CONDENSATION REACTIONS OF A NITRODIENAMINE WITH GRIGNARD AND ORGANOCOPPER REAGENTS PREPARED FROM INDOLE DERIVATIVES

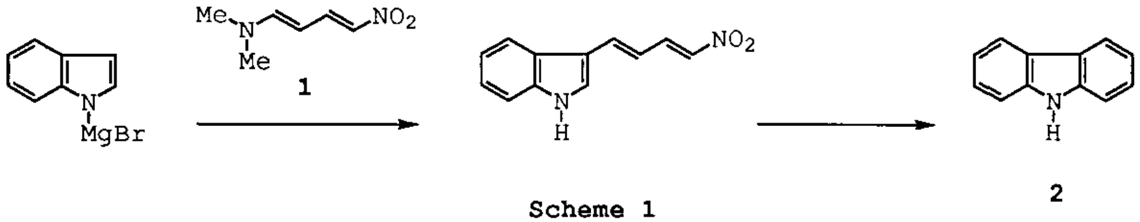
Takeshi Koike,* Naoki Takeuchi, Masanori Hagiwara, Kaori Yamazaki, and Seisho Tobinaga

Showa College of Pharmaceutical Sciences, Higashitamagawagakuen 3-3165, Machida, Tokyo 194-8543, Japan

Abstract - Condensation reactions of a nitrodienamine (**1**) with Grignard and organocopper reagents prepared from indole derivatives were investigated. Indolyl Grignard reagents were prepared from 4-bromoindole (**3a**), 5-bromoindole (**3b**), 6-bromoindole (**3c**), and 5-nitroindole (**3d**) using methylmagnesium bromide. Indolyl organocopper reagents were prepared from indole (**3e**), 2-methylindole (**3f**), and 3-methylindole (**3g**) using dimethylcopperlithium.

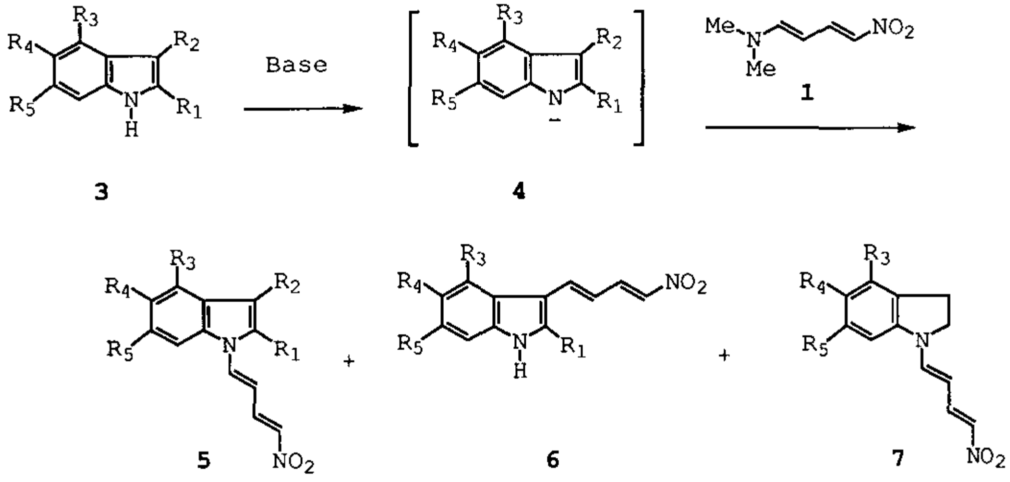
We are interested in the reactivities of the nitrodienamines containing enamine, olefinic, and nitro attracting moiety as well as aminodienyl esters and aminoacrylates synthons, because of their electronic "push-pull" character which can lead to interesting cycloaddition reactions.[1-5] In a previous study,[6] we reported a synthesis of nitrodienamine, 1-(*N*,*N*-dimethylamino)-4-nitro-1,3-butadiene(**1**), some cycloadditions of **1** with α,β-unsaturated carbonyl compounds and quinones, and condensation reactions of **1** with Grignard reagents prepared from indoles and carbazole using arylmagnesium halide and alkylmagnesium halide. In this paper we describe the condensation reactions of **1** with Grignard and organocopper reagents to afford the corresponding products(**5**), (**6**), and (**7**). Indolyl Grignard reagents were prepared from 4-bromoindole(**3a**), 5-bromoindole(**3b**), 6-bromoindole(**3c**), and 5-nitroindole(**3d**) using methylmagnesium bromide. Indolyl organocopper reagents were prepared from indole(**3e**), 2-methylindole(**3f**), and 3-methylindole(**3g**) using dimethylcopperlithium.

Previously, we reported the condensation reactions of nitrodienamine (**1**) with 2- and/or 3-substituted alkylindoles, and indole which yielded the cyclization product, carbazole (**2**), as shown in Scheme 1.[6] Haloindoles, especally bromoindoles, have been known to be able to lead to useful indole derivatives by substitution reaction.[7] Therefore, we planned to study the condensation reaction of nitrodienamine (**1**) with bromoindoles which do not possess substituent at 1-, 2- and/or 3-positions. First, we investigated reactivities of nitrodienamine (**1**) toward indolyl Grignard reagent, 4-bromoindolylmagnesium bromide as shown in Scheme 2. Treatment of 4-bromoindole (**3a**) with methylmagnesium bromide in THF, followed by reaction with **1** afforded two condensation products, 1-[1-(4-bromoindolyl)]-4-nitro-1,3-butadiene (**5a**) (29.7% yield) and 1-[1-(4-bromoindolinyl)]-4-nitro-1,3-butadiene (**7a**) (1.7% yield). The structures of **5a** and **7a** were confirmed by the following spectral data. The IR spectrum of **5a** and **7a** show absorption band ascribable to a nitro function at 1520 cm^{-1}, and show no absorption due to an NH group, respectively. The ^{1}H-NMR spectrum of **5a** reveals the presence of two protons at 2- and 3-positions, and **7a** reveals the presence of four methylenic protons at δ 4.07 (2H, t, *J* = 8.5 Hz) and 3.26 (2H, t, *J* = 8.5 Hz) of the indolinyl ring. Compound (**7a**) may be obtained from the reduction reaction of dissolved magnesium in Grignard THF solution. On the other hand, the condensation reaction of **1** with **3a** using methyllithium afforded the product (**5a**) in 5.5% yield.



Scheme 1

Similarly, we investigated the reactivities of nitrodienamine (**1**) with indolyl Grignard reagents prepared from 5-bromoindole (**3b**), 6-bromoindole (**3c**), and 5-nitroindole (**3d**). The reaction of 5-bromoindolylmagnesium bromide with **1** in THF gave two condensation products, 1-[1-(5-bromoindolyl)]-4-nitro-1,3-butadiene (**5b**) (33.4% yield) and 1-[3-(5-bromoindolyl)]-4-nitro-1,3-butadiene (**6b**) (1.0% yield). The structures of **5b** and **6b** were identified by the following spectral data. The IR spectrum of **5b** does not have absorption band by an NH group, and **6b** shows absorption bands at 3470 and 1520 cm^{-1} due to an amino group and a nitro group, respectively. The ^{1}H-NMR spectrum of **5b** indicates the presence of two protons at δ 7.89 (1H, d, *J* = 3.7 Hz) and 6.85 (1H, d, *J* = 3.7 Hz) at 2- and 3-positions, and **6b** exhibits a singlet at δ 7.92 due to a proton at the 2-position. The 6-bromoindolylmagnesium bromide reacted with **1** to give two condensation products, 1-[1-(6-bromoindolyl)]-4-nitro-1,3-butadiene (**5c**) (32.4% yield) and 1-[3-(6-bromoindolyl)]-4-nitro-1,3-butadiene (**6c**) (0.9% yield), respectively. The 5-nitroindolylmagnesium bromide was allowed to react with **1** to afford a condensation product, 1-[3-(2-methyl-5-nitroindolyl)]-4-nitro-1,3- butadiene (**6d**) (2.6% yield). However, attempts to the condensation reaction of **1** with 4 and 6-nitroindoles were unsuccessful.



Entry	Starting material	R$_1$	R$_2$	R$_3$	R$_4$	R$_5$	Base	Yield (%)		
								5	**6**	**7**
1	**3a**	H	H	Br	H	H	MeMgBr	**5a** (29.7)		**7a** (1.7)
2	**3a**	H	H	Br	H	H	MeLi	**5a** (5.5)		
3	**3b**	H	H	H	Br	H	MeMgBr	**5b** (33.4)	**6b** (1.0)	
4	**3c**	H	H	H	H	Br	MeMgBr	**5c** (32.4)	**6c** (0.9)	
5	**3d**	H	H	H	NO$_2$	H	MeMgBr		**6d** (R$_1$=Me,2.6)	
6	**3e**	H	H	H	H	H	BuLi	No Reaction		
7	**3e**	H	H	H	H	H	Me$_2$CuLi	**5e** (16.2)	**6e** (21.3)	
8	**3f**	Me	H	H	H	H	Me$_2$CuLi	**5f** (12.4)	**6f** (38.5)	
9	**3g**	H	Me	H	H	H	Me$_2$CuLi	**5g** (73.2)		

Scheme 2

Next, from consideration of reactivity and stability of nitrodienamine (**1**), we investigated the condensation reactions of **1** with indolyl organocopper reagents prepared from indole derivatives using dimethylcopperlithium. Dimethylcopperlithium reagents are considerable by less basic and less nucleophilic than the corresponding alkyllithiums. Although the condensation reaction of **1** with indole (**3e**) using butyllithium in ether-benzene was unsuccessful, use of Me_2CuLi in ether-benzene afforded two condensation products, 1-(1-indolyl)-4-nitro-1,3-butadiene (**5e**) (16.2% yield) having a nitrobutadiene and an indole ring, mp 131-133 ℃ (lit.,[6] mp 131-133 ℃), and 1-(3-indolyl)-4-nitro-1,3-butadiene (**6e**) (21.3% yield), mp 175.5-177.5 ℃ (lit.,[6] mp 175.5-177.5 ℃) as shown in Scheme 2. Grignard and organocopper reagents exhibit widely divergent behavior toward 1,3-butadiene, depending on the nature of the Grignard and organocopper reagents, the degree of substitution or steric crowding on the diene (or Grignard, organocopper), the reaction conditions including solvent. In this study, we indicated the synthesis of useful indole derivatives by introducing 4-nitro-1,3-butadiene group.

Similarly, we studied the reactivity of **1** with indolyl organocopper reagents prepared from 2-methylindole (**3f**), 3-methylindole (**3g**), and *N*-methylindole, under the same conditions. The condensation reaction of **1** with lithium methyl(2-methylindolyl)cuprate (I) in ether-benzene provided 1-[1-(2-methylindolyl)]-4-nitro-1,3-butadiene (**5f**) (12.4% yield) and 1-[3-(2-methylindolyl)]-4-nitro-1,3-butadiene (**6f**) (38.5% yield). Compound (**5f**) contains a nitro (1550 cm^{-1}), and **6f** shows an amino (3300 cm^{-1}) and a nitro (1527 cm^{-1}) IR absorption bands, respectively. The ^1H-NMR spectrum reveals that **5f** has a singlet proton at the 3-position [δ 6.51], and **6f** has a broad singlet proton at the N-1 position [δ 10.82]. The reaction of **1** with organocopper reagents prepared from 3-methylindole (**3g**) using Me_2CuLi afforded 1-[1-(3-methylindolyl)]-4-nitro-1,3-butadiene (**5g**) (73.2% yield), mp 204-206 ℃ (lit.,[6] mp 204-206 ℃). However, attempt to the condensation reaction of **1** with *N*-methylindole was unsuccessful.

These results provide a new condensation reaction of nitrodienamine (**1**) with Grignard and organocopper reagents prepared from indole derivatives.

EXPERIMENTAL

All melting points were determined on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were recorded with a JASCO FT/IR-8000, JASCO FT/IR-200 spectrophotometer, ^{1}H-NMR spectra with a JEOL EX-90, JEOL JNM-GX 270, JEOL JNM-α 500 spectrometer with tetramethylsilane as an internal standard, MS with a JEOL JMS-D 300 spectrometer. Elemental analyses were performed with a Yanaco CHN-corder MT-3. Silica gel 60 (Cica-MERCK) and Merck Kieselgel 60 F_{254} (silica gel) were used for column chromatography and TLC, respectively.

General Procedure for Reactions of the Nitrodienamine(1) with Grignard Reagents Prepared from Indoles(3a-d) Using Methylmagnesium Bromide

The 0.95 M MeMgBr in THF solution (1.05 mL, 1.0 mmol) was added to a solution of substrate (**3a-d**) (1.0 mmol) in dry THF (2 mL) with stirring at rt under an argon atmosphere. The whole was stirred at rt for 2 h. A solution of **1** (14.2 mg, 0.1 mmol) in dry THF (1.5 mL) was added dropwise to the reaction mixture with stirring at rt for 2 h. The reaction mixture was poured into saturated aqueous NH_4Cl. The whole was stirred at rt for 10 min, and then extracted with ethyl acetate. The organic layer was washed with brine, then dried over $MgSO_4$ and evaporated under reduced pressure. The residue was subjected to silica gel chromatography with appropriate solvents. The isolated yield of **5**, **6**, and **7** was based on the **1**.

1-[1-(4-Bromoindolyl)]-4-nitro-1,3-butadiene(5a) and 1-[1-(4-Bromoindolinyl)]-4-nitro-1,3-butadiene(7a)

4-Bromoindole (**3a**). Solvent for chromatography: 12% ethyl acetate in hexane. First eluate product: 8.7 mg (29.7%) of **5a** as red prisms ($CHCl_3$-hexane), mp 173-174 ℃. IR (KBr) cm^{-1}: 1630, 1600, 1580, 1520. ^{1}H-NMR (acetone-d_6) δ: 8.34 (1H, d, J = 13.7 Hz, olefinic H), 8.01 (1H, t, J = 12.5 Hz, olefinic H), 7.96 (1H, d, J = 3.7 Hz, aromatic H), 7.85 (1H, d, J = 8.2 Hz, aromatic H), 7.44 (1H, d, J = 8.2 Hz, aromatic H), 7.44 (1H, d, J = 13.1 Hz, olefinic H), 7.29 (1H, t, J = 7.9 Hz, aromatic H), 6.92 (1H, t, J = 13.4 Hz, olefinic H), 6.83 (1H, d, J = 3.7 Hz, aromatic H). High MS m/z: Calcd for $C_{12}H_9N_2O_2Br$ (M^+ for ^{79}Br): 291.9846. Found: 291.9861. Anal. Calcd for $C_{12}H_9N_2O_2Br$: C, 49.17; H, 3.09; N, 9.56. Found: C, 49.23; H, 3.22; N, 9.53. Second eluate product 0.5 mg (1.7%) of **7a** as orange prisms ($CHCl_3$-hexane), mp 200-201 ℃. IR ($CHCl_3$) cm^{-1}: 1620, 1600, 1580, 1520. ^{1}H-NMR (acetone-d_6) δ: 8.03 (1H, d, J = 12.8 Hz, olefinic H), 7.93 (1H, t, J = 12.5 Hz, olefinic H), 7.24 (1H, d, J = 7.9 Hz, aromatic H), 7.20 (1H, d, J = 12.5 Hz, olefinic H), 7.19 (1H, t, J = 7.9 Hz, aromatic H), 7.14 (1H, dd, J

= 7.9, 1.2 Hz, aromatic H), 5.72 (1H, t, *J* = 12.5 Hz, olefinic H), 4.07 (2H, t, *J* = 8.5 Hz, methylenic H), 3.26 (2H, t, *J* = 8.5 Hz, methylenic H). High MS *m/z*: Calcd for $C_{12}H_{11}N_2O_2Br$ (M^+ for ^{79}Br): 294.0003. Found: 294.0005.

1-[1-(5-Bromoindolyl)]-4-nitro-1,3-butadiene(5b) and 1-[3-(5-Bromoindolyl)]-4-nitro-1,3-butadiene(6b)

5-Bromoindole (**3b**). Solvent for chromatography: benzene. First eluate product: 9.8 mg (33.4%) of **5b** as orange plates ($CHCl_3$), mp 182-183 ℃. IR ($CHCl_3$) cm^{-1}: 1630, 1610, 1530. ^1H-NMR (acetone-d_6) δ: 8.33 (1H, d, *J* = 13.4 Hz, olefinic H), 8.01 (1H, t, *J* = 12.8 Hz, olefinic H), 7.89 (1H, d, *J* = 3.7 Hz, aromatic H), 7.84 (1H, d, *J* = 1.5 Hz, aromatic H), 7.79 (1H, d, *J* = 8.5 Hz, aromatic H), 7.47 (1H, dd, *J* = 8.5, 1.8 Hz, aromatic H), 7.43 (1H, d, *J* = 12.8 Hz, olefinic H), 6.87 (1H, t, *J* = 13.7 Hz, olefinic H), 6.85 (1H, d, *J* = 3.7 Hz, aromatic H). High MS *m/z*: Calcd for $C_{12}H_9N_2O_2Br$ (M^+ for ^{79}Br): 291.9844. Found: 291.9809. Anal. Calcd for $C_{12}H_9N_2O_2Br$: C, 49.17; H, 3.09; N, 9.56. Found: C, 49.23; H, 3.20; N, 9.51. Second eluate product: 0.3 mg (1.0%) of **6b** as red prisms ($CHCl_3$-hexane), mp 102-104 ℃. IR ($CHCl_3$) cm^{-1}: 3470, 1600, 1580, 1520. ^1H-NMR (acetone-d_6) δ: 11.09 (1H, br s, NH), 8.17 (1H, d, *J* = 1.8 Hz, aromatic H), 7.92 (1H, s, aromatic H), 7.89 (1H, t, *J* = 12.2 Hz, olefinic H), 7.62 (1H, dd, *J* = 15.6, 0.6 Hz, olefinic H), 7.50 (1H, d, *J* = 8.5 Hz, aromatic H), 7.50 (1H, d, *J* = 12.2 Hz, olefinic H), 7.37 (1H, dd, *J* = 8.5, 1.8 Hz, aromatic H), 7.18 (1H, dd, *J* = 15.6, 11.6 Hz, olefinic H). High MS *m/z*: Calcd for $C_{12}H_9N_2O_2Br$ (M^+ for ^{79}Br): 291.9846. Found: 291.9867.

1-[1-(6-Bromoindolyl)]-4-nitro-1,3-butadiene(5c) and 1-[3-(6-Bromoindolyl)]-4-nitro-1,3-butadiene(6c)

6-Bromoindole (**3c**). Solvent for chromatography: benzene. First eluate product: 9.5 mg (32.4%) of **5c** as yellow needles ($CHCl_3$), mp 202-203 ℃. IR ($CHCl_3$) cm^{-1}: 1630, 1610, 1520, 1495. ^1H-NMR (acetone-d_6) δ: 8.37 (1H, d, *J* = 13.4 Hz, olefinic H), 8.05 (1H, s, aromatic H), 8.03 (1H, t, *J* = 12.5 Hz, olefinic H), 7.86 (1H, d, *J* = 3.4 Hz, aromatic H), 7.60 (1H, d, *J* = 8.2 Hz, aromatic H), 7.43 (1H, d, *J* = 12.8 Hz, olefinic H), 7.37 (1H, dd, *J* = 8.6, 1.8 Hz, aromatic H), 6.86 (1H, d, *J* = 3.4 Hz, aromatic H), 6.86 (1H, t, *J* = 13.4 Hz, olefinic H). High MS *m/z*: Calcd for $C_{12}H_9N_2O_2Br$ (M^+ for ^{79}Br): 291.9843. Found: 291.9798. Anal. Calcd for $C_{12}H_9N_2O_2Br$: C, 49.17; H, 3.09; N, 9.56. Found: C, 49.32; H, 3.20; N, 9.52. Second eluate product: 0.3 mg (0.9%) of **6c** as red prisms ($CHCl_3$-hexane), mp 183-185 °C. IR ($CHCl_3$) cm^{-1}: 3470, 1610, 1580, 1540. ^{1}H-NMR (acetone-d_6) δ: 11.04 (1H, br s, NH), 7.96 (1H, d, J = 8.5 Hz, aromatic H), 7.89 (1H, s, aromatic H), 7.89 (1H, t, J = 12.8 Hz, olefinic H), 7.73 (1H, d, J = 1.5 Hz, aromatic H), 7.62 (1H, dd, J = 15.6, 0.6 Hz, olefinic H), 7.48 (1H, d, J = 12.8 Hz, olefinic H), 7.34 (1H, dd, J = 8.2, 1.5 Hz, aromatic H), 7.16 (1H, dd, J = 15.6, 11.6 Hz, olefinic H). High MS m/z: Calcd for $C_{12}H_9N_2O_2Br$ (M^+ for ^{79}Br): 291.9847. Found: 291.9874.

1-[3-(2-Methyl-5-nitroindolyl)]-4-nitro-1,3-butadiene(6d)

5-Nitroindole (**3d**). Solvent for chromatography: 50% ethyl acetate in hexane. Product: 2.3 mg (2.6%) of **6d** as orange prisms (acetone-hexane), mp 230-232 °C. IR (KBr) cm^{-1}: 3370, 1620, 1610, 1590, 1515. ^{1}H-NMR (acetone-d_6) δ: 11.36 (1H, br s, NH), 7.91 (1H, t, J = 11.3 Hz, olefinic H), 7.90 (1H, d, J = 8.9 Hz, aromatic H), 7.50 (1H, d, J = 15.6 Hz, olefinic H), 7.46 (1H, d, J = 13.1 Hz, olefinic H), 7.41 (1H, d, J = 8.9 Hz, aromatic H), 7.21 (1H, d, J = 1.5 Hz, aromatic H), 7.14 (1H, dd, J = 15.3, 11.3 Hz, olefinic H), 2.80 (3H, s, Me). CI MS m/z: 274 $(M+H)^+$.

General Procedure for Reactions of the Nitrodienamine(1) with Organocopper Reagents Prepared from Indoles(3e-g) Using Dimethylcopperlithium

The 1.06 M MeLi in ether solution (1.9 mL, 2.0 mmol) was added to a suspension of CuI (190 mg, 1.0 mmol) in anhydrous ether (4 mL) with stirring at 0°C under an argon atmosphere. A solution of substrate (**3e-g**) (0.17 mmol) in dry benzene (1.5 mL) was added to the mixture and the whole was stirred at 0 °C for 10 min under the same conditions. To resultant solution, a solution of **1** (142 mg, 1.0 mmol) in dry benzene (6.5 mL) was added at 0 °C and then the reaction mixture was stirred at rt for 2 h. The reaction mixture was poured into 10% NH_4Cl and extracted with ether. The organic layer was washed with brine, then dried over $MgSO_4$ and evaporated under reduced pressure. The residue was subjected to silica gel chromatography with appropriate solvents. The isolated yield of **5** and **6** was based on the corresponding starting indoles.

1-(1-Indolyl)-4-nitro-1,3-butadiene(5e) and 1-(3-Indolyl)-4-nitro-1,3-butadiene(6e)

Indole (**3e**). Solvent for chromatography: chloroform. First eluate product: 5.9 mg (16.2%) of **5e** as yellow plates (ethyl acetate-hexane), mp 131-133 ℃ (lit.,[6] mp 131-133 ℃). Second eluate product: 7.7 mg (21.3%) of **6e** as dark red prisms (ethyl acetate-hexane), mp 175.5-177.5 ℃ (lit.,[6] mp 175.5-177.5 ℃).

1-[1-(2-Methylindolyl)]-4-nitro-1,3-butadiene(5f) and 1-[3-(2-Methylindolyl)]-4-nitro-1,3-butadiene(6f)

2-Methylindole (**3f**). Solvent for chromatography: chloroform. First eluate product: 4.7 mg (12.4%) of **5f** as yellow prisms (ethyl acetate-hexane), mp 128-130 ℃. IR (KBr) cm^{-1}: 1634, 1593, 1550. ^{1}H-NMR (acetone-d_6) δ: 2.60 (3H, s, -Me), 6.51 (1H, s, aromatic H), 7.02 (1H, dd, J = 14.2, 12.8 Hz, olefinic H), 7.19 (1H, t, J = 7.3 Hz, aromatic H), 7.26 (1H, dd, J = 8.0, 7.3 Hz, aromatic H), 7.53 (1H, d, J = 7.3 Hz, aromatic H), 7.55 (1H, d, J = 12.8 Hz, olefinic H), 7.89 (1H, d, J = 8.0 Hz, aromatic H), 8.05 (1H, t, J = 12.8 Hz, olefinic H), 8.12 (1H, d, J = 14.2 Hz, olefinic H). High MS m/z: Calcd for $C_{13}H_{12}N_2O_2$ (M$^+$): 228.0896. Found: 228.0889. Second eluate product: 14.6 mg (38.5%) of **6f** as dark brown prisms (ethyl acetate), mp 201-203 ℃. IR (KBr) cm^{-1}: 3300, 1591, 1527. ^{1}H-NMR (acetone-d_6) δ: 2.63 (3H, s, -Me), 7.11 (1H, dd, J = 15.3, 12.2 Hz, olefinic H), 7.18 (2H, m, aromatic H), 7.41 (1H, m, aromatic H), 7.49 (1H, d, J = 12.2 Hz, olefinic H), 7.68 (1H, d, J = 15.3 Hz, olefinic H), 7.94 (1H, m, aromatic H), 7.95 (1H, t, J = 12.2 Hz, olefinic H), 10.82 (1H, br s, NH). CI-MS m/z: 229 (M+H)$^+$. Anal. Calcd for $C_{13}H_{12}N_2O_2$: C, 68.41; H, 5.30; N, 12.27. Found: C, 68.06; H, 5.49; N, 12.43.

1-[1-(3-Methylindolyl)]-4-nitro-1,3-butadiene(5g)

3-Methylindole (**3g**). Solvent for chromatography: benzene. Product: 27.8 mg (73.2%) of **5g** as yellow brown prisms (ethyl acetate), mp 204-206 ℃ (lit.,[6] mp 204-206 ℃).

REFERENCES

1. S. Rajappa, *Tetrahedron*, 1981, **37**, 1453.
2. a) T. Severin and I. Ipack, *Chem. Ber.*, 1976, **109**, 3541; b) *idem, ibid.*, 1978, **111**, 692.
3. a) R. A. Heacock and S. Kašpárek, *Advan. Heterocycl. Chem.*, 1969, **10**, 43; b) G. S. Silverman and P. E. Rakita, "Handbook of Grignard Reagent", Marcel Dekker, New York, 1996.
4. J. E. Bäckvall, N. A. Plobeck, and S. K. Juntunnen, *Tetrahedron Lett.*, 1989, **30**, 2589.

5. a) T. Koike, M. Tanabe, N. Takeuchi, and S. Tobinaga, *Chem. Pharm. Bull.*, 1997, **45**, 27; b) *idem, ibid.*, 1997, **45**, 243; c) *idem, ibid.*, 1997, **45**, 1117; d) T. Koike, N. Takeuchi, and S. Tobinaga, *ibid.*, 1998, **46**, 1497; e) *idem, ibid.*, 1999, **47**, 128.

6. a) N. Takeuchi, J. Ohki, and S. Tobinaga, *Chem. Pharm. Bull.*, 1988, **36**, 481; b) N. Takeuchi, M. Tanabe, M. Hagiwara, K. Goto, T. Koike, and S. Tobinaga, *Heterocycles*, 1994, **38**, 613; c) T. Koike, M. Hagiwara, N. Takeuchi, and S. Tobinaga, *ibid.*, 1997, **45**, 1271.

7. W. E. Noland and C. Reich, *J. Org. Chem.*, 1967, **32**, 828.

Received, 30th June, 1999