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Sulfamic acid as a green, efficient, recyclable and reusable catalyst for direct addition of aliphatic acid with cyclic olefins

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Sulfamic acid has been used as a catalyst for esterification of cyclic olefins with aliphatic acids, and good olefins conversion as well as excellent esters selectivity was obtained. The catalyst could be recycled easily by filtration and directly reused in the next run with satisfactory results.

KEY WORDS: esterification; sulfamic acid; cyclic olefin; norbornyl carboxylate.

The esterification of aliphatic acids with cyclic olefins, such as dicyclopentadiene or norbornene, yields compounds of industrial value [1]. For instance, the esterification of dicyclopentadiene with saturated carboxylic acids, such as acetic acid and propionic acid, leads to starting materials for the flavor and fragrance industry, as well as resulting the corresponding alcohol in the consecutive hydrolysis [2]. From unsaturated carboxylic acids as nucleophiles, the obtained esters are useful compounds in the manufacture of the binders for polymer concrete [3].

The esterification was quite well catalyzed by a number of acidic catalysts, such as ion exchange resins [4,5], heteropoly acids [6,7], silica-supported sulfuric acid [8], zeolite [9], *p*-toluenesulfonic acid [10] and $BF_3 \cdot Et_2O$ [11], etc. However, those catalysts have some problems so that any of these catalysts has not yet been used in industrial production [8]. For example, silica-supported sulfonic acid, a gas reaction catalyst, suffers from intense volatilization and dissolving-away of the effective catalytic components during the reaction, and therefore, it is not possible substantially to carry out a continuous operation for a long time. Nafion catalyst is very expensive and in addition, is not stable at a temperature (200 °C) at which the reaction could be effectively carried out and, however, the deterioration of the catalyst is inevitable [8]. The good results for this kind of esterification could be obtained from some liquid reaction systems, but these homogeneous liquid phase catalysts are considerably corrosive because of their very strong acidity. Furthermore, though the homogeneous liquid phase catalysts could be easily separated from the products, it is very difficult to separate them from by-products formed during the reaction, in particular, high boiling point by-products. Therefore, the recovery and regeneration of the catalysts are substantially not possible and as a result, the catalytic activity is disturbed and the life of catalyst is shortened.

The development of mild, low-cost and high performance acid catalysts has attracted much interest for green chemistry [12]. Sulfamic acid (NH_2SO_3H), with mild acidity, involatility and incorrosivity, is amino acid containing sulfur element. It is inexpensive and insoluble in common organic solvents, and very stable [13], which makes it a catalyst recycling very conveniently. However, a little attention has been given to the use of sulfamic acid as a catalyst in organic reactions. In the last year, it was used as an efficient heterogeneous acid catalyst for ketalization [14]. In our laboratory, sulfamic acid was successfully used for catalyzing the tetrahydropyranylation of hydroxy compounds under solvent-free conditions [15], the transesterification of β-ketoesters in ionic liquids [16] and the Beckmann rearrangement [17]. In these studies, as an acidic catalyst, sulfamic acid displayed a great potential in the replacement of conventional mineral and solid acid because of its intrinsic properties. In continuation of our research to explore new reactions promoted by sulfamic acid, we report herein, for the first time, the synthesis of the esters by the addition reaction of aliphatic acids with cyclic olefins in the present of catalytic amount of sulfamic acid (scheme 1).

Initially, the esterification of norbornene as a model substrate was investigated by using acetic acid at 120 °C in the presence of sulfamic acid. The esterification was almost performed with the conversion and selectivity of 100% in the presence of the catalyst of 10% (calculated by olefins), which was much better than in 5% or in the

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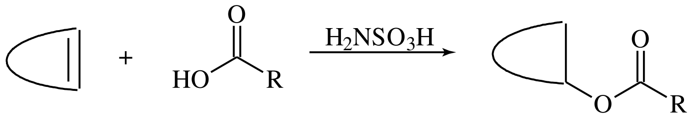


Scheme 1. Sulfamic acid catalyzed esterification of cyclic olefins with aliphatic acids.

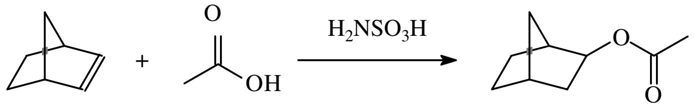
absence of any catalyst (table 1, entries 1, 2 and 3). However, by using the equimolar amounts of norbornene and acetic acid, the reaction rate was slow, and only 73.1% of olefin conversion was obtained after 4 h though the desired ester was obtained with perfect selectivity (entry 4). The further experiments revealed that under the condition of 2.5 h reaction time or 90 °C reaction temperature, the conversion only reached 74% and 70%, respectively (entries 5 and 6). It should be pointed that the catalyst recovery could be easily achieved by the simple filtration at room temperature after the reaction because the catalyst, sulfamic acid, is insoluble in the reaction mixture. The recovered sulfamic acid could be directly used in the next run without any treatment and, no considerable activity loss was observed in the reaction of norbornene with acetic acid even if sulfamic acid has been reused four times, (entry 7).

The sulfamic acid catalyzed esterification under the optimized conditions of 4 h reaction time and 120 °C reaction temperature is comparable with that obtained in the presence of Nafion-H resin [4]. However, the low cost, convenient recovery, good stability and reusability are the features of the sulfamic acid catalytic system over the former.

In addition, the esterification of various cyclic olefins with aliphatic acids was studied in the presence of sulfamic acid and the results are summarized in table 2. Initially, the poor reactivity of esterification between acetic acid and linear alkene was shown in the entry 1. All saturated aliphatic acids reacted with norbornene smoothly to give the corresponding esters with good olefin conversions and near 100% selectivity (entries 2 to 5). Furthermore, with norbornene and unsaturated aliphatic acids, such as acrylic acid and crotonic acid, the reaction of the addition esterification could selectively reacted with the double bonds in norbornene to give the corresponding carboxylates with satisfying olefin conversions (entries 6 and 7). However, when using cyclic olefins such as cyclohexene and cyclooctene as well as acetic acid as substrates, the olefins conversion was only 24.7% and 30.2%, respectively, which implied that the double bond in the single circle was more stable than that in the fused circle. Analogous to norbornene, dicyclopentadiene underwent the addition reaction with acetic acid to furnish the corresponding acetate in 80.4% olefin conversion (entry 10), which is a cost-effective process for the preparation of a new class of fragrance [2]. Again, 77.8% of dicyclopentadiene conversion was obtained over this catalytic system using acrylic acid (entry 11). It should be noted that, with an exception of the result for norbornene and acetic acid, all the reaction results could be probably improved further after the reaction condition optimization.

When acetic acid and propionic acid were used, the yields of the corresponding 2-norbornyl carboxylates by distillation were 97% and 92%, respectively. It indicated that the separation of products was very convenient and the results were in agreement with the quantitative analysis by GC.

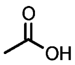
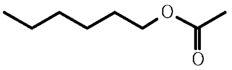
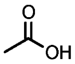
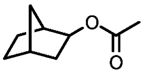
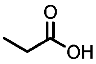
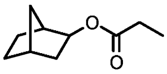
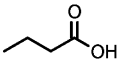
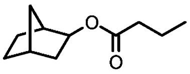
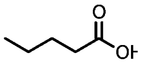
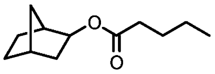
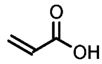
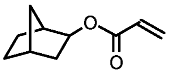
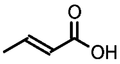
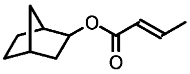
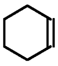
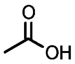
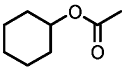
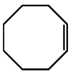
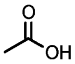
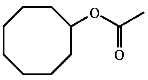
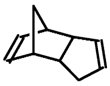
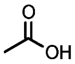
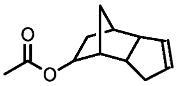
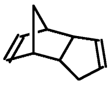
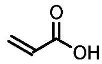
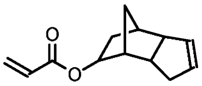
Table 1
Esterification of norbornene with acetic acid catalyzed by sulfamic acid under different conditions.



Entry	Amount of catalyst (%)	Olefin/acid (M/M)	Temp. (°C)	Time (h)	Con. (%)[a]	Sel. (%)[b]
1	0	3	120	4	1.6	100
2	5	3	120	4	24.1	99.8
3	10	3	120	4	99.6	99.5
4	10	1	120	4	73.1	99.4
5	10	3	90	4	70.0	99.6
6	10	3	120	2.5	74.0	99.4
7 [c]	10	3	120	4	97.1	99.2

[a] Conversion of norbornene.
[b] Selectivity to the ester.
[c] Fourth time reused.

Table 2
Esterification of cyclic olefins with aliphatic acids over H_2NSO_3H[a]

Entry	Cyclic olefins	Aliphatic acids	Con. (%)[b]	Products	Sel. (%)
1			2.2		91.0
2[c]			99.6		99.5
3[d]			94.3		99.1
4			89.4		99.1
5			91.6		99.6
6			86.9		99.4
7			82.6		99.8
8			24.7		100
9			30.2		100
10			80.4		100
11			77.8		100

[a] Reaction conditions: olefin, 20° mmol; aliphatic acid, 60○ mmol; sulfamic acid, 2° mmol; temperature, 120°C; reaction time, 4 h.

[b] Conversion of olefins.

[c] Isolated yield of desired ester was 97% (78–81°C/12 mm Hg).

[d] Isolated yield of desired ester was 92% (89–93°C/12 mm Hg).

In conclusion, a simple and an efficient method for the preparation of esters from cyclic olefins and aliphatic acids was developed by using sulfamic acid which could be recycled for the esterification without obvious loss in the substrate conversion and the product selectivity. In comparison with the previously reported methods, this method for the esterification should be admired for green chemistry process because of its simple operation, convenient separation, the recycle of the catalyst, as well as the other intrinsic properties of the catalyst.

Typical procedure of esterification: To a stirred mixture of an olefin (20 mmol) and aliphatic acid (60 mmol) in a reaction flask, H_2NSO_3H (2 mmol, 0.194 g) was added. The mixture was stirred at desired temperature for a certain period. Then the reaction mixture was cooled to ambient temperature and followed by the GC analysis. The qualitative analysis and the quantitative analysis were carried out on a Hewlett-Packard 6890/5793 GC/MS equipped with a HP 5MS column (30 m) with helium as carrier gas and on a temperature-programmed Hewlett-Packard GC-5790 equipped with a 3 × 3000 mm PTFE column, respectively. The concentration of reactant and product was directly given by the system of GC chemstation according to the area of each chromatograph peak. The isolation of products was achieved by distillation under reduced pressure.

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