

## A New Efficient Access to Cyclic Imines

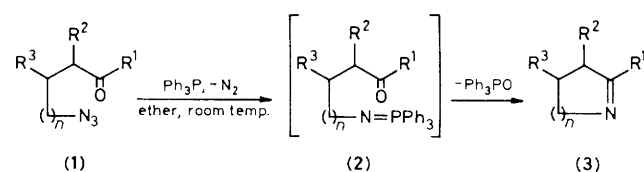
Pierre H. Lambert, Michel Vaultier, and Robert Carrié

Groupe de Physicochimie Structurale, Université de Rennes, Campus de Beaulieu, 35042 Rennes Cedex, France

Cyclic imines can be conveniently prepared from  $\omega$ -azidoketones by an intramolecular 'aza-Wittig' reaction.

The addition of a tertiary phosphine (*i.e.* triphenylphosphine) to an organic azide producing an iminophosphorane after nitrogen extrusion originally reported by Staudinger<sup>1</sup> has received little attention by synthetic chemists.<sup>2</sup> The iminophosphoranes are known to react with benzaldehyde, for example, to give the corresponding Schiff base in a Wittig-like ('aza-Wittig') reaction.<sup>3</sup> This route to imines is of no use if the corresponding primary amine is easily accessible and if both reagents and product are stable under the reaction conditions usually used for such a condensation. If this is not the case, the 'aza-Wittig' reaction could be very useful. We report a new efficient route to the cyclic imines (**3**), involving an intramolecular 'aza-Wittig' reaction according to Scheme (1). Although there are a number of methods in the literature for the preparation of cyclic imines,<sup>4</sup> they all suffer from severe limitations.

The addition of 1.0 equiv. of triphenylphosphine to a solution of the azide (**1**) in anhydrous ether under nitrogen



Scheme 1

produces an exothermic reaction which leads quantitatively to the cyclic imine (**3**), through the intermediate iminophosphorane (**2**), where  $n = 1, 2, \text{ or } 3$  (5, 6, or 7 membered ring). The results are summarized in Table 1. The spectroscopic data for the compounds (**3**) are in agreement with their structure. In particular, the <sup>13</sup>C n.m.r. spectra show a signal for C-2 at 175–180 p.p.m. and in the i.r. spectra the C=N absorption appears at 1620–1680 cm<sup>-1</sup>.

This reaction offers several advantages over the known methods. Since no reduction step is involved and the reaction occurs under anhydrous conditions, the method is useful

Table 1. Synthesis of cyclic imines (**3**).

	<i>n</i>	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Yield (%) <sup>a</sup>	b.p. (°C)/mmHg or m.p. (°C)
(3a)	1	Me	H	H	92	105–106/760
(3b)	1	Me	Me	H	65	122–124/760
(3c)	1	Me	Et	H	60	88–89/105
(3d)	1	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	H	H	82	89–90
(3e)	2	Me	H	H	65	135–136/760
(3f)	2	Me	H	SPh	78	<sup>b</sup>
(3g)	3	Me	H	H	60	70–80/18

<sup>a</sup> Yields of the isolated pure products and are not optimized. All these compounds give correct combustion analysis and/or mass spectra. <sup>b</sup> Isolated by column chromatography on silica gel (ether, light petroleum, methanol, 2:2:1, *R<sub>f</sub>* = 0.6).

with a variety of other substituents. The starting azides (**1**) are easily prepared from the corresponding chloro- or bromo-ketones which are themselves easily accessible.<sup>5</sup> As a consequence of the Wittig-like reaction, the cyclisation is regio-specific (this is not the case for the rearrangement of tertiary cycloalkylazides in the presence of sulphuric acid).<sup>4c</sup>

The reaction we have described represents a versatile preparation of this important class of heterocyclic compounds which are intermediates in alkaloid synthesis.

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### References

- 1 H. Staudinger and I. Meyer, *Helv. Chim. Acta*, 1919, **2**, 635.
  - 2 Y. G. Gololobov, I. N. Zhmurova, and L. F. Kasukhin, *Tetrahedron*, 1981, **37** (3), 437, and references therein; J. I. G. Cadogan, 'Organophosphorus Reagents in Organic Synthesis,' Academic Press, New York and London, 1979, pp. 241—249, and references therein; M. Pailer and E. Haslinger, *Monatsh. Chem.*, 1970, **101**, 508; E. Öhler and U. Schmidt, *Chem. Ber.*, 1975, **108**, 2907.
  - 3 A. W. Johnson, 'Ylid Chemistry,' Academic Press, New York and London, 1966, pp. 222—236, and references therein.
  - 4 (a) K. Blaha and O. Cervinka, *Adv. Heterocycl. Chem.*, 1966, **6**, 147, and references therein; (b) A. Etienne and Y. Correia, *Bull. Soc. Chim. Fr.*, 1969, **10**, 3704; (c) A. Astier and M. M. Plat, *Tetrahedron Lett.*, 1978, 2051; (d) J. Bielawski, S. Brandage, and L. Lindblom, *J. Heterocycl. Chem.*, 1978, 97.
  - 5 J. A. Wilt and J. W. Hill, *J. Org. Chem.*, 1961, **26**, 3523; G. W. Cannon, R. C. Ellis, and J. R. Leal, *Org. Synth.*, 1963, Coll. Vol. IV, 597; T. Cuvigny, M. Larchevêque, and H. Normant, *Liebigs Ann. Chem.*, 1975, 719.
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