Dimerization and Oxidation of Azirines by Silver(I)

By Howard Alper* and John E. Prickett

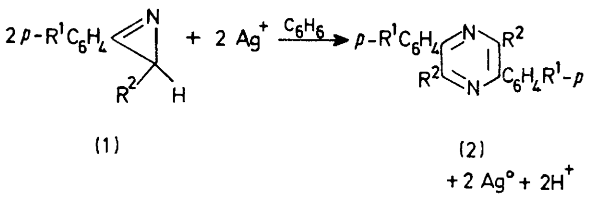
(*Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada* K1N 6N5)

Summary 2-Aryl-azirines are converted into 2,5-diarylpyrazines by silver perchlorate, metallic silver being formed as a by-product.

There has been great interest in the silver(I)-induced cleavage of strained ring systems.[1] While such processes generally occur with net retention of the oxidation state of silver, we know of two examples of the reduction of Ag^I to metallic silver and oxidation of the organic reactant.[2,3] We now report that Ag^I effects an interesting oxidative dimerization of azirines.

Reaction of a 2-aryl-azirine (**1**)[4] with silver perchlorate in benzene for 4–5 days at room temperature gave 2,5-diarylpyrazines (**2**) and metallic silver (Table).† The structures of the pyrazines were determined by comparison (m.p.; n.m.r., i.r., u.v., and mass spectra) with authentic materials. The reaction is not catalysed by Ag^+ ions.

Possible mechanistic pathways for the redox reaction are outlined in the Scheme. Initial complexation of the azirine to silver(I) would give (**3**), which could then undergo cycloaddition to another molecule of azirine affording a diazatricyclohexane (**4**). An analogous cyclization of cyclopropenes to tricyclo[3.1.0.0^{2,4}]hexanes, in the presence of palladium chloride[5] or zeolites,[6] has been



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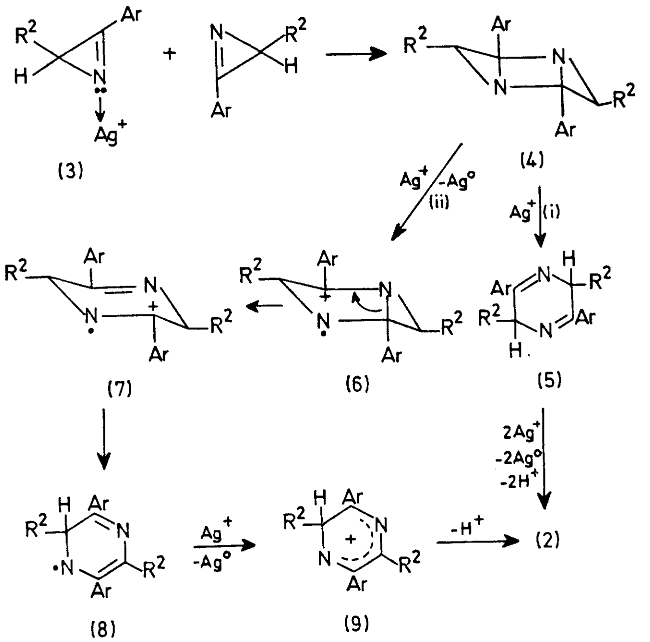
† The following general procedure was used. A mixture of the azirine (10 mmol) and $AgClO_4$ (25–30 mmol) in dry benzene (250 ml) was stirred at room temperature for 4–5 days under nitrogen. A silver mirror was deposited. Extraction with $CHCl_3$ and flash-evaporation of the organic layer gave an oil which was triturated with n-hexane to give a semi-solid which was treated with CH_2Cl_2 and the resulting mixture filtered and chromatographed on Florisil with toluene as eluent to give the pure pyrazine.



Ar = p-R^{1}C$_6$H$_4$

SCHEME

Table. Yields and m.p.s of (**2**).

(**2**) R^1	R^2	% Yield	M.p./°C
H	H	33	195—197[a]
Me	H	35	200—201[b]
OMe	H	16	275—276[c]
Br	H	12	233—234[d]
H	Me	30	122—124[e]

[a] L. Wolff, *Ber.*, 1887, **20**, 432. [b] D. Demus, K. H. Kolz, and H. Sackmann, *Z. Phys. Chem.*, 1972, **249**, 217. [c] E. Zbiral and J. Stroh, *Annalen*, 1969, **727**, 231. [d] O. Dann, H. Fick, B. Pietzner, E. Walkenhorst, R. Fernbach, and D. Zeh, *ibid.*, 1975, 160. [e] J. Fellman, S. H. Wilen, and C. A. VanderWerf, *J. Org. Chem.*, 1956, **21**, 713.

described. Ring cleavage of (**4**) may occur in a concerted fashion (i) to give (**5**) which is then convertible into the pyrazine by oxidative dehydrogenation. Alternatively, electron transfer (ii, stepwise cleavage)[1,3] would give the radical cation (**6**), and metallic silver. Isomerization of (**6**) to (**7**) and subsequent proton loss would afford (**8**). A second electron transfer (**8**→**9**) and proton loss would give the pyrazine.

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[1] P. E. Eaton, L. Cassar, R. A. Hudson, and D. R. Hwang, *J. Org. Chem.*, 1976, **41**, 1445; K. C. Bishop III, *Chem. Rev.*, 1976, **76**, 461, and refs. cited therein.

[2] G. F. Koser and J. N. Faircloth, *J. Org. Chem.*, 1976, **41**. 583.

[3] K. L. Kaiser, R. F. Childs, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1971, **93**, 1270.

[4] A. G. Hortmann, D. A. Robertson, and B. K. Gillard, *J. Org. Chem.*, 1972, **37**, 322.

[5] F. J. Weigert, R. L. Baird, and J. R. Shapley, *J. Amer. Chem. Soc.*, 1970, **92**, 6630.

[6] A. J. Schipperijn and J. Lukas, *Tetrahedron Letters*, 1972, 231.