]
9		P_2O_5-SiO_2	20	Orange-brown	NR [d]
10		P_2O_5-Al_2O_3	20	Orange-brown	NR [d]
11		P_2O_5-SiO_2	20	Orange-brown	NR [d]
12		P_2O_5-Al_2O_3	20	Orange-brown	NR [d]

[a] 1 gram of P_2O_5-Al_2O_3 (50 % W/W) for mixture of aromatic alcohol (1 mmol) and arene (1 mmol) is used.
[b] Competitively a trace amount benzohydrol ether is produced (<10 %).
[c] Only para isomer is obtained and all the compounds are characterized by IR and NMR spectroscopy and compared with those of authentic samples.
[d] No reaction happens at r.t.; however, at 60 °C and 90 °C the products entirely become benzhydryl ether and benzophenone, respectively.[25]

Mechanistically, it is believed that the synthesis of di- and triarylmethanes is achieved *via* Friedel-Crafts reaction type. P_2O_5 plays a powerful role as a dehydrating agent in this reaction. A proposed mechanism for the reaction is presented in Scheme 2.

The reusability of both reagents for the synthesis of diarylmethane and triarylmethane was studied at room temperature, under solvent-free conditions, for five successive runs. In each run, the reaction was stopped after 120 min, cooled and suspended in anhydrous CH_2Cl_2. The suspension was then filtered and the reagent washed with anhydrous CH_2Cl_2 (2 × 50 mL). The reagents were dried in vacuum oven (50 °C, 15 min) and



R, R'=aryl, H

Scheme 2

Table 4 Reactivity study of recycled P_2O_5-SiO_2 and P_2O_5-Al_2O_3 on reaction anisole with benzhydrol under solvent-free conditions after 120 min.

Run	Temp.	Yield% [a]/ (P_2O_5-SiO_2)	Yield% [a]/ (P_2O_5-Al_2O_3)
1	r.t.	78	75
2	r.t.	52	48
3	r.t.	28	27
4	r.t.	11	9
5	r.t.	8	5

[a] Isolated yield.

Table 5 Reactivity study of recycled P_2O_5-SiO_2 and P_2O_5-Al_2O_3 on reaction anisole with *p*-chlorobenzyl alcohol under solvent-free condition after 120 min.

Run	Temp.	Yield% [a]/ (P_2O_5-SiO_2)	Yield% [a]/ (P_2O_5-Al_2O_3)
1	r.t.	85	82
2	r.t.	60	57
3	r.t.	30	23
4	r.t.	17	10
5	r.t.	6	3

[a] Isolated yield.

were immediately used for a subsequent reaction. The results are depicted in Tables 4 and 5. As these tables indicate, the strong hygroscopic nature of both reagents causes their reactivity to decrease remarkably after the first run. This is due to readily conversion of P_2O_5 into phosphoric acids upon the absorption of water.

The reagents have been used for solvent-free synthesis of some diarylmethane and triarylmethane at room temperature and are superior to previously reported methods in terms of yields, molar ratio, shorter reaction times, and use of none toxic solvents. The advantages of our method compared to other methods are illustrated in Tables 6 and 7. As these Tables indicate, our method readily utilizes the routes for facile and mild synthesis of diarylmethane and triarylmethane at room temperature.

The scalability of this diarylmethane and triarylmethane synthesis using both supported P_2O_5: SiO_2 or P_2O_5: Al_2O_3 (50 % W/W) were examined at room temperature under solvent-free conditions. As the data in Table 8 indicate, various quantities of arene and aromatic alcohol (0.01–0.03 mol) were used to afford

Table 6 Preparation of diarylmethane(1-benzyl-4-methylbenzene) by supported P_2O_5-SiO_2 or P_2O_5-Al_2O_3 (50 % W/W) in comparison with other reagents.

Entry	Reagent	Ratio of reagent: arene:substrate	Time/min	Temp	Yield/% (o:m:p)	Solvent	Ref.
1	P_2O_5-SiO_2	P_2O_5(0.5 g)-SiO_2(0.5 g):1 (toluene): 1(benzyalcohol)	15	r.t.	88 (40:0:60)	–	–
2	P_2O_5-Al_2O_3	P_2O_5(0.5 g)-Al_2O_3(0.5 g):1(toluene): 1(benzyalcohol)	18	r.t.	85 (39:0: 61)	–	–
3	1) NH_3-$NH_3.H_2O$ 2) $AlCl_3$-CS_2	1) 1:0: 2(phenyl(p-tolyl)methanone) 2) 1: 0: 2.5(N,N-bis(1-methyl)azine)	1) 840 2) 1200	1) 25 2) 100–120	– 62	C_2H_5OH CS_2	17
4	$FeCl_3$	10 mol %: 1(toluene):1(benzyl phenyl ether)	720	90	90 (42:0:58)		26
5	In	1M %: 30(toluene):1(benzyl bromide) 1M %: 30(toluene):1(benzyl chloride)	180 180	70 110	99 (45:8:47) 97 (46:8:48)	–	16 16
6	$FeCl_3$-Montmorillonite K10	0.1 g:2: 30(toluene):2(benzyl chloride)	5	80	100 (45.3:8.1:45.2) [a]	–	27
7	$Bi(OTf)_3$	1M %: 3 (toluene):1(benzyl acetate)	120	r.t.	69 (42:0:58)	–	28
8	MoO_3	1M %:Excess (toluene):1(benzylalcohol)	20	110	95 (44:9:47)	–	29
9	$PdCl_2$ (dppf). CH_2Cl_2	2 mol %: 1(benzyl bromide):1(4-methyl phenyltrifluoroborate)	720	77	81 (0:0:81)	THF/H_2O (10:1)	30
10	TFSA	0.05: 5 (toluene):1(benzyl acetal)	420	110	94 (42:8:50)	di,2-chloroethane	31
11	$Sc(OTf)_3$	0.1:5 mL (benzen):1(p-methylbenzylalcohol) 0.1:5 mL (toluene):1(benzylalcohol)	180 240	115–125 115–125	91 (0:0:91) Quant: (48:7:45)	 –	 32
12	$PdCl_2$(dppf). CH_2Cl_2	2 mol %: 1(benzyl bromide):1(4-methyl phenyltrifluoroborate)	1200	60	100 (40:5.0:56)	[BMIM][OTf] ionic liquid	33 [b]
13	TFSA	0.05: 5 (toluene):1(benzyl acetal)	1200	65	96 (43:0:57)	[BMIM][OTf] ionic liquid	33 [b]
14	$Sc(OTf)_3$	0.1:5 mL (benzen):1(p-methylbenzylalcohol) 0.1:5 mL (toluene):1(benzylalcohol)	1200	80	100 (59:0:41)	[BMIM][OTf] ionic liquid	33[b]
15	$HAuCl_4$	10 mol %: 12(toluene):1(1-phenylethyl acetate) 10 mol %: 12(toluene):1(1-phenylethylacetate)	1200	80	52 (86:0:14) 80 (40:7:53)	$MeNO_2$	34 35
16	$H_2[PtCl_6].6H_2O$ $IrCl_3.nH_2O$	10 mol %: 12(toluene):1(1-phenylethyl acetate) 10 mol %: 12(toluene):1(1-phenylethyl acetate)	1200 1200	80 80	88 (40:7:53)	– –	35

[a] Competitively a trace amount dibenzylation was produced (1.4 %).
[b] $ArCH_2Ph$ isomers plus dibenzylether are formed.
[a] Isolated yield,

Table 7 Preparation of triarylmethane (1-benzhydryl-4-methylbenzene) by supported P_2O_5-SiO_2 or P_2O_5-Al_2O_3 (50% W/W) in comparison with other reagents.

Entry	Reagent	Ratio of reagent: arene:substrate	Time/min	Temp	Yield/% (o:m:p)	Solvent	Ref.
1	P_2O_5-SiO_2	P_2O_5(0.5g)-SiO_2(0.5):1 (toluene): 1(benzhydrol)	25	r.t.	70 (0:100)	–	–
2	P_2O_5-Al_2O_3	P_2O_5(0.5g)-Al_2O_3(0.5):1 (toluene): 1(benzhydrol)	30	r.t.	65 (0:100)	–	–
3	Nafion-H	Nafion-H (0.4 2 mL(benzene): 0.5(4-methyl benzhydrol)	90	150	21	–	36 [a]
4	H_2SO_4	5: 1 (toluene):1 (p-toluenesulfonamide):	1440	60–80	70	–	37
5	$ZnBr_2/SiO_2$	0.8 $ZnBr_2$ /SiO_2:8 benzene: 2 (4-methylbenzaldehyde)	60	r.t.	81	Benzene	38 [b]
6	Pd(II)/bpy	1) 2.5 mol %: 2 $PhB(OH)_2$:1 (4-methylbenzaldehyde) 2) Benzene	1440	80	89	CH_3NO_2	39
7	$FeCl_3$	10 mol%: 4 benzene: 1(4-methylbenzaldehyde)	1240	r.t.	89	CH_2Cl_2	40 [c]

[a] 50–150 W, 2–7 bar pressure.
[b] Acetyl bromide is added.
[c] Ac_2O is added.

Table 8 The scalability of diarylmethane and triarylmethane synthesis using P_2O_5.

Entry	Ar-H	mol	R-OH	mol	Reagent	Gram	Isolated yield/%
1	PhMe	0.01	$PhCH_2OH$	0.01	P_2O_5-SiO_2	5	82
2	PhMe	0.01	$PhCH_2OH$	0.01	P_2O_5-Al_2O_3	5	80
3	PhMe	0.02	$PhCH_2OH$	0.02	P_2O_5-SiO_2	7	78
4	PhMe	0.02	$PhCH_2OH$	0.02	P_2O_5-Al_2O_3	7	70
5	PhMe	0.03	$PhCH_2OH$	0.03	P_2O_5-SiO_2	10	76
6	PhMe	0.03	$PhCH_2OH$	0.03	P_2O_5-Al_2O_3	10	64
7	PhMe	0.01	Ph_2CHOH	0.01	P_2O_5-SiO_2	5	69
8	PhMe	0.01	Ph_2CHOH	0.01	P_2O_5-Al_2O_3	5	60
9	PhMe	0.02	Ph_2CHOH	0.02	P_2O_5-SiO_2	7	61
10	PhMe	0.02	Ph_2CHOH	0.02	P_2O_5-Al_2O_3	7	59
11	PhMe	0.03	Ph_2CHOH	0.03	P_2O_5-SiO_2	10	60
12	PhMe	0.03	Ph_2CHOH	0.03	P_2O_5-Al_2O_3	10	55

the diarylmethane and triarylmethane in good yields. Thus, the present method can be applied to large-scale (up to several grams) synthesis of the title compounds.

In summary, a highly efficient procedure has been established for the preparation di- and triphenylmethanes using supported P_2O_5 under solvent-free conditions. Using these reaction conditions, excellent yields of corresponding di- and triphenylmethanes at room temperature were obtained using both P_2O_5-SiO_2 (50 % W/W) and P_2O_5-Al_2O_3 (50 % W/W) at room temperature.

3. Experimental

3.1. Preparation of Supported P_2O_5 on Alumina or Silica Gel [50 % (W/W)]

To an anhydrous alumina (5 g, 50 mmol) (neutral, 0.063–0.200 mm) or anhydrous silica gel (5 g, 83 mmol) (0.040–0.063 mm) which was previously dried and kept at 120 °C for 24 h in vacuum oven, was added P_2O_5 (5 g, 35 mmol) and mixed. The obtained white solid was sealed and stored at room temperature in a vacuum-desiccator flask for subsequent use.

3.2. General Procedure for Synthesis of Diarylmethane and Triarylmethane using Supported P_2O_5 on Alumina and/or Silica Gel [50 % (W/W)]

A mixture of aromatic alcohol (1 mmol) and arene (1 mmol) was added to P_2O_5 supported on alumina or silica gel (1 g, 50 % W/W). When TLC monitoring (acetone: *n*-hexane 1:10 (V/V), R_f = 0.7–0.9, for example R_f for *p*-chlorobenzylchlorobenzene in acetone: *n*-hexane 1:10 (V/V) = 0.9) indicated no further progress in reaction, the reaction was stopped and diluted with anhydrous Et_2O (100 mL). The Et_2O solution was dried over anhydrous Na_2SO_4, filtrated and the solvent evaporated to obtain the pure product. Where necessary, the ratio of *ortho* and *para* isomers were determined by GC analysis.

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