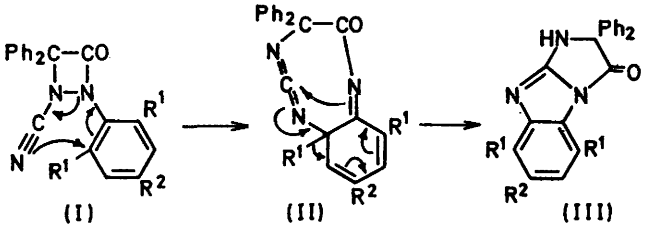
1,2-Halogen Migration accompanying a Sigmatropic Rearrangement

By C. W. BIRD

(*Department of Chemistry, Queen Elizabeth College, Campden Hill, London, W.8*)

Summary The 1,2-migration of halogen has been observed during the sigmatropic thermal rearrangement of certain diphenylketen–arenediazocyanide adducts.

THE ready thermal rearrangement of diphenylketen–arenediazocyanide adducts [*e.g.* (Ia)] to derivatives of the 1*H*-imidazo[1,2-*a*]benzimidazole ring system [*e.g.* (IIIa)] was reported several years ago.[1] In the course of carrying out a quantitative study of this transformation by differential scanning calorimetry it has been found that the 2,6-dichlorophenyldiazetidinone (Ib) is smoothly converted at 150° into the dichloroimidazobenzimidazole (IIIb) and 2,6-dichlorophenyl isocyanate. The expected *N*-cyanodiphenylketimine has not yet been isolated. The structure of (IIIb) is confirmed by its quantitative formation from the 2,5-dichloro-isomer of (Ib) at 120°. An analogous migration of bromine occurs in the conversion of (Ic) into (IIIc).



(a) $R^1 = H, R^2 = Cl$
(b) $R^1 = Cl, R^2 = H$
(c) $R^1 = R^2 = Br$

The mechanism originally suggested for this rearrangement and supported by the above-mentioned quantitative study, envisages an initial sigmatropic rearrangement of the diazetidinone to (II) with subsequent intramolecular cyclisation to (III). It now emerges that when the group R^1 in the intermediate (II) is halogen the substituent either migrates to the adjacent ring carbon atom with formation of (III), or that (II) fragments yielding the aryl isocyanate. The alternative genesis of the aryl isocyanate from direct thermal dissociation of the diazetidinone can probably be discounted, firstly on the grounds that closely related diazetidinones incapable of forming such an intermediate have far greater thermal stabilities, and secondly because little if any diphenylketen is formed, although it would be expected[2] to arise in any simple thermal dissociation of the diazetidinone.

Although halogen displacement has been encouraged in the Claisen rearrangement of allyl phenyl ethers, the foregoing conversions appear to be the first recorded examples of 1,2-halogen shifts in sigmatropic thermal rearrangements.

(*Received, October* 15*th*, 1969; *Com.* 1565.)

---

[1] C. W. Bird, *J. Chem. Soc.*, 1964, 5284; *Tetrahedron*, 1965, **21**, 2179.
[2] A. H. Cook and D. G. Jones, *J. Chem. Soc.*, 1941, 184.
[3] C. D. Hurd and C. N. Webb, *J. Amer. Chem. Soc.*, 1936, **58**, 2190; D. S. Tarbell and J. W. Wilson, *ibid.*, 1942, **64**, 1066.