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A New Mode of Reactivity for Nitrile Ylides?

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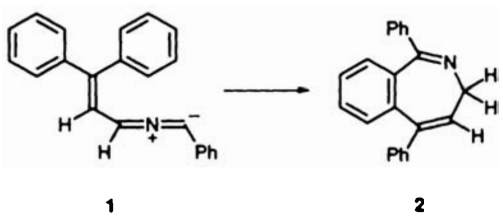
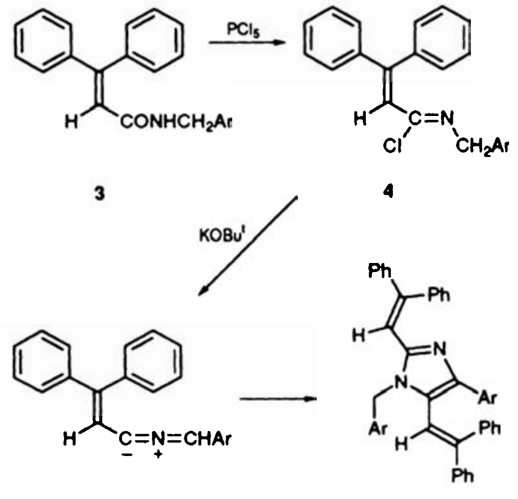
Treatment of the imidoyl chlorides **4** with base afforded the imidazoles **6**; these formal dimerisation products are the opposite regioisomers to those predicted by an analysis of the frontier molecular orbitals for the cycloaddition of the nitrile ylides **5** to their imidoyl chloride **4** precursors.

Recent studies on the cyclisation of diene-conjugated nitrile ylides, in which the γ,δ-bond forms part of an aromatic ring **1**,[1,2] have shown that the cyclisation proceeds *via* a 1,7-electrocyclisation, followed by a [1,5]-H shift, to give the 3*H*-2-benzazepines **2**, Scheme 1.



Scheme 1

The aim of this present work was to generate systems in which the nitrile ylide moiety had been inverted to investigate the effect of this inversion on the cyclisation of these species. The nitrile ylides **5** were generated by the well-established[3] 1,3-dehydrochlorination of the imidoyl chlorides **4**, which were prepared from the corresponding amides **3**, Scheme 2. This produced the deep-red solution characteristic of nitrile ylides but, upon work-up, no evidence for benzazepine formation was observed and the major product (in 50% yield when Ar = Ph and 25% when Ar = C_6H_4Cl-*p*) was shown by mass spectrometry to be a dimer. The head-to-head dimerisation of nitrile ylides is known to afford pyrazines[4] but the products of the dimerisation of the nitrile ylides **5** were shown to be *N*-arylmethyl-2,5-bis(2′,2′-diphenylethenyl)-4-arylimidazoles **6**†. This dimerisation could theoretically have taken place *via* a 1,3-cycloaddition of the nitrile ylide **5** to its imidoyl chloride precursor **4** followed by an elimination of HCl to give the imidazole **6**, Scheme 3 but the imidazole regioisomer **7** predicted by FMO theory is not that which is obtained.



(Ar = Ph, – C_6H_4Cl – *p*)

Scheme 2

With all dipolarophiles, except the very electron rich, nitrile ylide cycloaddition reactions are dipole HOMO controlled according to Sustmann's classification.[5] That is, the interaction of the dipole HOMO with the dipolarophile LUMO is the dominant frontier orbital interaction. Houk[6] has shown that the formonitrile methylide HOMO **8** is heavily localised on the

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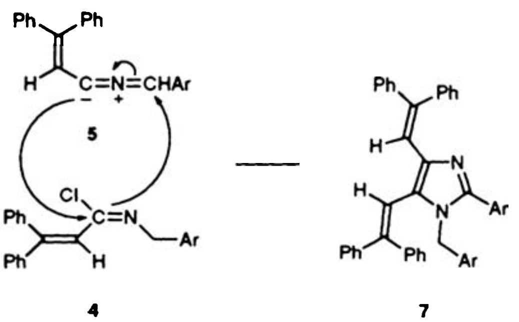

Scheme 3

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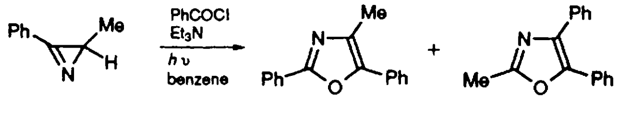
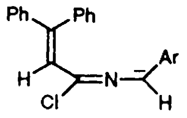
† All compounds gave satisfactory analytical and spectroscopic data. The structures of imidazoles **6** were confirmed by NOE experiments.



9 **10** **11**



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methine (C-1) terminus and this is compatible with protonation at this carbon in substituted nitrile ylides[7] and the regioisomers obtained in bimolecular nitrile ylide cycloadditions.[8] Interaction of the 3-phenylcinnamonitrile arylmethyl ylide **5** HOMO with the imidoyl chloride **4** LUMO would thus be predicted to produce the imidazole regioisomer **7**. Dimerisation of the nitrile ylide *via* this mechanism is therefore unlikely.

A number of other examples of nitrile ylides giving the 'wrong' regioisomer in [3 + 2] cycloaddition reactions have been reported.[9,10] For example, the photolysis of azirine **9** with benzoyl chloride in the presence of triethylamine gave mostly oxazole **10** together with a small amount of the expected product **11**. It has been proposed[10] that those processes that lead to the formation of the 'wrong' regioisomer involve the trapping of a deprotonated imidoyl chloride, *e.g.* **12**, rather than a nitrile ylide cycloaddition with inverse regioselectivity.

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References

1 P. W. Groundwater, C. Struthers-Semple and J. T. Sharp, *J. Chem. Soc., Chem. Commun.*, 1987, 1367.
2 P. W. Groundwater and J. T. Sharp, *Tetrahedron*, 1992, **48**, 7951.
3 R. Huisgen, H. Stangl, H. J. Sturm and H. Wagenhofer, *Angew. Chem., Int. Edn. Engl.*, 1962, **1**, 50.
4 A. Orahovats, H. Heimgartner, H. Schmid and W. Heinzelman, *Helv. Chim. Acta*, 1975, **58**, 2662.
5 R. Sustmann, *Tetrahedron Lett.*, 1971, 2717; 2721.
6 P. Caramella and K. N. Houk, *J. Am. Chem. Soc.*, 1976, **98**, 6397.
7 A. Padwa and J. Smolanoff, *J. Chem. Soc., Chem. Commun.*, 1973, 342.
8 K. Bunge, R. Huisgen, R. Raab and H. J. Sturm, *Chem. Ber.*, 1972, **105**, 1307.
9 U. Schmid, P. Gilgen, H. Heimgartner, H. J. Hansen and H. Schmid, *Helv. Chim. Acta*, 1974, **57**, 1393.
10 H. J. Hansen and H. Heimgartner, Nitrile Ylides, in *1,3-Dipolar Cycloaddition Chemistry*, ed. A. Padwa, Wiley, New York, 1984, vol. 1, pp. 177–290.