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PHOTOCHEMICAL N-α-CYANOETHYLATION OF SOME NH-HETEROCYCLES[1]

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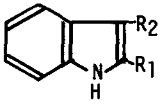
The conjugate addition of anions to acrylonitrile enables convenient synthesis of 3-substituted propionitriles (β-cyanoethylation).[2] In contrast to this, it has been reported that aromatic hydrocarbons[3] and heteroaromatic compounds such as imidazoles[4] or indoles[5] undergo facile photochemical reaction with acrylonitrile to yield the corresponding C-α-cyanoethylated products via exiplex formation. We now wish to report that irradiation of some NH-heterocycles such as indoles, benzimidazole, or carbazole in polar solvents give the corresponding N-α-cyanoethylated products,thus providing a convenient method for the N-α-cyanoethylation of NH-heterocycles.

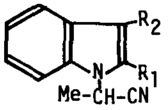
In a typical experiment, when a solution of indole (1a) (3×10^{-2}M) and acrylonitrile (0.3M) in acetonitrile was irradiated with a 200 W medium-pressure mercury lamp under nitrogen atomosphere, 1-(2-cyanoethyl)-indole (2a) (8%)[6] was obtained as an oil by preparative tlc, together with 3-(2-cyanoethyl)-indole (12%) which has been reported earlier[5]. Under similar conditions, 3-methylindole (1b) gave the corresponding N-cyanoethylated product 2b[6] in 41 % yield. It should be noted that in methanol 1a and 1b only gave the corresponding C-α-cyanoethylated products.[5]

On the other hand, irradiation of 2,3-disubstituted indoles (1c, 1d), benzimidazole (3) and carbazole (4) in methanol gave the corresponding N-α-cyanoethylated product 2c[6](5 %), 2d[6](8 %), 5[6](10 %) and 6[6] (8 %),respectively, as the only isolable product. Irradiation of these compounds in acetonitrile gave essentially the same results as those obtained in methanol. The poor yields of these reactions can be ascribed to the concurrent polymerization of acrylonitrile.

These photocyanoethylations may be best explained by a mechanism involving exiplex formation as has been reported earlier.[5]

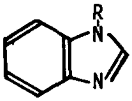


1a,b,c,d

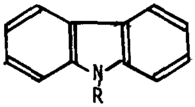


2a,b,c,d

a; $R_1=R_2=H$
b; $R_1=H$, $R_2=Me$
c; $R_1=R_2=Me$
d; $R_1=R_2=-CH_2-CH_2-$



3; R=H
5; R=-CH(Me)-CN



4; R=H
6; R=-CH(Me)-CN

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6. Satisfactory elemental analyses and the expected ir, uv and mass spectra were obtained for all new compounds. 2a; δ $(CDCl_3)$ 1.92 (d, 3H, J=7Hz), 5.30 (q, 1H, J=7Hz), 6.55 (d, 1H, J=3Hz), 7.08~7.73 (m, 5H). 2b; mp 61° ; δ$(CDCl_3)$ 1.87 (d, 3H, J=7Hz), 2.35 (s, 3H), 5.36 (q, 1H, J=7Hz), 7.03 (s, 1H), 7.20~7.73 (m, 4H). 2c; δ $(CDCl_3)$ 1.51 (d, 3H, J=7Hz), 2.20 (s, 3H), 2.35 (s, 3H), 5.24 (q, 1H, J=7Hz), 7.00~7.50 (m, 4H). 2d; mp 54-56° ;δ $(CDCl_3)$ 1.78 (d, 3H, J=7Hz), 1.93 (m, 4H), 2.72 (m, 4H), 5.30 (q, 1H, J=7Hz), 7.00~7.50 (m, 4H). 5; δ $(CDCl_3)$ 1.92 (d, 3H, J=7Hz), 5.42 (q, 1H, J=7Hz), 7.20~7.50 (m, 3H), 7.69~7.92 (m, 1H), 8.04 (s, 1H). 6 ; mp 103°; δ $(CDCl_3)$ 1.80 (d, 3H, J=7Hz), 5.60 (q, 1H, J=7Hz), 7.08~7.45 (m, 6H), 8.00~8.12 (m, 2H).