

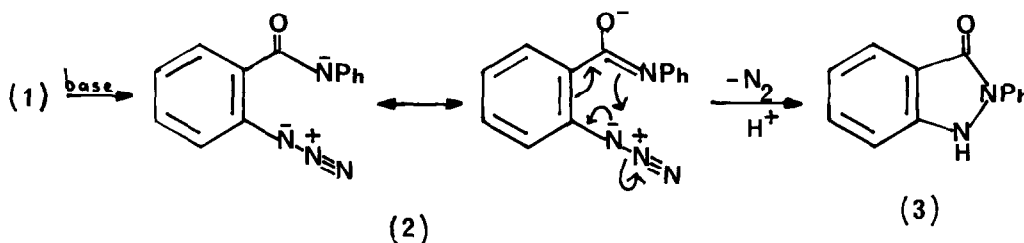
THERMOLYSIS OF N-(o-AZIDOBENZOYL)-IMINOPYRIDINIUM YLIDE: A NEW ROUTE TO 3H-INDAZOL-3-ONE

Stuart P. Darwen and Robert K. Smalley,*

Department of Chemistry and Applied Chemistry, University of Salford, Salford. M5 4WT

Summary. 3H-Indazol-3-one has been generated by thermolysis of N(o-azidobenzoyl)iminopyridinium ylide, and trapped as its Diels-Alder cycloadducts with several dienes.

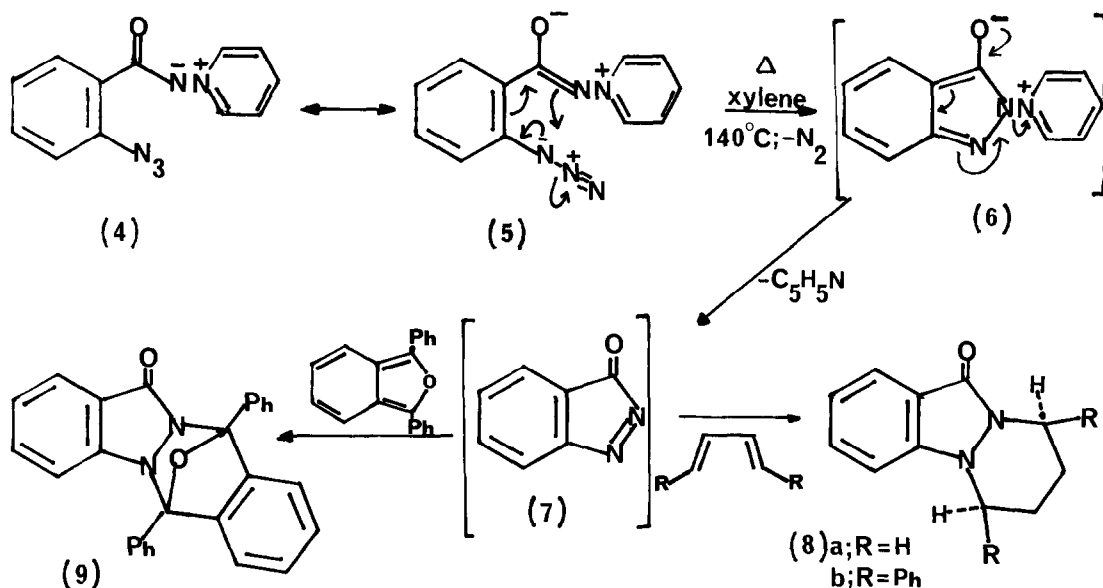
Thermal decompositions of o-azidoaryl ketones yield 2,1-benzisoxazoles by assisted loss of nitrogen from the azide group.¹ In contrast, o-azidobenzamides and o-azidobenzoates on thermolysis fail to produce the corresponding 3-amino-, or 3-alkyloxanthranils. Recently, however, it has been shown² that under base conditions (NaH-DMF) o-azidobenzanilide (1) cyclises in high yield (> 80%) to 2-phenyl-1,2-dihydroindazol-3-one (3) probably via an assisted loss of nitrogen from the mesomeric anion (2) as outlined in Scheme 1.



Scheme 1

As an extension of this simple and effective cyclisation process the thermal decomposition of N-(o-azidobenzoyl)iminopyridinium ylide (4), prepared by o-azidobenzoylation of N-aminopyridinium iodide³ has been investigated. In keeping with other N-acyliminopyridinium ylides³ the o-azidobenzoyl derivative (4) [off white needles, m.p. 125°C (decomp.) (from EtOAc); yield 41%] exhibits ν (C=O) and ν (C=N) at 1550-1620 cm^{-1} , values that indicate a large degree of delocalisation of the negative charge and the dominance of the 'imine' mesomer (5) over that of the 'amide' mesomer (4). On this basis it was anticipated that on thermolysis the azide would undergo nitrogen loss and cyclisation, probably via an assisted process rather than via a nitrene intermediate, to yield the N-pyridinium-indazole

(6), which by loss of pyridine would produce 3H-indazol-3-ones (7) as outlined in Scheme 2.



The formation of this unstable α -azocarbonyl compound⁴ was confirmed by trapping experiments (Scheme 2) from which the dienophilic indazolone (7) was isolated as its Diels-Alder cycloadducts with a number of dienes. For example, the (azidobenzoyl)imino-pyridinium ylide (0.1 g) was heated under reflux in xylene (20 ml) for 1.5-2 h. during which time 1,3-butadiene was bubbled through the mixture. Removal of solvent, and chromatography (preparative t.l.c. or flash column) (SiO_2 - EtOAc) gave adduct (8a) (12%) m.p. 96°C (Lit.⁵ 97°C). Prepared similarly were the trans-trans-1,4-diphenylbutadiene adduct (8b) (18%) [m.p. 176°C; m/z (M^+) 338] and the 1,3-diphenylisobenzofuran adduct (9) (22%), [m.p. 141°C; m/z (M^+) 402].⁸

Notes and References

1. R.K. Smalley, *Adv. Heterocycl. Chem.*, 1981, **29**, 1.
2. M. Azadi-Ardakani and R.K. Smalley, *Tetrahedron Lett.*, 1979, 4765.
3. Y. Tamura and M. Ideda, *Adv. Heterocycl. Chem.*, 1981, **29**, 73.
4. C.J. Moody, *Adv. Heterocycl. Chem.*, 1982, **30**, 1.
5. E.F. Ullman and E.A. Bartkus, *Chem. Ind. (London)*, 1962, 93.
6. Both of these new adducts have been fully characterised by elemental analysis, and by i.r. and ^1H n.m.r. spectral data.

(Received in UK 20 September 1985)