Photo-isomerization of Biphenyl-2-yl Isocyanide into Phenanthridine

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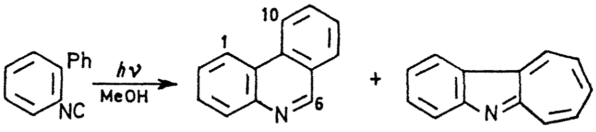
Summary In methanol photo-isomerization of biphenyl-2-yl isocyanide (**1**) requires solvent interaction for the formation of the predominant product phenanthridine (**2**) but not for the minor product cyclohept[*b*]indole (**3**).

In a new photo-isomerization biphenyl-2-yl isocyanide (**1**) is transformed into phenanthridine (**2**). The reaction is very efficient in methanol and requires solvent participation, presumably *via* hydrogen bonding. A competitive but less efficient isomerization affords cyclohept[*b*]indole (**3**) without solvent participation.[1] In cyclohexane (**3**) (62%) but no (**1**) is produced. These are apparently excited state isomerizations since (**1**) in refluxing diphenyl ether, at *ca.* 250°, rapidly isomerizes quantitatively into 2-cyanobiphenyl.

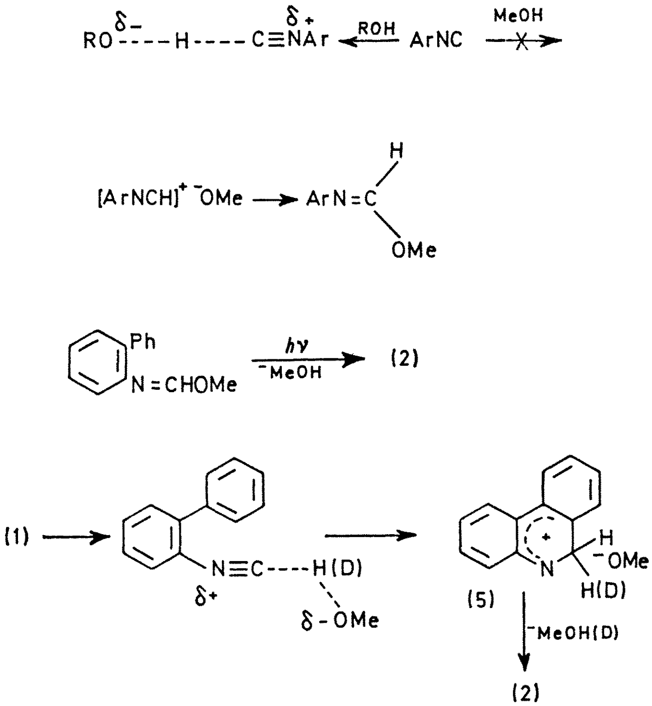


(1) (2) (3)

A solution of biphenyl-2-yl isocyanide (**1**) (6 mmol) in dry MeOD† (400 ml) was flushed with dry nitrogen for 3 h. The solution was irradiated for 64 h at 254 nm in a Rayonet Photochemical Reactor equiped with 16 low-pressure mercury lamps. After removal of solvent, chromatographic separation of the residue (silica gel) gave unchanged

† Greater than 99% isotope purity.

isocyanide [53·6%; eluted with n-hexane–benzene (3:2)], partially deuteriated phenanthridine [29·1%; benzene–chloroform (1:3)], and compound (**3**) (8·2%; chloroform).‡ Phenanthridine sublimed (85—90° at 0·1 mm Hg) as a colourless solid, m.p. and mixed m.p. 103·5—105° (lit.[2] 104°); ν_{max} ($CHCl_3$) 2220 cm^{-1} (6-^{2}H); δ ($CDCl_3$) 9·22 (0·5 H, s, 6-H), 8·50 2H, m, 1,10-H), and 8·28—7·45 (6H, m). Comparison of integrated n.m.r. peak areas for 6-H and for 1,10-H in samples of unlabelled phenanthridine with those for (**2**) partially deuteriated at the 6-position gave D/H = 1·23 ± 0·16 for the 6-position. A plot of peak heights for M^+ at m/e 180 *vs.* m/e 179 (obtained from a solid sample) gave a straight line with a slope of 1·24.§ After natural abundance isotope correction,[3] the ratio D:H was 1·09 (assigned to the 6-position as required by the above n.m.r. data).



Irradiation in MeOH rather than MeOD, for a shorter time, of the isocyanide gave a higher yield of phenanthridine and a lower yield of the indole (**3**). After irradiation for 2·0 and for 3·5 h in each solvent, the average amount of phenanthridine formed (g.l.c.) in methanol was 1·65 ± 0·07 times the amount formed in [^{2}H]methanol, and the yield was the same for both irradiation times. Instability of the indole (**3**) in methanol on prolonged irradiation was shown by g.l.c. and i.r. While the products were not identified, the formation of phenanthridine and acridine could not be detected.[4]

For partial substitution of hydrogen by deuterium in the 6-position of phenanthridine, solvent participation, presumably by hydrogen bonding to the excited isocyanide (**1**), is required. The hydrogen bonding between an alcohol and isocyano-carbon has been measured by i.r. absorption.[5] The difference of 127 cm^{-1} between the absorption for free methanol at 3635 cm^{-1} and that for (**1**) hydrogen bonded to methanol is in agreement with values for other isocyanide–alcohol systems.

Representations of an isocyanide in the ground state hydrogen bonded to an alcohol have shown separation of ions.[6] This is incorrect since in methanol this would lead to methyl formimidate which is not formed. A better representation shows hydrogen with partial covalent bonds to both oxygen and carbon.

Irradiation at 254 nm quantitatively transforms the formimidate (**4**) into phenanthridine in cyclohexane. Since there is no substitution of deuterium for hydrogen in the product in MeOD, the formimidate ester cannot be an intermediate in the transformation (**1**) → (**2**). It is significant that the product did not exchange hydrogen for deuterium from the solvent.

Since isomerization in the absence of hydrogen bonding transforms (**1**) into (**3**), it is assumed that cyclization must be concerted with or follow hydrogen bonding. Indole could not be detected in the unidentified mixture obtained by the irradiation of *o*-tolyl isocyanide in methanol. The apparent lack of isocyano-carbenoid insertion into a C–H bond of the adjacent methyl group confirms the absence of cyclization from (**1**) *via* isocyano-carbenoid insertion into the *o*-C–H bond. Further bond development at carbon with ultimate separation from oxygen of the methanolic hydrogen apparently controls the faster formation of phenanthridine in methanol. Hydride transfer, concerted with or following cyclization, generates an intermediate (**5**) from which hydrogen and deuterium compete for separation from the same ring-carbon atom.

We thank NASA for a grant.

(*Received, May* 10*th*, 1971; *Com.* 738.)

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‡ Yields are based on recovered isocyanide. Compounds were identified by comparison of R_T and R_F values, i.r., mass, and u.v. spectra with corresponding data for authentic samples.

§ The slope was determined from 13 points by a TR 4 computer using the method of least squares. We thank the Rekencentrum of the University, Groningen (The Netherlands) for assistance.

[1] J. H. Boyer and J. de Jong, *J. Amer. Chem. Soc.*, 1969, **91**, 5929.

[2] A. Pictet and H. J. Ankersmit, *Ber.*, 1889, **22**, 3340. C. E. van der Donckt, R. H. Martin, and F. Geerts-Evrard, *Tetrahedron*, 1964, **20**, 1500, reported δ (CCl_4) 9·06 (s, 6-H) and 8·43 (m, 1,10-H).

[3] An isotope correction on m/e 180 due to m/e 179 for thirteen carbon atoms and one nitrogen was made; see J. H. Beynon, "Mass Spectrometry and its Applications to Organic Chemistry", Elsevier, Amsterdam, 1960, p. 555.

[4] M. Comtet and H. D. Mettee, *Mol. Photochem.*, 1970, **2**, 63, describe the photo-isomerization of azulene into naphthalene.

[5] L. L. Ferstandig, *J. Amer. Chem. Soc.*, 1962, **84**, 1323, 3553; P. von R. Schleyer and A. Allerhand, *J. Amer. Chem. Soc.*, 1962, **84**, 1322; *ibid.*, 1963, **85**, 866.

[6] L. L. Ferstandig, *J. Amer. Chem. Soc.*, 1962, **84**, 3555.