Stable Diazotransfer Reagent against Heat and Impact/Friction

[A2457]

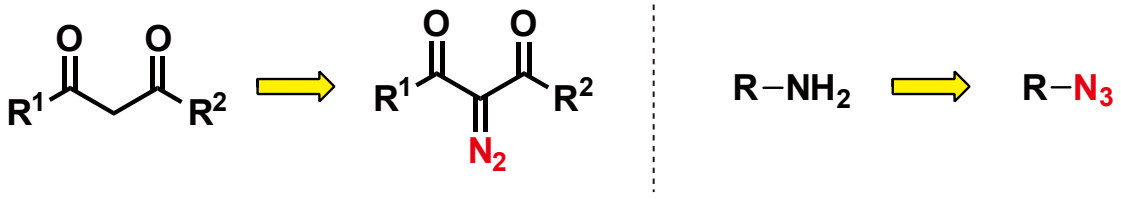
Advantages

- **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-dimethylimidazolinium 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)]

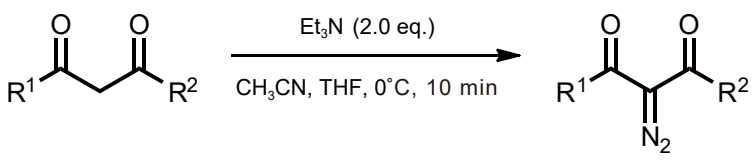
Application

Diazotransfer Reagent to 1,3-Diketones or Amines



Example 1.

Reaction of 1,3-Dicarbonyl Compounds with A2457[1)]

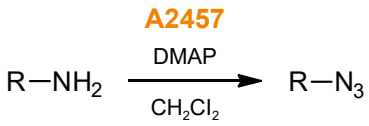


Entry	R^1	R^2	Yield (%)
1	Me	Me	83
2	Ph	Ph	90
3	OEt	OEt	quant.
4	—$CH_2C(Me)_2CH_2$—		86

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

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_6H_4	1.15	1.1	rt	1.5	94
3	4-$O_2NC_6H_4$	2	3	50 ˚C	4	61
4	$PhCH_2CH_2$	1.15	5[a)]	rt	0.25	74
5	1-adamantyl	1.15	1.1	rt	0.33	71

[a)] Et_3N is used instead of DMAP.

Procedure

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 Et_3N (1.0 mmol) in THF (2.0 mL) is added and the reaction mixture is stirred for 10 min. The reaction is quenched with H_2O (5 mL), and the reaction product is extracted with CH_2Cl_2 (3 x 10 mL). The combined extracts are washed with brine (15 mL), and then dried over anhydrous Na_2SO_4. 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.

References 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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