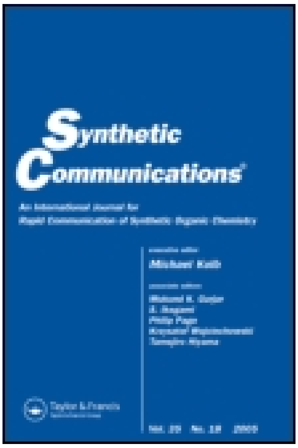

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Solvent-Free Esterification of Carboxylic Acids and Alcohols in the Presence of Silphos $[PCl_{3-n}(SiO_2)_n]$ as a Heterogeneous Phosphine Reagent

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SOLVENT-FREE ESTERIFICATION OF CARBOXYLIC ACIDS AND ALCOHOLS IN THE PRESENCE OF SILPHOS [$PCl_{3-n}(SiO_2)_n$] AS A HETEROGENEOUS PHOSPHINE REAGENT

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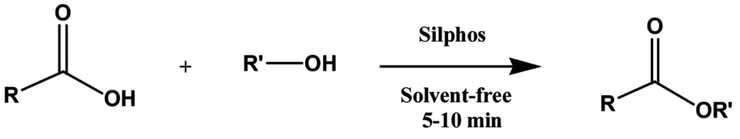
GRAPHICAL ABSTRACT



R, R'= Alkyl , Aryl group

Abstract *An efficient solvent-free method for the preparation of esters from various aromatic and aliphatic acids with primary, secondary, and tertiary alcohols using a heterogeneous phosphine reagent, silphos [$PCl_{3-n}(SiO_2)_n$], in good yields is reported.*

Keywords Alcohols; carboxylic acids; esterification; heterogeneous; silphos

INTRODUCTION

Esterification is an important reaction because of the wide utility of esters in organic and bioorganic synthesis.[1] Esterification is extensively employed for the protection and further manipulation of the carboxylic acid functional group as well as the synthesis of natural products. Thus esterification of carboxylic acids has been the subject of numerous accounts throughout the years owing to the fundamental importance of this synthetic transformation. Early methods called for heating the carboxylic acid in an alcoholic solvent under acid or base catalysis. Other conventional procedures involve conversion of the carboxylic acid to its corresponding acid chloride or mixed anhydride, followed by the addition of an alcohol nucleophile. Many coupling reagents have been utilized extensively for the synthesis of esters from their corresponding carboxylic acids.[2,3] Among these, the direct esterification

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reaction of carboxylic acids with alcohols in the presence of a large number of different reagents and various conditions was established.[4]

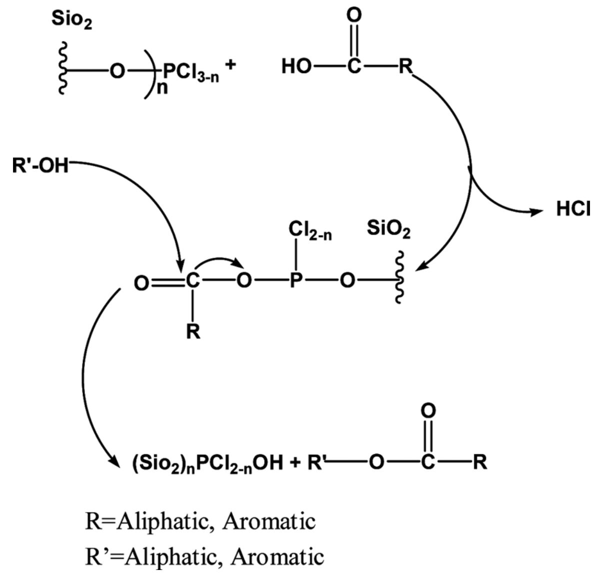
Few reports that have exemplified the esterification of alcohols via carboxylic salts include Mitsunobu conditions.[5–8] The mentioned methods have several drawbacks such as nongenerality for various types of alcohols and carboxylic acids, the use of expensive diethylazo-dicarboxylate or diisopropyl azodicarboxylate, poor yields, long reaction times, tedious workup, as well as cumbersome separation from the side product, triphenylphosphine oxide, and unreacted Ph_3P. Hence, there is still scope to develop practical and convenient methods for the esterification of alcohols with carboxylic acids.

Esterification of carboxylic acids with alcohols using homogeneous and heterogeneous catalysts is well known in the literature.[9–12] However, several limitations such as an excess of the catalysts or amounts of reactants to achieve efficient conversion, removal of water during the reaction, long reaction times, and large amounts of effluent generation during workup are associated with these processes, along with the additional limitation of lower yields in the case of acids and alcohols with chain lengths greater than C14. Ionic liquids (ILs) are an extensively used, ecofriendly, unconventional reaction medium for many chemical and biochemical transformations.[13] Fraga-Dubreuil et al.[14] reported the first esterification of acetic acid and methyl malonic acid with alcohols of chain lengths C_5–C_{10}. In an imidazolium-based IL with acidic counterions, HSO_4^- and $H_2PO_4^-$, no attempt was made at the esterification of long-chain carboxylic acids with long-chain alcohols. A new approach using a Brønsted acidic IL in the dual role of solvent/catalyst for esterificaiton as also been reported in the literature.[15–17] However, the success of this chemistry was limited to esters less than C_{10} in either carboxylic acid or alcohol chain length.

Hence, there is still a need to develop practical and convenient methods for the esterification of carboxylic acid with alcohols as well as need to develop an environmentally benign synthetic method for the synthesis of long-chain esters. In the present work, we report the highly efficient esterification of long-chain aliphatic carboxylic acids with long-chain alcohols using silphos $[PCl_{3-n}(SiO_2)_n]$ as a heterogeneous phosphine reagent.

For the first time, we introduce silphos $[PCl_{3-n}(SiO_2)_n]$ as a new heterogeneous phosphine reagent for the ester synthesis. This reagent is easily prepared from the reaction of silica gel and PCl_3.[18] In this article, syntheses of aliphatic long-chain esters as well as various aromatic esters from different acids and alcohols in very short reaction times at room temperature under solvent-free conditions are reported.

The first step of this synthetic approach involved optimization of reaction conditions. The esterification of undecanoic acid with 1-decanol was chosen as a model reaction (Scheme 1) to standardize the reaction parameters such as the amount of silphos and time. The effect of various amounts of silphos was optimized using the reaction of undecanoic acid and 1-decanol with different amounts of silphos (0.2–1.5 g for 1 mmol of acid/alcohol). Although 0.4 g of silphos was enough to synthesize decyl undecanoate in quantitative yield, the reaction time was long (8 h; Table 1, entry 2). Therefore, 0.6 g of silphos was considered to be the optimum for 100% conversion at room temperature within 5 min.



Scheme 1. The proposed mechanism.

The condensation of carboxylic acids and alcohols of different chain lengths (C_1 to C_{20}) were carried out, and the results are outlined in Table 2. All the substrates reacted smoothly to give the corresponding aliphatic long-chain esters (having 21 carbon atoms) in excellent yields.

To optimize the reaction conditions for the preparation of aromatic esters, 1.0 mmol of aromatic acid was reacted with 1-propanol in the presence of different amounts of silphos (0.2–1.2 g) at room temperature. It was observed that both 1.0 g and 1.2 g silphos gave 100% conversion in 10 min. We therefore used 1.0 g of silphos for synthesis of aromatic esters from various aromatic acids with 1-propanol. Moreover, reactions were also carried out with 1°, 2°, and 3° alcohols with benzoic acid. The results are summarized in Tables 3 and 4 respectively.

To examine the scope and limitations of the present process, we then carried out the reaction with various aromatic carboxylic acids with 1-propanol using

Table 1. Optimization of the reaction conditions for the preparation of decyl undecanoate[a]

Entry	Silphos (g)	Reaction time	Conversion (%)
1	0.2	17 h	80
2	0.4	8 h	100
3	0.6	5 min	100
4	0.8	5 min	100
5	1.0	5 min	100

[a] Reaction conditions: undecanoic acid (1 mmol), 1-decanol (1 mmol) without solvent and at ambient temperature (20 °C).

Table 2. Synthesis of aliphatic long-chain C-21 esters of aliphatic carboxylic acids with aliphatic alcohols of different chain lengths[a]

Entry	Carboxylic acid	Alcohol	Ester[b,c]
1	$CH_3(CH_2)_{18}COOH$	CH_3OH	$CH_3(CH_2)_{18}COOCH_3$
2	$CH_3(CH_2)_{17}COOH$	CH_3CH_2OH	$CH_3(CH_2)_{17}COOCH_2CH_3$
3	$CH_3(CH_2)_{16}COOH$	$CH_3CH_2CH_2OH$	$CH_3(CH_2)_{16}COOCH_2CH_2CH_3$
4	$CH_3(CH_2)_{15}COOH$	$CH_3(CH_2)_2CH_2OH$	$CH_3(CH_2)_{15}COOCH_2(CH_2)_2CH_3$
5	$CH_3(CH_2)_{14}COOH$	$CH_3(CH_2)_3CH_2OH$	$CH_3(CH_2)_{14}COOCH_2(CH_2)_3CH_3$
6	$CH_3(CH_2)_{13}COOH$	$CH_3(CH_2)_4CH_2OH$	$CH_3(CH_2)_{13}COOCH_2(CH_2)_4CH_3$
7	$CH_3(CH_2)_{12}COOH$	$CH_3(CH_2)_5CH_2OH$	$CH_3(CH_2)_{12}COOCH_2(CH_2)_5CH_3$
8	$CH_3(CH_2)_{11}COOH$	$CH_3(CH_2)_6CH_2OH$	$CH_3(CH_2)_{11}COOCH_2(CH_2)_6CH_3$
9	$CH_3(CH_2)_{10}COOH$	$CH_3(CH_2)_7CH_2OH$	$CH_3(CH_2)_{10}COOCH_2(CH_2)_7CH_3$
10	$CH_3(CH_2)_9COOH$	$CH_3(CH_2)_8CH_2OH$	$CH_3(CH_2)_9COOCH_2(CH_2)_8CH_3$
11	$CH_3(CH_2)_8COOH$	$CH_3(CH_2)_9CH_2OH$	$CH_3(CH_2)_8COOCH_2(CH_2)_9CH_3$
12	$CH_3(CH_2)_7COOH$	$CH_3(CH_2)_{10}CH_2OH$	$CH_3(CH_2)_7COOCH_2(CH_2)_{10}CH_3$
13	$CH_3(CH_2)_6COOH$	$CH_3(CH_2)_{11}CH_2OH$	$CH_3(CH_2)_6COOCH_2(CH_2)_{11}CH_3$
14	$CH_3(CH_2)_5COOH$	$CH_3(CH_2)_{12}CH_2OH$	$CH_3(CH_2)_5COOCH_2(CH_2)_{12}CH_3$
15	$CH_3(CH_2)_4COOH$	$CH_3(CH_2)_{13}CH_2OH$	$CH_3(CH_2)_4COOCH_2(CH_2)_{13}CH_3$
16	$CH_3(CH_2)_3COOH$	$CH_3(CH_2)_{14}CH_2OH$	$CH_3(CH_2)_3COOCH_2(CH_2)_{14}CH_3$
17	$CH_3(CH_2)_2COOH$	$CH_3(CH_2)_{15}CH_2OH$	$CH_3(CH_2)_2COOCH_2(CH_2)_{15}CH_3$
18	CH_3CH_2COOH	$CH_3(CH_2)_{16}CH_2OH$	$CH_3CH_2COOCH_2(CH_2)_{16}CH_3$
19	CH_3COOH	$CH_3(CH_2)_{17}CH_2OH$	$CH_3COOCH_2(CH_2)_{17}CH_3$

[a] Reaction conditions: acid (1 mmol), alcohol (1 mmol), silphos (0.6 g), and room temperature.

[b] All compounds were characterized by IR, NMR, and GCMS. Identification of the products was confirmed by comparison with available physical and spectroscopic data of authentic compounds.[19]

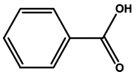
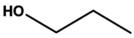
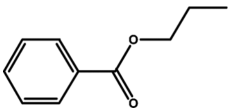
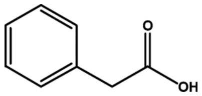
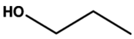
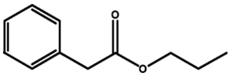
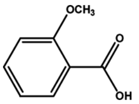
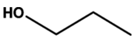
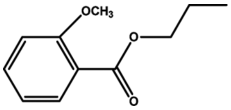
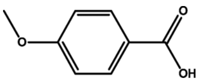
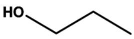
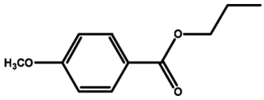
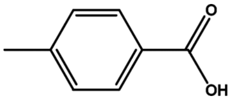
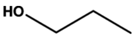
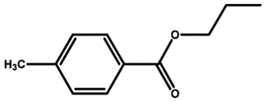
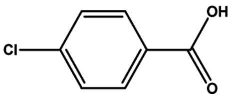
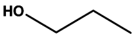
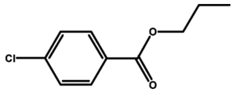
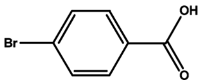
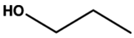
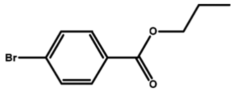
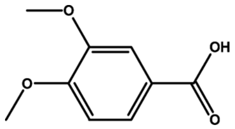
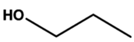
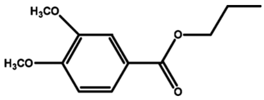
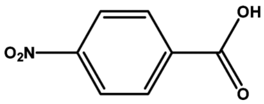
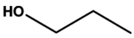
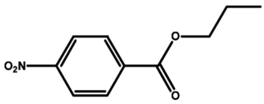
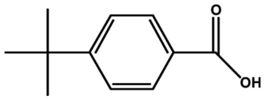
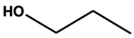
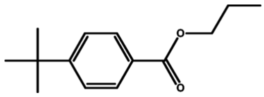
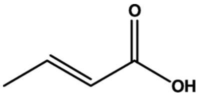
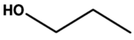
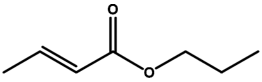
[c] Isolated yields >90%.

silphos as heterogeneous reagent. These results are presented in Table 3. Under these reaction conditions, aromatic carboxylic acids with electron-releasing groups such as methoxy, methyl, and dimethoxy reacted and produced the corresponding esters in good yields (entries 4, 5, and 8). The treatment of slightly deactivated aromatic carboxylic acids such as chloro and bromo under the same conditions gave the corresponding esters in moderate yields (entries 6 and 7). The yields of esters decreased with aromatic carboxylic acid that has electron-withdrawing groups such as nitro (entry 9). We also carried out reaction with various acids five-member rings such as cyclopentanoic acid, furan-2-carboxylic acid, and thiophene-2-carboxylic acid under the present reaction conditions, which gave moderate yields of the corresponding esters (entries 12, 13, and 14).

Then, we examined the generality of the present process by varying the alcohols at the next step, and the results are presented in Table 4. The reaction with primary and secondary alcohols under the present reaction conditions gave good yields of the corresponding esters, while the reaction with sterically hindered alcohols, ^tBuOH, gave smaller yields of the corresponding esters (entry 3, Table 4).

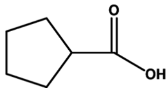
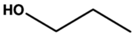
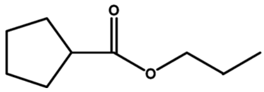
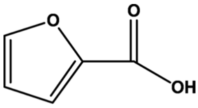
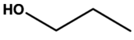
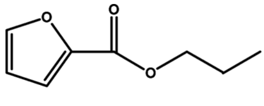
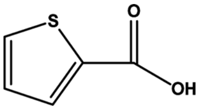
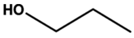
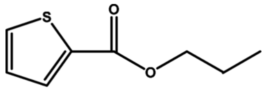
We also carried out the reaction of sterically hindered carboxylic acid with sterically hindered alcohols under the present conditions, with gave poor yields of the corresponding esters (entry 7, Table 4). The reaction carried out with secondary cyclic alcohol as cyclohexanol with benzoic acid under the same conditions to gave the corresponding ester with moderate yields (entry 8, Table 4).

Table 3. Synthesis of esters from various carboxylic acids with 1-propanol using silphos under solvent-free conditions[c]

Entry	Acid	Alcohol	Product	Yield[a] (%)	Bp/mp (°C)[b]
1				90	Liquid bp 231/760 mm Hg
2				92	Liquid bp 243/760 mm Hg
3				91	Liquid bp 114/1.5 mm Hg
4				94	Liquid bp 176/45 mm Hg
5				94	Liquid bp 120/5 mm Hg
6				78	Liquid bp 110/4 mm Hg
7				79	Liquid bp 293/760 mm Hg
8				95	Liquid bp 315/760 mm Hg
9				56	Liquid bp 128/16 mm Hg
10				90	Liquid bp 295/760 mm Hg
11				91	Liquid bp 146/760 mm Hg

(Continued)

Table 3. Continued

Entry	Acid	Alcohol	Product	Yield[a] (%)	Bp/mp (°C)[b]
12				79	Liquid bp 83/15 mm Hg
13				78	Liquid bp 89/4 mm Hg
14				79	Liquid bp 57/0.45 mm Hg

[a] Isolated yield.

[b] Identification of the all products was confirmed by comparison with available data.

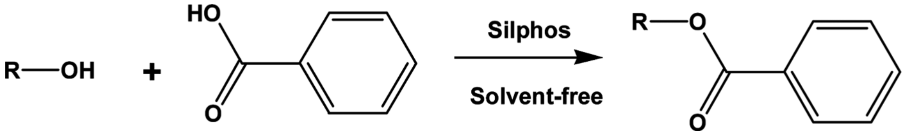
[c] Reaction conditions: acid (1 mmol), alcohol (1 mmol), silphos (1.0 g), and room temperature without any solvent.

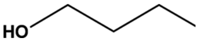
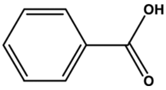
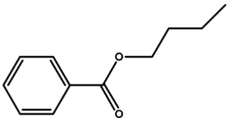
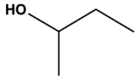
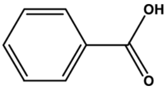
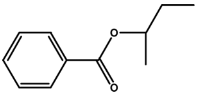
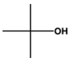
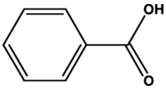
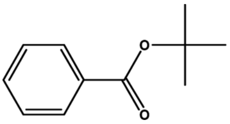
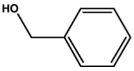
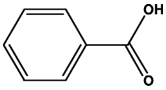
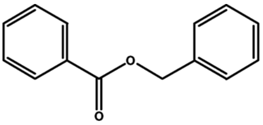
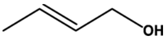
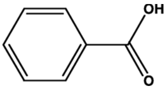
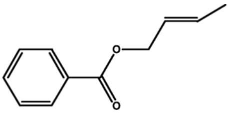
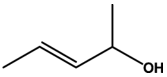
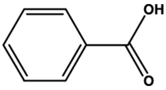
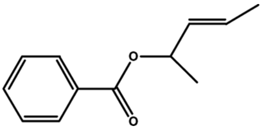
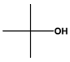
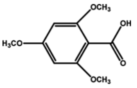
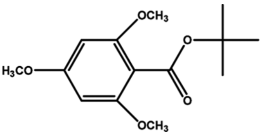
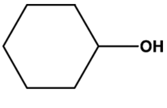
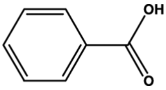
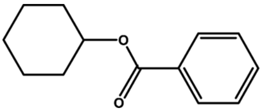
The reaction mechanism probably involves intermolecular attack of alcohols to the activated carboxylic acid, so the activity of the alcohol decreases as it gets bulkier.

The mechanism of the reaction is not clear as yet. In the literature, formylation and acetylation of alcohols and amines with ethyl formate and acetate using phosphine reagent is reported.[20] In our method, direct reaction of acid and alcohols with silphos without the use of solvent alone completes the formation of esters. The catalytic role of HCl is also ruled out because HCl was produced and eliminated during the reaction. On this basis, Scheme 1 may show the probable mechanism for the preparation of esters from carboxylic acids and alcohols.

In conclusion, an efficient and simple method for the synthesis of aliphatic long-chain esters and aromatic esters has been described using the silphos as a heterogeneous catalyst. The esterification with primary alcohols was complete in 5 min, whereas secondary alcohols and aromatic alcohol took comparatively longer time (10–12 min) for complete esterifcation. Tertiary alcohols did not react at 10–12 min; they took a long time. The reaction is slow essentially because of the bulkiness of the corresponding alcohol. The present methods have the following advantages: (a) Silphos shows activity superior to reported systems. (b) Silphos is cheap, easy to prepare, and easy to work up. The produced silphos oxide can be readily removed by simple filtration. (c) This method requires mild reaction conditions and short reaction times, takes place at room temperature, is operationally simple and has excellent yields. In summary, this procedure provides an efficient, clean, and simple methodology for the direct preparation of esters form carboxylic acids at room temperature with good yields under solvent-free conditions. This method can be easily applied for preparation of aliphatic and aromatic esters.

Table 4. Preparation of various esters from benzoic acid[a]



Entry	Alcohols	Acids	Product	Yield[b] (%)	Bp/mp (°C)[c]
1				92	Liquid bp 250/760 mm Hg
2				90	Liquid bp 234/760 mm Hg
3				70	Liquid b.p 70/1.5 mm Hg
4				90	Solid mp 42
5				91	Liquid bp 263/760 mm Hg
6				90	Liquid bp 274/760 mm Hg
7				52	Liquid bp 212/2 mm Hg
8				78	Liquid bp 179/20 mm Hg

[a] Reaction conditions: acid (1 mmol), alcohol (1 mmol), Silphos (1.0 g), and room temperature.

[b] Isolated yield.

[c] Identification of the products was confirmed by comparison with available data of authentic compounds.

EXPERIMENTAL

Preparation of Silphos [$PCl_{3-n}(SiO_2)_n$]

Silphos [$PCl_{3-n}(SiO_2)_n$] was prepared from cheap and easily available starting materials as reported earlier.[21] Under a nitrogen atmosphere, PCl_3 (13.8 g, 0.1 mol) was added at room temperature to a flask containing dried silica gel (60–120 mesh, 18.0 g, 0.3 mol), and the mixture was stirred slowly with a mechanical stirrer for 20 min. The mixture was then heated to 60 °C with stirring (500 cycle/min) using a flow of nitrogen for 2 to 3 h to remove all HCl. The reaction mixture was washed with 50 ml of dry CH_2Cl_2 and dried under vacuum. Silphos was obtained as a white solid (22 g), which was stored in a sealed bottle. IR (KBr disk) $v = 3200, 1100, 1000, 800, 680, 500\,cm^{-1}$ matched earlier reports. The presence of chloride in the reagent was determined by collecting the produced HCl in H_2O followed by titration with 0.1 M aq. NaOH. The results obtained from several runs showed that each mole of silphos contains 1.35–1.44 mol of chloride atoms in its structure. To determine the amount of active phosphorus content of the reagent, silphos was reacted with excess bromine in CH_3CN and stirred for 1 h under reflux conditions. The unreacted bromine was titrated with an aqueous solution of $Na_2S_2O_3$. The amount of active phosphorus content was determined to be 1 mmol per 0.6 g of silphos.

Typical Procedure for Synthesis of Aliphatic Long-Chain C-21 Ester

To a heterogeneous mixture of 0.6 g silphos and 1.0 mmol acid was added 1.1 mmol alcohol at room temperature with stirring or shaking. The progress of the reaction was followed by thin-layer chromatography (TLC). After completion of the reaction (Table 1), the resulting mixture was filtered to remove reacted Silphos. The organic layer was washed with 10% $NaHCO_3$ and water, dried with Na_2SO_4, and concentrated in vacuo to give the product. Identification of the products was ascertained by ^1H NMR and mass spectroscopy and by comparison with available physical and spectroscopic data. These products were found to be highly pure by the analytical methods.

Typical Procedure for Synthesis of Aromatic Ester

To a heterogeneous mixture of 1.0 of silphos and 1.0 mmol of aromatic acid was added 1.0 mmol aromatic alcohol at room temperature with stirring or shaking. The progress of the reaction was followed by TLC. After completion of the reaction (Tables 3 and 4), the resulting mixture was filtered to remove reacted silphos. The organic layer was washed with 10% $NaHCO_3$ and water, dried with Na_2SO_4, and concentrated in vacuo to give the product. Identification of the products was ascertained by ^1H NMR and mass spectroscopy and by comparison with available spectroscopic data. These products were found to be highly pure by the analytical methods.

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