

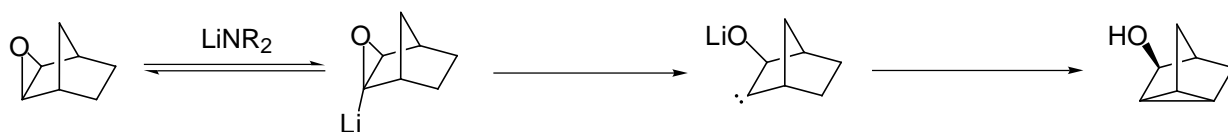
BASE-PROMOTED REARRANGEMENT OF *N*-TOSYL-2,3-*exo*-AZIRIDINO[2,3]NORBORNANE

Odón Arjona, Roberto Menchaca, and Joaquín Plumet*

Universidad Complutense, Facultad de Química, Dpto. Química Orgánica I, 28040 Madrid, Spain

Abstract-The first experimental evidence of the generation of an imino carbene from the tittle compound is reported.

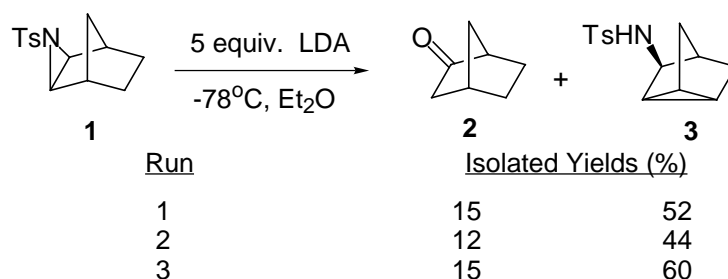
Although the chemistry of oxiranyl anions has been extensively considered in the literature,¹ more limited work on the related aziridinyl anions has been published to date.^{1b} The base-promoted α -abstraction of hydrogen in epoxides to give oxiranyl anions which rearrange to α -hydroxy carbenes is a well-known process which has been considered in the case of bicyclic systems providing intramolecular C-H insertion products (Scheme 1).²



Scheme 1

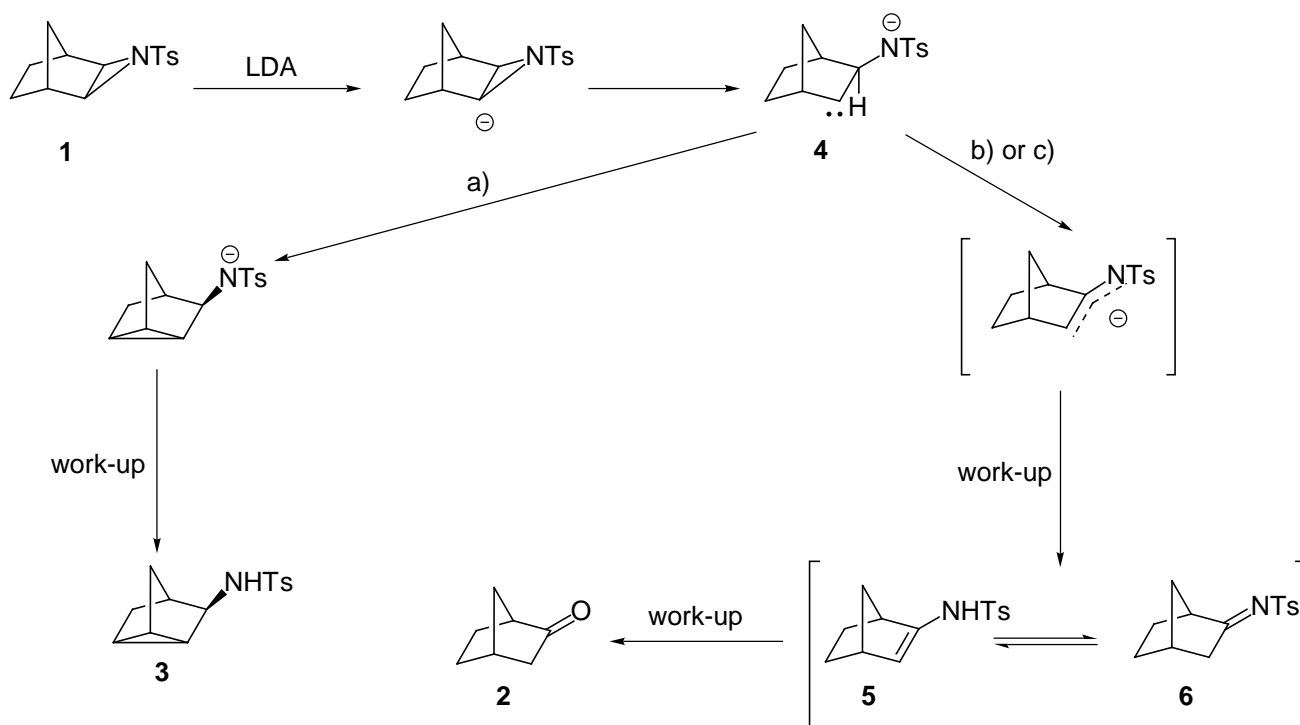
However, an analogous study in the case of bicyclic aziridines has not been, to the best of our knowledge, reported. Thus, the formation of an α -imino carbene (or carbenoid) generated from a nonstabilized α -aziridinyl anion³ has never been observed.

In this communication we wish to account for the first direct observation of the formation of this intermediate by treatment of compound (**1**)^{4, 5} with LDA (Scheme 2). Thus, reaction of **1** (1.0 equiv.) with 5 equiv. of LDA (Et₂O, -78°C, 2 h)⁶ affords a mixture of norbornanone (**2**) and *N*-Tosyl nortricyclylamine (**3**).⁷ The structure of compound (**3**) was determined by comparison with the previously described *N*-benzenesulfonyl derivative.⁸ The ratio **2**/**3** and the overall yield of the reaction have been fairly well reproduced in three independent experiments indicated in Scheme 2.



Scheme 2

Under these reaction conditions (LDA/Et₂O), the isolation of the tricyclic amine (**3**) indicates the presence of an α -imino carbenoid intermediate (**4**) (arising from α -deprotonation of the aziridine ring) which undergoes transannular insertion into a C-H bond to afford, after work-up, compound (**3**) (Scheme 3, path a). On the other hand, formation of norbornanone (**2**) can be justified by one of the following pathways: *i*) a hydrogen shift analogous to the Wagner-Meerwein process in carbocation chemistry (path b),⁹ or alternatively *ii*) a hydrogen migration in a pinacol-type rearrangement (path c). In both cases, the α -imino carbanion formed would afford, during work-up, the *N*-tosylenamine (**5**) equilibrated with the related *N*-tosylimine (**6**). Hydrolysis during the work-up of the reaction would finally give rise to compound (**2**).



Scheme 3

In summary, in this communication we have accounted for the first example of generation of an α -imino carbene from the related aziridine on the basis of the isolation of the intramolecular insertion product (**3**).

ACKNOWLEDGEMENTS

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REFERENCES AND NOTES

1. For selected reviews, see a) E. Doris, L. Dechoux, and Ch. Miokowski, *Synlett*, 1998, 337. b) T. Satoh, *Chem. Rev.*, 1996, **96**, 3303, and references therein. For more recent studies on the chemistry of oxiranylanions including synthetic

- applications, see: c) K. Kuramochi, H. Itaya, S. Nagata, H. Takao, and S. Kobayashi, *Tetrahedron Lett.*, 1999, **40**, 7367 and 7371. d) G. Maier, H. P. Reisenauer, and M. Cibulka, *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 105.
2. For selected references, see: a) J. K. Crandall, *J. Org. Chem.*, 1964, **29**, 2830. b) J. K. Crandall, L. C. Crawley, D. B. Banks, and L. C. Lin, *J. Org. Chem.*, 1971, **36**, 510. For an enantioselective version of this process, see: D. M. Hodgson, and R. Wisedale, *Tetrahedron: Asymmetry*, 1996, **7**, 1275. c) J. R. Neff, and J. E. Nordlander, *Tetrahedron Lett.*, 1971, 499. d) R. M. McDonald, R. N. Steppel, and R. C. Cousins, *J. Org. Chem.*, 1985, **50**, 135. e) O. Arjona, R. Menchaca, and J. Plumet, *Tetrahedron*, 2000, **56**, 3901.
 3. For an excellent account on the generation and evolution of stabilized and nonstabilized aziridinyl anions, see: a) ref. 1b, pp. 3321-3324. For related reviews, see: b) R. S. Atkinson, *Tetrahedron*, 1999, **55**, 1519. c) D. Tanner, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 599. d) For an account on the lithiation of aziridine using Lewis acid activation, see: E. Vedejs, and J. T. Kendall, *J. Am. Chem. Soc.*, 1997, **119**, 6941.
 4. *N*-Tosylaziridine (**1**) was prepared from norbornene according to the method previously described: D. A. Evans, M. F. Margaret, and M. T. Bilodeau, *J. Am. Chem. Soc.*, 1994, **116**, 2742. Isolated yields were described by Evans depending on the Cu (II) salts employed: Cu(ClO₄)₂, 90%; Cu(acac)₂, 95%; Cu(OTf)₂, 50%. Full details will be provided upon request.
 5. For a review on the asymmetric synthesis of aziridines, see: H. M. Osborn, and J. Sweeney, *Tetrahedron: Asymmetry*, 1997, **8**, 1693.
 6. Experimental procedure. To a solution of diisopropylamine (0.52 mL, 3.68 mmol) in 4 mL of ether cooled at -78°C under argon, *n*-BuLi (2.35 mL, 3.76 mmol, 1.6 M solution in hexane) was added dropwise and stirring was kept for 15 min. Then, a solution of **1** (194 mg, 0.74 mmol) in 7 mL of ether was added and the resulting yellow solution was stirred for 2 h at -78°C. The reaction mixture was quenched with brine and extracted with ether. The organic phases were dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with hexanes/ethyl acetate (4:1) afforded norbornanone (**2**) (12 mg, 15%) and nortricyclylamine (**3**) (116.3 mg, 60%), both as white solids.
 7. Spectroscopic data for **3**. mp: 91-92°C (hexane-acetate). ¹H-NMR (CDCl₃, 300 Mz): δ 7.78 (d, 2 H, *J* = 8.3 Hz), 7.28 (d, 2 H, *J* = 8.3 Hz), 4.95 (d, 1 H, *J* = 7.3 Hz), 3.18 (d, 1 H, *J* = 7.3 Hz), 2.41 (s, 3 H), 1.77 (br s, 1 H), 1.53 (br d, 1 H, *J* = 11.0 Hz), 1.27 (br d, 1 H, *J* = 11.0 Hz), 1.24-0.80 (m, 4 H), 0.89 (t, 1 H, *J* = 5.1 Hz). ¹³C-NMR (CDCl₃, 75 Mz): δ 143.2, 138.1, 129.7, 127.1, 59.0, 34.1, 31.4, 29.4, 21.5, 14.7, 11.9, 10.4. Anal. calc. for C₁₄H₁₇O₂NS: C, 63.88; H, 6.46; N, 5.32; found: C, 63.76; H, 6.62; N, 5.36. Copies of ¹H- and ¹³C-NMR spectra of **3** will be provided upon request. Norbornanone (**2**) was identified upon comparison with an authentic sample.
 8. For the isolation of other derivatives of nortricyclylamine from norbornyl derivatives in basic media, see: L. H. Zalkow, and E. M. Calhoun, *Tetrahedron Lett.*, 1975, 2149. For the isolation of 3-*N*-carbethoxyaminonortricyclene from ethyl-2,3-*exo*-aziridino[2,3]norborn-5-ene-1'-carboxylate, by reaction with HBr followed by treatment with Li-NH₃, see: H. Tanida, T. Tsuji, and T. Irie, *J. Org. Chem.*, 1966, **31**, 3941.
 9. Carbenes, like other electron deficient intermediates, undergo a facile rearrangement with simultaneous formation of a new C=C bond. This hydrogen shift can be regarded as an intramolecular insertion of the carbene into the adjacent C-H bond, see: Ch. J. Moody, and G. H. Whitham, 'Reactive Intermediates', ed by S. G. Davies, Oxford Chemistry Primers, Oxford, 1995, p. 42.