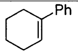
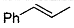
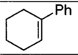
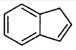
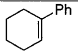
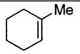
J|A|C|S

ADDITIONS AND CORRECTIONS

Epoxidation of Alkenes by Amine Catalyst Precursors: Implication of Aminium Ion and Radical Cation Intermediates [*J. Am. Chem. Soc.* **2000**, *122*, 8317−8318]. Mauro F. A. Adamo, Varinder K. Aggarwal,* and Matthew A. Sage.

Page 8317. We have recently become aware of certain inconsistencies relating to our amine-catalyzed oxidation of alkenes and regret that the results presented in Table 3 of the above paper have been found to be irreproducible.[1] The original results are shown in normal font and the new results are given in bold.

Table 3. Competition Experiments with Structurally Similar Alkenes and Comparison of Different Oxidation Procedures[a]

Entry	Alkenes		Amine[b]		$Ar_3N^+ \,^\bullet SbCl_6^-$ [c]	MTO[d]
	A	**B**	Pyrrolidine	**1**		
1			100:0 **55:11**	100:0 **100:36**	100:0 **decomposition**	70:50
2			100:0 **58:25**	100:0 **99:23**	100:0 **decomposition**	70:50
3			4:100 **90:93**	7:100 **99:99**[e]	5:100 **decomposition**	65:75

[a] 1 equiv of each alkene is used in all experiments. ^1H NMR conversion of the two alkenes A:B are given relative to an internal standard (1,4-dimethoxybenzene). [b] Alkene (each 0.424 mmol), amine (0.04 mmol), Oxone (0.85 mmol), $NaHCO_3$ (4.24 mmol), 0.5 mL of *d*-MeCN:D_2O (95:5), pyridine (0.424 mmol), 4 h, rt. [c] 20 mol % of $Ar_3N^+ \,^\bullet SbCl_6^-$, 3 equiv of SeO_2, *d*-CH_2Cl_2, rt, 5 min. [d] 0.5 mol % of MTO (methyltrioxorhenium), 12 mol % of pyridine, 1.5 equiv of H_2O_2, *d*-CH_2Cl_2, 6 h. [e] Using only 0.21 mmol of Oxone, a 24:20 ratio of alkenes consumed is observed after 10 min.

In fact, we have not been able to reproduce Bauld and Mirafzal's epoxidation[2] using $Ar_3N^+ \,^\bullet SbCl_6^-$ and either SeO_2 or $(PhSeO)_2O$; while the starting alkenes were consumed, only products of decomposition were observed. Even when the reaction was stopped part way, only starting material and products of decomposition were obtained. In a control experiment, the intermediate epoxide was treated to the same radical cation conditions and the same signals corresponding to decomposition products were identified in the ^1H NMR.

The similarity in selectivity between the "established" radical cation oxidations and our own results led us to propose a related radical cation mechanism (shown in Scheme 2 of the above paper). However, as we have been unable to reproduce the "established" radical cation oxidations, the proposed mechanism is much less compelling and therefore less credible.

The enantioselectivity given in Table 2 (entry 5) (57% ee) should be 32−38% ee.

We thank Franck Sandrinelli and Chrystel Lopin for performing these additional experiments.

---

(1) Adamo, M. F. A.; Aggarwal, V. K.; Sage, M. *J. Am. Chem. Soc.* **2000**, *122*, 8317−8318.

(2) Bauld, N.; Mirafzal, G. A. *J. Am. Chem. Soc.* **1991**, *113*, 3613−3614. Kim, T.; Mirafzal, G. A.; Liu, J.; Bauld, N. L. *J. Am. Chem. Soc.* **1993**, *115*, 7653−7664.

JA027285V

10.1021/ja027285v