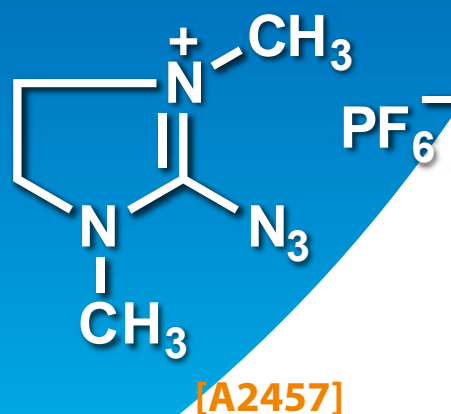


New Stable Diazotransfer Reagent against Heat and Impact/Friction

Advantages

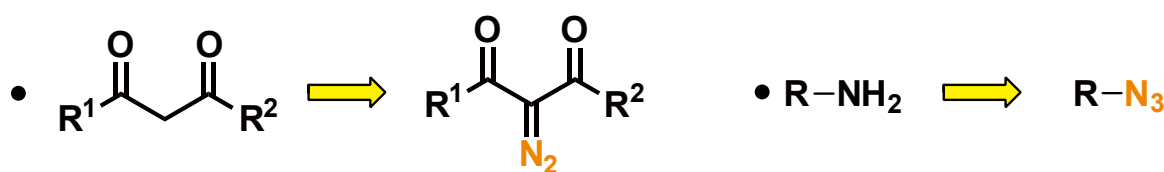
- Stable crystalline solid against heat, impact, and friction
- Reaction proceeds under mild conditions
- By-products can be easily removed by ordinary extraction procedures

2-Azido-1,3-dimethylimidazolium Hexafluorophosphate (**A2457**), which was developed by Kitamura *et al.*, is a crystalline diazotransfer reagent having high thermal stability and low explosibility. The differential scanning calorimetry (DSC) experiment of **A2457** has revealed that the exothermic decomposition temperature was approximately 200 °C. Moreover, **A2457** has tested negative for the impact and friction-sensitivity tests.¹⁾



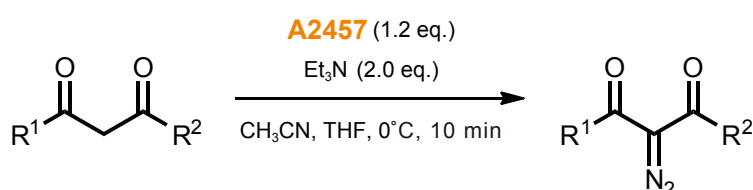
Application

Diazotransfer Reagent to 1,3-Diketones or Amines



Example 1.

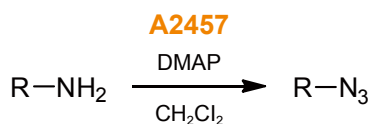
Reaction of 1,3-Dicarbonyl Compounds with **A2457**¹⁾



Entry	R ¹	R ²	Yield (%)
1	Me	Me	83
2	Ph	Ph	90
3	OEt	OEt	quant.
4	—CH ₂ C(Me) ₂ CH ₂ —		86

Example 2.

Reaction of Aromatic and Aliphatic Amines with **A2457**²⁾



Entry	R	A2457 (eq.)	DMAP (eq.)	Temp.	Time (h)	Yield (%)
1	Ph	1.15	1.1	rt	2.5	87
2	4-MeC ₆ H ₄	1.15	1.1	rt	1.5	94
3	4-O ₂ NC ₆ H ₄	2	3	50 °C	4	61
4	PhCH ₂ CH ₂	1.15	5 ^{a)}	rt	0.25	74
5	1-adamantyl	1.15	1.1	rt	0.33	71

^{a)} Et₃N is used instead of DMAP.

Application Example

Synthesis of 2-Diazo-1,3-dicarbonyl Compounds using **A2457**¹⁾

A2457 (0.6 mmol) in MeCN (0.5 mL) is cooled to 0 °C. A solution of 1,3-dicarbonyl compound (0.5 mmol) and Et₃N (1.0 mmol) in THF (2.0 mL) is added and the reaction mixture is stirred for 10 min. The reaction is quenched with H₂O (5 mL), and the reaction product is extracted with CH₂Cl₂ (3 x 10 mL). The combined extracts are washed with brine (15 mL), and then dried over anhydrous Na₂SO₄. The solvent is removed in vacuo to afford the almost pure diazo compound. This diazo compound is purified by flash column chromatography (silica gel; Hexane-EtOAc) to give the pure 2-diazo-1,3-dicarbonyl compound.

A2457 2-Azido-1,3-dimethylimidazolinium Hexafluorophosphate 5g

1) M. Kitamura, N. Tashiro, S. Miyagawa, T. Okauchi, *Synthesis* **2011**, 1037.

2) M. Kitamura, M. Yano, N. Tashiro, S. Miyagawa, M. Sando, T. Okauchi, *Eur. J. Org. Chem.* **2011**, 458.

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