

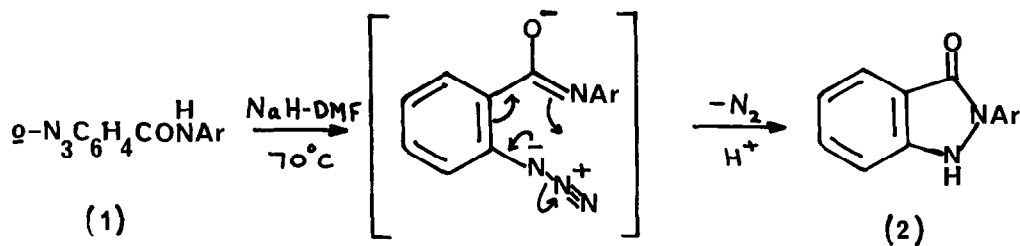
THE BASE-INDUCED DECOMPOSITION OF ETHYL N-(*o*-AZIDOARYL) CARBAMATES.
AN UNEXPECTED FORMATION OF AZO-COMPOUNDS.

Robert K. Smalley* and Antony W. Stocker

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

Summary: A mechanistic rationale is offered to explain the formation of dihydrobenzimidazolones and azo-compounds in the base-induced (NaH-DMF) decompositions of ethyl N-(*o*-azidoaryl) carbamates.

Recently¹, we have shown that under base conditions (NaH-DMF) *o*-azidoanilides (1) cyclise in high yield to 2-aryl-1,2-dihydro-3H-indazol-3-ones (2) via a concerted assisted loss of nitrogen from the amide anion as indicated in Scheme 1.

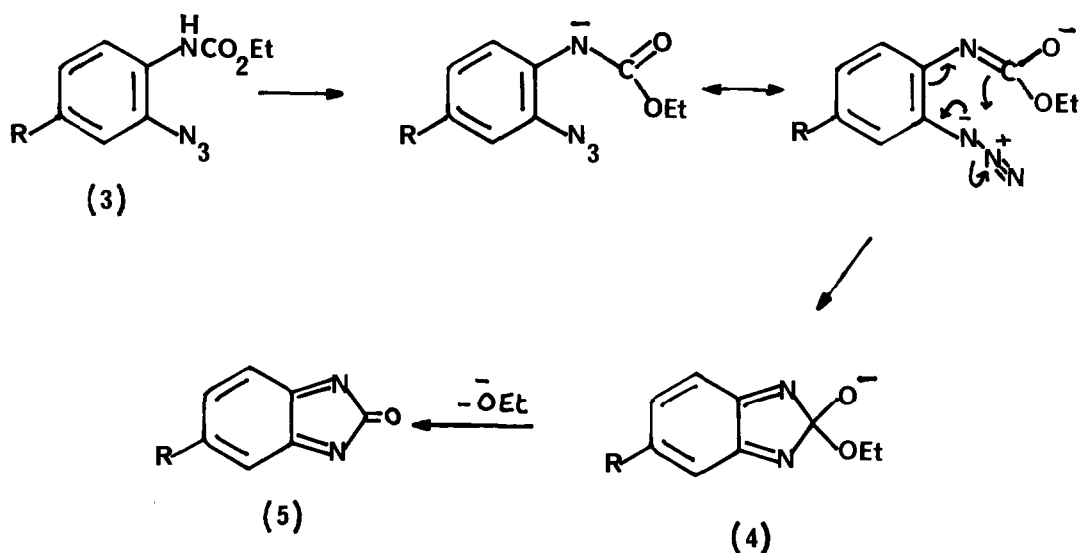


Scheme 1

As an extension to this work we have investigated the effect of base on ethyl N-(*o*-azidoaryl) carbamates (3) as a possible route to the hitherto unknown 2H-benzimidazol-2-ones (5) (Scheme 2).

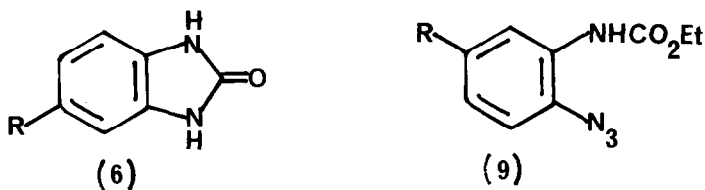
The carbamate (3; R = H)², prepared from *o*-azidoaniline³ and ethyl chloroformate in pyridine, with NaH in DMF at 70°C for 3 hours undergoes loss of nitrogen to give a mixture of products. Chromatographic separation (SiO₂) yielded 1,3-dihydrobenzimidazolone (6; R = H) (30%) m.p. 305°C; lit.⁴ 308°C; and an azo-compound (8; R = H) (35%), m.p. 176°C identical to that produced by thermolysis of the azido carbamate (3; R = H) in xylene.⁵

The moderate yield of azo-compound is surprising as generally azo-compound formation during the decomposition of aryl azides is indicative of nitrene participation⁶ and is not to



Scheme 2

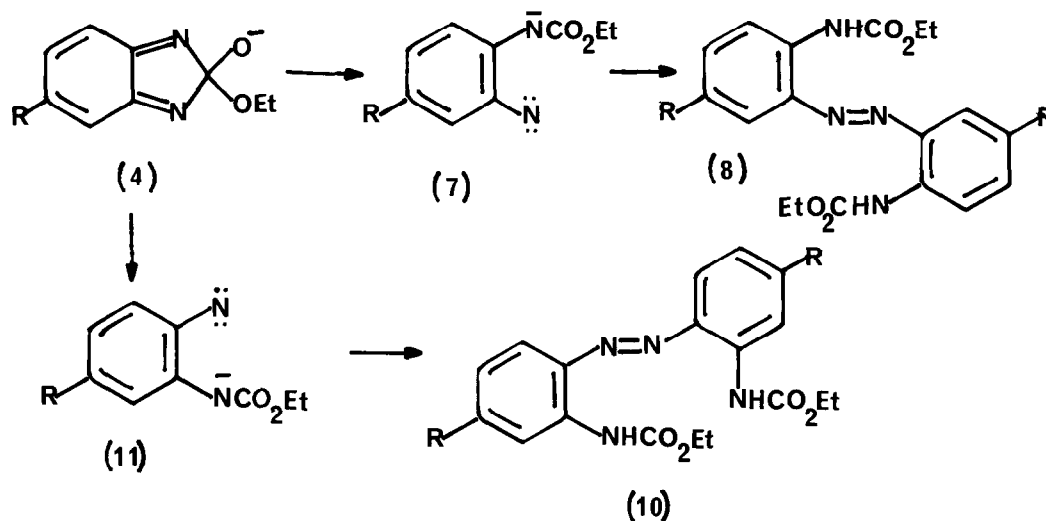
be expected at these relatively low reaction temperatures. In fact, we find that on heating the azidocarbamate in DMF at 70°C for several hours only a low yield (<5%) of azo-compound is produced.



A possible precursor of the azo-compound and the dihydrobenzimidazolone⁷ is the hemiacetal anion (4). Cleavage⁸ of the N-C bond would generate *o*-nitrenocarbamate (7; R = H) which, on dimerisation⁶ can yield azo-compound (8; R = H), or dihydrobenzimidazolone by hydrogen abstraction and cyclisation of the resulting ethyl *N*-(*o*-aminophenyl)carbamate.

It is apparent, however, that an intermediate of type (4; R = H) can give rise to two different nitrenes depending on which C-N bond is cleaved. As a result mixtures of azo-compounds are likely (Scheme 3). In order to check this possibility the isomeric chlorocarbamates (3 and 9; R = Cl) were decomposed separately in NaH-DMF to produce in each case the same azo-compound, m.p. 217°C in 18% and 16% yield respectively, along with the chlorobenzimidazolinone (6; R = Cl), m.p. 320°C (lit.⁹ 326°C). This azo-compound (8; R = Cl) proved

to be identical to that obtained by thermolysis of the *p*-chlorocarbamate (3; R = Cl) in boiling xylene. No product corresponding to the isomeric azo-compound (10; R = Cl; m.p. 236°C), prepared separately by thermolysis of the *m*-chlorocarbamate (9; R = Cl) could be detected (t.l.c. and h.p.l.c.) in the base-induced decomposition of carbamate (3; R = Cl).¹⁰



Scheme 3

A plausible explanation of this apparent regioselective ring-opening of (4) is that an electron-withdrawing chlorine at the *para* position destabilises the developing nitrene (11; R = Cl) but stabilises the carbamate anion (7; R = Cl). If this is so, then, an electron-donating substituent in azidocarbamate (3) should have the opposite effect and hence promote ring-opening to nitrenocarbamate (11). We find this to be so, with the *p*-tolyl carbamate (3; R = Me), which with NaH-DMF yields 5-methyl-1,2-dihydrobenzimidazolone (6; R = Me) m.p. 292°C; lit.⁴ 292°C and a 1:5 mixture of azo-compounds. Separation of the latter was tedious¹¹ but finally yielded two azo-compounds (m.p.'s 195°C and 199°C) identical to those obtained by thermolysis of the (azidotolyl) carbamates (3 and 9; R = Me). Significantly, the major isomer has structure (10; R = Me; m.p. 199°C) i.e. the azo-compound derived from the more stable nitrene (11; R = Me). The small amount of isomer (8; R = Me; m.p. 195°C) can again¹⁰ be accounted for by a competing thermal reaction.

Further work is in progress to confirm the intermediacy of a nitrene in these base induced decompositions and to investigate more fully the effects of substituents on the

reaction.

We thank S.E.R.C. for a research studentship to A.W.S.

References and Notes

1. M. Azadi-Ardakani and R.K. Smalley, *Tetrahedron Lett.*, 1979, 4765.
2. All new compounds gave satisfactory analysis and spectroscopic (i.r. ^1H n.m.r.) data.
3. J.H. Hall and E. Patterson, *J. Amer. Chem. Soc.*, 1967, 89, 5856 and references cited therein.
4. A. Hartmann, *Ber.*, 1890, 23, 1046.
5. W.A. Strachan, Ph.D. thesis, University of Salford, 1974.
6. The actual mode of formation of azo-compounds from aryl azides is still obscure; for a recent discussion see W.H. Waddell and N.B. Feilchenfeld, *J. Amer. Chem. Soc.*, 1983, 105, 5499.
7. This product could also arise by hydride ion reduction of (5).
8. The ring-opening of hemi-acetal anion (4) in preference to elimination of ^-OEt is reminiscent of the proposed stereo-electronic controlled ring-opening of similar systems as delineated by P. Deslongchamps, *Tetrahedron* 1975, 31, 2463 and recently confirmed by C.L. Perrin and G.M.L. Arrhenius, *J. Amer. Chem. Soc.*, 1982, 104, 2839.
9. W.B. Wright jnr., *J. Heterocycl. Chem.*, 1965, 2, 41.
10. A low yield (<4%) of azo-compound (10; R = Cl) m.p. 236°C was obtained from the base-induced decomposition of the *m*-chlorocarbamate (9; R = Cl). This is attributed to a competing thermal decomposition of the azide.
11. Separation was by t.l.c. ($\text{SiO}_2:\text{CH}_2\text{Cl}_2$) and then h.p.l.c.

(Received in UK 30 January 1984)