Successive Electron Transfer Reaction of the Lithium Salt of 5-Methyl-5,10-dihydrophenazine Anion with 4-Nitrophenethyl Bromide *via* 4-Nitrostyrene

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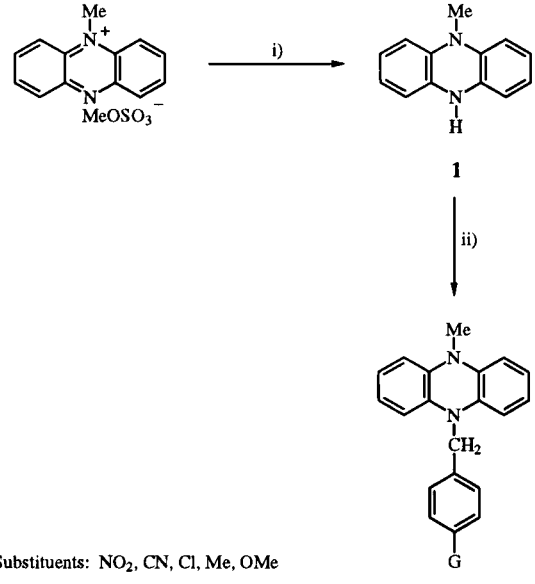
Received August 27, 1998
Revised March 22, 1999

The reaction of lithium salt of 5-methyl-5,10-dihydrophenazine anion with 4-nitrophenethyl bromide in 1,2-dimethoxyethane gave unexpected compounds, 1,2-bis[5-(10-methyl-5,10-dihydrophenazinyl)]-1-(4-nitrophenyl)ethane and 1,4-bis(4-nitrophenyl)-1,4-bis[5-(10-methyl-5,10-dihydrophenazinyl)]butane, while the reaction in dimethyl sulfoxide brought about the formation of 5-methyl-10-(4-nitrophenethyl)-5,10-dihydrophenazine. The successive electron transfer mechanism is proposed for the former reaction *via* 4-nitrostyrene.

J. Heterocyclic Chem., **36**, 849 (1999).

N,N'-Disubstituted 5,10-dihydrophenazine serves as a powerful electron donor [1]. The formation of charge transfer complexes with appropriate electron acceptors, their properties, and the reactivities have so far been published [2]. In the course of our investigation of dihydrophenazines, we have found that, *N,N'*-disubstituted 5,10-dihydrophenazines are easily obtained by reaction of lithiated 5,10-dihydrophenazine with alkyl halide in 1,2-dimethoxyethane [3]. Similarly 5-methyl-5,10-dihydrophenazine (**1**) is converted into 10-(*p*-substituted benzyl)-5-methyl-5,10-dihydrophenazines by the lithiation of **1** followed by reaction with *p*-substituted benzyl halide (substituent: NO_2, CN, Cl, Me, OMe) in 1,2-dimethoxyethane (Equation 1) [4].



Substituents: NO_2, CN, Cl, Me, OMe

(1)

i) $Na_2S_2O_4$-H_2O
ii) BuLi, 1,2-Dimethoxyethane solution, then *p*-substituted benzyl bromide in 1,2-Dimethoxyethane

Under similar reaction conditions, however, the reaction of the lithium salt of anion of **1** with *p*-nitrophenethyl bromide afforded mainly 1,2-bis[5-(10-methyl-5,10-dihydrophenazinyl)]-1-(4-nitrophenyl)ethane (**2**) and 1,4-bis(4-nitrophenyl)-1,4-bis[5-(10-methyl-5,10-dihydrophenazinyl)]butane (**3**) (see Experimental), although 5-methyl-10-(*p*-nitrophenethyl)-5,10-dihydrophenazine (**4**) is obtained from the same reagents by reaction in dimethyl sulfoxide. In this paper we propose the mechanisms for the formation of the unexpected products **2** and **3**.

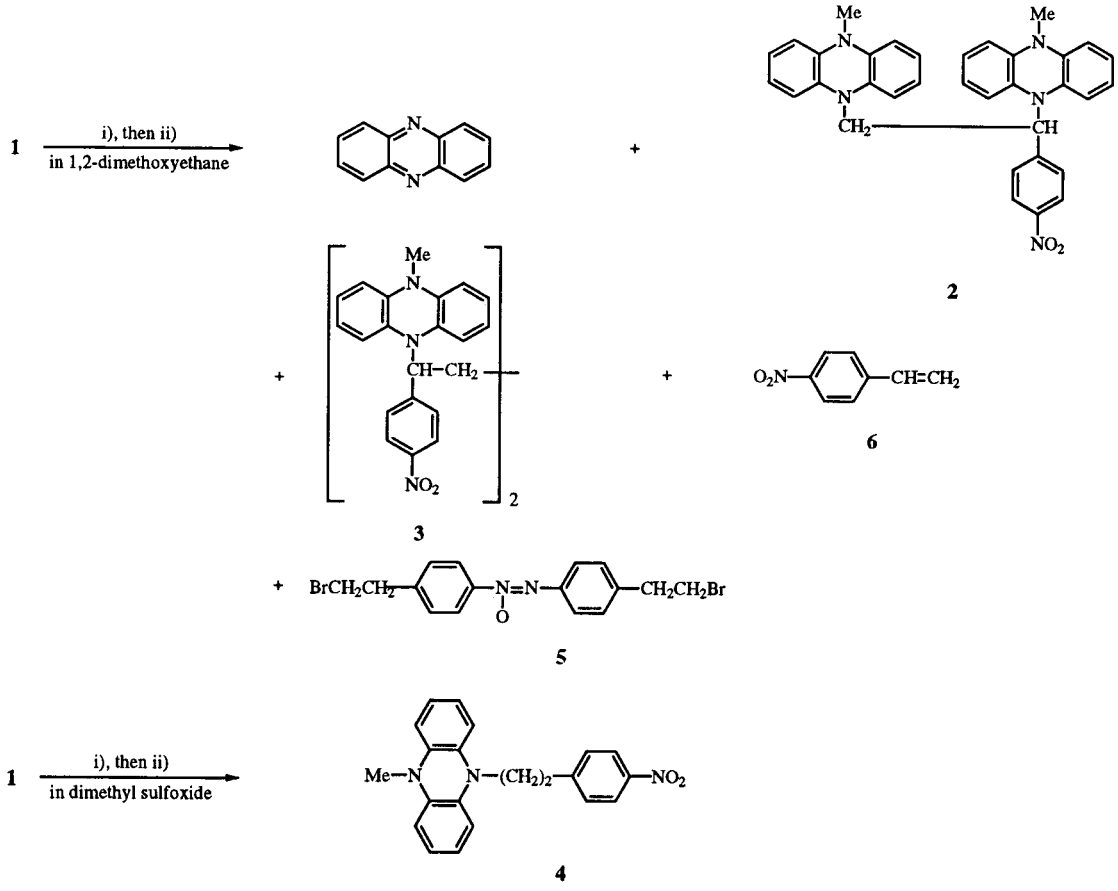
The reaction of lithiated **1** with *p*-nitrophenethyl bromide was carried out under an argon atmosphere in 1,2-dimethoxyethane or dimethyl sulfoxide at room temperature. As compound **1** is very sensitive to air, unchanged **1** is hardly recovered and a mixture of unidentified dark brown substances and phenazine were formed during the workup treatment. The isolated products of the reaction in 1,2-dimethoxyethane were **2**, **3**, phenazine, 4,4'-bis(2-bromoethyl)azoxybenzene (**5**), and 4-nitrostyrene (**6**) in 36, 5, 23, 1, and 19% isolated yields, respec-

tively, along with the recovery of *p*-nitrophenethyl bromide (25%) (Scheme 1). These products were identified by the spectroscopic method. Furthermore, the structures of **2** and **3** were confirmed by X-ray crystal structure analysis [5]. ORTEP drawings of them are shown in Figure 1 and the crystallographic analysis data of them are summarized in Table 1 along with those of compound **4**. The bond lengths, bond angles, atomic coodinates and B_{eq} of **2**, **3**, and **4** are shown in Tables 2-7. Compound **3** is a mixture of *dl*- and *meso*-isomers, both of which were isolated for crystallographic samples (see Experimental).

The use of dimethyl sulfoxide instead of 1,2-dimethoxyethane for the reaction of *p*-nitrophenethyl bromide with sodium salt of **1** resulted in the formation of **4** in 20% yield and no detectable amount of **2** or **3** was isolated. Furthermore, the reaction even in *N*,*N*-dimethylformamide also gave **4** in 16% yield. In this reaction, **2** or **3** was not detected, either. Reaction of the lithiated **1** with phenethyl iodide, instead of *p*-nitrophenethyl bromide, gave a usual product, 5-methyl-10-phenethyl-5,10-dihydrophenazine (**7**) in 1,2-dimethoxyethane. However, 5-methyl-10-[3-(4-nitrophenyl)propyl]-5,10-dihydrophenazine (**8**) was not obtained by the reaction with 3-(4-nitrophenyl)propyl bromide in 1,2-dimethoxyethane, but obtained by the reaction in dimethyl sulfoxide. Furthermore, the mixing of 5,10-dihydrophenazine and *p*-nitrophenethyl bromide under the same reaction conditions (in 1,2-dimethoxyethane) afforded the starting materials unchanged, indicating that the anion of **1** is neccessary for the present reaction. These results suggested that compound **6** is a primary product and that electron transfer from the anion of **1** to **6** gives a radical anion of **6** and a phenazinyl radical.

To obtain further informations, reaction of **6** with lithiated **1** in 1,2-dimethoxyethane was investigated. A solution of **6** was added dropwise to a solution of lithiated **1** (reaction conditions of excess of the anion of **1**) followed by the usual workup gave **2** in 8% yield and only a detect-

Scheme 1



i) BuLi; ii) *p*-Nitrophenethyl bromide.

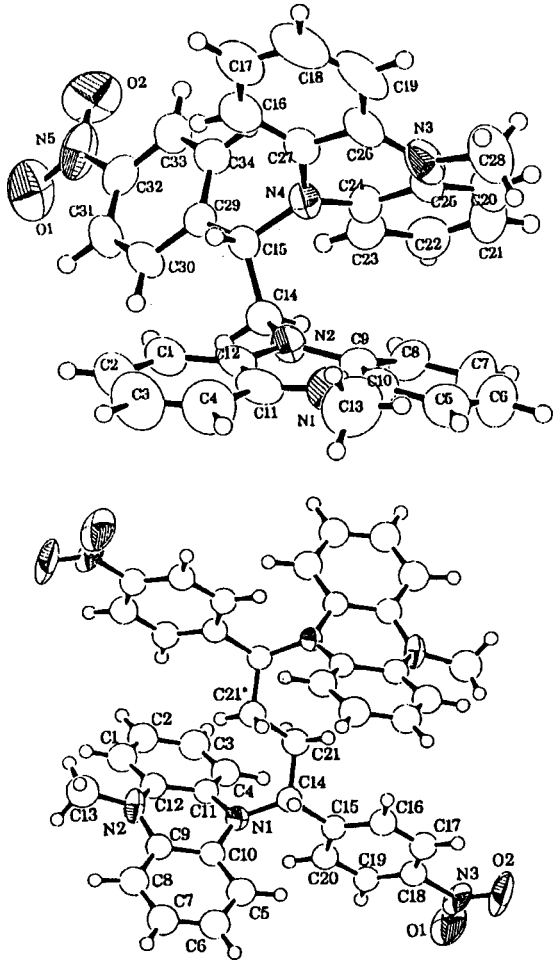


Figure 1. ORTEP drawings of **2** (top) and **3** (bottom).

able amount of **3**, respectively, along with phenazine in 21% yield. Conversely, an addition of a solution of lithiated **1** to that of **6** (reaction conditions of excess **6**) resulted in the formation of **2** and **3** in the yields of 5% and 15%, respectively, with 11% yield of phenazine. Namely, under the reaction conditions of the presence of excess lithiated **1**, **2** was produced preferentially and under that of the presence of excess of **6**, **3** was a major product. On the other hand, unchanged **1** was recovered by mixing of styrene with lithiated **1** in 1,2-dimethoxyethane indicating that nitro group is essential for the present reaction.

On the basis of these observations, we wish to propose a plausible formation pathway of the present products, **2** and **3**, as shown in Scheme 2. The first step of the reactions should be elimination of hydrogen bromide from *p*-nitrophenethyl bromide by anion of **1** to form **6**. Electron transfer from anion of **1** to **6** gives a pair of a phenazinyl radical (**R**•) and an anion radical of **6** (**6**$^{-\bullet}$). Coupling of them affords an anion **9** which reacts with another **R**• after an electron transfer (to *p*-nitrophenethyl bromide) to form compound **2**. On the other hand, the addition of the anion radical **6**$^{-\bullet}$ to **6** gives a butyl radical anion **10**, which couples with radical **R**• followed by an electron transfer and coupling with another **R**• to afford compound **3**.

Table 1

Crystallographic Analysis of Compounds **2**, **3** and **4**

	Compound **2**	Compound **3**	Compound **4**
Crystal Parameters			
Formula	$C_{34}H_{29}N_5O_2$	$C_{42}H_{36}N_6O_4$	$C_{21}H_{19}N_3O_2$
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1 (#2)	$P2_1/c$ (#14)	$P2_1/a$ (#14)
Lattice parameters	a = 10.385(2) Å	a = 10.972(3) Å	a = 7.679(2) Å
	b = 27.731(4) Å	b = 11.210(2) Å	b = 22.860(3) Å
	c = 9.670(3) Å	c = 14.531(2) Å	c = 9.932(2) Å
	α = 96.49(2)°		
	β = 90.31(2)°	β = 106.21(1)°	β = 102.12(2)°
	γ = 83.75(1)°		
V	2750(1) Å^3	1716.2(6) Å^3	1704.7(5) Å^3
Z	4	2	4
Dcalc (g/cm^3)	1.303	1.333	1.346
μ (MoKα) (cm^{-1})	0.83	0.88	0.83
Refinement Parameters			
Number of reflections	4396 (I>2.0σ)	807 (I>1.5σ)	1182 (I>2.0σ)
R [a]	0.071	0.074	0.062
Rw [b]	0.099	0.071	0.045
GOF	2.44	1.90	1.60

[a] R index = $\Sigma \| Fo \| - | Fc \| / \Sigma | Fo |$; [b] Rw index = $\{\Sigma w(| Fo | - | Fc |)^2/\Sigma wFo^2\}^{1/2}$ where $w = [\sigma^2(Fo) + (p^2/4)(Fo)^2]^{-1}$.

Table 2

Selected Bond Lengths (Å) and Bond Angles (°) for **2**

O(1)-N(5)	1.233(8)	C(8)-C(9)	1.388(9)
O(2)-N(5)	1.204(8)	C(9)-C(10)	1.395(9)
N(1)-C(10)	1.390(9)	C(11)-C(12)	1.414(9)
N(1)-C(11)	1.367(9)	C(14)-C(15)	1.509(8)
N(1)-C(13)	1.470(9)	C(15)-C(29)	1.512(8)
N(2)-C(9)	1.406(7)	C(16)-C(17)	1.381(10)
N(2)-C(12)	1.401(7)	C(16)-C(27)	1.381(9)
N(2)-C(14)	1.464(7)	C(17)-C(18)	1.34(1)
N(3)-C(25)	1.415(9)	C(18)-C(19)	1.36(1)
N(3)-C(26)	1.399(9)	C(19)-C(26)	1.40(1)
N(3)-C(28)	1.457(9)	C(20)-C(21)	1.39(1)
N(4)-C(15)	1.461(7)	C(20)-C(25)	1.42(1)
N(4)-C(24)	1.418(8)	C(21)-C(22)	1.37(1)
N(4)-C(27)	1.410(8)	C(22)-C(23)	1.400(9)
N(5)-C(32)	1.471(8)	C(23)-C(24)	1.361(9)
C(1)-C(2)	1.382(10)	C(24)-C(25)	1.388(9)
C(1)-C(12)	1.391(9)	C(26)-C(27)	1.387(9)
C(2)-C(3)	1.38(1)	C(29)-C(30)	1.385(8)
C(3)-C(4)	1.39(1)	C(29)-C(34)	1.394(8)
C(4)-C(11)	1.38(1)	C(30)-C(31)	1.377(9)
C(5)-C(6)	1.40(1)	C(31)-C(32)	1.359(9)
C(5)-C(10)	1.366(10)	C(32)-C(33)	1.370(9)
C(6)-C(7)	1.35(1)	C(33)-C(34)	1.393(8)
C(7)-C(8)	1.356(10)		

C(10)-N(1)-C(11)	120.8(6)	C(25)-N(3)-C(26)	116.5(5)
C(10)-N(1)-C(13)	119.3(7)	C(25)-N(3)-C(28)	117.6(7)
C(11)-N(1)-C(13)	119.1(7)	C(26)-N(3)-C(28)	122.4(7)
C(9)-N(2)-C(12)	119.6(5)	C(15)-N(4)-C(24)	122.0(5)
C(9)-N(2)-C(14)	121.5(5)	C(15)-N(4)-C(27)	120.4(5)
C(12)-N(2)-C(14)	117.6(5)	C(24)-N(4)-C(27)	117.0(5)
O(1)-N(5)-O(2)	123.9(7)	C(17)-C(18)-C(19)	121.8(8)
O(1)-N(5)-C(32)	116.3(7)	C(18)-C(19)-C(26)	119.9(7)
O(2)-N(5)-C(32)	119.8(7)	C(21)-C(20)-C(25)	118.9(7)
C(2)-C(1)-C(12)	122.2(7)	C(20)-C(21)-C(22)	122.2(7)
C(1)-C(2)-C(3)	118.9(8)	C(21)-C(22)-C(23)	117.8(7)
C(2)-C(3)-C(4)	119.3(8)	C(22)-C(23)-C(24)	121.8(7)
C(3)-C(4)-C(11)	122.6(8)	N(4)-C(24)-C(23)	124.1(6)
C(6)-C(5)-C(10)	121.5(8)	N(4)-C(24)-C(25)	115.3(6)
C(5)-C(6)-C(7)	117.9(8)	C(23)-C(24)-C(25)	120.4(6)
C(6)-C(7)-C(8)	121.5(9)	N(3)-C(25)-C(20)	122.3(7)
C(7)-C(8)-C(9)	121.7(7)	N(3)-C(25)-C(24)	119.0(6)
N(2)-C(9)-C(8)	123.4(6)	C(20)-C(25)-C(24)	118.7(7)
N(2)-C(9)-C(10)	119.2(6)	N(3)-C(26)-C(19)	123.8(7)
C(8)-C(9)-C(10)	117.4(6)	N(3)-C(26)-C(27)	117.6(7)
N(1)-C(10)-C(5)	121.1(7)	C(19)-C(26)-C(27)	118.6(8)
N(1)-C(10)-C(9)	118.9(6)	N(4)-C(27)-C(16)	123.4(6)
C(5)-C(10)-C(9)	120.0(8)	N(4)-C(27)-C(26)	117.2(6)
N(1)-C(11)-C(4)	122.7(7)	C(16)-C(27)-C(26)	119.4(7)
N(1)-C(11)-C(12)	119.2(6)	C(15)-C(29)-C(30)	121.4(5)
C(4)-C(11)-C(12)	118.1(8)	C(15)-C(29)-C(34)	120.2(5)
N(2)-C(12)-C(1)	122.6(6)	C(30)-C(29)-C(34)	118.3(5)
N(2)-C(12)-C(11)	118.6(6)	C(29)-C(30)-C(31)	119.9(5)
C(1)-C(12)-C(11)	118.8(6)	C(30)-C(31)-C(32)	120.6(6)
N(2)-C(14)-C(15)	113.6(5)	N(5)-C(32)-C(31)	120.2(7)
N(4)-C(15)-C(14)	110.2(5)	N(5)-C(32)-C(33)	118.0(6)
N(4)-C(15)-C(29)	114.4(4)	C(31)-C(32)-C(33)	121.7(6)
C(14)-C(15)-C(29)	114.0(5)	C(32)-C(33)-C(34)	117.8(6)
C(17)-C(16)-C(27)	120.7(7)	C(29)-C(34)-C(33)	121.6(6)
C(16)-C(17)-C(18)	119.4(8)		

Table 3

Atomic Coordinates (x 10^4) and B_{eq}* for Compound **2**

Atom	x	y	z	B_{eq}(Å^2)
O(1)	1971(6)	8539(2)	-871(6)	8.1(2)
O(2)	2811(6)	7801(2)	-748(6)	8.6(2)
N(1)	8671(6)	10152(2)	6714(7)	5.9(2)
N(2)	6805(5)	9635(2)	5405(5)	4.1(1)
N(3)	8914(6)	8197(2)	5967(7)	5.7(2)
N(4)	7197(5)	8586(2)	4212(5)	3.7(1)
N(5)	2768(6)	8234(3)	-414(6)	6.0(2)
C(1)	6844(7)	10131(2)	3467(8)	5.1(2)
C(2)	7292(9)	10508(3)	2854(9)	7.1(3)
C(3)	8190(10)	10777(3)	3560(10)	9.4(3)
C(4)	8610(10)	10662(3)	4860(10)	8.4(3)
C(5)	8272(9)	9830(3)	8854(10)	6.8(2)
C(6)	7640(10)	9529(4)	9622(9)	8.9(3)
C(7)	6730(10)	9273(3)	8967(9)	8.0(3)
C(8)	6425(8)	9310(3)	7614(8)	5.5(2)
C(9)	7060(6)	9599(2)	6822(7)	4.0(2)
C(10)	8014(7)	9859(2)	7478(8)	4.7(2)
C(11)	8200(7)	10282(2)	5470(8)	5.2(2)
C(12)	7271(6)	10011(2)	4764(7)	4.1(2)
C(13)	9763(9)	10388(4)	7350(10)	9.3(3)
C(14)	5838(6)	9361(2)	4657(6)	3.9(2)
C(15)	6412(6)	8967(2)	3560(6)	3.3(1)
C(16)	8799(7)	8413(2)	2311(8)	5.1(2)
C(17)	10054(8)	8258(3)	1872(9)	6.3(2)
C(18)	10914(8)	8079(3)	2770(10)	7.4(3)
C(19)	10577(8)	8036(2)	4110(10)	6.5(2)
C(20)	7150(10)	7901(2)	7249(8)	6.3(2)
C(21)	5830(10)	7895(3)	7432(8)	6.9(3)
C(22)	4939(8)	8091(3)	6550(8)	5.6(2)
C(23)	5399(7)	8311(2)	5444(7)	4.6(2)
C(24)	6686(7)	8335(2)	5246(6)	3.9(2)
C(25)	7590(8)	8141(2)	6154(7)	4.5(2)
C(26)	9327(7)	8210(2)	4599(8)	4.5(2)
C(27)	8437(6)	8403(2)	3679(7)	3.7(2)
C(28)	9804(9)	8070(3)	7071(10)	8.6(3)
C(29)	5438(6)	8780(2)	2522(6)	3.5(1)
C(30)	4505(6)	9095(2)	1957(7)	4.3(2)
C(31)	3651(7)	8913(3)	991(7)	5.2(2)
C(32)	3695(6)	8425(3)	605(6)	4.3(2)
C(33)	4610(7)	8099(2)	1117(7)	4.5(2)
C(34)	5486(6)	8282(2)	2080(6)	4.0(2)

* Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(8/3)\pi^2[(aa^*)^2U_{11} + (bb^*)^2U_{22} + (cc^*)^2U_{33} + 2aa^*bb^*(\cos\gamma)U_{12} + 2aa^*cc^*(\cos\beta)U_{13} + 2bb^*cc^*(\cos\alpha)U_{23}]$.

Table 4

Selected Bond Lengths (Å) and Bond Angles (°) for **3**

O(1)-N(3)	1.24(1)	C(5)-C(10)	1.38(1)
O(2)-N(3)	1.21(1)	C(6)-C(7)	1.34(1)
N(1)-C(10)	1.42(1)	C(7)-C(8)	1.38(1)
N(1)-C(11)	1.41(1)	C(8)-C(9)	1.40(1)
N(1)-C(14)	1.47(1)	C(9)-C(10)	1.39(1)
N(2)-C(9)	1.37(1)	C(11)-C(12)	1.41(1)
N(2)-C(12)	1.40(1)	C(14)-C(15)	1.54(1)
N(2)-C(13)	1.45(1)	C(14)-C(21)	1.52(1)
N(3)-C(18)	1.46(1)	C(15)-C(16)	1.39(1)
C(1)-C(2)	1.39(1)	C(15)-C(20)	1.39(1)
C(1)-C(12)	1.40(1)	C(16)-C(17)	1.40(1)
C(2)-C(3)	1.38(1)	C(17)-C(18)	1.36(1)
C(3)-C(4)	1.39(1)	C(18)-C(19)	1.37(1)
C(4)-C(11)	1.38(1)	C(19)-C(20)	1.40(1)
C(5)-C(6)	1.41(1)	C(21)-C(21*)	1.57(2)

C(10)-N(1)-C(11)	119.0(8)	C(6)-C(7)-C(8)	121(1)
C(10)-N(1)-C(14)	119.1(8)	C(7)-C(8)-C(9)	119(1)
C(11)-N(1)-C(14)	120.2(8)	N(2)-C(9)-C(8)	122.7(10)
C(9)-N(2)-C(12)	118.8(9)	N(2)-C(9)-C(10)	119(1)
C(9)-N(2)-C(13)	121.7(9)	C(8)-C(9)-C(10)	118(1)
C(12)-N(2)-C(13)	117.8(9)	N(1)-C(10)-C(5)	121.1(9)
O(1)-N(3)-O(2)	122(1)	N(1)-C(10)-C(9)	117.2(10)
O(1)-N(3)-C(18)	117(1)	C(5)-C(10)-C(9)	121(1)
O(2)-N(3)-C(18)	120(1)	N(1)-C(11)-C(4)	124.3(9)
C(2)-C(1)-C(12)	119.9(10)	N(1)-C(11)-C(12)	116.3(9)
C(1)-C(2)-C(3)	120(1)	C(4)-C(11)-C(12)	119.4(9)
C(2)-C(3)-C(4)	119(1)	N(2)-C(12)-C(1)	121.8(10)
C(3)-C(4)-C(11)	121(1)	N(2)-C(12)-C(11)	118.6(9)
C(6)-C(5)-C(10)	118(1)	C(1)-C(12)-C(11)	119.5(10)
C(5)-C(6)-C(7)	120(1)	N(1)-C(14)-C(15)	114.4(8)
N(1)-C(14)-C(21)	114.8(8)	N(3)-C(18)-C(17)	117(1)
C(15)-C(14)-C(21)	110.5(8)	N(3)-C(18)-C(19)	119(1)
C(14)-C(15)-C(16)	118.7(9)	C(17)-C(18)-C(19)	122.7(10)
C(14)-C(15)-C(20)	121.6(9)	C(18)-C(19)-C(20)	119.4(10)
C(16)-C(15)-C(20)	119.7(9)	C(15)-C(20)-C(19)	119.1(10)
C(15)-C(16)-C(17)	120(1)	C(14)-C(21)-C(21*)	109(1)
C(16)-C(17)-C(18)	118(1)		

Table 5

Atomic Coordinates (x 10^4) and B_{eq}* for Compound **3**

Atom	x	y	z	B_{eq}(Å^2)
O(1)	3533(9)	6812(7)	8657(7)	8.6(3)
O(2)	5360(10)	6557(7)	8435(7)	8.6(3)
N(1)	2708(7)	659(6)	8995(6)	3.4(2)
N(2)	1347(8)	-1349(7)	9003(6)	4.3(2)
N(3)	4410(10)	6164(8)	8584(7)	5.6(3)
C(1)	1274(10)	-951(9)	10640(8)	4.8(3)
C(2)	1570(10)	-209(10)	11439(8)	4.9(3)
C(3)	2230(10)	841(10)	11430(8)	5.2(3)
C(4)	2751(10)	1165(9)	10615(8)	4.3(2)
C(5)	2024(10)	698(9)	7250(7)	4.5(3)
C(6)	1330(10)	151(9)	6392(8)	4.8(3)
C(7)	600(10)	-799(10)	6411(8)	5.2(3)
C(8)	563(10)	-1320(10)	7263(8)	4.8(3)
C(9)	1285(9)	-838(9)	8133(8)	3.6(2)
C(10)	1982(9)	190(8)	8107(8)	3.3(2)
C(11)	2319(9)	429(9)	9825(7)	3.3(2)
C(12)	1617(10)	-622(9)	9818(7)	3.6(2)
C(13)	850(10)	-2530(10)	9073(8)	5.9(3)
C(14)	3990(9)	1109(8)	9079(7)	3.4(2)
C(15)	4066(10)	2465(8)	8954(7)	3.4(2)
C(16)	5140(10)	2941(9)	8757(7)	4.2(2)
C(17)	5250(10)	4173(9)	8644(7)	4.4(2)
C(18)	4280(10)	4888(9)	8724(7)	3.9(2)
C(19)	3221(10)	4456(9)	8924(7)	3.7(2)
C(20)	3086(10)	3221(9)	9021(7)	3.8(2)
C(21)	5000(10)	697(9)	9973(8)	3.9(2)

* See footnote of Table 3.

Table 6

Selected Bond Lengths (Å) and Bond Angles (°) for **4**

O(1)-N(24)	1.215(6)	C(6)-C(13)	1.377(7)
O(2)-N(24)	1.227(6)	C(7)-C(8)	1.375(9)
N(5)-C(12)	1.394(7)	C(8)-C(9)	1.372(9)
N(5)-C(13)	1.420(7)	C(9)-C(14)	1.387(8)
N(5)-C(15)	1.464(6)	C(11)-C(12)	1.403(8)
N(10)-C(11)	1.402(7)	C(13)-C(14)	1.388(7)
N(10)-C(14)	1.384(7)	C(15)-C(16)	1.532(7)
N(10)-C(23)	1.456(7)	C(16)-C(17)	1.498(7)
N(24)-C(20)	1.473(7)	C(17)-C(18)	1.366(7)
C(1)-C(2)	1.384(9)	C(17)-C(22)	1.365(7)
C(1)-C(11)	1.389(8)	C(18)-C(19)	1.377(7)
C(2)-C(3)	1.375(9)	C(19)-C(20)	1.354(7)
C(3)-C(4)	1.379(8)	C(20)-C(21)	1.358(7)
C(4)-C(12)	1.381(8)	C(21)-C(22)	1.384(7)
C(6)-C(7)	1.381(8)		

C(12)-N(5)-C(13)	118.4(5)	C(7)-C(8)-C(9)	119.4(8)
C(12)-N(5)-C(15)	118.1(5)	C(8)-C(9)-C(14)	121.4(7)
C(13)-N(5)-C(15)	118.6(5)	N(10)-C(11)-C(1)	123.2(7)
C(11)-N(10)-C(14)	117.6(5)	N(10)-C(11)-C(12)	118.0(7)
C(11)-N(10)-C(23)	117.6(6)	C(1)-C(11)-C(12)	118.8(7)
C(14)-N(10)-C(23)	119.3(6)	N(5)-C(12)-C(4)	124.1(7)
O(1)-N(24)-O(2)	124.8(6)	N(5)-C(12)-C(11)	117.2(7)
O(1)-N(24)-C(20)	117.9(6)	C(4)-C(12)-C(11)	118.7(7)
O(2)-N(24)-C(20)	117.3(6)	N(5)-C(13)-C(6)	122.4(6)
C(2)-C(1)-C(11)	122.0(7)	N(5)-C(13)-C(14)	117.4(7)
C(1)-C(2)-C(3)	118.4(7)	C(6)-C(13)-C(14)	120.1(7)
C(2)-C(3)-C(4)	120.7(7)	N(10)-C(14)-C(9)	123.3(7)
C(3)-C(4)-C(12)	121.4(7)	N(10)-C(14)-C(13)	118.2(7)
C(7)-C(6)-C(13)	120.3(7)	C(9)-C(14)-C(13)	118.5(7)
C(6)-C(7)-C(8)	120.2(7)	N(5)-C(15)-C(16)	114.5(4)
C(15)-C(16)-C(17)	111.4(4)	N(24)-C(20)-C(19)	119.5(6)
C(16)-C(17)-C(18)	120.6(6)	N(24)-C(20)-C(21)	119.0(6)
C(16)-C(17)-C(22)	121.0(6)	C(19)-C(20)-C(21)	121.4(6)
C(18)-C(17)-C(22)	118.3(5)	C(20)-C(21)-C(22)	118.2(6)
C(17)-C(18)-C(19)	120.8(6)	C(17)-C(22)-C(21)	121.7(6)
C(18)-C(19)-C(20)	119.5(6)		

Scheme 2

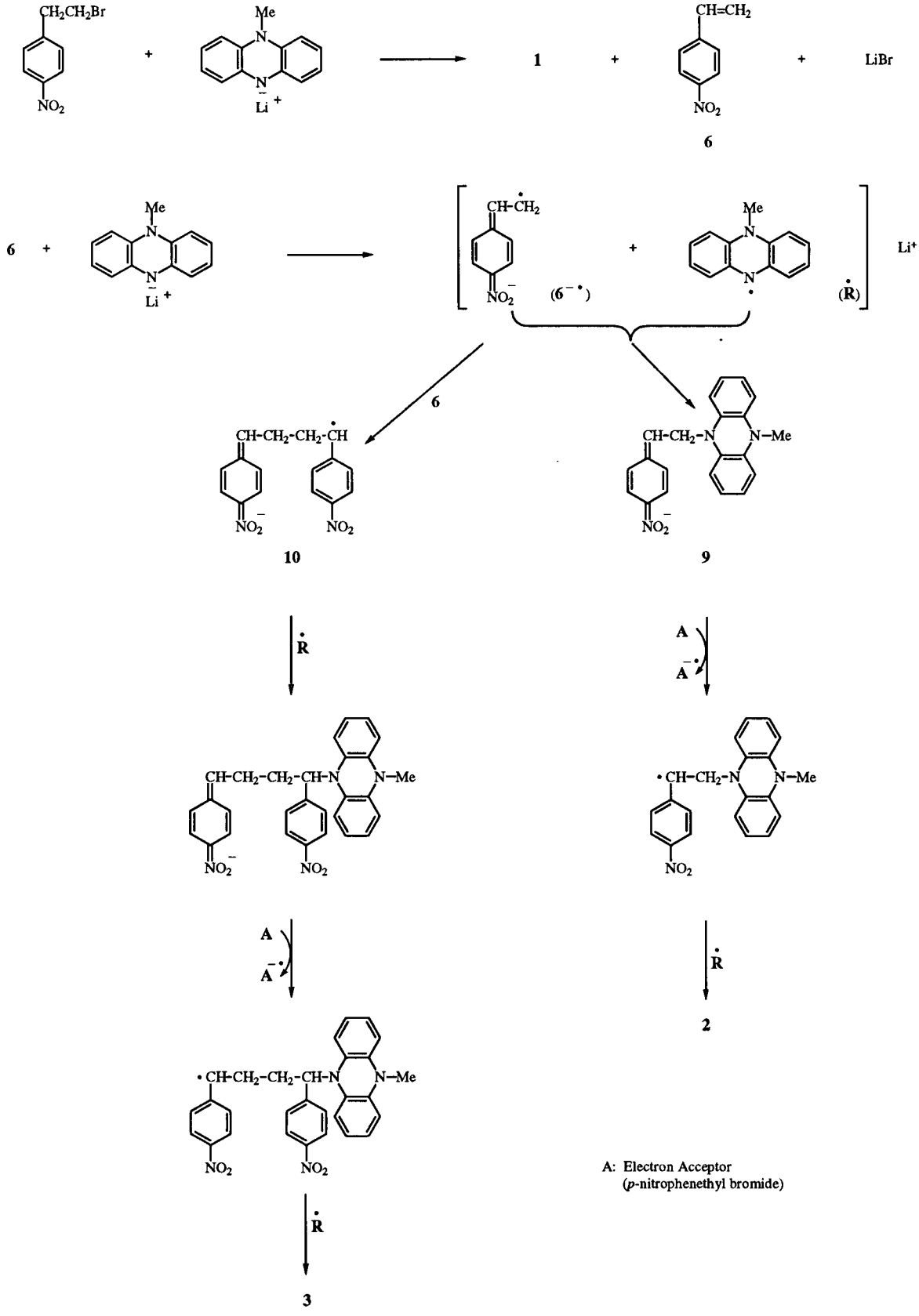

CH2CH2Br
NO2
Me
N
Li+
1
CH=CH2
6
LiBr
CH-CH2
(6−•)
(R•)
Li+
CH-CH2-CH2-CH
10
CH-CH2-N
N-Me
9
R•
A
A−•
CH-CH2-CH2-CH-N
2
3
A: Electron Acceptor
(p-nitrophenethyl bromide)

Table 7

Atomic Coordinates (x 10^4) and B_{eq}* for Compound **4**

Atom	x	y	z	B_{eq}(Å^2)
O(1)	4120(6)	589(2)	216(5)	7.1(3)
O(2)	5991(6)	554(2)	2176(5)	7.6(3)
N(5)	-2738(7)	-1120(2)	4609(6)	4.8(3)
N(10)	-5019(7)	-1730(2)	5799(7)	5.7(3)
N(24)	4590(8)	418(2)	1395(6)	5.3(3)
C(1)	-2780(10)	-1778(3)	7960(10)	6.2(4)
C(2)	-1120(10)	-1631(3)	8737(8)	7.3(5)
C(3)	10(10)	-1312(3)	8120(9)	6.9(4)
C(4)	-480(10)	-1151(3)	6756(8)	5.8(4)
C(6)	-4300(8)	-1467(3)	2342(8)	5.3(4)
C(7)	-5640(10)	-1798(3)	1552(8)	7.0(4)
C(8)	-6710(10)	-2143(3)	2170(10)	7.4(4)
C(9)	-6440(10)	-2149(3)	3580(10)	6.5(4)
C(11)	-3320(10)	-1608(3)	6593(8)	5.1(4)
C(12)	-2130(10)	-1292(2)	5974(8)	4.7(3)
C(13)	-4067(8)	-1464(2)	3754(8)	4.5(3)
C(14)	-5178(9)	-1794(3)	4393(9)	5.2(4)
C(15)	-1546(7)	-768(2)	3963(6)	5.2(3)
C(16)	-73(7)	-1118(2)	3499(6)	5.0(3)
C(17)	1168(7)	-724(2)	2943(7)	3.9(3)
C(18)	2569(8)	-462(3)	3807(6)	4.6(3)
C(19)	3686(7)	-88(3)	3304(7)	4.9(3)
C(20)	3390(8)	21(2)	1935(7)	3.7(3)
C(21)	2032(9)	-240(3)	1039(6)	5.3(3)
C(22)	910(7)	-609(3)	1566(7)	5.5(4)
C(23)	-6281(9)	-2027(3)	6474(7)	7.9(4)

* See footnote of Table 3.

In conclusion, we have found the unusual vicinal addition of phenazinyl group to 4-nitrostyrene double bond *via* the successive electron transfer although the yield was not high.

EXPERIMENTAL

Reaction of **1** with *p*-Nitrophenethyl Bromide in 1,2-Dimethoxyethane.

To a hot solution of 5-methylphenazinium methylsulfate (1.56 g, 5.1 mmoles) [6] in ethanol (40 ml) was added successively sodium dithionite (25 g) and water (800 ml) under vigorous stirring. After cooling, the solids deposited were filtered and dried under vacuum to give **1** (0.87 g, 87% yield) recrystallized from hexane under argon atmosphere, mp 168-172° in capillary sealed under vacuum (lit mp 164° [7]). To a stirred solution of **1** (0.606 g, 3.1 mmoles) in 1,2-dimethoxyethane (21 ml) was added a solution of *n*-butyllithium in hexane (3.4 mmoles, 2.3 ml of 15% solution) under argon atmosphere. To this reaction mixture was added a solution of *p*-nitrophenethyl bromide (0.78 g, 3.4 mmoles) in 1,2-dimethoxyethane (10 ml) over 20 minutes. After stirring for 3 hours at room temperature, the reaction mixture was treated with water (aqueous solution of sodium dithionite)-toluene mixture, the toluene layer was separated, dried (sodium sulfate), and evaporated to dryness. The residue was flash chromatographed under argon with toluene-hexane (1:1, v/v) to give the compounds in the following order: *p*-nitrostyrene (65 mg, 13%), unchanged *p*-nitrophenethyl bromide (199 mg, 25%), 4,4'-bis(2-bromoethyl)azoxybenzene (**5**) (11 mg, 1%), 1,2-bis[5-(10-methyl-5,10-dihydrophenazinyl)]-1-(4-nitrophenyl)ethane (**2**) (138 mg, 17%), 1,4-bis(4-nitrophenyl)-1,4-bis[5-(10-methyl-5,10-dihydrophenazinyl)]butane (**3**) (146 mg, 14%), and phenazine (155 mg, 28%).

1,2-Bis[5-(10-methyl-5,10-dihydrophenazinyl)]-1-(4-nitrophenyl)ethane (**2**).

This compound was obtained as dark violet prisms (crystallized from hexane), mp 130-132° dec; ir (potassium bromide): ν NO_2 1515 and 1345 cm^{-1}; uv (hexane): λ max 246 (log ε 4.79), 335 (4.00), and 410 (2.89); ^{1}H nmr (benzene-d_6): δ 2.48 (s, 6H, CH_3), 4.14-4.43 (m, 2H, CH_2), 5.32 (t, 1H, CH), 5.94-5.97 (m, 2H, ArH), 6.15-6.19 (m, 4H, ArH), 6.46-6.74 (m, 10H, ArH), 7.11-7.12 (m, 2H, ArH), and 7.54-7.57 (m, 2H, ArH).

Anal. Calcd. for $C_{34}H_{29}N_5O_2$: C, 75.68; H, 5.42; N, 12.98. Found: C, 75.80; H, 5.41; N, 13.03.

1,4-Bis(4-nitrophenyl)-1,4-bis[5-(10-methyl-5,10-dihydrophenazinyl)]butane (**3**).

This compound was obtained as dark red prisms (from toluene-hexane) and a mixture of *meso*- and *dl*-forms (see X-ray data), mp 155-157° dec; ir (potassium bromide): ν NO_2 1516 and 1344 cm^{-1}; uv (dichloromethane): λ max 248 (log ε 5.04), 335 (4.00), and 410 (2.89); ^{1}H nmr (benzene-d_6): δ 2.25-2.48 (m, 4H), 2.56 and 2.58 (s and s, together 6H), 4.37-4.39 and 4.94 (m, together 2H), 5.92-5.99 (m, 4H), 6.24 (d, 4H), 6.48-6.50 (m, 4H), 6.73-6.79 and 6.97-6.80 (m, together 8H), and 7.75 (m, 4H).

Crystal data for **3** are shown in Table 1. These crystals are made up of *meso*-type molecules. Crystals from toluene gave other crystal data: $C_{42}H_{36}N_6O_4 \cdot C_7H_8$; monoclinic; space group $P2_1/n$ (# 14), a = 14.201(4), b = 19.091(8), c = 16.871(8)Å β = 113.69(3)°, U = 4188(3)Å^3; D_c = 1.238 gcm^{-3}, Z = 4, μ = 0.80 cm^{-1}. The final R (Rw) values converged to 0.076 (0.082). S = 2.09. This is *dl*-type-isomer containing toluene molecules in the crystals.

Anal. Calcd. for $C_{42}H_{36}N_6O_2$: C, 73.24; H, 5.27; N, 12.20. Calcd. for $C_{49}H_{44}N_6O_2$: C, 75.36; H, 5.68; N, 10.76. Found: C, 74.54; H, 5.34; N, 12.11.

4,4'-Bis(2-bromoethyl)azoxybenzene (**5**).

This compound was obtained as pale yellow needles (from hexane), mp 144-146° dec; ir (potassium bromide): 2956, 1595, 1458, 1308, 1212, 837, and 636 cm^{-1}: uv (hexane): λ max 237 (log ε 3.84), 264 (3.78), and 330 (4.14); ^{1}H nmr (deuteriochloroform): δ 3.23-3.27 (m, 4H), 3.58-3.62 (m, 4H), 7.31-7.37 (m, 4H), 8.14-8.17 (m, 2H), and 8.24-8.27 (m, 2H).

4-Nitrostyrene (**6**) had mp 17-19° (lit [8], mp 21.4°; ir (potassium bromide): ν NO_2 1517 and 1344 cm^{-1}; uv (hexane): λ max 289 (log ε 4.17).

Reaction of **1** with *p*-Nitrophenethyl Bromide in Dimethyl Sulfoxide.

Metallic sodium (0.03 g, 1.22 mmoles) was allowed to react with dimethyl sulfoxide (0.6 ml) under stirring and the solution was added dropwise to a solution of **1** (0.24 g, 1.22 mmoles) in

dimethyl sulfoxide (3 ml). To the mixture was added a solution of *p*-nitrophenethyl bromide (0.56 g, 2.44 mmoles) in dimethyl sulfoxide (2 ml) and the mixture was stirred for 12 hours. The similar workup as the reaction in 1,2-dimethoxyethane gave a dark violet solid which was chromatographed with toluene-hexane (1:1, v/v) to give **4** (0.08 g) in 20% yield. Compounds **2** and **3** was not isolated from the reaction mixture even in a detectable amount.

Similar results were obtained by use of *n*-butyllithium for metallation instead of sodium methylsulfinyl carbanion.

5-Methyl-10-(*p*-nitrophenethyl)-5,10-dihydrophenazine (**4**).

This compound was obtained as dark violet prisms (hexane), mp 191.5-194°; ir (potassium bromide): ν NO_2 1516 and 1347 cm^{-1}; uv (hexane): λ max 249 (log ε 4.66), 346 (4.01), and 417 (2.95); ^1H nmr (benzene-d_6): δ 2.45 (s, 3H, CH_3), 2.51 (t, 2H, CH_2), 3.28 (t, 2H, CH_2), 6.11-6.15 (m, 2H, ArH), 6.22-6.25 (m, 2H, ArH), 6.51-6.54 (d, 2H, ArH), 6.71-6.75 (m, 4H, ArH), and 7.76-7.79 (d, 2H, ArH).

Anal. Calcd. for $C_{21}H_{19}N_3O_2$: C, 73.02; H, 5.54; N, 12.16. Found: C, 73.33; H, 5.48; N, 11.91.

X-Ray diffraction data were collected by using Rigaku AFC5R diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71069Å) and an 18 kw rotating anode generator. Cell dimensions were obtained by least-square fitting from 20 high angle reflections. All computations for the structure determination were carried out on VAX station 3100 and on INDY R5000 using a crystallographic program package TEXSAN and teXsan [5]. Details of the crystal structure analysis are available on request from the authors.

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