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THE REACTIONS OF ALLYL o-BROMOARYL ETHERS, N-ALLYL o-BROMOACETANILIDE, AND RELATED COMPOUNDS WITH TRIBUTYLTIN HYDRIDE IN THE PRESENCE OF ACTIVATED OLEFINS

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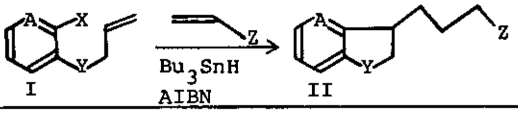
Abstract —— o-Bromophenyl allyl ether, N-allyl o-bromoacetanilide, and related compounds reacted with tributyltin hydride in the presence of activated olefins to give 2,3-dihydrobenzofuran, 2,3-dihydroindole, and analogous derivatives in modest yields respectively via both intra- and intermolecular radical C-C bond formations.

Recently, free radical reactions which mediated C-C bond formations have been studied extensively.1) In those reactions, the reaction with tributyltin hydride is one of the powerful synthetic tools and the radical cyclization reaction via the intramolecular pathway on an olefinic double bond or an acetylenic triple bond in aliphatic compound has been developed by Stork, Beckwith, Giese, and others.1) While, the reactions of aromatic compounds, i.e., free radical arylation reactions are less widely studied. Hitherto the reactions of o-substituted aryl halides with tributyltin hydride were reported to give dihydroindole, dihydrobenzofuran, and tetrahydro-ß-naphthol via intramolecular radical reactions by Ueno,2) Snieckus,3) Dittami,4) and Kuwajima.5)

We now report the direct preparations of 3-substituted 2,3-dihydrobenzofuran and 2,3-dihydroindole derivatives from o-bromophenyl allyl ether and N-allyl o-bromoacetanilide(A=CH), and the activated olefins in the presence of tributyltin hydride via both intramolecular(arylation) and intermolecular(alkylation) radical C-C bond formations as shown in eq. 1.6)

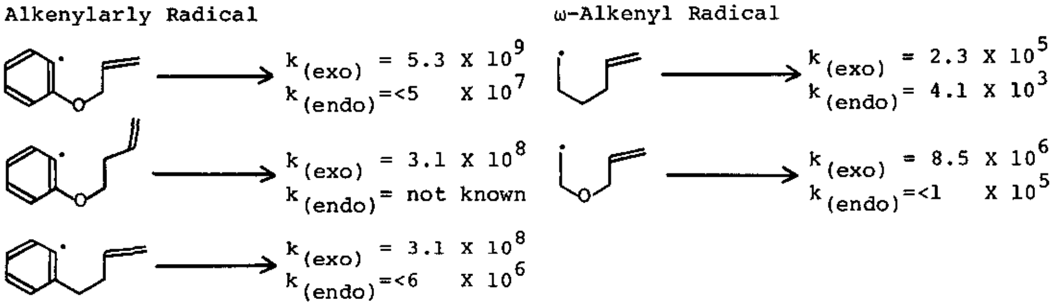


A: CH and N
X: Halogen
Y: O and NR
Z: Electron-Withdrawing Group
(1)

Dedicated with gratitude to Prof. Derek H. R. Barton on the occasion of his 70th birthday.

The rates for ring closure of alkenylaryl radicals are much faster than those of the corresponding ω-alkenyl radicals as shown below.7) Thus the ring closure in alkenylaryl radicals produced in the reaction (1) is expected to proceed very fast. Furthermore the rates of exo cyclization are much faster than those of the corresponding endo cyclization.

Rate Constants for Ring Closure at 25°C in s^{-1} 7)



Alkenylarly Radical

$k_{(exo)} = 5.3 \times 10^{9}$, $k_{(endo)} =< 5 \times 10^{7}$

$k_{(exo)} = 3.1 \times 10^{8}$, $k_{(endo)} =$ not known

$k_{(exo)} = 3.1 \times 10^{8}$, $k_{(endo)} =< 6 \times 10^{6}$

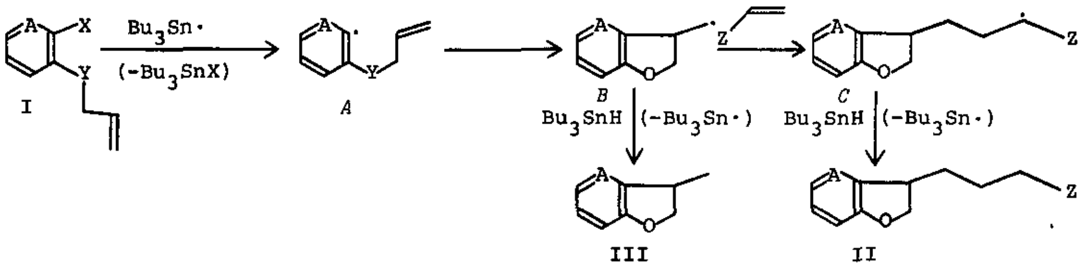
ω-Alkenyl Radical

$k_{(exo)} = 2.3 \times 10^{5}$, $k_{(endo)} = 4.1 \times 10^{3}$

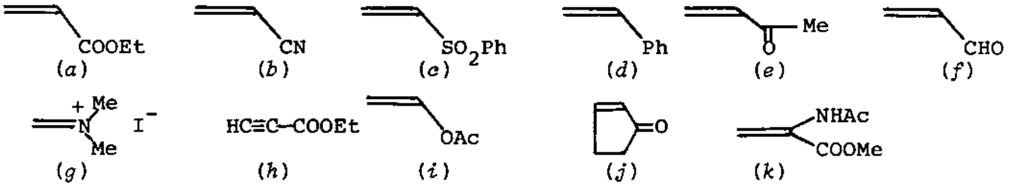
$k_{(exo)} = 8.5 \times 10^{6}$, $k_{(endo)} =< 1 \times 10^{5}$

Based on these physical properties, the reaction (1) is understood as the following Scheme. Once the radical *A* is formed, it immediately cyclizes to give *B* which can react both with tributyltin hydride and with an olefin to give III and *C*, respectively. Since the carbon radicals are nucleophilic in nature,8) the presence of electron-withdrawing group (Z) in side chain promotes the addition of *B* to the olefin to form another radical *C* . In the presence of tributyltin hydride, these radicals *B* and *C* are subjected to hydrogen abstraction to give III and II as final products respectively.

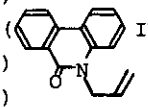
Scheme



Olefins



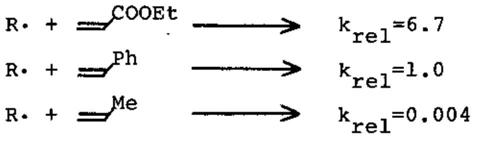
Table

run	I			Olefin(eq)		Yields(%)	
	X	Y	A		Z	II	III
1	Br	NAc	CH		COOEt(3.5)	54	18
2	"	"	"		CN (2.5)	46	b)
3	"	NCOPh	"		COOEt(3.5)	0	100 ( IV)
4	"	O	"		" (2.0)	60	b)
5	"	"	"		" (3.5)	49	b)
6	"	"	"		" (5.0)	22	0
7	"	"	"	a)	" (2.0)	16	b)
8	"	"	"	c)	" (2.0)	43	b)
9	I	"	"		" (2.0)	47	b)
10	Cl	"	"		" (2.0)	no reaction	
11	Br	"	"		CN (2.5)	57	b)
12	"	"	"		Ph (2.5)	58	25
13	"	"	"		SO_2Ph(2.0)	53	21
14	"	"	"		" (3.5)	60	15
15	"	"	"		 (2.5)	0	76
16	"	"	"		OAc (2.5)	0	84
17	"	"	N		COOEt(2.0)	55	b)
18	"	"	"		CN (2.5)	48	b)

a) Bu_3SnH was added to the mixture of I and olefin, and then the reaction was carried out under refluxing conditions in toluene. b) Small amount of III was observed but not isolated. c) Benzene was used as a solvent instead of toluene, and the reaction was carried out for 5 h.

The results are summarized in Table supporting the above assumption. As shown in runs 4, 5, and 6, when the amount of olefin was increased, the yield of II was decreased and formation of the other products was also observed on TLC. The optimun result was obtained when 2.0∿3.5 equimolar amount of olefin was used based on I. Run 3 shows that the aryl radical produced reacts at the ortho position of benzoyl group instead of allyl group to give tricyclic compound, IV. Runs 15 and 16 show that the reaction don't occur with a β-substituted olefin and an electron rich olefin, respectively. Though the phenyl group(z=Ph) is not a strong electron-withdrawing group, the addition reaction with carbon radical (R·) proceeds much faster than that of electron-donating group as shown below.[8]

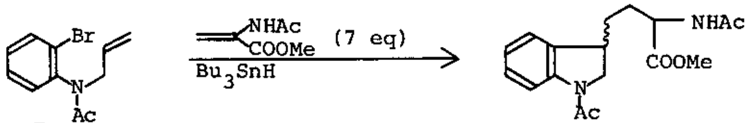
Relative Rate Constants for Addition Reactions[8)]



Thus the reaction with styrene in eq. 1 can proceed smoothly. The reaction of methyl N-acetyldehydroalanate(*k*), which has both electron-donating and electron-withdrawing groups, with carbon radical *B* gave a mixture of III, V, and further addition products with olefin(eq. 2), though it gave homologous compound of 2,3-dihydrotryptophan. The compound VI, which has two kind of halogens, reacted on iodine atom predominantly to give VII and VIII(eq. 3).

In conclusion, the cyclized carbon radical *B* reacts with ethyl acrylate(*a*), acrylonitrile(*b*), phenyl vinyl sulfone(*c*), and styrene(*d*) smoothly. While in the presence of methyl vinyl ketone(*e*), acrolein(*f*), Eschenmoser's salt(*g*), and ethyl propiolate(*h*), tributyltin hydride reacts faster with them than with compound I. In vinyl acetate(*i*) and cyclopentenone(*j*), the intermediate radical *B* produced reacts faster with tributyltin hydride than those olefins. In all these reactions, the products of exo ring closure, II and III, were major and those of endo ring closure were not observed. Finally, o-bromophenyl 3-butenyl ether IX gave X in 24% yield as a major product(eq. 4).

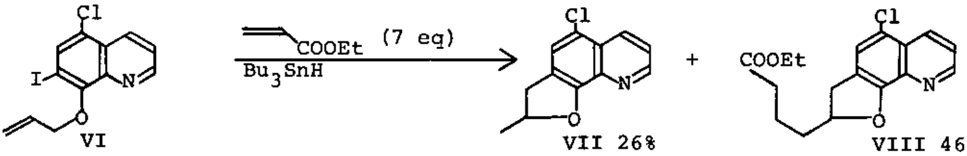
We are convinced that the reactions of aryl halides with tributyltin hydride in the presence of an activated olefin for making C-C bonds will be of value in organic synthesis



I

V 24%

(2)

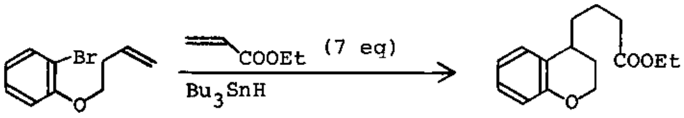


VI

VII 26%

VIII 46%

(3)



IX

X 24%

(4)

EXPERIMENTAL

Apparatus. ^{1}H-Nmr spectra were obtained on a JEOL FX-100 spectrometer. The chemical shifts are in ppm using TMS as an internal standard. Ir spectra were measured on Hitachi 260-50 spectrophotometer.

Preparation of Starting Materials. All o-haloaryl allyl ethers and N-allyl o-bromoacetanilide were prepared from the corresponding o-halophenol derivatives and o-bromoacetanilide with allyl bromide in DMF in the presence of sodium hydride.

o-Bromophenyl allyl ether: bp 83∿87°C/3 mmHg(lit.,[9] bp 130∿134°C/20 mmHg)

o-Iodophenyl allyl ether: bp 84∿97°C/3 mmHg(lit.,[9] bp 141∿144°C/8 mmHg)

2-Bromo-3-allyloxypyridine: Oil; ir(NaCl) 1565, 1450, 1415, and 1300 cm^{-1}; nmr(CDCl$_3$) δ=4.7∿4.55(m, 2H, CH$_2$), 5.50(d, 1H, J=17.1 Hz, trans CH$_2$=), 5.36(d, 1H, J=11.4 Hz, cis CH$_2$=), 5.90∿6.25(m, 1H, -CH=), 7.05∿7.25(m, 2H, aromatic), 8.00(dd, 1H, J=4.3 and 2.3 Hz, aromatic); Found: C, 45.14; H, 3.91; N, 6.45%. Calcd for C_8H_8NOBr: C, 44.89; H, 3.77; N, 6.54%.

N-Allyl o-bromoacetanilide: Oil; ir(NaCl) 1660 cm^{-1}; nmr(CDCl$_3$) δ=1.80(s, 3H, CH$_3$), 3.72(dd, 1H, J=14.3 and 7.7 Hz, CH$_2$), 4.78(dd, 1H, J=14.3 and 5.7 Hz, CH$_2$), 4.90∿5.20(m, 2H, CH$_2$=), 5.70∿6.10(m, 1H, -CH=), 7.10∿7.48(m, 3H, aromatic), 7.64∿7.77(m, 1H, aromatic); Found: C, 51.55; H, 4.82; N, 5.44%. Calcd for $C_{11}H_{12}NBrO$: C, 51.99; H, 4.76; N, 5.51%.

N-Allyl Benz(o-bromo)anilide: mp 88∿90°C; ir(Nujol-NaCl) 1620 and 1570 cm^{-1}; nmr (CDCl$_3$) δ=3.97(dd, 1H, J=14.6 and 7.7 Hz), 5.10∿4.70(m, 2H), 5.20(s, 1H), 6.20∿5.80 (m, 1H), 7.60∿6.90(m, 9H, aromatic); Found: C, 60.68; H, 4.44; N, 4.40; Br, 25.43%. Calcd for $C_{16}H_{14}NBrO$: C, 60.77; H, 4.46; N, 4.42; Br, 25.27%.

5-Chloro-7-iodo-8-allyloxyquinoline: mp 75∿76°C; ir(Nujol-NaCl) 1560 and 1080 cm^{-1}; nmr(CDCl$_3$) δ=4.95(dt, 2H, J=5.9 and 1.0 Hz, CH$_2$=), 5.17∿5.54(m, 2H, CH$_2$), 6.49∿6.10(m, 1H, -CH=), 7.53(dd, 1H, J=8.6 and 4.3 Hz, aromatic), 7.96(s, 1H, aromatic), 8.51(dd, 1H, J=8.6 and 1.7 Hz, aromatic), 8.95(dd, 1H, J=4.3 and 1.7 Hz, aromatic). Found: C, 41.91; H, 2.62; N, 3.98%. Calcd for $C_{13}H_9NOClI$: C, 41.71; H, 2.63; N, 4.05%.

3-Butenyl o-bromophenyl ether: Oil; ir(NaCl) 1580, 1465, 1275, and 1240 cm^{-1}; nmr (CDCl$_3$) δ=2.60(t, 2H, J=7.1 Hz, CH$_2$), 4.06(t, 2H, J=7.1 Hz, OCH$_2$), 5.05∿5.30(m, 2H, CH$_2$=), 5.75∿6.15(m, 1H, -CH=), 6.70∿6.95(m, 2H, aromatic), 7.24(td, 1H, J=8.0 and 2.0 Hz, aromatic), 7.52(dd, 1H, J=8.0 and 2.0 Hz, aromatic). Found: C, 52.96; H, 4.95%. Calcd for $C_{10}H_{11}BrO$: C, 52.89; H, 4.88%.

Phenyl vinyl sulfone[10) and methyl N-acetyldehydroalanate[11) were prepared by the known procedures.

Phenyl vinyl sulfone: mp 63∿66°C(lit.,[10) mp 68.5°C); nmr($CDCl_3$) δ=6.04(d, 1H, J=8.9 Hz, CH_2=), 6.44(d, 1H, J=16.3 Hz, CH_2=), 6.70(dd, 1H, J=8.9 and 16.3 Hz, -CH=), 7.40∿7.70(m, 3H, aromatic), 7.80∿8.00(m, 2H, aromatic).

Methyl N-acetyldehydroalanate: mp 45∿47°C(lit.,[11) mp 52∿54°C); nmr($CDCl_3$) δ=2.13(s, 3H, acetyl CH_3), 3.84(s, 3H, OCH_3), 5.88(m, 1H, CH_2=), 6.59(s, 1H, CH_2=), 7.76(bs, 1H, NH).

Radical Reactions of I *with Tributyltin hydride in the Presence of Olefin.*

The typical procedure was carried out as follows. To a refluxing toluene solution (10 ml) of I(2 mmol) and an olefin was added a toluene solution(8 ml) of tributyltin hydride(0.7 ml, 2.5 mmol) and azobisisobutyronitrile(AIBN, 30 mg) over 30∿40 min. After the addition, the reaction was continued further 20∿30 min under the same conditions. In these conditions, the starting material was consumed completely. Then the solvent was removed and the residue was separated by flash column chromatography on silica gel(eluent; chloroform) to give II and III.

In the cases of pyridine and quinoline derivatives I, 10 mg of dry p-toluenesulfonic acid was added to the toluene solution of I and then an olefin was added to the mixture before the addition of tributyltin hydride.

Ethyl 4-[(2,3-dihydrobenzofuran)-3-yl]butyrate: Oil; ir(NaCl) 1730, 1480, 1230, and 1170 cm^{-1}; nmr($CDCl_3$) δ=1.26(t, 3H, J=7.1 Hz, CH_3), 1.50∿1.90(m, 4H, CH_2CH_2), 2.20∿2.40(m, 2H, CH_2COO), 3.30∿3.60(m, 1H, CH), 4.14(q, 2H, J=7.1 Hz, OCH_2), 4.22(dd, 1H, J=8.6 and 5.7 Hz, CH), 4.64(t, 1H, J=8.6 Hz, CH), 6.70∿6.93(m, 2H, aromatic), 7.02∿7.24(m, 2H, aromatic). Found: C, 71.77; H, 7.86%. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74%.

4-[(2,3-Dihydrobenzofuran)-3-yl]butyronitrile: Oil; ir(NaCl) 2950, 2255, 1600, and 1230 cm^{-1}; nmr($CDCl_3$) δ=1.40∿2.00(m, 4H, CH_2CH_2), 2.20∿2.50(m, 2H, CH_2CN), 3.30∿3.60(m, 1H, CH), 4.20(dd, 1H, J=8.6 and 5.7 Hz, CH_2O), 4.63(t, 1H, J=8.6 Hz, CH_2O), 6.70∿6.95(m, 2H, aromatic), 7.00∿7.30(m, 2H, aromatic). Found: C, 76.75; H, 7.09; N, 7.48 %. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48%.

3-(3-Phenylpropyl)-2,3-dihydrobenzofuran: Oil; ir(NaCl) 3040, 2940, 1600, 1480, 1460, and 1230 cm^{-1}; nmr($CDCl_3$) δ=1.40∿1.90(m, 4H, CH_2CH_2), 2.50∿2.70(m, 2H, CH_2Ph), 3.20∿3.60(m, 1H, CH), 4.15(dd, 1H, J=8.6 and 5.7 Hz, OCH_2), 4.60(t, 1H, J=8.6 Hz, OCH_2), 6.70∿6.90(m, 2H, aromatic), 7.00∿7.40(m, 7H, aromatic). Found: C, 85.73; H, 7.63%. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61%.

4-(N-Acetyl-2,3-dihydro-3-indolyl)butyronitrile: mp 72∿74°C; ir(Nujol-NaCl) 2250, 1660, and 1595 cm^{-1}; nmr($CDCl_3$) δ=1.60∿2.00(m, 4H, CH_2CH_2), 2.24(s, 3H, CH_3), 2.30∿2.50(m, 2H, CH_2CN), 3.20∿3.70(m, 1H, CH), 3.70(dd, 1H, J=10.0 and 5.7 Hz, CH_2N), 4.20(t, 1H, J=10.0 Hz, CH_2N), 6.90∿7.40(m, 3H, aromatic), 8.23(d, 1H, J=7.1 Hz, aromatic). Found: C, 73.55; H, 7.12; N, 12.28%. Calcd for $C_{14}H_{16}N_2O$: C, 73.66; H, 7.06; N, 12.27%.

3-(3-Benzenesulfonylpropyl)-2,3-dihydrobenzofuran: Oil; ir(NaCl) 1600, 1300, 1230, 1140, and 1090 cm^{-1}; nmr($CDCl_3$) δ=1.50∿2.00(m, 4H, CH_2CH_2), 3.00∿3.20(m, 2H, CH_2SO_2), 3.20∿3.60(m, 1H, CH), 4.16(dd, 1H, J=8.6 and 5.7 Hz, CH_2O), 4.60(t, 1H, J=8.6 Hz, CH_2O), 6.80∿6.70(m, 2H, aromatic), 7.00∿7.20(m, 2H, aromatic), 7.70∿7.40(m, 3H, aromatic), 7.80∿8.00(m, 2H, aromatic). Found: C, 66.54; H, 6.13%. Calcd for $C_{17}H_{18}SO_3$: C, 67.52; H, 6.00%.

Ethyl 4-(N-acetyl-2,3-dihydro-3-indolyl)butyrate: Oil; ir(NaCl) 1725, 1660, 1600, 1480, 1405, and 1180 cm^{-1}; nmr($CDCl_3$) δ=1.25(t, 3H, J=7.1 Hz, CH_3), 1.40∿2.00(m, 4H, CH_2CH_2), 2.24(s, 3H, CH_3), 2.50∿2.10(m, 2H, CH_2COO), 3.20∿3.55(m, 1H, CH), 3.70(dd, 1H, J=10.6 and 5.7 Hz, CH_2), 4.14(q, 2H, J=7.1 Hz, OCH_2), 4.20(t, 1H, J=10.6 Hz, CH), 6.90∿7.30(m, 3H, aromatic), 8.20(d, 1H, J=7.1 Hz, aromatic). Found: C, 68.62; H, 7.83; N, 4.55%. Calcd for $C_{16}H_{21}NO_3$: C, 69.79; H, 7.69; N, 5.09%.

Ethyl 4-[(4-aza-2,3-dihydrobenzofuran)-3-yl]butyrate: Oil; ir(NaCl) 1725, 1435, 1260, and 1160 cm^{-1}; nmr($CDCl_3$) δ=1.25(t, 3H, J=7.1 Hz, CH_3), 1.60∿2.00(m, 4H, CH_2CH_2), 2.20∿2.50(m, 2H, CH_2COO), 3.30∿3.64(m, 1H, CH), 4.15(q, 2H, J=7.1 Hz, OCH_2), 4.34 (dd, 1H, J=8.6 and 5.7 Hz, CH_2), 4.76(t, 1H, J=8.6 Hz, CH_2), 7.01(d, 2H, J=2.8 Hz, aromatic), 8.05(t, 1H, J=2.8 Hz, aromatic). Found: C, 65.78; H, 7.39; N, 5.32%. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95%.

4-[(4-aza-2,3-dihydrobenzofuran)-3-yl]butyronitrile: Oil; ir(NaCl) 2140, 1600, 1570, 1420, and 1250 cm^{-1}; nmr($CDCl_3$) δ=2.10∿1.70(m, 4H, CH_2CH_2), 2.30∿2.55(m, 2H, CH_2CN), 3.33∿3.66(m, 1H, CH), 4.30(dd, 1H, J=9.1 and 6.8 Hz, CH_2), 4.78(t, 1H, J=9.1 Hz, CH_2), 7.05(d, 2H, J=2.9 Hz, aromatic), 8.06(t, 1H, J=2.9 Hz, aromatic). Found: C, 69.83; H, 6.48; N, 14.78%. Calcd for $C_{11}H_{12}N_2O$: C, 70.19; H, 6.43; N, 14.88%.

Ethyl pyrido[2,3-g]-5-chloro-2,3-dihydrobenzofuran-2-ylbutyrate: Oil; ir(NaCl) 1715, 1450, 1345, 1240, 1180, and 1080 cm^{-1}; nmr($CDCl_3$) δ=1.25(t, 3H, J=6.9 Hz, CH_3), 1.50 2.00(m, 4H, CH_2CH_2), 2.50∿2.20(m, 2H, CH_2COO), 3.50∿3.85(m, 1H, CH), 4.13(q, 2H, J=6.9 Hz, OCH_2), 4.54(dd, 1H, J=9.1 and 5.7 Hz, CH_2), 4.94(t, 1H, J=9.1 Hz, CH_2), 7.50∿7.30(m, 2H, aromatic), 8.44(dd, 1H, J=8.6 and 1.5 Hz, aromatic), 8.87(dd, 1H, J=4.6 and 1.5 Hz, aromatic). Found: C, 62.97; H, 5.69; N, 4.29%. Calcd for $C_{17}H_{18}NClO_3$:

C, 63.85; H, 5.67; N, 4.38%.

Pyrido[2,3-g]-2-methyl-5-chloro-2,3-dihydrobenzofuran; Oil; ir(NaCl) 1605, 1580,1445, 1340, and 1080 cm^{-1}; nmr($CDCl_3$) δ=1.40(d, 3H, J=7.1 Hz, CH_3), 3.56∿3.94(m, 1H, CH), 4.38(dd, 1H, J=9.1 and 7.7 Hz, CH_2), 4.97(t, J=9.1 Hz, CH_2), 7.30∿7.50(m, 2H, aromatic), 8.44(dd, 1H, J=8.6 and 1.5 Hz, aromatic), 8.87(dd, 1H, J=5.1 and 1.5 Hz, aromatic), Found: C, 65.15; H, 4.62; N, 6.39%. Calcd for $C_{12}H_{10}NOCl$: C, 65.61; H, 4.59; N, 6.38%.

Ethyl 4-chromanylbutyrate: Oil; ir(NaCl) 1720, 1595, and 1570 cm^{-1}; nmr($CDCl_3$) δ= 1.26(t, 3H, J=7.4 Hz, CH_3), 2.20∿1.50(m, 6H, CH_2CH_2 and CH_2), 2.20∿2.45(m, 2H, CH_2COO), 2.65∿2.95(m, 1H, CH), 4.15(q, 2H, J=7.4 Hz, OCH_2), 4.17(t, 2H, J=5.7 Hz, OCH_2), 6.70∿6.95(m, 2H, aromatic), 7.00∿7.15(m, 2H, aromatic). Found: C, 72.32; H, 8.19%. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12%.

N-Acetyl 3-methyl-2,3-dihydroindole: mp 82∿84°C; ir(Nujol-NaCl) 1650, 1595, and 1270 cm^{-1}; nmr($CDCl_3$) δ=1.36(d, 3H, J=6.6 Hz, CH_3), 2.22(s, 3H, CH_3), 3.30∿3.70(m, 2H, CH_2), 4.05∿4.40(m, 1H, CH), 8.20(d, 1H, J=7.1 Hz, aromatic), 6.90∿7.33(m, 3H, aromatic). Found: C, 75.16; H, 7.53; N, 7.88%. Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99%.

Methyl 2-acetylamino-4-(N-acetyl-2,3-dihydro-3-indolyl)butyrate: mp 123∿127°C; ir (Nujol-NaCl) 3260, 1725, and 1640 cm^{-1}; nmr($CDCl_3$) δ=2.10∿1.50(m, 4H, CH_2CH_2), 2.03 (s, 3H, CH_3), 2.22(s, 3H, CH_3), 3.20∿3.60(m, 1H, CH), 3.60(dd, 1H, J=10.0 and 5.7, CH_2N), 3.77(s, 3H, CH_3), 4.16(t, 1H, J=10.0 Hz, CH_2N), 4.50∿4.80(m, 1H, CHCOO), 6.16(d, 1H, J=7.4 Hz, NH), 6.90∿7.30(m, 3H, aromatic), 8.19(d, 1H, J=8.6 Hz, aromatic). Found: C, 63.34; H, 7.03; N, 8.69%. Calcd for $C_{17}H_{22}N_2O_4$: C, 64.13; H, 6.97; N, 8.69%.

5,6-Dihydro-6-oxo-N-allylphenanthridine: mp 98∿100°C; ir(Nujol-NaCl) 1635, 1605, and 1580 cm^{-1}; nmr($CDCl_3$) δ=4.95∿5.35(m, 4H, CH_2 and CH_2=), 5.85∿6.25(m, 1H, -CH=), 7.20∿7.90(m, 5H, aromatic), 8.30(d, 2H, J=7.1 Hz, aromatic), 8.60(dd, 1H, J=7.1 and 1.4 Hz, aromatic). Found: C, 81.46; H, 5.60; N, 5.92%. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95%.

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