

Thermal Carbenoid Insertion Reactions of Isocyanides

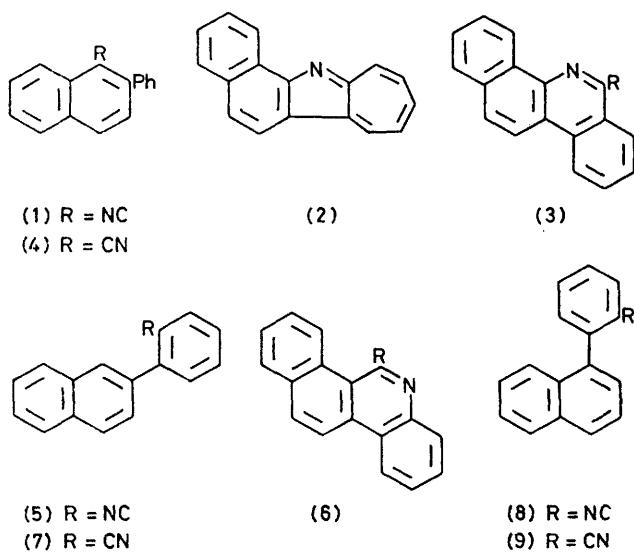
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Summary The thermal isomerisation, in *n*-tetradecane, of 1-isocyano-2-phenylnaphthalene into benzo[*g*]cyclohept[*b*]indole and benzo[*c*]phenanthridine and of 2-(2-isocyanophenyl)naphthalene into benzo[*i*]phenanthridine and the accompanying formation of tetradecylbenzophenanthridines by solvent participation reveal ground state isocyano carbenoid properties.

THE first examples of thermal insertion of a *C*-isocyano carbon atom into CC and CH bonds have been found in the isomerization of the isocyanonaphthalene (**1**) into the benzocycloheptindole (**2**) and benzophenanthridine (**3**; R = H) and of the isocyanophenylnaphthalene (**5**) into the benzophenanthridine (**6**; R = H). Each isocyanide also isomerised into the corresponding cyanide (**4**) or (**7**).†

† Each structural assignment is supported by i.r., u.v., and mass spectroscopic analyses and by n.m.r. and elemental analyses except for the phenanthridines (**3**) and (**6**) (R = C₁₄H₂₉) obtained in trace amounts. Identical spectroscopic and m.p. data were obtained for authentic samples of the indole (**2**) and the phenanthridines (**3**) and (**6**) (R = H). Mixed m.p.s were not depressed.



Products from each isocyanide (1), m.p. 94.5–95.5 °C, or (5), m.p. 116–117 °C, after being heated in refluxing (253 °C) n-tetradecane for 35 and 90 min respectively were isolated by silica gel column chromatography. The indole

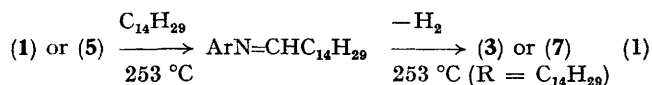
¹ C. W. Muth and E. S. Hanrahan, *J. Org. Chem.*, 1958, **23**, 395.

² G. M. Badger and J. A. Siedler, *J. Chem. Soc.*, 1954, 2329.

³ I. Ugi, 'Isonitrile Chemistry,' Academic Press, London, 1971, describes other reactions which can be attributed to a carbenoid isocyano carbon atom.

(2), m.p. 189–191 °C¹ (3%), the phenanthridine (3; R = H), m.p. 130–133 °C² (31%), and the naphthalene (4), m.p. 118–119 °C (35%), were obtained from the isocyanide (1). The phenanthridine (6; R = H), m.p. 178–180 °C (3%) and the naphthalene (7), m.p. 110–112 °C (15%) were obtained from the isocyanide (5). Trace amounts of the phenanthridines (3; R = C₁₄H₂₉) and (6; R = C₁₄H₂₉) (oils) were also detected by n.m.r. and mass spectroscopy.¹ After similar treatment the isocyanophenylnaphthalene (8), m.p. 82.5–83 °C, rearranged into the cyanophenyl-naphthalene (9), m.p. 122–123 °C (56%).

These insertion reactions reveal that the isocyanides (1) and (5) undergo ground-state electrophilic carbenoid reactions.³ It is assumed that the phenanthridines (3) and (6) (R = C₁₄H₂₉) were dehydrogenated electrocyclic products from intermediate imines which were, in turn, the result of intermolecular insertion of the appropriate isocyano carbon into a tetradecane CH bond [reaction (1)].



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