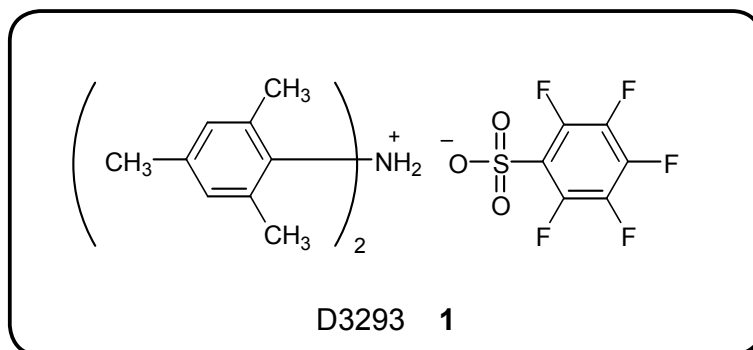


Dehydrative Ester Condensation Catalyst

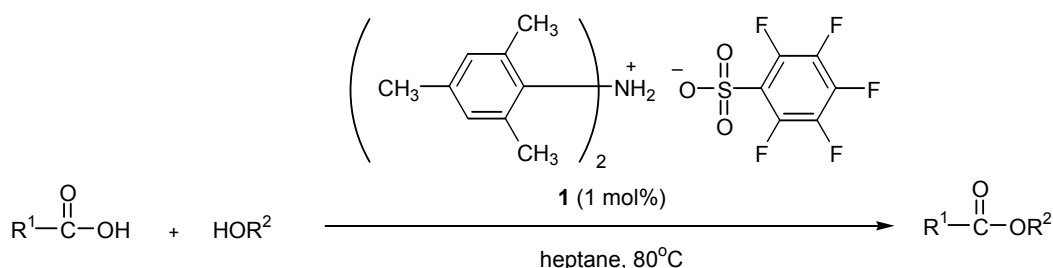


Dimesitylammonium Pentafluorobenzenesulfonate **1** is a catalyst developed by Ishihara et al. for the ester condensation reaction of carboxylic acids with equimolar amounts of alcohols. It has a major advantage in that when used, it is not necessary to remove the water generated as a byproduct.

The esterification reaction of carboxylic acids and alcohols is one of the most fundamental and widely used reactions in organic synthesis. The classical esterification reaction involves dehydrative condensation under acidic conditions, which is an equilibrium reaction between the ester condensation and hydrolysis of the generated ester. To obtain esters efficiently, this equilibrium has to be shifted to the ester formation side and this is normally achieved either by using the carboxylic acid or alcohol in large excess, or removing the generated water azeotropically. However, when both the carboxylic acid and alcohol are expensive, and either the carboxylic acid or alcohol is acid or heat sensitive, this classical esterification method is difficult to apply. Therefore, esterification methods which proceed under mild conditions without the need to use either carboxylic acids or alcohols in large excess are required, and many excellent condensation catalysts have been reported which help to achieve this.^{1,2)}

Dimesitylammonium Pentafluorobenzenesulfonate **1**, developed by Ishihara et al. in recent years, is one such ester condensation catalyst, and the yields obtained from equimolar amounts of carboxylic acids and alcohols is high. In addition, it is not necessary to remove the water generated as a byproduct.³⁾ **1** consists of bulky diarylamine and bulky pentafluorobenzenesulfonic acid, and the hydrophobicity in the NH_2^+ neighborhood, that is the active center of this catalyst, increase by steric hindrance of both components. Therefore, the elimination of water is promoted during condensation, and hydrolysis of the ester by the water is restricted. As a result, desired ester is obtained in high yields. Moreover, the acidity of pentafluorobenzenesulfonic acid is low [$\text{pK}_a(\text{CD}_3\text{COOD})=11.1$, $H_0=-3.98$] and **1** can therefore also be applied to acid labile substrates.

To show its versatility, Ishihara et al. reported the ester condensation reaction of various carboxylic acids and alcohols in the presence of 1mol% of **1**.



Keywords : dehydrative ester condensation catalyst

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Entry	R ₁ CO ₂ R ₂	Time (h)	Yield (%) ^a	Entry	R ₁ CO ₂ R ₂	Time (h)	Yield (%) ^a
1		7	91	7		24	90
2		24	96	8		24	82 (5)
3		3	98	9		30	88 (0)
4		4	95 (0)	10 ^b		24	73
5		10	93 (0)	11		72	92
6		6	93	12		24	91

- a. Yield of alkenes is shown in parentheses.
b. **1** (10mol%) was used at 115°C.

When secondary alcohols are used as the substrate, there is little or no generation of olefins as byproduct (Entry 4,5,8,9). When tertiary alcohols (Entry 11) and phenol (Entry 10) are used as the substrate, the corresponding esters are generated in high yields. Moreover, **1** is also applicable to a wide variety of carboxylic acids such as α,β -unsaturated carboxylic acids (Entry 2,7,9), aromatic carboxylic acid (Entry 12), 2-alkyloxycarboxylic acid (Entry 4,10,11), 2-alkylcarboxylic acids (Entry 1,6,7), and 4-oxocarboxylic acid (Entry 3,8).

1 is a versatile dehydrative condensation catalyst, and many future applications are expected.

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