Furopyridines. XVIII [1]. Photocycloaddition of Furo[2,3-*c*]pyridin-7(6*H*)-one with Acrylonitrile

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The photocycloaddition of furo[2,3-*c*]pyridin-7(6*H*)-one (**1**) and its *N*-methyl derivative (**1-Me**) to acrylonitrile has been studied. The structures of the photoadducts isolated by colum chromatography were determined by the nuclear magnetic resonance spectroscopy and single crystal X-ray analysis. The cycloaddition of **1** afforded an adduct **2** at the carbonyl oxygen and 8-cyano-8,9-dihydrofuro[*d*]azocin-7(6*H*)-one (**3**), and the addition of **1-Me** the *N*-methyl derivative **3-Me** of **3**, (9*S**)-9-cyano-6-methyl-3a,7a-dihydro-3a,7a-ethanofuro[2,3-*c*]pyridin-7(6*H*)-one (**4**), (2*S**, 2a*R**, 7b*R**)- (**5**) and (1*R**, 2a*S**, 7b*S**)-2-cyano-3-methyl-4-oxo-1,2,2a,3,4,7b-hexahydrocyclobuta[*e*]furo[2,3-*c*]pyridine (**6**).

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In continuation of our interest in the chemistry of furopyridines, we had reported the syntheses and chemical properties of the furopyridine derivatives having substituents at the 2- and/or 3-position [2]. In order to extend our chemical studies of furopyridines, we planned the photo-[2+2]cycloaddition of furopyridines to prepare new heterocycles and to see the effect of the furan ring upon the regio- and stereoselectivity of the addition. In the previous paper [3], we reported the cycloaddition of furo[3,2-*c*]-pyridin-4(5*H*)-one to acrylonitrile. In this paper, we describe the photo[2+2]cycloaddition of furo[2,3-*c*]pyridin-7(6*H*)-one (**1**) [4] and its *N*-methyl derivative **1-Me** with acrylonitrile.

Irradiation of **1** (1.0 mmole) in methanol (200 ml) containing large excess of acrylonitrile (100 mmoles) by high pressure mercury lamp (400 w, Pyrex filter) until disappearance of the starting furopyridone afforded a mixture of addition products. The mixture was chromatographed on a silica gel column to isolate two crystalline compounds **2** (mp 91-93°) (4.3%) and **3** (mp 236-239°) (13%). The structure of **2** was determined by its elemental analysis and its ir and nmr spectra. The elemental analysis indicated the molecular formula $C_{10}H_8N_2O_2$. The ir spectrum showed no carbonyl and NH absorption but an absorption of cyano group at 2245 cm^{-1} (very weak). The ^1H-nmr exhibited signals of eight protons. Two doublets at 7.90 and 7.20 ppm (J = 5.2 Hz) were assigned to the protons of the pyridine ring (H-5 and H-4) and two doublets at 7.68 and 6.77 ppm (J = 2.0 Hz) to the protons of the furan ring (H-2 and H-3) respectively. The quartet at 5.92 ppm (1H, J = 6.8 Hz) and the doublet at 1.84 ppm (3H, J = 6.8 Hz) suggested the presence of a partial structure O-CH-CH_3. Thus, the structure of compound **2** was confirmed as 7-(1-

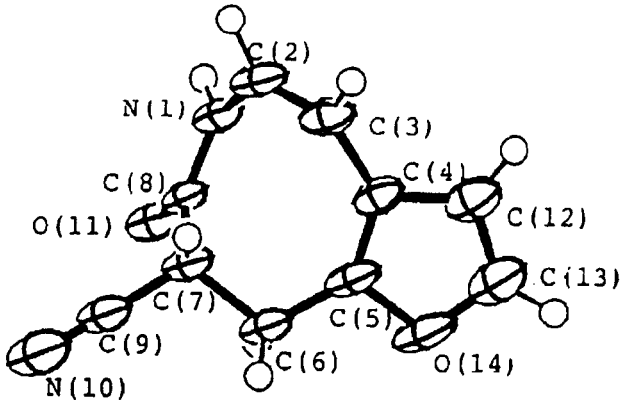


Figure 1. ORTEP drawing of compound **3**.

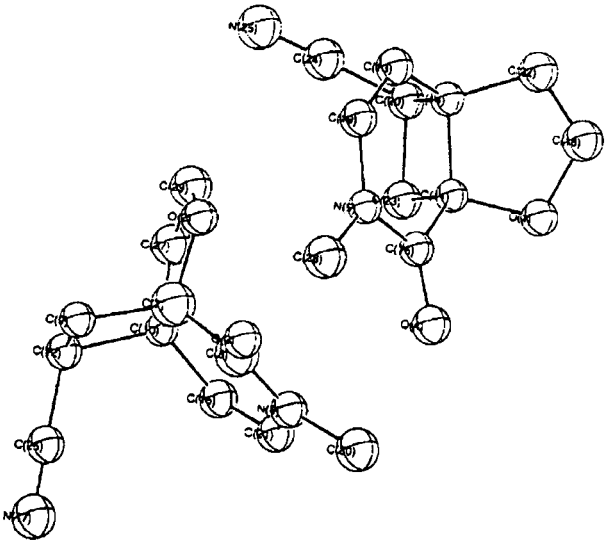


Figure 2. ORTEP drawing of compound **4**.

cyanoethoxy)furo[2,3-*c*]pyridine.

The elemental analysis of compound **3** suggested the molecular formula $C_{10}H_8N_2O_2$. The ir spectrum showed a carbonyl, NH and -CN absorption at 1671, 3441 (broad) and 2254 cm^{-1}, respectively. The ^{1}H-nmr of compound **3** exhibited signals of the furan protons at 7.32 ppm (1H, d, J = 1.6 Hz, H-2) and 6.18 ppm (1H, d, J = 1.6 Hz), two olefinic protons at 6.16 ppm (1H, d, J = 8.8 Hz) and 6.07 ppm (1H, dd, J = 8.8, 3.0 Hz; changed to a doublet, on treatment with deuterium oxide), a proton of NH at 6.93 ppm (1H, broad s; disappeared on treatment with deuterium oxide) and three aliphatic protons at 4.25 (1H, dd, J = 11.6, 4.0 Hz), 3.57 (1H, dd, J = 17.2, 11.6 Hz) and 3.51 ppm (1H, dd, J = 17.2, 4.0 Hz). Though these data suggested two frameworks, cyano substituted 8,9-dihydrofuro[*d*]azocin-7(6*H*)-one, and cyano substituted 3a,7a-dihydro-3a,7a-ethanofuro[2,3-*c*]pyridin-7(6*H*)-one, the framework and the position and configuration of the cyano group could not be determined. Thus, the final structure was determined by a single crystal X-ray analysis performed by the Osaka group of the authors. The X-ray data of **3** unambiguosly established **3** as 8-cyano-8,9-dihydrofuro[*d*]azocin-7(6*H*)-one (Figure 1). Methylation of compound **3** with sodium hydride and iodomethane afforded 8-cyano- 6,8-dimethyl-8,9-dihydrofuro[*d*]azocin-7(6*H*)-one (**3-Me'**).

The photocycloaddition of 6-methylfuro[2,3-*c*]pyridin-7(6*H*)-one (**1-Me**) with acrylonitrile in methanol afforded a mixture of the addition products, from which compound **3-Me** (mp 180-181.5°) (25%), **4** (mp 90-90.5°) (6.5%) and **5** (mp 187.5-191°) (4.5%) and **6** (mp 151-156°) (1.1%) were isolated by column chromatography on silica gel. The elemental analyses of these compounds indicated the molecular formula $C_{11}H_{10}N_2O_2$. The ir spectrum of compound **3-Me** showed a carbonyl and a cyano absorption at 1648 cm^{-1} and 2252 cm^{-1} respectively. The ^{1}H-nmr spectrum exhibited signals of two protons of the furan ring at 7.31 (1H, d, J = 2.0 Hz) and 6.18 ppm (1H, d, J = 2.0 Hz), of two olefinic protons at 6.13 (1H, d, J = 9.0 Hz) and 6.04 ppm (1H, d, J = 9.0 Hz), of three aliphatic protons at 4.38 (1H, dd, J = 12.0, 3.6 Hz), 3.57 (1H, dd, J = 16.8, 12.0 Hz) and 3.48 ppm (1H, dd, J = 16.8, 3.6 Hz)

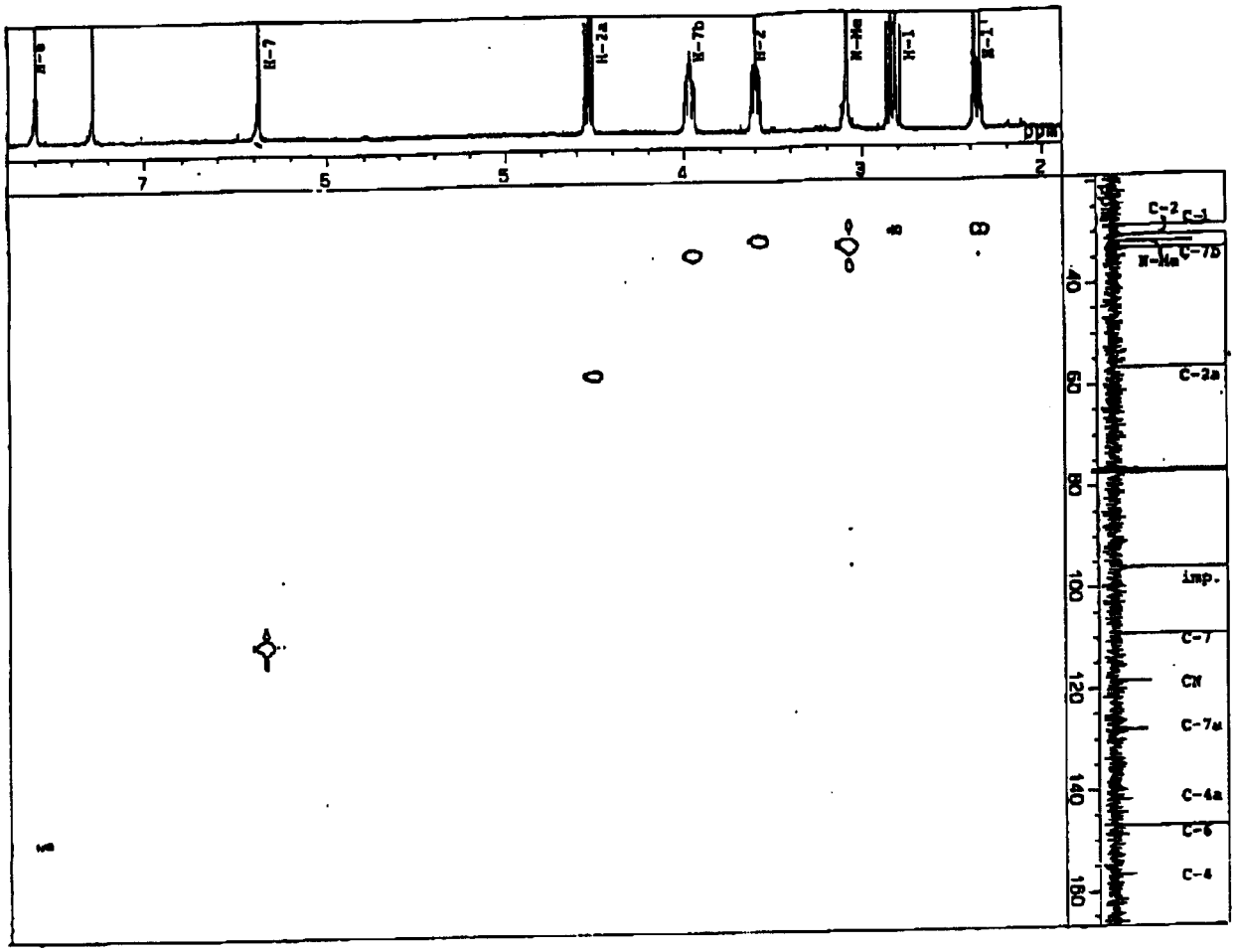


Figure 3. HSQC Spectrum of compound **5**.

and of *N*-methyl protons at 3.09 ppm (3H, s). The chemical shift and coupling pattern of the furan, olefinic and aliphatic protons resemble those of compound **3**. Thus, compound **3-Me** was converted to compound **3-Me'** and confirmed its structure.

Compound **4** also exhibited absorptions of carbonyl and cyano group in its ir spectrum. The ^{1}H-nmr spectrum showed two pairs of olefinic protons at 6.56 (1H, d, J = 2.8 Hz) and 5.18 ppm (1H, d, J = 2.8 Hz), and at 6.17 (1H, d, J = 8.0 Hz) and 5.05 ppm (1H, d, J = 8.0 Hz), three aliphatic protons at 3.34 (1H, dd, J = 10.0, 6.4 Hz), 3.12 (1H, dd, J = 14.4, 10.0 Hz) and 3.05 ppm (1H, dd, J = 14.4, 6.4 Hz), and *N*-methyl at 3.16 ppm (3H, s). The ^{13}C-nmr spectrum showed signals of an *N*-methyl (34.9 ppm), a methylene (37.7 ppm), five methine (33.2, 102.5, 105.8, 131.8 and 148.8 ppm), two quaternary (55.7 and 80.9 ppm), a carbonyl (δ 164.0 ppm) and a cyano carbon (118.5 ppm). The ^{13}C-^{1}H COSY spectrum of **4** indicated that the carbon at 37.7 ppm is connected to the protons at 3.05 and 3.12 ppm, and the carbon at 33.2 ppm to the proton at 3.34 ppm. Though the larger up-field shift of the signals of protons due to H-2, H-3, H-4 and H-5 (by 0.8-1.0 ppm) and carbons due to C-3a (55.7 ppm) and C-7a (80.9 ppm) comparing to those of 6-methylfuro-[2,3-*c*]pyridin-7(6*H*)-one indicated the 3a,7a-ethanofuropyridine structure for compound **4**, it was difficult to determine the final structure by common spectroscopic methods including HMBC and NOE technique of nmr spectroscopy. Thus, the final structure of **4** was again confirmed by single crystal X-ray analysis as (9*S**)-9-cyano-6-methyl-3a,7a-dihydro-3a,7a-ethanofuro[2,3-*c*]pyridin-7-(6*H*)-one (Figure 2). It is worth noting that the crystal of compound **4** contained two different conformers concerning the cyclobutane conformation.

Compound **5** and **6** exhibited the absorption of carbonyl at 1664 and 1664 cm^{-1} and cyano group at 2232 and 2239 cm^{-1} in their ir spectra, respectively. The ^{1}H-nmr spectra showed no signal of aromatic pyridine ring. Thus, compound **5** and **6** were estimated as cyclobutane-fused adducts at 4- and 5-position of the furopyridone. The proton resonating at the furthest down field of the aliphatic protons (4.52 for **5** and 4.54 ppm for **6**), and the carbon at

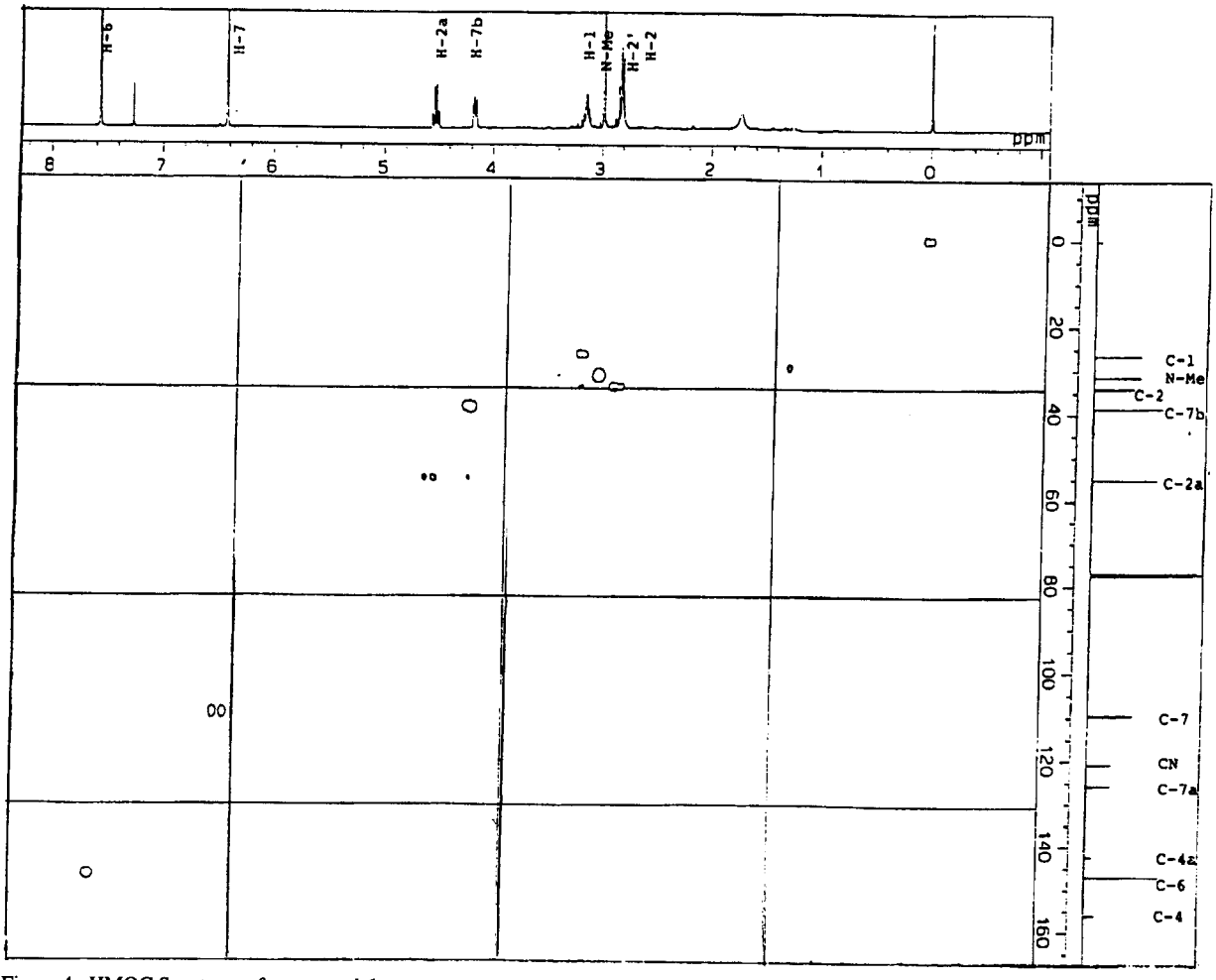


Figure 4. HMQC Spectrum of compound **6**.

the furthest down field of the sp^3 carbons (56.7 for **5** and 55.0 ppm for **6**) for each compound can be assigned to a nitrogen bearing methine, H-2a and C-2a, unambiguously. From the HSQC spectrum of **5** (Figure 3) and the HMQC

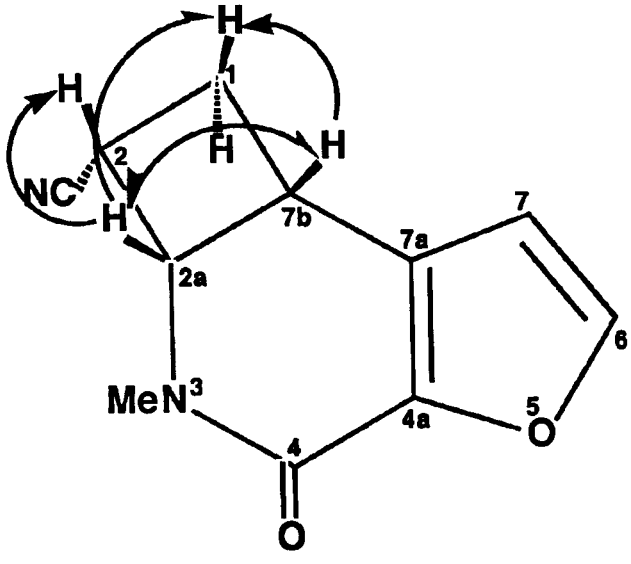


Figure 5. Main NOE correlation of **5**.

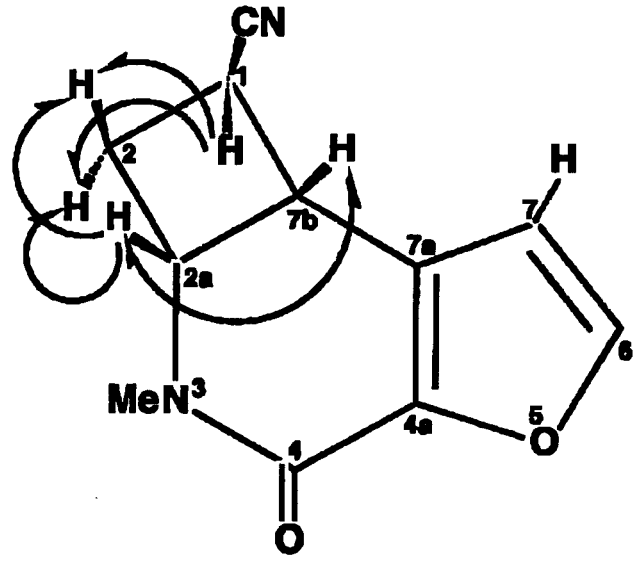


Figure 6. Main NOE correlation of **6**.

Chart 1

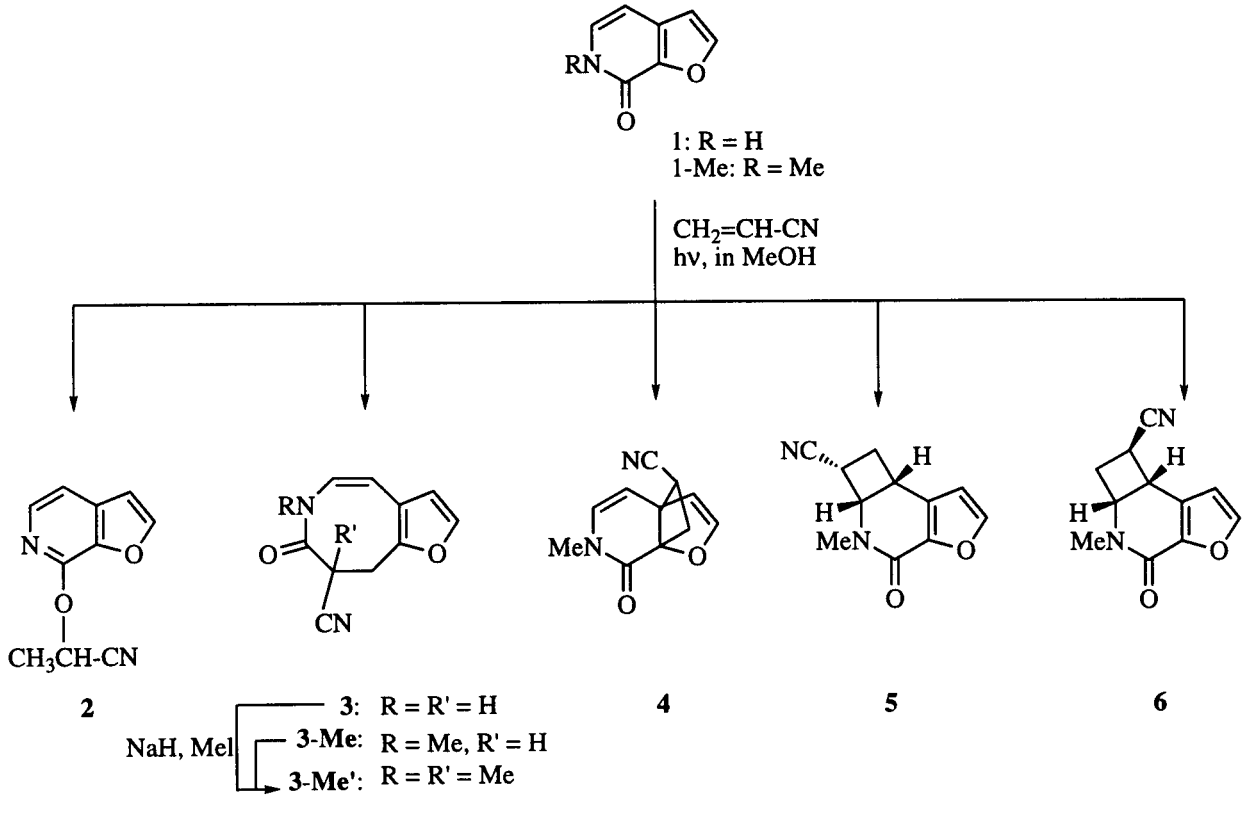
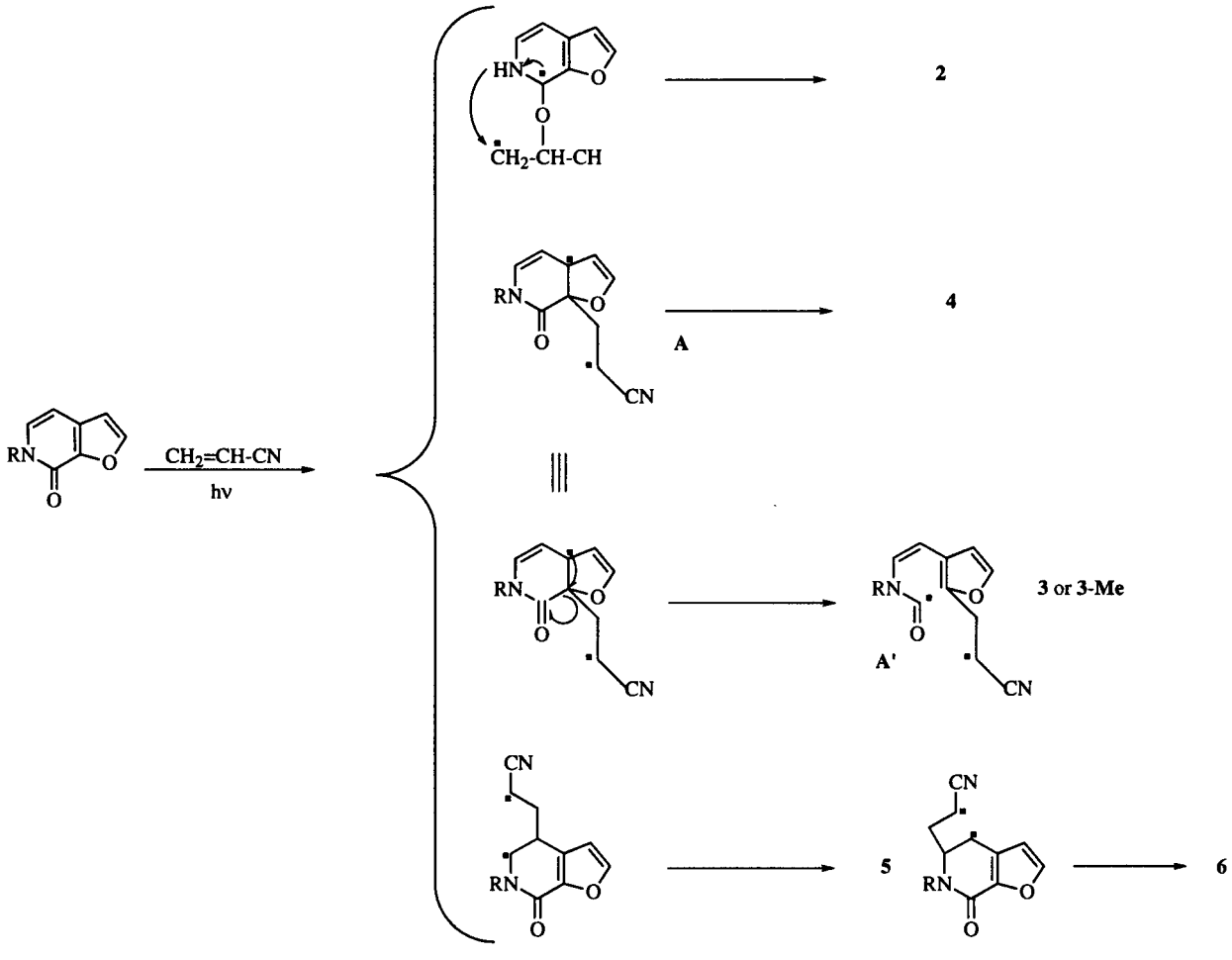


Chart 2



spectrum of **6** (Figure 4), it is observed that the proton corresponding to H-2a is attached to the carbon assigned to C-2a in each compound. Both of the spectra also showed that the proton resonating at 3.95 ppm is attached to the carbon resonating at 33.2 ppm, the proton at 3.58 ppm to the carbon at 30.7 ppm and the protons at 2.81 and 2.34 ppm to the carbon at 28.7 ppm for compound **5**, and that the proton resonating at 4.18 ppm is attached to the carbon resonating at 38.5 ppm, the proton at 3.40 ppm to the carbon at 26.5 ppm and the protons at 2.82 and 2.83 ppm to the carbon at 34.0 ppm for **6**. The carbon connectivity was established by spin decoupling, NOE and HMBC studies.

In the spectrum of **5**, irradiation at 4.52 ppm changed the signal at 3.95 ppm (1H, dt, J = 3.6, 8.8 Hz) to a double doublet and the signal at 3.58 ppm (1H, dt, J = 3.6, 8.8 Hz) to a double doublet, while the signals at 2.81 (1H, dt, J = 8.8, 12.8 Hz) and 2.34 ppm (1H, dt, J = 3.6, 12.8 Hz) were unchanged. Irradiation at 3.95 ppm changed the triplet at 4.52 ppm to a doublet, the double triplets at 2.81 and 2.34 ppm to double doublets, while it did not change the double triplet at 3.58 ppm. Irradiation at 3.58 ppm changed the triplet at 4.52 ppm to a doublet, the double triplets at 2.81 and 2.34 ppm to double doublets, while it did not change the signal at 3.95 ppm. Irradiation at 2.81 ppm changed the double triplets at 3.95 and 3.58 ppm to double doublets and the double triplet at 2.34 ppm to a triplet, while the signal at 4.52 ppm remained unchanged. Irradiation at 2.34 ppm changed the double triplets at 3.95, 3.58 and 2.81 ppm to triplets, respectively, while it did not change the signal at 4.52 ppm. These facts suggested that the signals at 2.81 and 2.34 ppm are assignable to H-1 and/or H-1', the signals at 3.95 ppm to H-7b and the signal at 3.58 ppm to H-2 (or H-2'). The long-range correlations observed in the HMBC spectrum (Table VI) provided additional evidence. The carbon resonating at

Table I

Crystal Data and Data Collection for **3** and **4**

Compound	**3**	**4**
Formula	$C_{10}H_8N_2O_2$	$C_{11}H_{10}N_2O_2$
Mr	188.186	202.21
Crystal System	monoclinic	monoclinic
Space group	P2/c	$P2_1/c$
Cell constant		
a(Å)	8.217(2)	12.439(4)
b(Å)	7.784(1)	12.119(3)
c(Å)	14.255(2)	14.279(4)
α(°)	90.00	90.00
β(°)	93.90(1)	114.20(2)
γ(°)	90.00	90.00
Volume ($Å^3$)	910.8(3)	1963(1)
Z	4	8
Dx, $g.cm^{-3}$	1.372	1.368
μ(Cu-Kα) (cm^{-1})	7.75	7.54
F(000)	392	848
Crystal size, mm^3	0.5 x 0.1 x 0.5	0.3 x 0.3 x 0.5
T of data collection, °C	20	20
Data collection method	ω-2θ scan	ω-2θ scan
Scan speed in 2θ, deg. min^{-1}	6	30
Scan range in ω, deg	1.628+0.15tanθ	1.680+0.15tanθ
Data range measd, deg	2<2θ<130	3<2θ<130
Data collected	-h, -k, ±l	-h, -k, ±l
No. of unique data measd	1436	3096
No. of data with Fo>2σ(Fo)	1397	2547
No. of variables	159	291
R_F	0.076	0.050
R_{wF}	0.100	0.073
Goodness of fit	0.550	0.949

Table II

Final Atomic Coordinates and Equivalent Values of Anisotropic Temperature Factors for Compound 3 (estimated standard deviations are in parentheses)

Atom	x	y	z	Ueq
N(1)	0.8616(2)	0.0048(2)	-0.1155(1)	0.033(1)
C(2)	0.7993(3)	-0.0511(3)	-0.2050(2)	0.037(1)
C(3)	0.7546(3)	0.0517(3)	-0.2774(2)	0.038(1)
C(4)	0.7680(3)	0.2363(3)	-0.2849(2)	0.035(1)
C(5)	0.7358(3)	0.3650(3)	-0.2244(2)	0.035(1)
C(6)	0.6607(3)	0.3776(3)	-0.1326(2)	0.038(1)
C(7)	0.6344(2)	0.2010(3)	-0.0902(2)	0.032(1)
C(8)	0.7982(3)	0.1184(2)	-0.0588(1)	0.031(1)
C(9)	0.5387(3)	0.2138(3)	-0.0072(2)	0.040(1)
N(10)	0.4617(4)	0.2205(4)	0.0570(2)	0.061(2)
O(11)	0.8654(2)	0.1613(2)	0.0176(1)	0.042(1)
C(12)	0.8230(3)	0.3186(4)	-0.3661(2)	0.047(2)
C(13)	0.8232(4)	0.4885(4)	-0.3498(2)	0.056(2)
O(14)	0.7675(3)	0.5217(2)	-0.2620(1)	0.049(1)

$Ueq = 1/3S_iS_jU_{ij}a_i^*a_j^*a_ia_j$

28.7 ppm correlates with the protons at 3.58 ppm (corresponds to H-2 or H-2') and at 3.95 ppm (H-7b), and therefore corresponds to C-1. The carbon resonating at 30.7 ppm correlates with the protons assignable to H-1, H-1', H-2a and weakly with H-7b thus identifying this as C-2.

Likewise, the carbon resonance at 33.2 ppm correlates with the protons corresponding to H-1, H-1', and H-2a and weakly with H-2 thus identifying this carbon as C-7b. The carbon resonating at 56.7 ppm (C-2a) correlates with the protons assignable to H-1, H-2, H-7b and N-Me. The

Table III

Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Compound **4** (estimated standard deviations are in parentheses)

Atom	x/a	y/b	z/c	U(iso)
O(1)	0.57594(13)	0.14513(13)	0.94084(12)	0.051
O(2)	0.81955(13)	-0.28265(12)	1.10223(10)	0.048
O(3)	0.79638(13)	-0.19983(14)	0.90774(12)	0.052
O(4)	0.69359(14)	0.07202(15)	0.82337(12)	0.055
N(5)	0.86462(14)	0.11710(15)	0.95633(13)	0.044
N(6)	0.62505(14)	-0.29487(15)	0.85802(13)	0.042
N(17)	0.7618(2)	-0.6463(2)	0.8518(2)	0.073
N(25)	0.9140(2)	-0.0795(2)	1.2728(2)	0.072
C(7)	0.79419(17)	-0.35092(15)	1.01325(15)	0.037
C(8)	0.73969(17)	-0.27561(17)	0.92152(15)	0.039
C(9)	0.89699(18)	-0.42347(18)	1.01724(18)	0.045
C(10)	0.72491(17)	-0.45307(16)	1.02262(15)	0.045
C(11)	0.68786(17)	0.8949(16)	0.98760(15)	0.039
C(12)	0.82543(18)	-0.52880(18)	1.01728(16)	0.045
C(13)	0.87638(19)	0.16760(18)	1.12437(17)	0.047
C(14)	0.75207(18)	0.13634(18)	1.09786(16)	0.044
C(15)	0.60529(18)	-0.46432(19)	0.93897(19)	0.051
C(16)	0.74736(16)	0.09364(16)	0.91407(15)	0.039
C(18)	0.5757(2)	0.2238(2)	1.0110(2)	0.060
C(19)	0.92316(19)	0.15720(18)	1.05698(18)	0.048
C(20)	0.7300(2)	0.0219(2)	1.1409(2)	0.052
C(21)	0.56287(18)	-0.38958(19)	0.86574(18)	0.048
C(22)	0.6693(2)	0.2249(2)	1.0992(2)	0.057
C(23)	0.6817(2)	-0.0254(2)	1.0297(2)	0.050
C(24)	0.8329(2)	-0.0342(2)	1.2151(2)	0.057
C(26)	0.79078(19)	-0.59551(18)	0.92517(19)	0.052
C(27)	0.7342(2)	-0.4389(2)	1.1303(2)	0.060
C(28)	0.9278(2)	0.1153(3)	0.8896(2)	0.066
C(29)	0.7879(2)	-0.3446(2)	1.1676(2)	0.058
C(30)	0.5651(2)	-0.2161(2)	0.7750(2)	0.064

$T = \exp[-2p^2U]$; $U = U_{iso}$ or $U = (U_{11} + U_{22} + U_{33})/3$

Table IV

Bond Length (Å) in Compound **3** and **4**

Compound **3**			
N(1) - C(2)	1.412(3)	C(6) - C(7)	1.524(3)
N(1) - C(8)	1.329(3)	C(7) - C(8)	1.531(3)
C(2) - C(3)	1.338(3)	C(7) - C(9)	1.468(3)
C(3) - C(4)	1.447(3)	C(8) - O(11)	1.232(3)
C(4) - C(5)	1.360(3)	C(9) - N(10)	1.148(4)
C(4) - C(12)	1.423(3)	C(12) - C(13)	1.345(4)
C(5) - C(6)	1.488(3)	C(12) - C(13)	1.345(4)
C(5) - O(14)	1.366(3)		
Compound **4**			
O(1) - C(11)	1.441(3)	C(9) - C(12)	1.556(4)
O(1) - C(18)	1.384(3)	C(10) - C(12)	1.578(3)
O(2) - C(7)	1.439(3)	C(10)- C(15)	1.484(3)
O(2) - C(29)	1.362(3)	C(10) - C(27)	1.504(4)
O(3) - C(8)	1.222(3)	C(11) - C(14)	1.552(3)
O(4) - C(16)	1.218(3)	C(11) - C(16)	1.513(3)
N(5) - C(16)	1.360(3)	C(11) - C(23)	1.531(4)
N(5) - C(19)	1.405(3)	C(12) - C(26)	1.451(4)
N(5) - C(28)	1.462(3)	C(13) - C(14)	1.483(3)
N(6) - C(8)	1.360(3)	C(13) - C(19)	1.319(4)
N(6) - C(21)	1.413(3)	C(14) - C(20)	1.586(4)
N(6) - C(30)	1.466(4)	C(14) - C(22)	1.493(4)
N(17) - C(26)	1.138 (4)	C(15) - C(21)	1.319(4)
N(25) - C(24)	1.147(4)	C(18) - C(22)	1.319(4)
C(7) - C(8)	1.510(3)	C(20) - C(23)	1.558(4)
C(7) - C(9)	1.534(3)	C(20) - C(24)	1.453(4)
C(7) - C(10)	1.545(3)	C(27) - C(29)	1.317(4)

carbon resonance at 128.1 ppm correlates with the protons corresponding to H-1, H-2a, H-7b, H-6 and H-7 identify-

Table V

Bond Angles (°) in Compound **3** and **4** (estimated standard deviations are in parentheses)

Compound **3**

C(2) - N(1) - C(8)	128.5(1)	C(6) - C(7) - C(8)	110.5(1)
N(1) - C(2) - C(3)	125.2(1)	C(6) - C(7) - C(9)	110.9(1)
C(2) - C(3) - C(4)	129.3(1)	C(8) - C(7) - C(9)	107.5(1)
C(3) - C(4) - C(5)	131.9(1)	N(1) - C(8) - C(7)	118.4(1)
C(3) - C(4) - C(12)	122.5(1)	N(1) - C(8) - O(11)	123.1(1)
C(5) - C(4) - C(12)	105.6(2)	C(7) - C(8) - O(11)	118.5(1)
C(4) - C(5) - C(6)	135.7(1)	C(7) - C(9) - N(10)	178.3(2)
C(4) - C(5) - O(14)	111.1(1)	C(4) - C(12) - C(13)	107.5(2)
C(6) - C(5) - O(14)	112.8(1)	C(12) - C(13) - O(14)	110.0(2)
C(5) - C(6) - C(7)	111.6(1)	C(5) - O(14) - C(13)	105.7(2)

Compound **4**

C(11) - O(1) - C(18)	106.0(2)	C(7) - O(2) - C(29)	105.4(2)
C(16) - N(5) - C(19)	122.5(2)	C(16) - N(5) - C(28)	118.2(2)
C(19) - N(5) - C(28)	118.7(2)	C(8) - N(6) - C(21)	123.0(2)
C(8) - N(6) - C(30)	118.3(2)	C(21) - N(6) - C(30)	118.6(2)
O(2) - C(7) - C(8)	106.0(2)	O(2) - C(7) - C(9)	114.8(2)
O(2) - C(7) - C(10)	108.2(2)	C(8) - C(7) - C(9)	116.7(2)
C(8) - C(7) - C(10)	119.4(2)	C(9) - C(7) - C(10)	91.4(2)
O(3) - C(8) - N(6)	122.6(2)	O(3) - C(8) - C(7)	120.7(2)
N(6) - C(8) - C(7)	116.7(2)	C(7) - C(9) - C(12)	90.1(2)
C(7) - C(10) - C(12)	88.9(2)	C(7) - C(10) - C(15)	114.5(2)
C(7) - C(10) - C(27)	100.7(2)	C(12) - C(10) - C(15)	117.4(2)
C(12) - C(10) - C(27)	112.7(2)	C(15) - C(10) - C(27)	117.7(2)
O(1) - C(11) - C(14)	107.2(2)	O(1) - C(11) - C(16)	108.5(2)
O(1) - C(11) - C(23)	114.4(2)	C(14) - C(11) - C(16)	119.8(2)
C(14) - C(11) - C(23)	91.2(2)	C(16) - C(11) - C(23)	114.9(2)
C(9) - C(12) - C(10)	89.3(2)	C(9) - C(12) - C(26)	114.5(2)
C(10) - C(12) - C(26)	114.9(2)	C(14) - C(13) - C(19)	121.0(3)
C(11) - C(14) - C(13)	113.7(2)	C(11) - C(14) - C(20)	88.5(2)
C(11) - C(14) - C(22)	101.8(2)	C(13) - C(14) - C(29)	116.9(2)
C(13) - C(14) - C(22)	117.8(2)	C(20) - C(14) - C(22)	113.2(2)
C(10) - C(15) - C(21)	121.2(2)	O(4) - C(16) - N(5)	122.6(2)
O(4) - C(16) - C(11)	121.3(2)	N(5) - C(16) - C(11)	116.1(2)
O(1) - C(18) - C(22)	115.8(3)	N(5) - C(19) - C(13)	125.5(2)
C(14) - C(20) - C(23)	89.0(2)	C(14) - C(20) - C(24)	116.8(2)
C(23) - C(20) - C(24)	115.3(2)	N(6) - C(21) - C(15)	124.4(3)
C(14) - C(22) - C(18)	108.9(3)	C(11) - C(23) - C(20)	90.3(2)
N(25) - C(24) - C(20)	179.2(3)	N(17) - C(26) - C(12)	178.6(3)
C(10) - C(27) - C(29)	109.2(3)	O(2) - C(29) - C(27)	115.7(3)

Table VI

^{13}C Assignments and HMBC Corrrelation of Compound **5**

Position	^{13}C	HMBC (^{1}H)
1	28.7 (t)	2, 7b
2	30.7 (d)	1, 1', 2a, 7b
2a	56.7 (d)	1', 2, 7b, N-Me
N-Me	31.8 (q)	2a
4	156.5 (s)	2a, N-Me
4a	141.9 (s)	6, 7
6	147.0 (d)	7
7	109.2 (d)	6
7a	128.1 (s)	1, 2a, 6, 7
7b	33.2 (d)	1, 1', 2, 2a
CN	118.4 (s)	1, 1', 2a

Table VII

^{13}C Assignments and HMBC Corrrelation of Compound **6**

Position	^{13}C	HMBC (^{1}H)
1	26.5 (d)	2, 2', 2a, 7b
2	34.0 (t)	1', 2a, 7b
2a	55.0 (d)	1', 2, 2', 7b, N-Me
N-Me	31.4 (q)	2a
4	156.0 (s)	2a, N-Me
4a	142.3 (s)	6, 7, 7b
6	147.0 (d)	7
7	109.5 (d)	6
7a	125.7 (s)	1', 2a, 6, 7, 7b
7b	38.5 (d)	1', 2, 2', 2a
CN	120.8 (s)	1', 2, 2', 7b

ing this as C-7a. The configuration at C-2 of compound **5** was determined by the NOE experiment. Upon irradiation at H-2a clear NOEs were observed from H-2a to H-2, to H-7b and weakly to H-1 and was absent from H-2a to H-1'; when irradiated at H-7b NOEs were observed clearly from H-7b to H-2a and to H-1. Therefore, the configuration of H-2a and H-2 is suggested to be *cis*. Thus, the structure of compound **5** was assigned to (2*S**,2a*R**,-7b*R**)-2-cyano-3-methyl-4-oxo-1,2,2a,3,4,7b-hexahydrocyclobuta[*e*]furo[2,3-*c*]pyridine [5].

In the spin decoupling studies of **6**, irradiation at 4.54 ppm changed the signal at 4.18 ppm (1H, ddd, J = 8.8, 3.6, 2.0 Hz) to a double doublet (J = 3.6, 2.0 Hz), the signal at 2.82 ppm (1H, dddd, J = 18.4, 8.8, 8.4, 2.0 Hz) to a

doublet of double doublet (J = 18.4, 8.4, 2.0 Hz) and the signal at 2.83 ppm (1H, ddd, J = 18.4, 8.8, 5.6 Hz) to a double doublet (J = 18.4, 5.6 Hz), while it did not change the signal at 3.14 ppm (ddd, J = 8.4, 5.6, 3.6 Hz). Irradiation at 4.18 ppm changed the signal at 4.54 ppm (q, J = 8.8 Hz) to a triplet (J = 8.8 Hz), the signal at 3.14 ppm to a double doublet (J = 8.4, 5.6 Hz), while the signals at 2.82 and 2.83 were almost unchanged. Irradiation at 3.14 ppm changed the signal at 4.18 ppm to a double doublet (J = 8.8, 2.0 Hz), the signal at 2.83 ppm to a double doublet (J = 18.4, 8.8 Hz) and the signal at 2.82 to a doublet of double doublet (J = 18.4, 8.8, 2.0 Hz), while it did not change the signal at 4.54 ppm. These facts suggested that the signal at 3.14 ppm is assignable to H-1 (or H-1'), the signals at 2.82 and 2.83 ppm to H-2 and/or H-2' and the signal at 4.18 ppm to H-7b. The HMBC spectrum of **6** provided evidence for the assignment of the carbon resonances (Table VII). The carbon resonating at 26.5 ppm correlates with the protons corresponding to H-2, H-2', H-2a and H-7b, and therefore corresponds to C-1. The carbon resonating at 34.0 ppm correlates with the protons assignable to H-1', H-2a and H-7b thus identifying this as C-2. The carbon resonance at 38.5 ppm correlates with the protons corresponding to H-1', H-2, H-2' and H-2a. These correlations identify the carbon at 38.5 ppm as C-7b. The carbon assigned to C-2a correlates with protons assignable to H-1', H-2, H-2' and N-Me. In the NOE experiment, upon irradiation at H-2a clear NOEs were observed from H-2a to H-2 and H-2' and to H-7b and was absent from H-2a to H-1'; upon irradiation at H-7b NOEs were observed clearly from H-7b to H-2a and very weakly to H-1', and was absent from H-7b to H-2 and H-2'. When irradiated at H-1' NOEs were observed from H-1' to H-2 and H-2' and very weakly to H-7b, and was absent from H-1' to H-2a. Therefore, the configuration of H-1' and H-7b is suggested to be *trans*. Thus, the structure of compound **6** was assigned to (1*R**,2a*S**,7b*S**)-1-cyano-3-methyl-4-oxo-1,2,2a,3,4,7b-hexahydrocyclobuta[*e*]furo-[2,3-*c*]pyridine [5,6].

It had been reported that in the photocycloaddition to monosubstituted olefin, isoquinolone-1 and/or its *N*-substituted derivatives afforded 1-substituted cyclobut[*c*]isoquinolones as the major products [7]. Recently we reported the photocycloaddition of furo[3,2-*c*]pyridin-4(5*H*)-one and its *N*-methyl derivative to acrylonitrile to afford a complex mixture from which 4-(1-cyanoethoxy)furo-[3,2-*c*]pyridine and four isomers of a cyclobutane-fused adduct with the acrylonitrile group incorporated at the 6- or the 7-position of the fused furopyridone were isolated [3]. This research has demonstrated that photocycloaddition of furo[2,3-*c*]pyridone and its *N*-methyl derivative with acrylonitrile afforded a complex mixture from which ethylene-inserted product **3** (and **3-Me**) with the acrylonitrile at the 7 and 7a-position, two cyclobutane-fused adducts with the acrylonitrile group incorporated at the 6- and 7-position (**5**) and (**6**), and at the 3a- and 7a-position (**4**), and an addition product at the carbonyl-oxygen (**2**) could be isolated. Both compound **3** (and **3-Me**) and **4** would be formed through the same biradical intermediate **A**. The minor product **2** formed in the reaction of furo[2,3-*c*]pyridin-7(6*H*)-one may be afforded by the addition at the carbonyl group in the excited state, which is similar to that in the reaction of furo[3,2-*c*]pyridin-4(5*H*)-one [3]. Formation of such an addition product in pyridones, quinolones and/or isoquinolones had not yet been reported.

EXPERIMENTAL

All melting points were determined on a micro-melting point apparatus (Yanagimoto) and are uncorrected. Infrared spectra were recorded on a JASCO FT/IR 7300 spectrometer. The ^{1}H- and ^{13}C-nmr spectra were recorded on a JEOL JNM-PMX 60 (60 MHz) or a JEOL FX-A400 spectrometer (400 MHz) with tetramethylsilane as an internal standard. The nmr spectral assignments were confirmed by spin-decoupling, ^{1}H-^{13}C correlation spectroscopy (^{1}H-^{13}C COSY) (512 x 256 data matrix size, 104 scans, interpulse delay 1.79 seconds) of **4**, HSQC (512 x 512 data matrix size, 80 scans, recycle delay 1.50 seconds) of **5**, HMBC (1024 x 512 data matrix size, 80 scans, recycle delay 1.00 second) and nuclear Overhauser effect (NOE) analysis of **4** and **5**.

Photolyses were carried out under nitrogen in a Pyrex immersion apparatus with Shigemi 400w high-pressure lamp cooled internally with running water, and correspond to irradiation at >300 nm.

Photoreaction of Furo[2,3-*c*]pyridin-6(7*H*)-one (**1**) with Acrylonitrile.

A solution of **1** (135 mg, 1.0 mmole) and acrylonitrile (5.3 g, 100 mmoles) in methanol (200 ml) was irradiated for 7 hours. The reaction mixture was filtered and evaporated to give a slightly yellow semi-solid residue. This reaction was repeated 7 times. The combined residue (1510 mg) was chromatographed on a silica gel (160 g) column eluting with chloroform-methanol. The first fraction eluted with chloroform-methanol (99:1) gave 63 mg of a crude sample of compound **2**, the second fraction eluted with chloroform-methanol (98:2) 200 mg of a crude sample of compound **3**.

Further processing of the crude products is indicated in the following paragraph.

7-(1-Cyanoethoxy)furo[2,3-*c*]pyridine (**2**).

The first fraction was recrystallized from ether to give 56.6 mg (4.3%) of the pure sample of **2** as colorless needles, mp 91-93°; ir (potassium bromide): 3130, 3107, 3003, 2941, 2245 (w), 1621, 1576, 1469, 1436, 1334, 1247, 1199, 1139, 1105, 1027, 919, 881, 839, 789 cm^{-1}; ^{1}H-nmr (deuteriochloroform, 60 MHz): δ 7.90 (d, J = 5.2 Hz, 1H, H-5), 7.68 (d, J = 2.0 Hz, 1H, H-2), 7.20 (d, J = 5.2 Hz, 1H, H-4), 6.77 (d, J = 2.0 Hz, 1H, H-3), 5.92 (q, J = 6.8 Hz, 1H, Me-C*H*(CN)-O-), 1.84 (d, J = 6.8 Hz, 3H, CH-CH_3).

Anal. Calcd. for $C_{10}H_8N_2O_2$: C, 63.83; H, 4.28; N, 14.89. Found: C, 63.77; H, 4.34; N, 14.84.

8-Cyano-8,9-dihydrofuro[*d*]azocin-7(6*H*)-one (**3**).

Recrystallization of the second fraction from methanol gave 171 mg (13%) of the pure sample of **3** as colorless needles of mp 236-239°; ir (potassium bromide): 3441 (broad), 3196, 3143, 3117, 3071, 2919, 2254, 1671, 1646, 1523, 1445, 1414, 1290, 1190, 1063, 964, 893, 866 cm^{-1}; ^1H-nmr (deuteriochloroform, 400 MHz): δ 7.32 (d, J = 1.6 Hz, 1H, H-2), 6.93 (broad s, 1H, NH), 6.18 (d, J = 1.6 Hz, 1H, H-3), 6.16 (d, J = 8.8 Hz, 1H, H-4), 6.07 (dd, J = 3.0, 8.8 Hz, 1H, H-5), 4.25 (dd, J = 4.0, 11.6 Hz, 1H, H-8), 3.58 (dd, J = 11.6, 17.2 Hz, 1H, H-9), 3.51 (dd, J = 4.0, 17.2 Hz, 1H, H-9').

Anal. Calcd. for $C_{10}H_8N_2O_2$: C, 63.83; H, 4.28; N, 14.89. Found: C, 63.91; H, 4.36; N, 14.92.

6-Methylfuro[2,3-*c*]pyridin-7(6*H*)-one (**1-Me**).

To a stirred suspension of sodium hydride (97 mg of 60% dispersion in mineral oil, 2.4 mmoles, washed with hexane) in dry tetrahydrofuran (15 ml) was added a solution of **1** (270 mg, 2.0 mmoles) in dry tetrahydrofuran. Stirring was continued for 2 hours at room temperature. To this mixture was added iodomethane (1.07 g, 7.5 mmoles). After stirring at room temperature for 15 hours, the solvent was evaporated. The residual mixture was treated with chloroform and water. The chloroform layer was dried and evaporated to give a crystalline mass, which was recrystallized from acetone/ether to afford 285 mg (96%) of **1-Me** as colorless cubes, mp 118.5-120°; ir (potassium bromide): 3134, 3094, 2920, 2852, 1667, 1590, 1557, 1500, 1467, 1275, 1235, 1109, 1028, 889, 807, 751 cm^{-1}; ^1H-nmr (deuteriochloroform, 60 MHz): δ 7.73 (d, J = 2.0 Hz, 1H, H-2), 7.15 (d, J = 7.0 Hz, 1H, H-5), 6.66 (d, J = 2.0 Hz, 1H, H-3), 6.45 (d, J = 7.0 Hz, 1H, H-4), 3.65 (s, 3H, N-Me).

Anal. Calcd. for $C_8H_7NO_2$: C, 64.42; H, 4.73; N, 9.39. Found: C, 64.63; H, 4.78: N, 9.37.

8-Cyano-6,8-dimethyl-8,9-dihydrofuro[*d*]azocin-7(6*H*)-one (**3-Me'**).

(a) To a stirred suspension of sodium hydride (77 mg of 60% dispersion in mineral oil, 1.9 mmoles, washed with hexane) in dry tetrahydrofuran (35 ml) was added a solution of **3** (120 mg, 0.64 mmole) in dry tetrahydrofuran. After being stirred for 2 hours at room temperature, to this mixture was added iodomethane (640 mg, 4.5 mmoles). Stirring at room temperature was continued for 20 hours. After evaporation of the solvent, the residual solid was treated with chloroform and water. The chloroform layer was dried and evaporated to give 130 mg of a solid mass, from which 117 mg (85%) of pure sample of **3-Me'** was obtained by recrystallization from ether, mp 112-113°; ir (potassium bromide): 3154, 3109, 2990, 2940, 1128, 1654, 1520, 1456, 1392, 1262, 1237, 1190, 1088, 1049, 894, 801, 782, 756 cm^{-1}; ^1H-nmr (deuteriochloroform, 400 MHz), δ 7.30 (d, J = 2.0 Hz, 1H, H-2), 6.21 (d, J = 2.0 Hz, 1H, H-3), 6.19 (d, J = 8.4 Hz, 1H, H-4), 6.15 (d, J = 8.4 Hz, 1H, H-5), 3.37 and 3.27 (AB-q, J = 17.6 Hz, 2H, H-9 and H-9'), 3.07 (s, 3H, N-Me), 1.82 (s, 3H, 8-Me).

Anal. Calcd. for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.88. Found: C, 66.87; H, 5.57; N, 12.88.

(b) Methylation of compound **3-Me** (20 mg, 0.1 mmole) with sodium hydride (20 mg of 60% dispersion in mineral oil, 0.5 mmole, washed with hexane) and iodomethane (142 mg, 1.0 mmole) by the same procedure described in the above yielded a sample of compound **3-Me'** (20 mg, 93%). The melting point and ir and nmr spectra of this sample were identical with those of the sample obtained from compound **3**.

Photoreaction of 6-Methylfuro[2,3-*c*]pyridin-7(6*H*)-one (**1-Me**) with Acrylonitrile.

A solution of **1-Me** (149 mg, 1.0 mmole) and acrylonitrile (530 mg, 10 mmoles) in methanol (200 ml) was irradiated for 5 hours. The reaction mixture was filtered and evaporated to leave a semi-solid mass. The reaction was repeated 5 times. The combined residue (1.25 g) was chromatographed on a silica gel (130 g) column eluting with hexane/ethyl acetate (1:1). The first fraction gave 305 mg of a crude sample of compound **3-Me**, the second 253 mg of a mixture of compound **4** and **5**, which was chromatographed on a silica gel (30 g) column eluting with hexane/ethyl acetate to give crude sample of compound **4** (75 mg), compound **5** (50 mg) and compound **6** (15 mg).

Further processing of the crude products is indicated in the following paragraph.

8-Cyano-6-methyl-8,9-dihydrofuro[*d*]azocin-7(6*H*)-one (**3-Me**).

The first fraction was recrystallized from acetone/ether to give 253 mg (25%) of the pure sample of **3-Me** as colorless cubes, mp 180.5-181.5°; ir (potassium bromide): 3139, 3103, 3042, 3001, 2960, 2922, 2861, 2252, 1648, 1424, 1400, 1312, 1238, 1188, 1096, 894, 782 cm^{-1}; ^1H-nmr (deuteriochloroform, 400 MHz): δ 7.31 (d, J = 2.0 Hz, 1H, H-2), 6.18 (d, J = 2.0 Hz, 1H, H-3), 6.13 (d, J = 8.8 Hz, 1H, H-4), 6.03 (d, J = 8.8 Hz, 1H, H-5), 4.37 (dd, J = 3.6, 12.0 Hz, 1H, H-8), 3.57 (dd, J = 12.4, 16.8 Hz, 1H, H-9), 3.48 (dd, J = 4.0, 16.8 Hz, 1H, H-9'), 3.09 (s, 3H, N-Me).

Anal. Calcd. for $C_{11}H_{10}N_2O_2$: C, 65.34; H, 4.98; N, 13.85. Found: C, 65.33; H, 5.08; N, 13.76.

(9*S**)-9-Cyano-6-methyl-3a,7a-dihydro-3a,7a-ethanofuro-[2,3-*c*]pyridin-7(6*H*)-one (**4**).

Recrystallization of the crude sample of compound **4** from acetone/ether afforded the pure sample (66 mg, 6.5%) of mp 90-90.5°; ir (potassium bromide): 3102, 2958, 2239, 1672, 1599, 1380, 1259, 1209, 1132, 1038, 758, 734 cm^{-1}; ^1H-nmr (deuteriochloroform, 400 MHz) δ 6.56 (d, J = 2.8 Hz, 1H, H-2), 6.17 (d, J = 8.0 Hz, 1H, H-5), 5.18 (d, J = 2.8 Hz, 1H, H-3), 5.05 (d, J = 8.0 Hz, 1H, H-4), 3.34 (dd, J = 6.4, 10.0 Hz, 1H, H-9), 3.16 (s, 3H, N-Me), 3.15 (dd, J = 10.0, 14.4 Hz, 1H, H-8), 3.05 (dd, J = 6.4, 14.4 Hz, 1H, H-8').

Anal. Calcd. for $C_{11}H_{10}N_2O_2$: C, 65.34; H, 4.98; N, 13.85. Found: C, 65.51; H, 5.19; N, 13.7.

(2*S**,2a*R**,7b*R**)-2-Cyano-3-methyl-4-oxo-1,2,2a,3,4,7b-hexahydrocyclobuta[*e*]furo[2,3-*c*]pyridine (**5**).

The crude sample of compound **5** was recrystallized from acetone to give 45.5 mg, 4.5%) of pure **5**, mp 187.5-191°; ir (potassium bromide): 3135, 3119, 2959, 2924, 2854, 2232, 1664, 1600, 1486, 1396, 1329, 1210, 1072, 1052, 897, 805, 795 cm^{-1}; ^1H-nmr (deuteriochloroform, 400 MHz) δ 7.57 (d, J = 2.0 Hz, 1H, H-6), 6.35 (d, J = 2.0 Hz, 1H, H-7), 4.52 (t, J = 8.8 Hz, 1H, H-2a), 3.95 (dt, J = 8.8, 3.6 Hz, 1H, H-7b), 3.58 (dt, J = 8.8, 3.6 Hz, 1H, H-2), 3.06 (s, 3H, N-Me), 2.81 (dt, J = 12.8, 8.8 Hz, 1H, H-1), 2.34 (dt, J = 12.8, 3.6 Hz, 1H, H-1').

Anal. Calcd. for $C_{11}H_{10}N_2O_2$: C, 65.34; H, 4.98; N, 13.85. Found: C, 65.40; H, 5.05; N, 14.15.

(1*R**,2a*S**,7b*S**)-1-Cyano-3-methyl-4-oxo-1,2,2a,3,4,7b-hexahydrocyclobuta[*e*]furo[2,3-*c*]pyridine (**6**).

The crude sample of compound **6** was recrystallized from acetone to give 11 mg (1.1%) of pure **6**, mp 151-156°; ir (potassium bromide): 3123, 3095, 3013, 2924, 2855, 2239, 1664, 1594, 1481, 1332, 1218, 1083, 888, 808 cm^{-1}; ^1H-nmr (deuteriochloroform, 400 MHz) δ 7.57 (d, J = 2.0 Hz, 1H, H-6), 6.43 (d, J = 2.0 Hz, 1H, H-7), 4.54 (q, J = 8.8 Hz, 1H, H-2a), 4.18 (ddd, J = 8.8, 3.6, 2.0 Hz, 1H, H-7b), 3.14 (ddd, J = 8.4, 5.6, 3.6 Hz, 1H, H-1'), 2.99 (s, 3H, N-Me), 2.83 (ddd, J = 18.4, 8.8, 5.6 Hz, 1H, H-2'), 2.82 (dddd, J = 18.4, 8.8, 8.4, 2.0 Hz, 1H, H-2).

Anal. Calcd. for $C_{11}H_{10}N_2O_2$: C, 65.34; H, 4.98; N, 13.85. Found: C, 65.15; H, 5.04; N, 13.76.

X-Ray Structural Determination of **3** and **4**.

After many attempts, the structures of **3** and **4** were finally solved by the direct method with the SHELX86 [8] and TEXSAN program [9]. Many non-H atoms were revealed on an E-map calculated by the tangent refinement method using the *E* values of 1.40-2.50 which were calculated from the observed intensities by the assistance of the atomic coordinates [10] of compound **3** and **4** as a random group. The positional parameters of the non-H atoms were refined by full-matrix least-squares with anisotropic thermal parameters. The positions of H atoms were obtained from a difference Fourier map and were included in the subsequent refinements with isotropic thermal parameters. The function minimized was $\Sigma w(|Fo| - |Fc|)^2$, where |Fo| and |Fc| are the observed and calculated amplitudes of structure factors, respectively. The weighting scheme used for the final refinement was $w = 1.0/\sigma(Fo)^2$, where $\sigma(Fo)^2$ is the standard deviation of each reflection intensity on the basis of counting statistics. Final $R = \Sigma(|Fo| - |Fc|) / \Sigma |Fo|$, $Rw = [\Sigma w(|Fo| - |Fc|)^2 / \Sigma w(|Fo|^2]^{1/2}$, and $S = [\Sigma w(|Fo| - |Fc|)^2 / (M-N)]^{1/2}$ are also given in Table I. None of the positional parameter for non-H atoms shifted more than their estimated standard deviations (e.s.d.s). The residual electron density in the final difference Fourier map ranged from -0.69e • $Å^{-3}$ to 0.65e • $Å^{-3}$. Final positional and isotropic thermal parameters for non-H atoms are listed in Table II and III [11], together with their e.s.d.s in parentheses. For all crystallographic computation, the UNICS program [12] was used, and the atomic scattering factors and terms of anomalous dispersion corrections were taken from ref 12 [13].

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[5] *cis*-Configuration between H-2a and H-7b of compounds **5** and **6** was confirmed from the experiment by treating compounds **5** and **6** with basic alumina, by which both compound did not epimerized.

[6] The fact that the cyclobutane fused compounds **5** and **6** were isolated from the photocycloaddition product suggests the possibility of formation of two other isomers of **5** and **6**; because in the case of furo[3,2-*c*]pyridin-7(6*H*)-one, four isomers of cyclobutane fused compound were isolated.

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