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Photoinitiated Substitution Reactions of Heterocyclic Bases: Reaction with Alkenes

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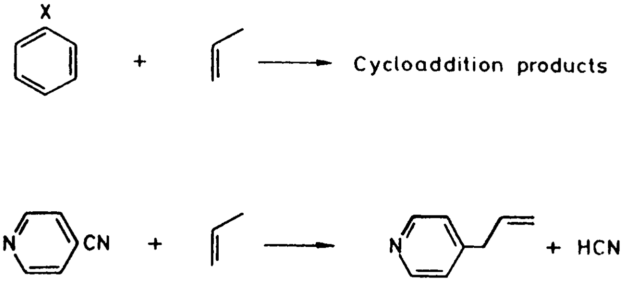
A method is described for the synthesis of allyl heterocyclic bases by a photoinduced substitution reaction of cyano-heterocyclic bases and certain alkenes.

THE photochemical reactions of heteroaromatic bases with alkenes are not well known. Recently we reported that when a solution of pyridine-4-carbonitrile and quinoline-2-carbonitrile in 2,3-dimethylbut-2-ene is irradiated a photoinitiated substitution reaction occurs leading to the formation of two isomeric 4-allylpyridines and 2-allylquinolines.[1] This reaction interested us considerably since under similar condition classical aromatic systems such as benzene yield instead photocycloaddition products.[2] The reaction, furthermore, appears to be a general synthetic route for the preparation of allyl heteroaromatic bases (Scheme).



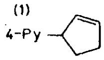
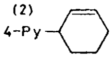
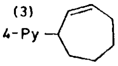
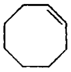
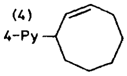
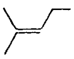
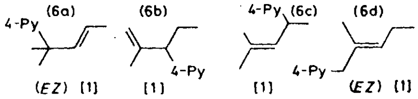
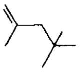
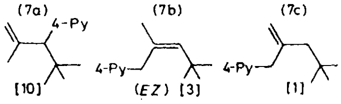
SCHEME

In order to establish the scope and synthetic value of this reaction, solutions of 4-cyanopyridine and cyclic or polysubstituted alkenes in acetone were irradiated at 254 nm. A summary of the results obtained is given in Table 1 and the spectroscopic data and elemental analyses of the products are reported in Table 2. In all cases 4-allylpyridines were obtained as the major or sole products. Cyclic alkenes led to only one photosubstitution product while polysubstituted alkenes led to mixtures containing all possible isomeric 4-allylpyridines. Furthermore it was found that hex-1-ene, hex-2-ene, and vinylcyclohexane do not react under these conditions.

With the aim of generalizing this new photochemical reaction, a range of different cyanoheteroaromatic bases were irradiated under the same reported general conditions in the presence of cyclohexene or 2,3-dimethylbut-2-ene. The results are reported in Table 3 and the spectroscopic data and elemental analyses of the products are reported in Table 4. In these cases also, only photosubstitution products were obtained. It is interesting to note that the irradiation of 4-cyanoquinoline and 1-cyanoisoquinoline with 2,3-dimethylbut-2-ene leads to only one isomer, probably owing to steric hindrance of the *peri*-hydrogen. For the reactions with the lower yields, the solutions darkened after being irradiated for a few minutes; working in much more dilute solutions gave better results.

TABLE 1

Reactions between 4-cyanopyridine and alkenes

Alkene	Products (relative ratio)	Yield (%)
	(1) 	49
	(2) 	45
	(3) 	23
	(4) 	17
	(5a) [2] (5b) [1] 	67
	(6a) (*EZ*) [1] (6b) [1] (6c) [1] (6d) (*EZ*) [1] 	60
	(7a) [10] (7b) (*EZ*) [3] (7c) [1] 	14

Although it is rather premature to speculate on the mechanism, some general statements may be made. One mechanism that was initially considered by us was alkylation originating through an allyl-hydrogen photoabstraction from the olefins by the excited heterocyclic base. This would be followed by cross coupling of the cyanopyridyl radical thus formed, with the delocalized alkenyl radicals and elimination of HCN.[3] In this mechanism, the reactivity of the alkenes should depend

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TABLE 2

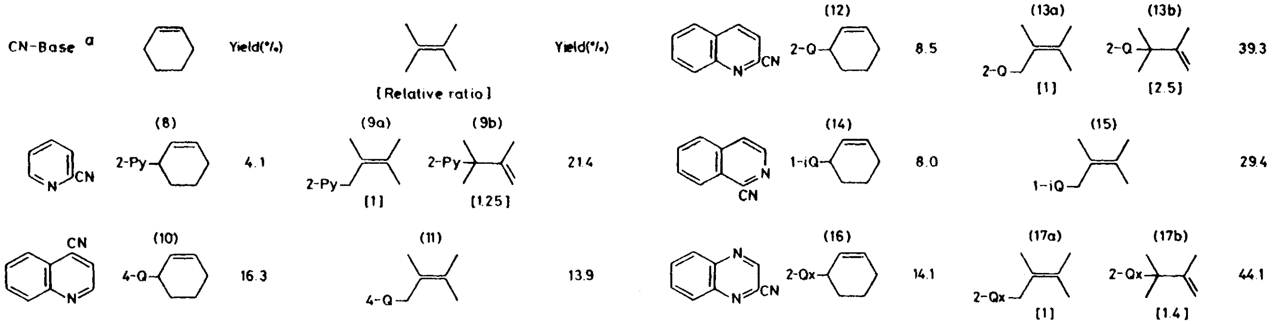
Spectroscopic data and elemental analyses for compounds (1)—(7)

Cmpd.[a]	m/e	^{1}H N.m.r. (δ)	Found (%) [Required (%)] C	H	N
(1)	145, 133, 120, 95, 78, 67	8.5 (dd, H_A and H_B, J_{AC} = J_{BD} = 4.5 Hz, J_{AB} = 1.8 Hz), 7.15 (dd, H_C and H_D, J_{CA} = J_{DB} = 4.5 Hz, J_{CD} = 1.8 Hz), 5.95 and 5.75 (2 m, 2 H, CH=CH], 3.87br (1 H, CHpy), 2.42br (4 H, [CH_2]$_2$)	82.6 [82.72]	7.75 [7.64]	9.7 [9.65]
(2)	159, 144, 130, 117, 105, 91, 78	8.5 (dd, H_A and H_B), 7.13 (dd, H_C and H_D), 5.91br and 5.61br (2s, 2 H CH=CH), 3.32 (m, 1 H, CHpy), 2.08 and 1.65 (2 m, 6 H [CH_2]$_3$)	83.15 [82.97]	8.15 [8.23]	8.65 [8.80]
(3)	173, 159, 145, 130, 117, 105, 91, 81, 78	8.5 (dd, H_A and H_B), 7.19 (dd, H_C and H_D), 5.82br (s, 2 H, CH=CH), 3.51 (m, 1 H, CHpy), 2.23 and 1.80 (2 m, 8 H, [CH_2]$_4$)	83.1 [83.19]	9.1 [8.73]	7.8 [8.09]
(4)	187, 172, 158, 144, 130, 118, 105, 91	8.51 (dd, H_A and H_B), 7.19 (dd, H_C and H_D), 5.66br (s, 2 H, CH=CH), 3.75 (m, 1 H, CHpy), 2.24 and 1.68 (2 m, 10 H [CH_2]$_5$)	83.5 [83.35]	8.85 [9.15]	7.6 [7.48]
(5a)	161, 146, 131, 117, 93, 77	8.5 (dd, H_A and H_B), 7.08 (dd, H_C and H_D), 3.4 (s, 2 H, CH_2Py), 1.75 (s, 6 H), 1.58 (s, 3 H)	82.3 [81.93]	9.2 [9.38]	8.55 [8.69]
(5b)	161, 146, 131, 120, 92, 77	8.5 (dd, H_A and H_B), 7.25 (dd, H_C and H_D), 4.97 (d, 2 H, CH_2=C), 1.51 (s, 3 H), 1.45 (s, 6 H)	81.6 [81.93]	9.15 [9.38]	8.25 [8.69]
(6a)	161, 146, 131, 117, 106, 91	8.5 (dd, H_A and H_B), 7.22 (dd, H_C and H_D), 5.75br [s, CH=CH (*E* + *Z*)], 1.71 (1.65) (s, 3 H, CH_3C=), 1.39 [s, 6 H, (*E* + *Z*)-(CH_3)$_2$CPy]	81.7 [81.93]	9.45 [9.38]	8.8 [8.69]
(6b)	161, 146, 132, 117, 106, 91	8.53 (dd, H_A and H_B), 7.15 (dd, H_C and H_D), 4.91br (s, 2 H, CH_2=C), 3.1 (t, 1 H C*H*pyCH_2, *J* 7.5 Hz), 1.65 (m, 2 H, CHC*H*$_2$$CH_3$, *J* 7.5 and 7.2 Hz), 0.90 (t, 3 H, C*H*$_3$$CH_2$, *J* 7.2 Hz)	82.05 [81.93]	9.2 [9.38]	8.8 [8.69]
(6c)	161, 146, 131, 117, 104, 91	8.5 (dd, H_A and H_B), 7.22 (dd, H_C and H_D), 5.21 (d, 1 H =C*H*–CHpy, *J* 9 Hz), 3.61 (m, 1 H, CH–C*H*py–CH_3, *J* 9 and 6.9 Hz), 1.7 (s) and 1.64 (s) [6 H, (CH_3)$_2$C=], 1.3 (d, 3 H, C*H*$_3$CHPy, *J* 6.9 Hz)	82.15 [81.93]	9.15 [9.38]	8.7 [8.69]
(6d)	161, 146, 144, 130, 117, 91, 69	8.53 (dd, H_A and H_B), 7.15 (dd, H_C and H_D), 5.55 [t, 1 H, =C*H*CH_2 (*E* + *Z*), *J* not determined] ,3.35 (3.25) (s, 2 H, CH_2Py), 2.05 [m, 2 H, =CHC*H*$_2$$CH_3$ (*E* + *Z*), one *J* not determined, other *J* 6 Hz], 1.35 (1.51) (s, 3 H, CH_3C=), 0.98 (0.97) (t, 3 H, C*H*$_3$$CH_2$, *J* 6 Hz)	81.6 [81.93]	9.4 [9.38]	8.9 [8.69]
(7a)	189, 174, 159, 144, 132, 117, 97	8.5 (dd, H_A and H_B), 7.12 (dd, H_C and H_D), 4.9br (s, 2 H, CH_2=C), 3.4 (s, 1 H, CHPy), 1.9 (s, 3 H, CH_3C=), 1.2 (s, 9 H, Bu^t)	82.6 [82.48]	10.4 [10.12]	7.7 [7.40]
(7b)	189, 133, 132, 93	8.5 (dd, H_A and H_B), 7.12 (dd, H_C and H_D), 5.45 (5.38) (s, 1 H, CH=C), 3.55 (3.22) (s, 2 H, CH_2Py), 1.55 (1.65) (s, 3 H, CH_3C=), 1.2 [s, 9 H, Bu^t (*E* + *Z*)]	82.6 [82.48]	10.2 [10.12]	7.7 [7.40]
(7c)[c]	189, 174, 135, 105, 93				

[a] All products are oils. [b] For solutions in $CDCl_3$. H_A, H_B, H_C, H_D refer respectively to the hydrogen atoms at positions 2, 6, 3, and 5 of the pyridine ring. J_{AC}, J_{BD}, J_{AB}, and J_{CD} values are reported only for the first product; in all the other cases the values are the same and are not further reported. In the case of *E* and *Z* isomers the n.m.r. values are reported for one isomer with those for the other isomer in parentheses; no attempt was made to identify the isomers. [c] This compound was not isolated. Its presence was checked by g.l.c.–mass spectrometry. The reported structure is only tentative.

TABLE 3

Reactions of cyano-bases with cyclohexene and tetramethylethylene



[a] In Tables 3 and 4, the heterocyclic bases are reported as: pyridine = Py, quinoline = Q, isoquinoline = iQ, and quinoxaline = Qx

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TABLE 4

Spectroscopic data and elemental analyses for compounds (8)—(17)

Cmpd.[a]	m/e	^{1}H N.m.r. (δ)[b]	Found (%) [Required (%)]		
			C	H	N
(8)	159, 158, 144, 130, 117, 93, 78	8.55 (t, $J_{6,5}$ 5 Hz, 1 H, H-6), 7.61 and 7.26 (2 m, 3 H, H-3, H-4, H-5), 5.82br (s, 2 H, CH=CH), 3.58br (s, 1 H, CHPy), 2.04br and 1.69br (2 s, 6 H $-[CH_2]_3-$)	82.75 [82.97]	8.1 [8.23]	8.85 [8.80]
(9a)	161, 160, 146, 131, 117, 93	8.52 (dd, 1 H, H-6, $J_{6,5}$ 4.8, $J_{6,4}$ 1.8 Hz), 7.54 and 7.11 (2 m, 3 H, H-3, H-4, H-4), 3.61 (s, 2 H, CH_2Py), 1.79 (6 H, s), and 1.65 (3 H, s) (3 CH_3)	81.75 [81.93]	9.25 [9.38]	8.45 [8.69]
(9b)	161, 160, 146, 131, 120, 93	8.6 (dd, 1 H, H-6, $J_{6,5}$ 5 Hz, $J_{6,4}$ 1.8 Hz), 7.61 and 7.19 (2 m, 3 H, H-3, H-4, H-5), 5.02 and 4.96 (2 s, 2 H, CH_2=), 1.56 (3 H, s) and 1.50 (6 H, s) (3 CH_3)	82.1 [81.93]	9.15 [9.38]	8.35 [8.69]
(10)	209, 208, 194, 180, 164, 143, 128	8.86 (d, 1 H, H-2, $J_{2,3}$ 4.5 Hz), 8.12 and 7.68 (2 m, 4 H, H-5, H-6, H-7, H-8), 7.30 (d, 1 H, H-3 $J_{3,2}$ 4.5 Hz), 5.8br (s, 2 H, CH=CH), 4.21br (s, 1 H, CHQ), 2.22br and 1.69br (2 s, 6 H, $-[CH_2]_3-$)	85.85 [86.08]	7.3 [7.22]	6.45 [6.69]
(11)	211, 210, 196, 181, 170, 143, 128	8.85 (d, 1 H, H-2, $J_{2,3}$ 4.5 Hz), 8.11 and 7.63 (m, 4 H, H-5, H-6, H-7, H-8), 7.17 (d, 1 H, H-3 $J_{3,2}$ 4.5 Hz), 3.83 (s, 2 H, CH_2Q), 1.82, 1.77, and 1.67 (3 s, 9 H, 3 CH_3)	85.35 [85.26]	8.05 [8.11]	6.5 [6.63]
(12)	209, 208, 194, 180, 164, 143, 129	8.08 (m, 2 H, H-4, H-8), 7.83 and 7.25 (m, 4 H, H-5, H-6, H-7, H-3), 5.91br (s, 2 H, CH=CH), 3.78br (s, 1 H, CHQ), 2.0br and 1.72br (2 s, 6 H, $-[CH_2]_3-$)	86.25 [86.08]	7.35 [7.22]	6.60 [6.69]
(13a)	211, 210, 196, 181, 170, 154, 143, 128	8.19 and 7.99 (m, 2 H, H-4, H-8), 7.90 and 7.19 (m, 4 H, H-5, H-6, H-7, H-3), 3.77 (s, 2 H, CH_2Q) 1.82, 1.77, and 1.67 (3 s, 9 H, 3 CH_3)	85.4 [85.26]	7.95 [8.11]	6.45 [6.63]
(13b)	211, 196, 181, 170, 154, 143, 128	8.18 and 8.08 (m, 2 H, H-4, H-8), 7.90 and 7.32 (m, 4 H, H-5, H-6, H-7, H-3), 5.07 and 4.98, (s, 2 H, CH_2=), 1.57 (s, 9 H, 3 CH_3)	85.45 [85.26]	8.25 [8.11]	6.45 [6.63]
(14)	209, 208, 194, 180, 167, 154, 143, 127	8.52 (d, 1 H, H-3, $J_{3,4}$ 6 Hz), 8.36—7.35 (m, 5 H, aromatic), 5.98br (s, 2 H, CH=CH), 4.41br (s, 1 H, CHiQ), 2.20br and 1.85br (2 s, 6 H, $-[CH_2]_3-$)	85.9 [86.08]	7.35 [7.22]	6.5 [6.69]
(15)	211, 196, 181, 167, 154, 143, 128	8.47 (d, 1 H, H-3, $J_{3,4}$ 6 Hz), 8.25—7.40 (m, 5 H, aromatic), 4.12 (s, 2 H, CH_2iQ), 1.84, 1.73, and 1.50 (s, 9 H, 3 CH_3)	85.45 [85.26]	8.25 [8.11]	6.8 [6.63]
(16)	210, 209, 195, 181, 169, 156, 144, 129	8.82 (s, 1 H, H-3), 8.12 (m, 2 H, H-5, H-8), 7.71 (m, 2 H, H-6, H-7), 5.96br (s, 2 H, CH=CH), 3.86br (s, 1 H, CHQx), 2.2br and 1.82br (2 s, 6 H, $-[CH_2]_3-$)	80.15 [79.97]	6.55 [6.71]	13.1 [13.32]
(17a)	212, 211, 197, 182, 169, 144, 129	8.71 (s, 1 H, H-3), 8.09 (m, 2 H, H-5, H-8), 7.70 (m, 2 H, H-7), 3.81 (s, 2 H, CH_2Qx), 1.89, 1.75, and 1.70 (3 s, 9 H, 3 CH_3)	79.4 [79.21]	7.45 [7.60]	13.3 [13.20]
(17b)	212, 197, 182, 171, 157, 144, 129	8.86 (s 1 H, H-3), 8.12 (m, 2 H, H-5, H-8), 7.73 (m, 2 H, H-6, H-7), 5.10 and 5.05 (2 s, 2 H, CH_2=), 1.64 (s, 9 H, 3 CH_3)	79.45 [79.21]	7.35 [7.60]	13.2 [13.20]

[a] All products are oils. [b] For solutions in $CDCl_3$.

on the bond-dissociation energy of the allylic hydrogen atom(s). Our results seem to exclude this possibility. Furthermore, we were not able to detect signals when the reactions were carried out in the e.s.r. cavity at low temperature. In another observation no bands corresponding to a charge-transfer complex were observed in the u.v. spectrum.

It is conceivable that this reaction proceeds by way of an exciplex between the alkene and the excited base. Studies are now in progress to check this possibility and to study the scope and limitations of the reaction.

EXPERIMENTAL

General Procedure.—A mixture of the cyano-base (1 mmol), acetone (2 ml), and the alkene (5 mmol) in a quartz reaction vessel was subjected to three freeze–vacuum–thaw cycles. The samples were then irradiated under nitrogen at 254 nm for 18 h in an RPR-100 Rayonet photochemical reactor. The solvent was removed under reduced pressure and the residue was chromatographed on a Jobin Yvon Chromatospac Prep instrument using Merck silica gel HF_{254} (TyP60) and hexane–ethyl acetate (9 : 1 v/v) as eluant. Evaporation of the solvent in the appropriate fractions gave the product(s) as oil(s). In the case of a complex mixture, separation was achieved with a Waters LiquiPrep instrument using hexane–ethyl acetate (9 : 1 v/v) and 0.5% isopropyl alcohol solvents. Gas chromatographic analyses were performed on a Hewlett–Packard 5750 gas chromatograph using a 2-m glass column (i.d. 2 mm) packed with 5% SP-1000 on 100/120 Supelcoport. Temperature programming from 110 to 220 °C (6 °C min^{-1} after the first minute) was used with a 2-m glass column (i.d. 2 mm) packed with 3% OV-225 on Chrom.w DMCS 100/120.

G.l.c.–mass spectral analyses were performed on a Perkin-Elmer model 270 instrument modified in the interface zone. The conditions used for g.l.c. were the same as those reported above. Mass spectra were taken using an electron energy of 70 eV with a filament emission of 80 mA and a source and interface temperature of 250 °C. N.m.r. spectra were recorded with a Varian EM 390 90-MHz spectrometer and chemical shifts are recorded as p.p.m. (δ) relative to internal Me_4Si.

[0/657 *Received*, 6*th May*, 1980]

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