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*]phenathridine 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**).†

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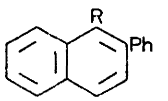
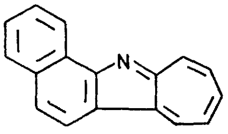
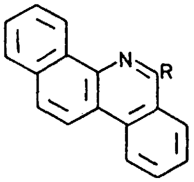
† Each structural assignment is supported by i.r., u.v., and mass spectroscopic analyses and by n.m.r. and elemental analyses except for the phenanthridines (**3**) and (**6**) (R = $C_{14}H_{29}$) obtained in trace amounts. Identical spectroscopic and m.p. data were obtained for authentic samples of the indole (**2**) and the phenanthridines (**3**) and (**6**) (R = H). Mixed m.p.s were not depressed.



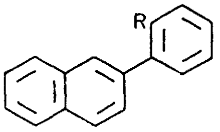
(1) R = NC
(4) R = CN



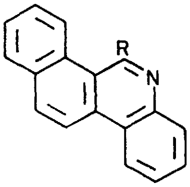
(2)



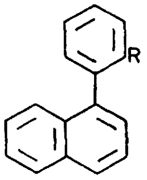
(3)



(5) R = NC
(7) R = CN



(6)



(8) R = NC
(9) R = CN

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 (**2**), m.p. 189—191 °C[1] (3%), the phenanthridine (**3**; R = H), m.p. 130—133 °C[2] (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 = $C_{14}H_{29}$) and (**6**; R = $C_{14}H_{29}$) (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 cyanophenylnaphthalene (**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 = $C_{14}H_{29}$) 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)].

$$(\mathbf{1}) \text{ or } (\mathbf{5}) \xrightarrow[253\ ^\circ\text{C}]{C_{14}H_{29}} \text{ArN=CHC}_{14}\text{H}_{29} \xrightarrow[253\ ^\circ\text{C}\ (\text{R} = C_{14}H_{29})]{-H_2} (\mathbf{3}) \text{ or } (\mathbf{7}) \qquad (1)$$

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[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.