REDUCTION OF AROMATIC NITROALKENES WITH BAKER'S YEAST

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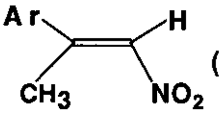
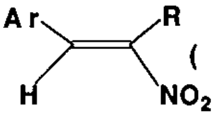
Abstract——Aromatic nitroalkenes were reduced chemoselectively with baker's yeast to give the corresponding nitroalkanes.

It is widely recognized that nitro compounds are useful in synthetic organic chemistry because of the easiness to convert into other compounds such as amines or ketones.[1] Among the syntheses of nitro compounds, nitroalkanes were prepared enzymatically from nitroalkenes in some cases.[2,3] In the reaction of 1-nitro-2-phenylpropene (**1**) with baker's yeast,[2] carbon-carbon double bond was reduced to give the corresponding nitroalkanes. However, few papers on the enzymatic reduction of aromatic nitroalkenes have been reported.[4] Herein, we would like to report the chemoselective reduction of heteroaromatic nitroalkenes with baker's yeast.

For extention of chemoselective reduction of *E*-β-nitrostyrene derivatives (**2**), we examined the influences of the sustituent on the aromatic ring for the enzymatic reduction.



(**1**)



(**2**) (R = H, CH_3)

As shown in Table I, fermentation of *E*-β-nitrostyrenes (**3 a-o**) with baker's yeast at 31-33 °C for 72-74 h gave the corresponding nitroalkanes (**4 a-o**) in 28-81% chemical yields. In these reactions, it was found that when an electron-withdrawing group such as Br, Cl and CN (**3i-o**) was substituted on the aromatic ring, chemical yields of *meta*- or *ortho*-substituted compounds were higher than those of *para*-substituted

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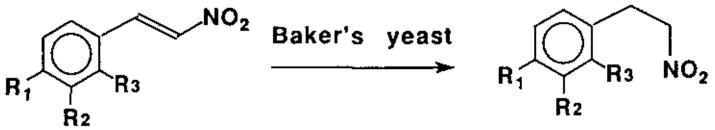
Dedicated to Professor Aran. R. Katritzky on the occasion of his 65th birthday.

compounds. But, distinct differences in reducibilities between an electron-donating group substituted compounds (**3b-h**) and electron-withdrawing group substituted compounds (**3i-o**) were slightly observed. (Table I)

The same reaction of methyl substituted *E*-β-nitrostyrene (**5**a-n) with baker's yeast also proceeded smoothly to give nitroalkanes (**6a-n**) in 42-73% chemical yields, although the optical rotations of the products were low because of racemization.[3] (Table II)

Interestingly, when a nitro group subustituted on the benzene ring (**7a-c**), selective reduction, as we reported previously,[5] took place to give nitroalkane (**8a-c**) in 42-65% chemical yields accompanied with amino derivatives (**9a-c**) as minor products (0-5% chemical yields). In contrast, when methyl substituted nitroalkenes (**7 d-f**) were treated with baker's yeast under the same conditions, amino derivatives (**9d-f**) were obtained (61 and16 %) in preference to nitroalkane (**8d-f**) (24 and 10%).

Table I. Reduction of *E*-Nitro Alkenes with Baker's Yeast

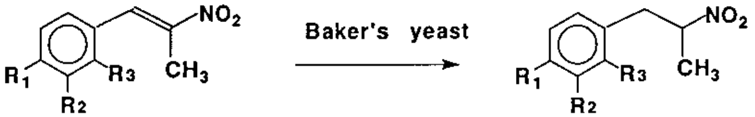


(3a-o) (4 a-o)

(3)				Temp	Time	(4)	(3)				Temp.	Time	(4)
	R_1	R2	R3	°C	h	Yield (%)		R_1	R2	R3	°C	h	Yield (%)
3a[a,b]	H	H	H	31	72	43[h,i]	3i[d,e,f]	CN	H	H	31	74	28[e,f]
3b[a,c,d]	CH_3O	H	H	33	74	75[c,h]	3j	H	CN	H	31	73	69
3c[a,d]	H	CH_3O	H	33	74	81[j]	3k[d]	Br	H	H	33	74	46[m]
3d[a]	H	H	CH_3O	33	74	57[h]	3l	H	Br	H	33	74	52
3e[b,d]	CH_3	H	H	32	72	67[c,i,k]	3m[g]	H	H	Br	33	74	61
3f[b]	H	CH_3	H	32	72	41	3n[d]	Cl	H	H	31	73	67[c,k,n]
3g[b]	H	H	CH_3	33	73	73[l]	3o[a,b]	H	H	Cl	31	72	73[l]
3h[a]	OH	H	H	33	74	37[k]							

a) see ref. 6a. b) see ref. 6b. c) see ref. 6c. d) see ref. 6d. e) see ref.6 e. f) see ref. 6f. g) see ref. 6g. h) see ref. 4. i) see ref. 6h. j) see ref. 6i. k) see ref. 6j. l) see ref. 6k. m) see ref. 6l. n) see ref. 6n.

Table II. Reduction of *E*-Aryl-2-nitropropenes with Baker's Yeast

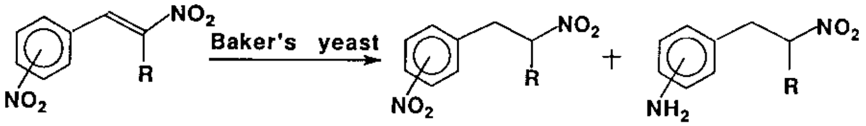


(5a-n) (6a-n)

(5)				Temp.	Time	(6)	(5)				Temp.	Time	(6)
	R_1	R_2	R_3	°C	h	Yield (%)		R_1	R_2	R_3	°C	h	Yield (%)
5a[a,b]	H	H	H	24	120	79[k]	5h[e,f]	CN	H	H	33	65	48[g]
5b[a,b,c,d]	CH_3O	H	H	33	75	42[k,l]	5i	H	CN	H	33	67	52
5c[a,c,f]	H	CH_3O	H	33	50	60[l]	5j[e,f,j]	Cl	H	H	33	64	73[c]
5d[c,f,g]	CH_3	H	H	33	71	61[l]	5k[e]	H	Cl	H	33	50	42[c]
5e[a,c]	H	CH_3	H	33	48	59[l]	5l[i,j]	H	H	Cl	33	50	48[n]
5f[h]	H	H	CH_3	33	71	69[l]	5m	H	Br	H	33	69	52[o]
5g[i]	OH	H	H	33	72	69[m]	5n	H	H	Br	33	70	44[o]

a) see ref. 7a. b) see ref. 7b. c) see ref. 7c. d) see ref. 7d. e) see ref. 7e. f) see ref. 6b. g) see ref. 7g. h) see ref. 6g. i) see ref. 6a. j) see ref. 6h. k) see ref. 4. l) see ref. 7f. m) see ref. 3. n) see ref. 6f. o) see ref. 7h.

Table III. Reduction of *E*-Nitrophenyl Nitroalkenes with Baker's Yeast



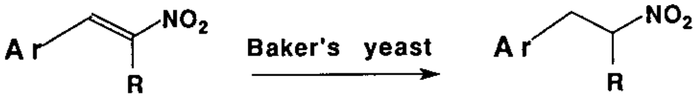
(7a-f) (8a-f) (9a-f)

(7)			Temp.	Time	(8)	(9)
	Phenyl	R	°C	h	Yield (%)	Yield (%)
7a[a]	4-NO_2	H	33	72	44[g,h]	5[h]
7b[a]	3-NO_2	H	33	70	42	0
7c[a]	2-NO_2	H	33	72	65	0
7d[b,c,d]	4-NO_2	CH_3	33	72	24[i,j]	61[i]
7e[b,d,e]	3-NO_2	CH_3	33	72	10[j]	28
7f[f]	2-NO_2	CH_3	33	52	24	16

a) see ref. 6a. b) see ref. 7a. c) see ref. 7b. d) see ref. 7d. e) see ref. 7e. f) see ref. 8a. g) see ref. 6j. h) see ref. 8b. i) see ref. 8c. j) see ref. 7c.

We next applied these enzymatic reduction to heteroaromatic nitroalkenes. When *E*-3-indolyl- or 3-pyridyl nitroalkenes (**10 a-d**) were treated with baker's yeast at 33 °C for 72-109 h, chemoselective reductions occurred to give the corresponding 3-indolyl- or 3-pyridyl nitroalkanes (**11a-d**) (44- 73% chemical yields), while reduction of *E*-*N*-phenyl-3-indolyl nitroethene (**10c**) did not proceed at all.

Table IV. Reduction of *E*-Heteroaromatic Nitroalkenes with Baker's Yeast.



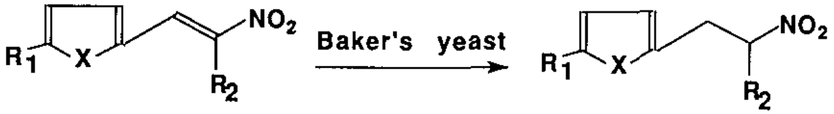
(10a-d) (11a-d)

(10)			Temp.	Time	(11)
	Ar	R	°C	h	Yield (%)
10a[a]	3-Indolyl	H	33	72	44[d]
10b[a]	3-Indolyl	CH_3	33	109	65
10c	*N*-Phenyl-3-indolyl	H	33	72	0
10d[b,c]	3-pyridyl	CH_3	33	72	73

a) see ref. 9a. b) see ref. 7a. c) see ref. 9b. d) see ref. 9c.

When five-membered ring (thiophene, furan, and pyrrol) substituted *E*-nitroalkenes (**12 a-h**) were treated with baker's yeast under the same conditions, carbon-carbon double bonds were selectively reduced to afford the corresponding nitroalkanes (**13a-h**) in 45-79% chemical yields. In the reactions, significant differences in reactivities among five-menbered heteroaromatics were not observed. But, to be notice, when a methyl group was substituted on the double bond (**10c,10d, 12e, 12g, 12h**), the yields of the products were higher than those in the case of unmethylated compounds (**10a-b, 12a, 12c, 12d**). Thus, it was found that heteroaromatic nitroolefins were reduced chemoselectively with baker's yeast to give the corresponding nitroalkanes in moderate to good chemical yields.

Table V. Reduction of *E*-Five-membered Heteroaromatic Nitroalkenes with Baker's Yeast.



(12a-h) (13a-h)

(12)				Temp.	Time	(13)
	X	R_1	R_2	°C	h	Yield (%)
12a[a,b]	S	H	H	33	72	61[f]
12b[c]	S	Br	H	33	50	79[g]
12c[a,b]	O	H	H	33	50	59[f]
12d[b]	*N*-CH_3	H	H	33	72	45[h]
12e[b,d]	S	H	CH_3	33	72	75[g,i]
12f[d]	S	Br	CH_3	33	64	46[i]
12g[e]	O	H	CH_3	33	72	74[g]
12h	*N*-CH_3	H	CH_3	33	72	79

a) see ref. 7f. a) see ref. 9a. c) see ref. 10a. d) see ref. 10b.
e) see ref. 9b. f) see ref. 4. g) see ref. 6j. h) see ref. 10c.
i) see ref. 10b.

EXPERIMENTAL

^{1}H-Nmr spectra were recorded on JEOL PMX-60si (60MHz) or JNM-GMX-400 (400MHz) spectrometers with tetramethylsilane as an internal standard. Mass spectra were recorded on a JEOL JMN-DX 303. Melting point were determined on a Yanagimotomelting point apparatus and are uncorrected. For column chromatography, silica gel (Wacogel C-200, from Wako Pure chemical Industries, Ltd.) was used. Configuration of β-nitrostyrenes was confirmed to be *E* by the coupling constant (J = 14Hz) and nOe effect in ^{1}H-nmr spectra.

General procedure for the reduction of *E*-β-nitrostyrenes (3a-o) with Baker's yeast. A mixture of *E*- β-nitrostyrenes (**3a-o**) (0.5 g) and baker's yeast (250 g)(purchased from Oriental Yeast Co.) in water (250 ml) was fermented for 72-74 h at 31-33° C. The mixture was extracted continuously with $CHCl_3$ using a Soxlet apparatus and the extract was dried over Na_2SO_4. The solvent was removed under reduced pressure to give the residue which was purified by silica gel (10-15 g) column chromatography using CH_2Cl_2 as eluent to yield 1-aryl-2-nitroetanes (**4a-o**)(Table I).

3j : a colorless powder, mp 110-112°C(MeOH-Et_2O);^{1}H-nmr ($CDCl_3$) δ : 7.57 (1H, d, *J*= 14Hz), 7.67-7.99 (5H, m); ms m/z : Calcd. for $C_9H_6N_2O_2(M^+)$: 174.0429. Found : 174.0406.

3l : an oil,^{1}H-nmr ($CDCl_3$) δ: 7.16-8.14 (6H, m); ms m/z : Calcd. for $C_8H_6BrNO_2(M^+)$: 226.9581. Found : 226.9627.

4f : an oil,^{1}H-nmr ($CDCl_3$) δ : 3.33 (3H, s), 3.60 (2H, t, *J*=7Hz), 4.57 (2H, t, *J*=7Hz), 7.22-7.80 (4H, m); ms m/z : Calcd. for $C_9H_{11}NO_2(M^+)$: 165.0790. Found : 165.0784.

4j : an oil,^{1}H-nmr ($CDCl_3$) δ: 3.33 (2H, t, *J*=7Hz), 4.60 (2H, t, *J*=7Hz), 7.57 (4H, s); ms m/z : Calcd. for $C_9H_8N_2O_2(M^+)$: 176.0586. Found : 176.0613.

4l : an oil,^{1}H-nmr ($CDCl_3$) δ: 3.30 (2H, t, *J*=7Hz), 4.60 (2H, t, *J*=7Hz), 7.01-7.73 (4H, m); ms m/z : Calcd. for $C_8H_8BrNO_2(M^+)$: 228.9738. Found : 228.9801.

4m : an oil,^{1}H-nmr ($CDCl_3$) δ: 3.33 (2H, t, *J*=7Hz), 4.57 (2H, t, *J*=7Hz), 6.80-7.87 (4H, m); ms m/z : Calcd. for $C_8H_8BrNO_2(M^+)$: 228.9738. Found: 228.9700.

General procedure for the reduction of *E*-α-methyl-β-nitrostyrenes (5a-n) with Baker's yeast. A mixture of *E*-α-methyl-β-nitrostyrenes (**5a-n**) (0.5 g) and baker's yeast (250 g)(purchased from Oriental Yeast Co.) in water (250 ml) was fermented for 48-120 h at 24-33° C. The mixture was extracted continuously with $CHCl_3$ using a Soxlet apparatus and the extract was dried over Na_2SO_4. The solvent was removed under reduced pressure to give the residue which was purified by silica gel (10-15 g) column chromatography using CH_2Cl_2 as eluent to yield 1-aryl-2-nitropropanes (**6a-n**) (Table II).

5i : a colorless powder, mp 107-109°C (MeOH-Et_2O); ^{1}H-nmr ($CDCl_3$) δ: 2.65 (3H,s), 7.64-7.83 (4H, m), 8.02 (1H,s); ms m/z : Calcd. for $C_{10}H_8N_2O_2(M^+)$: 188. 0586. Found : 188.0592.

5m : an oil,^{1}H-nmr ($CDCl_3$) δ: 2.75 (3H,s), 7.20-7.90 (4H, m), 7.99 (1H, s); ms m/z : Calcd. for $C_9H_8BrNO_2(M^+)$: 240.9738. Found : 240.9800.

5n : an oil, ^{1}H-nmr ($CDCl_3$) δ: 2.33 (3H, s), 7.17-7.87 (4H, m), 8.15 (1H, s); ms m/z : Calcd. for $C_9H_8BrNO_2(M^+)$: 240.9738. Found : 240.9844.

6i : an oil, ^{1}H-nmr ($CDCl_3$) δ: 1.57 (3H, d, *J*=7Hz), 2.83-3.63 (2H, m), 4.50-5.16 (2H, m), 7.20-7.60 (4H, m); ms m/z : Calcd. for $C_{10}H_{10}N_2O_2(M^+)$: 190.0720. Found : 190.0740.

General procedure for the reduction of *E*-1-Nitrophenyl-2-nitroalkenes (7a-f) with Baker's yeast. A mixture of *E*-1-Nitrophenyl-2-nitropropenes (**7a-f**) (0.5 g) and baker's yeast (250 g)(purchased from Oriental Yeast Co.) in water (250 ml) was fermented for 70-72 h at 33° C. The mixture was extracted continuously with $CHCl_3$ using a Soxlet apparatus and the extract was dried over Na_2SO_4. The solvent was removed under reduced pressure to give the residue which was purified by silica gel (10-15 g) column chromatography usig CH_2Cl_2 as eluent to yield 1-nitrophenyl-2-nitroalkanes (**8a-f**) and CH_2Cl_2 : MeOH (98 : 2) as eluent to yield 1-aminophenyl-2-nitroalkanes(**9a-f**)(Table III).

8b : an oil,^{1}H-nmr ($CDCl_3$) δ : 3.50 (2H, t, *J*=7Hz), 4.73 (2H, t, *J*=7Hz), 7.18-8.34 (3H, m); ms m/z: Calcd. for $C_8H_8N_2O_4(M^+)$: 196.0484. Found : 196.0475.

8c : an oil, ^{1}H-nmr ($CDCl_3$) δ: 3.57 (2H, t, *J*=7Hz), 4.77 (2H, t, *J*=7Hz), 6.98-8.17 (4H, m); ms m/z: Calcd. for $C_8H_8N_2O_4(M^+)$: 196.0484. Found : 196.0473.

8f : an oil, ^{1}H-nmr ($CDCl_3$) δ: 1.63 (3H, d, *J*=7Hz), 3.16 (1H, dd, *J*=7, 14Hz), 3.47 (1H, dd, *J*=7, 14Hz), 4.57-5.17 (1H, m), 7.20-8.27 (4H, m); ms m/z: Calcd. for $C_{10}H_{10}N_2O_2(M^+)$: 210.0641. Found : 210.0601.

9e : an oil,^{1}H-nmr ($CDCl_3$) δ : 1.50 (3H, d, *J*=7Hz), 2.86 (1H, dd, *J*=7, 14Hz), 3.27 (1H, dd, *J*=7, 14Hz), 4.42-5.10 (1H, m), 6.48-7.23 (4H, m); ms m/z : Calcd. for $C_9H_{12}N_2O_2(M^+)$: 180.0899. Found : 180.0914.

9f : an oil,^{1}H-nmr ($CDCl_3$) δ : 1.50 (3H, d, *J*=7Hz), 2.89 (1H, dd, *J*=7, 14Hz), 3.27 (1H, dd, *J*=7, 14Hz), 4.51- 5.13 (1H, m), 6.83-7.42 (4H, m); ms m/z : Calcd. for $C_9H_{12}N_2O_2(M^+)$: 180.0899. Found :

180.0886

General procedure for the reduction of *E*-1-Heteroaryl-2-nitroalkenes (10a-d) with Baker's yeast. A mixture of *E*-1-heteroaryl-2-nitropropenes(**10 a-d**) (0.5 g) and baker's yeast (250 g)(purchased from Oriental Yeast Co.) in water (250 ml) was fermented for 72 -109 h at 33° C. The mixture was extracted continuously with $CHCl_3$ using a Soxlet apparatus and the extract was dried over Na_2SO_4. The solvent was removed under reduced pressure to give the residue which was purified by silica gel (10-15 g) column chromatography usig CH_2Cl_2 as eluent to yield 1-heteroaryl-2-nitroalkanes(**11a-d**) (Table IV).

11d : an oil, ^{1}H-nmr (CDCl3) δ : 1.53 (3H, d, *J*=7Hz), 3.03 (1H, dd, *J*=7, 14Hz), 3.37 (1H, dd, *J*=7, 14 Hz), 4.50-5.20 (1H, m), 7.15-8.71 (4H, m); ms m/z : Calcd. for $C_8H_{10}N_2O_2(M^+)$: 166.0742. Found : 166.0734.

General procedure for the reduction of Five-membered *E*-Heteroaryl-2-nitroalkenes (12a-h) with Baker's yeast. A mixture of five-membered *E*-heteroaryl-2-nitroalkenes(**12a-h**) (0.5 g) and baker's yeast (250 g)(purchased from Oriental Yeast Co.) in water (250 ml) was fermented for 50-72 h at 33° C. The mixture was extracted continuously with $CHCl_3$ using a Soxlet apparatus and the extract was dried over Na_2SO_4. The solvent was removed under reduced pressure to give the residue which was purified by silica gel (10-15 g) column chromatography using CH_2Cl_2 as eluent to yield five-membered heteroaryl-2-nitroalkanes(**13a-h**). (Table V)

12h : pale yellow powder, mp 62-64 °C(EtOH); ^{1}H-nmr ($CDCl_3$) δ: 2.50 (3H, s), 3.76 (3H, s), 6.21-7.02 (3H, m), 8.11 (1H, s); ms m/z : Calcd. for $C_8H_{10}N_2O_2(M^+)$: 166.0742. Found : 166.0727.

13h : an oil, ^{1}H-nmr ($CDCl_3$) δ: 1.56 (3H, d, *J*=7Hz), 2.90 (1H, dd, *J*=7, 14Hz), 3.33 (1H, dd, *J*=7, 14Hz), 4.43-5.01(1H, m), 5.86-6.65(3H, m); ms m/z: Calcd. for $C_8H_{12}N_2O_2(M^+)$: 168.0899. Found: 168.0914.

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