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Base catalyzed sustainable synthesis of phenyl esters from carboxylic acids using diphenyl carbonate†

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Phenyl esters were obtained in moderate to high yields by reaction of aliphatic and aromatic carboxylic acids with one equivalent of diphenyl carbonate in the presence of catalytic amounts of tertiary amine bases, such as DBU, TBD and DMAP under neat conditions at elevated temperatures (>100 °C).

Introduction

Diphenyl carbonate (DPC) is a sustainable and environmentally benign reagent mainly, used as phosgene-substitute for the synthesis of polycarbonates.¹ Several eco-friendly procedures for the synthesis of DPC are reported,² including the oxidative carbonylation of phenol in the presence of palladium catalysts³ and the transesterification of dimethyl carbonate (DMC) with phenol using diverse catalysts.⁴ Moreover, transesterification reactions of dimethyl oxalate with phenol to DPC are described.⁵ A modern and promising method is the direct synthesis of DPC from phenol and carbon dioxide.⁶ DPC is often used for the synthesis of bisphenol A derived polycarbonates,⁷ but also found application in the preparation of other aliphatic and aromatic polycarbonates.⁸ Moreover, DPC is used for the protection of sugars and other vicinal diols as cyclic carbonates.⁹ Generally, however, the application of DPC as sustainable and environmentally-friendly reagent in organic chemistry is rarely described. A few articles reported the use of DPC for the synthesis of heterocycles,¹⁰ as well as for *N*-carbonylations of amines and *N*-heteroaromatics.¹¹ Moreover, in 1998 Chiriac *et al.* reported that DPC is a suitable reagent for the synthesis of phenyl esters from carboxylic acids.¹² They demonstrated that aromatic carboxylic acids react with DPC in the presence of one equivalent of 4 (dimethylamino)pyridine (DMAP) as base and pyridine as solvent to the corresponding phenyl esters in moderate to good yields.

Typically, phenyl esters are prepared by reacting phenols with carboxylic acid chlorides or anhydrides.¹³ Besides, coupling reagents such as phosphorus pentoxide,¹⁴ carbodiimides,¹⁵ 2-chloro-1-methylpyridinium iodide (Mukaiyama reagent),¹⁶ chlorosulfonyl isocyanate,¹⁷ as well as numerous conventional and modern reagents were successfully applied for the synthesis of phenyl esters.¹⁸ Direct acid catalyzed esterifications of carboxylic acids with phenol are described as well,¹⁹ but difficult to perform and only low yields are obtained and side reactions occur. Moreover, transesterification reactions of esters with phenols are reported.²⁰ Another useful method for the preparation of phenyl esters is the well-known Mitsunobu reaction.²¹ However, these procedures rely on the use of activated carboxylic acid derivatives or an *in situ* activation and thus produce a large amounts of waste.

Results and discussion

Here, we report a catalytic procedure to obtain phenyl esters of different carboxylic acids. Tertiary amine bases were used as catalyst under neat conditions, which offers significant advantages to similar procedures, such as the one described by Chiriac and coworkers.¹² In a first experiment, we performed the reaction of castor-oil derived 10-undecenoic acid **2a**²² with DPC **1** (1 eq.) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 1 eq.) as strong organic base by heating the mixture to 100 °C (Scheme 1). Immediately, an acute gas formation occurred and subsequent analysis by thin layer chromatography (TLC) indicated a complete conversion of the carboxylic acid under release of phenol. After purification of the crude reaction mixture by column chromatography, the phenyl ester **3a** was obtained in nearly quantitative yields. Inspired by this result, other tertiary amine bases were investigated in stoichiometric and catalytic quantities (Table 1, entry 1–6). Potassium carbonate, as a cheap inorganic base, did not induce the phenyl ester formation. Similar to reactions with pyridine, the formation of **3a** was very slow and after 8 hours reaction time only traces of the respective phenyl ester were obtained (entries 2 and 3). Applying

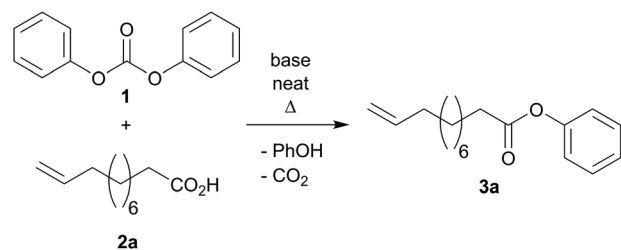
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1,4-diazabicyclo[2.2.2]octane (DABCO) as amine base in stoichiometric quantities led to full conversion after seven hours (entry 4). As also observed by Chiriac,¹² DMAP gave very good results in stoichiometric amounts. Indeed, similar to DBU, full conversion was reached within 15 minutes using DMAP (entry 5). Also the strong cyclic guanidine base 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD)²³ resulted in a complete conversion to **3a** in short reaction times (entry 6). Next, we were interested if also catalytic quantities of the successfully tested bases can be applied for the phenyl ester formation. However, reactions with 0.2 equivalents of DBU at 100 °C only showed a very slow conversion of the carboxylic acid (entry 7). In order to accelerate the reaction, higher temperatures were applied to favor the phenyl ester formation. If 0.4 equivalents of DBU were used at 130 °C, after one hour, a complete conversion to **3a** was detected (entry 8), while reactions with 0.2 equivalents of DBU showed full conversion after three hours (entry 9). Interestingly, a further increase of the temperature to 160 °C significantly reduced the reaction time without observing the formation of side products (entries 10–13). Thus, full conversion was achieved after one hour utilizing only 0.2 equivalents of DBU. Reducing the amount of DBU to only 3.0 mol% also yielded complete conversion, although longer, but still acceptable, reaction times were needed (entry 13). These results clearly demonstrate that the temperature has a strong influence on the reaction time and, more importantly, phenyl ester formation using DPC is possible by using only catalytic amounts of amine bases.

As a next step, several other aliphatic and aromatic carboxylic acids were investigated for their performance in this catalytic phenyl ester formation. Similarly to **2a**, oleic acid **2b** and stearic acid **2c** were fully converted in the presence of 5.0 mol% DBU after eight hours at 160 °C. After purification by column chromatography, phenyl oleate **3b** (82%) and phenyl stearate **3c** (90%) were obtained in good yields (Scheme 2). The phenolic acid derivative **2d**, derived from renewable ferulic acid,²⁴ was also successfully converted to the corresponding phenyl ester **3d** (yield 79%). In case of levulinic acid **2e**, a valuable renewable platform chemical,²⁵ the preparation of the corresponding phenyl ester **3e** was less successful and pure **3e** was isolated only in a yield of 44%. Lower temperatures and/or applying higher amounts of DBU did not lead to improved yields in this case.

Moreover, the fatty acid derived dicarboxylic acids sebacic acid **2f**,²² azelaic acid **2g**,²⁶ and adipic acid **2h** (ref. 27) were



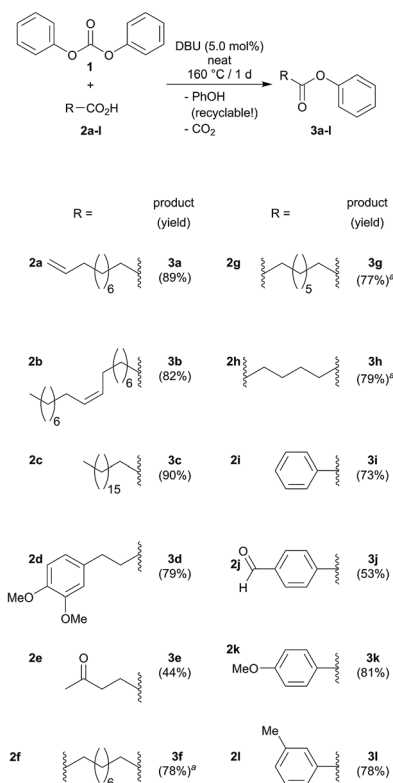
Scheme 1 Synthesis of phenyl 10-undecenoate **3a** by the reaction of 10 undecenoic acid **2a** with DPC **1** in the presence of different bases under neat conditions.

Table 1 Results for the synthesis of phenyl 10-undecenoate **3a** using different bases and conditions

Entry	Base [eq.]	T [°C]	Complete conversion reached in ^a
1	DBU [1]	100	15 min
2	K ₂ CO ₃ [1]	100	Very slow
3	Pyridine [1]	100	Very slow
4	DABCO [1]	100	7 hours
5	DMAP [1]	100	15 min
6	TBD [1]	100	15 min
7	DBU [0.2]	100	Very slow
8	DBU [0.4]	130	1 hour
9	DBU [0.2]	130	3 hours
10	DBU [0.2]	160	1 hour
11	DBU [0.1]	160	2 hours
12	DBU [0.05]	160	4 hours
13	DBU [0.03]	160	8 hours

^a Reactions were monitored by thin layer chromatography (TLC) and the conversions were determined by ¹H NMR.

successfully converted to the corresponding diphenyl esters **3f–h**. After removal of phenol *via* vacuum distillation, the diphenyl esters **3f–3h** were obtained as colorless solids in good yields of almost 80% by simple recrystallization. It is noteworthy that the phenol can be recycled by simple vacuum distillation and almost recovered quantitatively (93%), thus increasing the sustainability of this process. Unfortunately, the conversions of

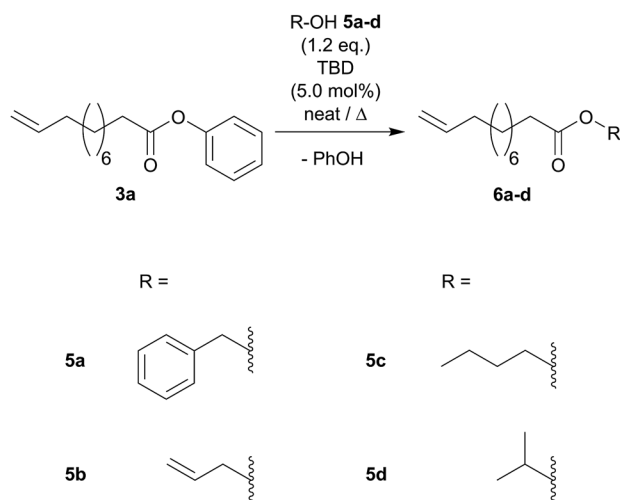


Scheme 2 Synthesis of phenyl esters **3a–l** from carboxylic acids **2a–l** with DPC **1** and DBU as catalyst under neat conditions. 10 mol% of DBU and two equivalents of DPC **1** were used.

amino acid derivatives, such as Boc- or Cbz-protected glycine, were not successful. Under the applied conditions, numerous side-reactions, *e.g.* polymerizations and fragmentations occurred, and only traces of the desired amino acid phenyl ester derivatives could be isolated. Nevertheless, several other functional groups, such as ketones, aldehydes and double bonds, are well tolerated in this reaction.

Since phenyl esters are “active esters”, they are valuable intermediates for the synthesis of versatile alkyl esters, thioesters and amides.²⁸ Under neutral and acidic conditions, they are quite stable and can even be considered as protective groups in peptide chemistry,²⁹ but under basic conditions or enzyme catalysis, phenyl esters hydrolyze quickly in the presence of water,³⁰ or can be transesterified with alcohols to alkyl esters.^{28,31} Moreover, in the presence of acidic catalysts, phenyl esters can undergo the so-called Fries rearrangement to obtain acyl phenols.³² This reaction can also be induced by light, known as the so-called photo-Fries rearrangement.³³

To verify the reactivity, diverse transesterification reactions were performed by reacting **3a** with different alcohols **5a–d** in the presence of catalytic amounts of TBD at higher temperatures and under solvent-free conditions (Scheme 3). The reaction of **3a** with a slight excess of benzyl alcohol **5a** and 5.0 mol% of TBD under neat conditions led to full conversion after 90 minutes at 120 °C and pure benzyl 10 undecenoate **6a** was isolated in a yield of 91% (Table 2, entry 1). For the transesterification with alcohols exhibiting low boiling points, reactions were performed in a microwave reactor. By applying a temperature of 140 °C under neat conditions, the reactions of **3a** with allyl alcohol **5b**, *n*-butanol **5c** and isopropanol **5d** yielded full conversion to the corresponding alkyl esters **6b–d** after 60 minutes of reaction time (entry 2–4). Contrary, the reaction of **3a** with isopropanol **5d** to **6d** was completed after three hours, probably due to steric hindrance. After purification *via* column chromatography, alkyl 10-undecenoates **6b–d** were obtained in almost quantitative yields. Moreover, the isolation of the phenyl esters is not necessary for the additional conversion with



Scheme 3 Transesterifications of phenyl 10-undecenoate **3a** with alcohols **5a–d** and TBD as catalyst under neat conditions.

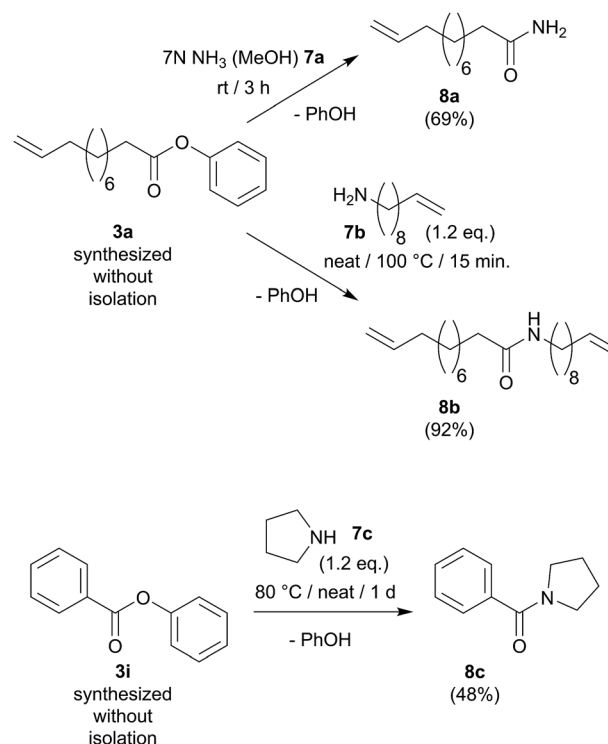
Table 2 Results for the transesterification of phenyl 10-undecenoate **3a** with alcohols **5a–d**

Entry	Product	Conditions ^a	Yield ^b [%]
1	6a	120 °C/90 min	91
2	6b	MW/140 °C/60 min	95
3	6c	MW/140 °C/60 min	95
4	6d	MW/140 °C/3 hours	93

^a MW = microwave reactor. ^b Isolated yields after column chromatography.

alcohols to the corresponding alkyl esters. In a one-pot procedure, an excess of a primary or secondary alcohol can add directly to the phenyl ester and stirring at higher temperature gives the wished alkyl ester derivative. Unfortunately, tertiary alcohols such as *tert*-butanol did not react with the phenyl esters to the desired *tert*-butyl ester derivatives. Other basic catalysts as well as high temperatures also did not yield the corresponding *tert*-butyl esters.

Moreover, phenyl esters can be coupled with ammonia as well as with primary or secondary amines to obtain the corresponding amide derivatives. In a one-pot procedure, the synthesized phenyl 10 undecenoate **3a** was subsequently reacted with an excess of ammonia (7 N solution in methanol **7a**) to obtain 10-undecenamide **8a** (Scheme 4). Complete conversion of **3a** was observed at room temperature after three hours. After recrystallization in *n*-hexane/ethyl acetate mixture, **8a** was obtained in a yield of 69%.



Scheme 4 Amidation reactions of phenyl esters **3a** and **3i** with ammonia **7a**, primary amine **7b** and pyrrolidine **7c**.

The reaction of **3a** with a slight excess of dec-9-en-1-amine **7b**, as representative primary amine, led to full conversion after 15 minutes at 100 °C and under neat conditions to obtain amide derivative **8b** (yield 92%) after recrystallization. The reaction with secondary amines is also feasible, but longer reaction times are required and the obtained yields are comparably low. As example, the one pot reaction of phenyl benzoate **3i** with pyrrolidine **7c** (1.2 equivalents) led to full conversion after one day at 80 °C. Isolation and purification of the crude product afforded the amide derivative **8c** in a yield of 48%. These examples demonstrate the use of DPC **1** as coupling agent for the synthesis of amides from carboxylic acids under neat conditions by a straightforward one-pot procedure.

To evaluate the sustainability of the catalytic phenyl ester synthesis, the environmental factor (*E* factor) was determined and compared to conventional phenyl ester synthesis procedures. The *E*-factor is defined by the ratio of the mass of waste per unit of generated product.³⁴ As an example, for the reaction of 10-undecenoic acid **2a** with DPC **1** and 5.0 mol% of DBU to phenyl 10 undecenoate **3a** (yield of 89%) an *E*-factor of 0.93 was calculated. Considering that phenol is not a waste product and can be recycled in an average yield of 93% (see performed recycling above), the *E*-factor reduces to a value of 0.51. Industrially, it should further be possible to recycle the released carbon dioxide, which would further reduce the *E* factor to a value of 0.30. Compared to the procedure of Chiriac *et al.*¹² using stoichiometric amounts of DMAP and pyridine as solvent, a considerably higher *E*-factor of 4.15 was estimated. The assumption that product **3a** will be synthesized according to a standard procedure^{13a} from **2a** with phenol in the presence of 0.4 equivalents of phosphorus(v) oxychloride and the yield will be the same, a higher *E* factor of 0.61 was calculated. Moreover, harmful organic solvents are often used and the isolated product yields of this reaction are normally lower. Furthermore, the *E*-factors of conventional coupling methods such as the Mitsunobu reaction²¹ or other reactions utilizing common coupling reagents (Mukaiyama reagent¹⁶ or chlorosulfonyl isocyanate¹⁷) were calculated. Although, the phenyl ester formation was assumed to be quantitative, high *E* factors were calculated for these procedures (19.1 for the Mitsunobu reaction, 78.4 applying the Mukaiyama reagent, and 26.9 using chlorosulfonyl isocyanate). The extremely high *E* factors mainly result from the high amounts of solvents (THF and dichloromethane). By considering that the solvent can be recycled completely for these procedures or the coupling reactions are possible under neat conditions, the values of the *E*-factors decrease dramatically (*E* = 1.96 for the Mitsunobu reaction, *E* = 2.96 with Mukaiyama reagent and *E* = 1.38 with chlorosulfonyl isocyanate). Nevertheless, the calculated *E*-factors of conventional phenyl ester synthesis procedures are significantly higher than the ones obtained by our new catalytic procedure with DPC as coupling reagent.

Conclusions

In summary, we developed a novel sustainable approach for the synthesis of phenyl esters. The reactions of aliphatic and

aromatic carboxylic acids with equimolar ratios of diphenyl carbonate in the presence of catalytic amounts of tertiary amine bases such as DBU, TBD and DMAP under neat conditions at temperatures over 100 °C gave phenyl esters in moderate to excellent yields. Noteworthy, only 3.0 mol% of catalyst is sufficient to achieve full conversion. Furthermore, in a one-pot procedure, the phenyl esters can be directly converted with primary and secondary alcohols to obtain alkyl esters in high yields. One-pot reactions with primary and secondary amines led to the corresponding amide derivatives. We demonstrated that phenol can be recovered with yields up to 93% *via* vacuum distillation. Since phenol and carbon dioxide are the only by-products, which can be easily recycled, the introduced catalytic procedure is more sustainable and environmental benign compared to other phenyl ester synthesis protocols. Generally, a more sustainable, efficient and straightforward method for the synthesis of phenyl esters is described.

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