CONDENSATION REACTIONS OF A NITRODIENAMINE WITH INDOLES IN TRIFLUOROACETIC ACID

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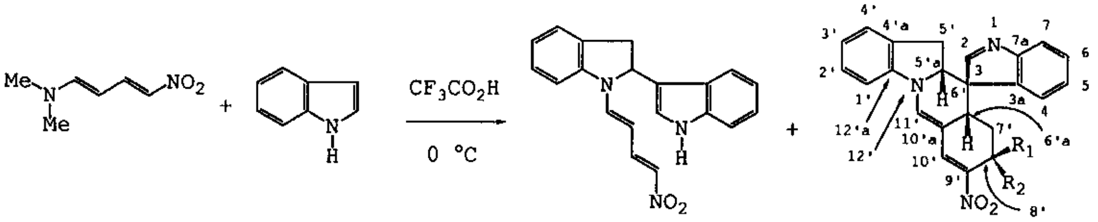
Abstract---Treatment of a nitrodienamine (**1**) with indoles in trifluoroacetic acid gave condensation products.

Considerable interest has been focused on the reactivities of nitroenamines because they may turn out to be useful intermediates in organic synthesis.[1] The center of interest in nitroenamine chemistry may lie in the enaminic character and the electronic "push-pull" nature. Reactions of *nitrodienamines are also of interest from* the viewpoint of the diene character, and also the analogy with nitroenamines. Nevertheless, only a few reports on the reactions using nitrodienamines have been published to date.[2] One reason may lie in the difficulty of preparation of nitrodienamines. Continuing to the previous report[3] in which we described a new and easy synthesis of nitrodienamines and some reactions with α, β-unsaturated carbonyl compounds and quinones, this paper reports a condensation reactions of a nitrodienamine (**1**) with indoles (**2**, **6**, **7**, and **8**) in trifluoroacetic acid.

The first, reactions of a nitrodienamine, 1-(*N,N*-dimethylamino)-4-nitro-1,3-

butadiene (**1**)[3] with indole (**2**) were investigated. Although several attempts to the condensation reaction of nitrodienamine (**1**) with indole (**2**) in various solvents such as xylene, ether, alcohol, and acetic acid were unsuccessful, use of trifluoroacetic acid at 0 °C for 1 h afforded three condensation products, namely, **3**, $C_{20}H_{17}N_3O_2$, mp 197-199 °C, (10.3% yield), **4**, $C_{24}H_{20}N_4O_4$, mp 238-240 °C, (21.8% yield), and **5**, $C_{24}H_{20}N_4O_4$, mp 229-231 °C, (19.9% yield), as shown in Scheme 1. The molecular formula of the product (**3**) suggested incorporation of two molecules of indole (**2**) in a condensation product. The infrared (ir) spectrum of **3** showed absorption bands at 3418 and 1585 cm^{-1} due to an indole N-H group and a nitro group, respectively. The proton nuclear magnetic resonance (^{1}H-nmr) spectrum of **3** showed the presence of four olefinic protons at δ 5.78 (1H, t, J = 12.4 Hz), 6.98 (1H, d, J = 12.4 Hz), 7.82 (1H, t, J = 7.3 Hz), and 8.03 (1H, d, J = 12.4 Hz), nine aromatic protons at δ 6.92-7.42, a proton of an indole N-H group at δ 10.25 (1H, s(br)), two protons of a methylene group at δ 3.23 (1H, dd, J = 16.3, 3.5 Hz) and 3.92 (1H, dd, J = 16.3, 10.1 Hz), and a methine proton at δ 5.82 (1H, dd, J = 10.1, 3.5 Hz), respectively. From these data, the product (**3**) was assigned as 2-(3"-indolyl)-1-(4'-nitro-1',3'-butadienyl)indoline having a nitrodiene, an indole ring, and an indoline ring in the molecule. The molecular formulas of the products (**4**) and (**5**)



1 **2** **3**

4 R^1=CH_2NO_2, R^2=H
5 R^1=H, R^2=CH_2NO_2

Scheme 1

suggested that **4** and **5** were prepared from two molecules of **1** and two molecules of **2**. The ir spectra of **4** and **5** showed absorption bands at 1566 and 1560 cm^{-1} and at 1580 and 1536 cm^{-1} and did not show any absorption bands at around 3000 cm^{-1}. The products (**4**) and (**5**) have consequently two nitro groups but do not have the indole N-H group and the hydroxy group. The ^{1}H-^{1}H and ^{1}H-^{13}C correlation spectroscopy (COSY) spectra of **4** and **5** were studied to identify the protons directly attached to the individual carbons.

Table 1: ^{1}H-Nmr (500.0 MHz) and ^{13}C-Nmr (125.6 MHz) Spectral Data for **4** in Acetone-d_6 *

Atom	δC (ppm)	DEPT	δH (ppm)	J_{H-H} (Hz)
2	175.17	CH	8.30 s	
3=6'	61.38	C		
3a	135.87	C		
4	125.26	CH	7.08 dd	7.3 (J_{4H-5H}), 1.2 (J_{4H-6H})
5	127.66	CH	7.11 t	7.3 ($J_{5H-4H,6H}$)
6	130.01	CH	7.39 dt	7.3 ($J_{6H-5H,7H}$), 1.2 (J_{6H-4H})
7	122.32	CH	7.66 d	7.3 (J_{7H-6H})
7a	158.63	C		
1'	109.72	CH	7.34 dd	7.3 ($J_{1'H-2'H}$), 1.2 ($J_{1'H-3'H}$)
2'	128.93	CH	7.24 t	7.3 ($J_{2'H-1'H,3'H}$)
3'	124.48	CH	6.92 dt	7.3 ($J_{3'H-2'H,4'H}$), 1.2 ($J_{3'H-1'H}$)
4'	126.51	CH	7.05 d	7.3 ($J_{4'H-3'H}$)
4'a	130.98	C		
5'	29.77	CH_2	1.81 dd	16.3 ($J_{5'\alpha H-5'a\beta H}$), 9.1 ($J_{5'\alpha H-5'\beta H}$)
			3.08 dd	16.3 ($J_{5'\beta H-5'a\beta H}$), 9.1 ($J_{5'\beta H-5'a\beta H}$)
5'a	62.95	CH	5.30 t	9.1 ($J_{5'a\beta H-5'\beta H,5'\alpha H}$)
6'a	32.27	CH	3.80 dd	13.1 ($J_{6'a\beta H-7'\alpha H}$), 4.1 ($J_{6'a\beta H-7'\beta H}$)
7'	25.30	CH_2	0.81 dt	13.1 ($J_{7'\alpha H-7'\beta H,6'a\beta H}$), 4.9 ($J_{7'\alpha H-8'\alpha H}$)
			1.44 ddd	13.1 ($J_{7'\beta H-7'\alpha H}$), 4.1 ($J_{7'\beta H-6'a\beta H}$), 1.8 ($J_{7'\beta H-8'\alpha H}$)
8'	34.56	CH	3.86 m	
9'	135.40	C		
10'	138.69	CH	8.11 s	
10'a	107.39	C		
11'	137.60	CH	8.27 s	
12'a	143.59	C		
13'	76.83	CH_2	4.62 dd	12.5 ($J_{13'H-13'H}$), 9.9 ($J_{13'H-8'\alpha H}$)
			4.78 dd	12.5 ($J_{13'H-13'H}$), 3.6 ($J_{13'H-8'\alpha H}$)

* All these assignments were confirmed by ^{1}H-^{1}H and ^{1}H-^{13}C COSY and HMBC spectra.

Table 2: ^{1}H-Nmr (500.0 MHz) and ^{13}C-Nmr (125.6 MHz) Spectral Data for **5** in DMSO-d_6 *

Atom	δC (ppm)	DEPT	δH (ppm)	J_{H-H} (Hz)
2	174.74	CH	8.33 s	
3=6'	59.82	C		
3a	135.51	C		
4	123.78	CH	6.93 dd	$7.3(J_{4H-5H}), 1.2(J_{4H-6H})$
5	126.69	CH	7.14 t	$7.3(J_{5H-4H,6H})$
6	128.94	CH	7.38 dt	$7.3(J_{6H-5H,7H}), 1.2(J_{6H-4H})$
7	121.06	CH	7.66 d	$7.3(J_{7H-6H})$
7a	156.83	C		
1'	108.84	CH	7.30 d	$8.0(J_{1'H-2'H})$
2'	127.94	CH	7.22 dd	$8.0(J_{2'H-1'H})\ 7.3(J_{2'H-3'H})$
3'	123.20	CH	6.88 t	$7.3(J_{3'H-2'H,4'H})$
4'	125.49	CH	7.02 d	$7.3(J_{4'H-3'H})$
4'a	129.54	C		
5'	28.53	CH_2	1.56 dd	$16.2(J_{5'\alpha H-5'a\beta H}), 9.2(J_{5'\alpha H-5'\beta H})$
			2.98 dd	$16.2(J_{5'\beta H-5'a\beta H}), 9.2(J_{5'\beta H-5'a\beta H})$
5'a	61.03	CH	5.12 t	$9.2(J_{5'a\beta H-5'\beta H,5'\alpha H})$
6'a	34.25	CH	3.58 dd	$12.2(J_{6'a\beta H-7'\alpha H}), 4.3(J_{6'a\beta H-7'\beta H})$
7'	27.41	CH_2	0.56 q	$12.2(J_{7'\alpha H-7'\beta H,6'a\beta H,8'\beta H})$
			1.46 ddd	$12.2(J_{7'\beta H-7'\alpha H}), 4.3(J_{7'\beta H-6'a\beta H})$ $3.4(J_{7'\beta H-8'\beta H})$
8'	33.15	CH	3.50 m	
9'	134.65	C		
10'	138.91	CH	8.09 s	
10'a	107.13	C		
11'	136.69	CH	8.40 s	
12'a	142.17	C		
13'	76.60	CH_2	4.69 dd	$15.3(J_{13'H-13'H}), 4.6(J_{13'H-8'\beta H})$
			4.72 dd	$15.3(J_{13'H-13'H}), 4.6(J_{13'H-8'\beta H})$

• All these assignments were confirmed by ^{1}H-^{1}H and ^{1}H-^{13}C COSY and HMBC spectra.

From the correlated peaks in **4** and **5**, we have been able to identify the pairs of carbons and directly bonded protons as shown in Tables 1 and 2. From the cross-peaks, by analyses of the networks of ^{1}H-^{1}H long range COSY spectra with delay (Figures 1 and 2) due to long range couplings, the connectivity of the carbon atoms in **4** and **5** could be determined as shown in Figure 3. However, at this stage, the connectivities of the quaternary carbons could not be determined (broken lines in Figure 3). In order to

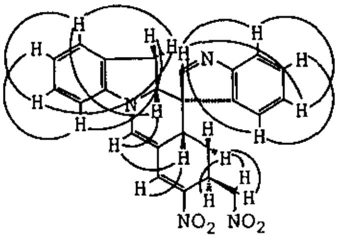


Figure 1
^1H-^1H Long Range COSY
of **4**

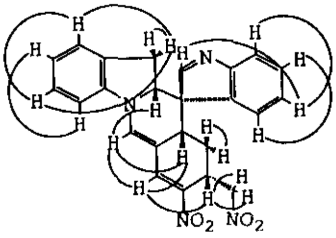


Figure 2
^1H-^1H Long Range COSY
of **5**

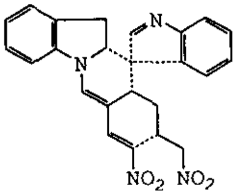
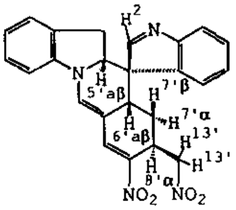


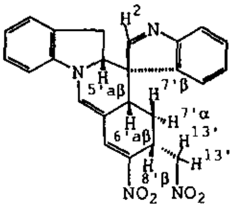
Figure 3
Skeletal Structures
of **4** and **5**

locate the carbons, the ^1H-detected multiple-bond heteronuclear multiple quantum coherrence (HMBC) spectra of **4** and **5** were measured. The presence of the cross-peaks due to the vicinal couplings between the protons of C(2), C(5'a), C(6'a) and the quaternary carbon C(3=6') showed the connectivity of the quaternary carbon C(3=6') to the methine carbons C(5'a) and C(6'a), the



NOE : $H^{7'\alpha} \frown H^{7'\beta}$ = 18.8%, $H^{7'\alpha} \frown H^{8'\alpha}$ = 16.9%,
$H^{6'a\beta} \frown H^{2}$ = 5.7%, $H^{6'a\beta} \frown H^{5'a\beta}$ = 5.7%,
$H^{6'a\beta} \frown H^{13'}$ = 3.5%,
$H^{13'} \frown H^{6'a\beta}$ = 15.4%

Figure 4
NOE Difference Spectra Observed in **4**



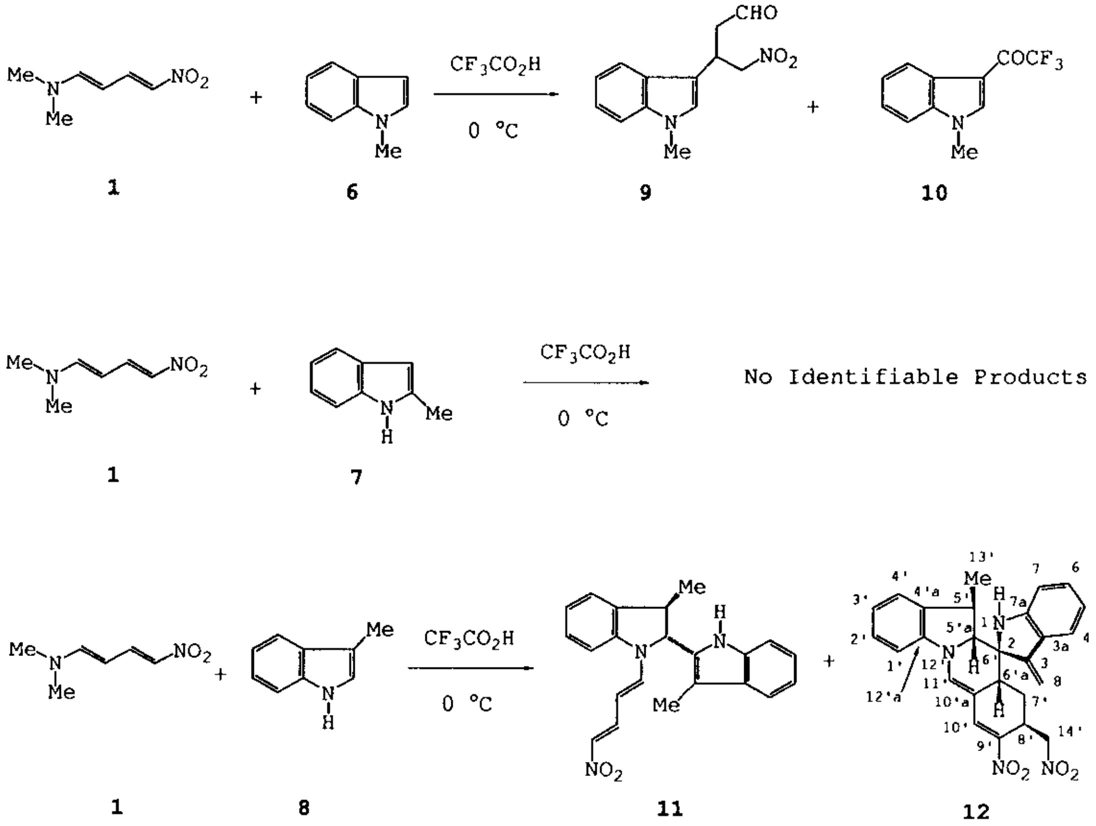
NOE : $H^{7'\alpha} \frown H^{7'\beta}$ = 16.2%,
$H^{6'a\beta} \frown H^{2}$ = 6.2%, $H^{6'a\beta} \frown H^{5'a\beta}$ = 5.7%,
$H^{6'a\beta} \frown H^{7'\beta}$ = 3.4%,
$H^{13'} \frown H^{8'\beta}$ = 7.9%, $H^{13'} \frown H^{7'\alpha}$ = 2.2%,
$H^{13'} \frown H^{7'\beta}$ = 1.5%

Figure 5
NOE Difference Spectra Observed in **5**

olefinic carbon C(2), and the quaternary carbon C(3a). In the same manner, the connectivity of the quaternary carbon C(9') to the methine carbon C(8') was established. Thus, the skeletal structures of **4** and **5** were established as shown in Figure 3. The three dimensional (3D) structures of **4** and **5** were determined by the nuclear Overhauser effect (NOE) difference spectra, based on the skeletal structure. Figure 4 shows the results of the NOE difference spectra of **4**. In particular, on irradiation at the methine proton resonance $H^{6'a\beta}$, NOE was observed on the olefinic proton resonance H^{2}, the methine proton resonance $H^{5'a\beta}$, and the methylene protons resonance $H^{13'}$, indicating that these protons protrude on one side of molecule. Figure 5 shows the results of the NOE difference spectra of **5**. On irradiation at the methine proton resonance $H^{6'a\beta}$, NOE was observed on the olefinic proton resonance H^{2} and the methine proton resonance $H^{5'a\beta}$, but was not observed the methylene protons resonance H^{13}, indicating that **4** and **5** are epimers with respect to the methine carbon C(8'). Therefore, the relative 3D-structures of **4** and **5** were determined as 9'-nitro-8'β-nitromethyl[spiro[3*H*-indole-3,6'-5'*H*,5'aβ*H*,6'*H*,6'aβ*H*,7'*H*,8'α*H*-indolo[1,2-*b*]isoquinoline]] and 9'-nitro-8'α-nitromethyl[spiro[3*H*-indole-3,6'-5'*H*,5'aβ*H*,6'*H*,6'aβ*H*,7'*H*,8'β*H*-indolo[1,2-*b*]-isoquinoline]}.

Second, we investigated the reactivities of nitrodienamine (**1**) with *N*-methylindole (**6**), 2-methylindole (**7**), and 3-methylindole (**8**) under the same conditions (Scheme 2).

The reaction of **1** with **6** afforded the products (**9**), $C_{13}H_{14}N_{2}O_{3}$, oil, (19.2% yield) and (**10**), mp 104-105 °C (lit.,[4] mp 105 °C), (11.0% yield). The ir spectrum of **9** showed absorption bands at 1722 and 1550 cm^{-1} due to a carbonyl group and a nitro group. The ^{1}H-nmr spectrum of **9** showed the presence of four protons of two methylene groups at δ 3.06 (2H, dd, J = 7.1,



Scheme 2

1.5 Hz) and 4.91 (2H, d, J = 7.1 Hz), three protons of a methyl group at δ 3.77 (3H, s), a methine proton at δ 4.42 (1H, quint, J = 7.1 Hz), five protons of an indole ring at δ 6.99-7.43 (4H, m) and 7.70 (1H, d, J = 7.7 Hz), and a proton of an formyl group at δ 9.71 (1H, t, J = 1.5 Hz), respectively. Thus, the product (**9**) was assigned as 3-(*N*-methylindolyl)-4-nitrobutanal. All physical data for the product (**10**), *N*-methyl-3-trifluoroacetylindole, were identical with those of an authentic sample.[4]

The reaction of **1** with **7** by the above methods gave no identifiable products.

The reaction of **1** with **8** afforded the products (**11**), $C_{22}H_{21}N_3O_2$, mp 128-131 °C (dec.), (15.5% yield), and (**12**), $C_{26}H_{24}N_4O_4$, mp 264-266 °C, (31.8% yield). The molecular formula of the product (**11**) showed that **11** was prepared from a molecule of **1** and two molecules of **8**. The ir spectrum of **11** showed absorption bands at 3387 and 1583 cm^{-1} due to an indole N-H group and a nitro group. The ^1H-nmr spectrum of **11** showed the presence of six protons of two methyl groups at δ 1.52 (3H, d, J = 6.5 Hz) and 2.42 (3H, s), two methine protons at δ 3.53 (1H, quint, J = 6.5 Hz) and 5.26 (1H, d, J = 6.5 Hz), four olefinic protons at δ 5.50 (1H, dd, J = 12.7, 12.1 Hz), 6.91 (1H, d, J = 12.1 Hz), 7.81 (1H, t, J = 12.1 Hz), and 8.03 (1H, d, J = 12.7 Hz), a proton of an indole N-H group at δ 10.05 (1H, br), and eight aromatic protons at δ 7.00-7.51 (8H, m). Thus, the product (**11**) was assigned as 1-(4'-nitro-1',3'-butadienyl)-2α-[2"-(3"-methylindolyl)]-3β-methylindoline. The molecular formula of the product (**12**) showed that **12** was prepared from two *molecules of* **1** *and two molecules of* **8**. *The ir spectrum of* **12** showed absorption bands at 3379, 1568, and 1550 cm^{-1} due to an indole N-H group and two nitro groups. The ^1H-nmr spectrum of **12** showed the presence of three protons of a methyl group at δ 1.35 (3H, d, J = 6.7 Hz) and two protons of an exomethylene group at δ 5.06 (1H, s) and 5.76 (1H, s). The ^1H-^1H and ^1H-^{13}C COSY spectra were studied to identify the protons directly attached to the individual carbons. From the correlated peaks in **12**, we have been able to identify the pairs of carbons and directly bonded protons as shown in Table 3. From the cross-peaks, by analyses of the networks of ^1H-^1H long range COSY spectrum with delay (Figure 6) due to long range couplings, the connectivity of the carbon atoms in **12** could be determined as shown in Figure 7. However, at this stage, the connectivities of quaternary carbons could not be determined (broken lines in Figure 7). In order to locate the quaternary carbons, the HMBC spectrum was measured. The presence of the cross-peaks due to the vicinal coupling between the protons of C(8) and N(1)

Table 3: ^{1}H-Nmr (500.0 MHz) and ^{13}C-Nmr (125.6 MHz) Spectral Data for **12** in Acetone-d_6 *

Atom	δC (ppm)	DEPT	δH (ppm)	J_{H-H} (Hz)
2=6'	65.23	C		
3	149.03	C		
3a	127.40	C		
4	121.57	CH	7.49 d	7.3 (J_{4H-5H})
5	118.66	CH	6.67 dd	7.3 (J_{5H-4H}), 6.7 (J_{5H-6H})
6	131.48	CH	7.06 dd	7.3 (J_{6H-7H}), 6.7 (J_{6H-5H})
7	110.29	CH	6.58 d	7.3 (J_{7H-6H})
7a	158.63	C		
8	101.62	CH_2	5.06 s 5.76 s	
1'	109.76	CH	7.25 or 7.26 d	6.7 ($J_{1'H \text{ or } 2'H-3'H}$)
2'	128.92	CH	7.25 or 7.26 d	6.7 ($J_{2'H \text{ or } 1'H-3'H}$)
3'	124.58	CH	7.01 m	
4'	125.23	CH	7.19 d	7.3 ($J_{4'H-3'H}$)
4'a	137.17	C		
5'	37.18	CH	3.17 qint	6.7 ($J_{5'\alpha H-5'a\beta H,13'H}$)
5'a	76.89	CH	4.05 d	6.7 ($J_{5'a\beta H-5'\alpha H}$)
6'a	39.35	CH	3.00 dd	13.2 ($J_{6'a\beta H-7'\alpha H}$), 4.2 ($J_{6'a\beta H-7'\beta H}$)
7'	24.17	CH_2	1.55 dt 1.82 ddd	13.2 ($J_{7'\alpha H-7'\beta H,6'a\beta H}$), 4.2 ($J_{7'\alpha H-8'\alpha H}$) 13.2 ($J_{7'\beta H-7'\alpha H}$), 4.2 ($J_{7'\beta H-6'a\beta H}$) 1.2 ($J_{7'\beta H-8'\alpha H}$)
8'	34.66	CH	4.00 m	
9'	135.00	C		
10'	139.09	CH	8.03 s	
10'a	108.78	C		
11'	137.60	CH	8.05 s	
12'a	143.09	C		
13'	20.12	CH_3	1.35 d	6.7 ($J_{13'H-5'\alpha H}$)
14'	77.32	CH_2	4.55 dd 4.80 dd	12.2 ($J_{14'H-14'H}$), 11.4 ($J_{14'H-8'\alpha H}$) 12.2 ($J_{14'H-14'H}$), 4.2 ($J_{14'H-8'\alpha H}$)

* All these assignments were confirmed by ^{1}H-^{1}H and ^{1}H-^{13}C COSY and HMBC spectra.

and the quaternary carbons C(3), C(2=6'), and C(3a) showed the connectivity of the carbon C(2=6') to the nitrogen N(1) and the carbon C(3) and the connectivity of the carbon C(3) to the carbons C(3a) and C(8). In the same manner, the connectivity of the carbon C(9') to the carbon C(8') was established. Thus, the skeletal structure of **12** was established as shown in

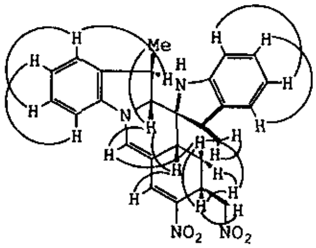


Figure 6
^{1}H-^{1}H Long Range COSY of **12**

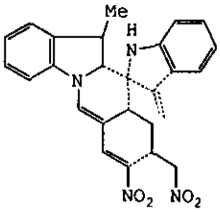


Figure 7
Skeletal Structure of **12**

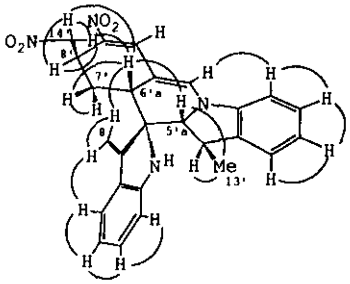
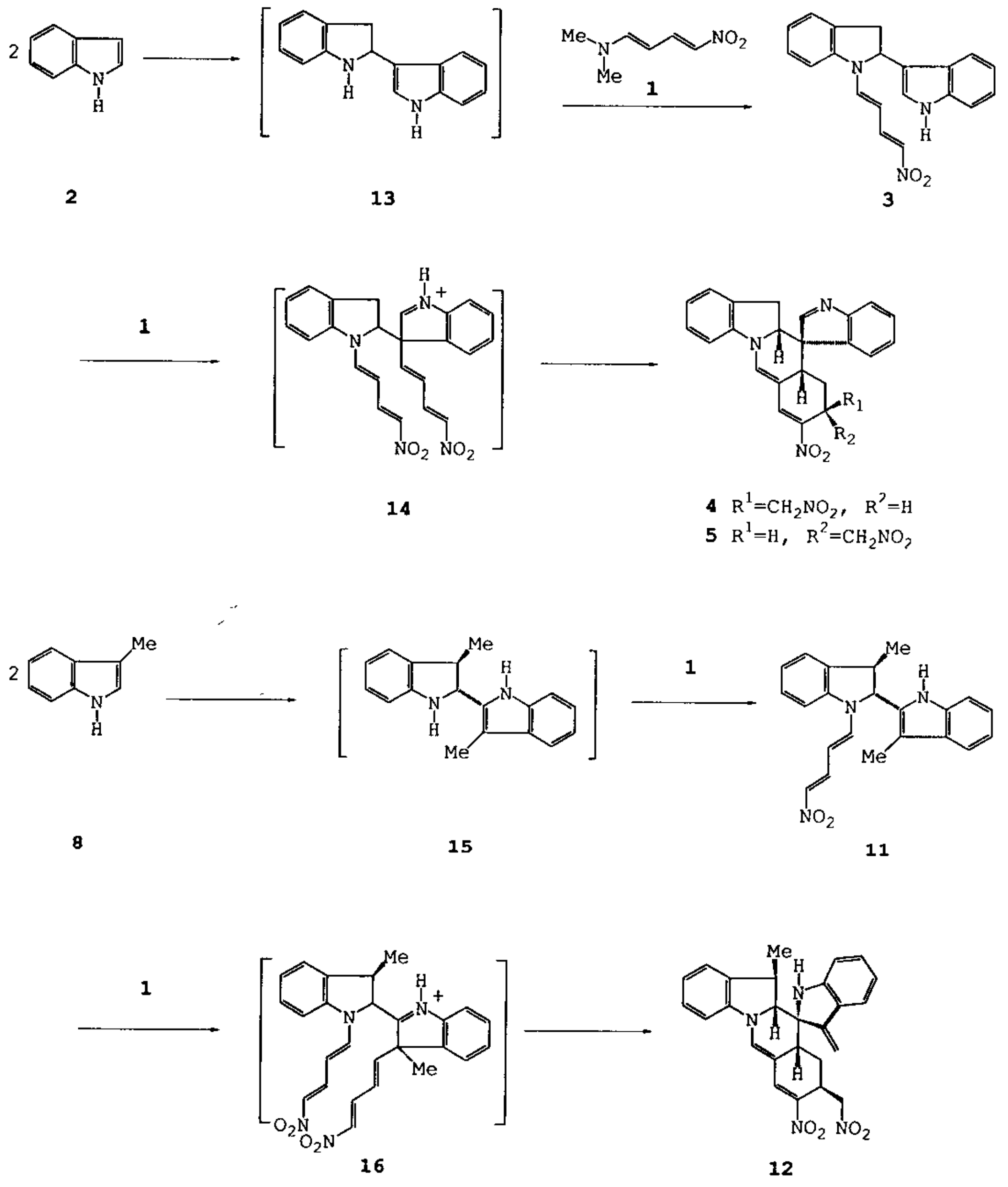


Figure 8
NOESY Observed in **12**

Figure 7. The 3D-structure of **12** was determined by a nuclear Overhauser and exchange spectroscopy (NOESY) spectrum, based on the skeletal structure as follows. The connectivity between observed ^{1}H-coupled sectors was provided by essential stereochemical information as shown in Figure 8. In particular, the presence of the cross-peaks between a proton of C(6'a) and the protons of C(8), C(5'a), C(7'), and C(14') and between a proton of C(5'a) and the protons of C(6'a) and C(13') showed the close proximity of the protons of C(8), C(5'a), C(7'), and C(14') to a proton of C(6'a) and the protons of C(6'a) and C(13') to a proton of C(5'a), indicating that these protons protrude on one side of the molecule. Therefore, the relative 3D-structure of **12** was determined as 5'β-methyl-3-methylene-9'-nitro-8'β-nitromethyl[spiro[2*H*,3*H*-indole-2,6'-5'α*H*,5'aβ*H*,6'aβ*H*,7'*H*,8'β*H*-indolo[1,2-*b*]-isoquinoline]].

The condensation reactions of a nitrodienamine (**1**) with indoles (**2**) and (**8**) may proceed as follows; the product (**3**) may form by the reaction of a nitrodienamine (**1**) with the indole dimer (**13**). Compounds (**4**) and (**5**) may be the further reaction products of **3** through the intermediate (**14**) by the reaction of **1** with **3** followed by ring closures of **14** to form **4** and **5**. Compound (**11**) may form by the reaction of **1** to the 3-methylindole dimer


2
2
13
Me
N
Me
NO2
1
3
1
14
4 R1=CH2NO2, R2=H
5 R1=H, R2=CH2NO2
2
Me
8
15
1
11
1
16
12

Scheme 3

(**15**),[5] and **12** may be a further reaction product of **11** through the intermediate (**16**) by the reaction of **1** with **11** followed by intramolecular rearrangement of 4-nitro-1,3-butadienyl group and ring closure to form **12** as shown in Scheme 3.

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 spectrophotometer, ^{1}H- and ^{13}C-nmr spectra with a JEOL EX-90, JEOL JNM-GX 270, JEOL JNM-α500 spectrometer with tetramethylsilane as an internal standard, ms with a JEOL JMS-D 300 spectrometer. ^{1}H-^{1}H COSY, ^{1}H-^{13}C COSY, ^{1}H-^{1}H long-range COSY, HMBC, and NOESY spectra were obtained with the usual pulse sequence and data processing was performed with the standard JEOL software. Elemental analyses were done by Miss. K. Nakamura, Kissei Pharmaceutical Company Ltd., Matsumoto, Japan. Wakogel C-200 (silica gel) and Merck Kieselgel G nach stahl (silica gel) were used for column chromatography and tlc, respectively.

General Procedure for Reactions of the Nitrodienamine (1) with Indoles (2, 6, and 8)

Indole (**2**, **6**, **7**, and **8**) (1.0 mmol) was added to a solution of **1** (170 mg, 1.2 mmol) in trifluoroacetic acid (2 ml) and the whole was stirred at 0 °C for 1 h under a nitrogen atmosphere and then at appropriate temperature for an appropriate period under the same conditions. The reaction mixture was poured into ice-water, and extracted with ethyl acetate. The organic layer was washed with saturated aqueous $NaHCO_3$ solution and brine, dried over dry Na_2SO_4 and concentrated. A solution of the residue in appropriate solvents was subjected to silica gel chromatography.

Reaction with Indole (2)

Reaction period at 0 °C: 1 h. Solvent for chromatography: 10% ethyl acetate in chloroform. The first eluate gave 17 mg (10.3%) of 2-(3"-indolyl)-1-(4'-nitro-1',3'-butadienyl)indoline (**3**) as bright red prisms (ethyl acetate), mp 197-199 °C. Ir (KBr) cm^{-1}: 3418, 1616, 1585. ^1H-Nmr (acetone-d_6) δ: 3.23 (1H, dd, *J* = 16.3, 3.5 Hz, H^3 in indoline), 3.92 (1H, dd, *J* = 16.3, 10.1 Hz, H^3 in indoline), 5.78 (1H, t, *J* = 12.4 Hz, olefinic H), 5.82 (1H, dd, *J* = 10.1, 3.5 Hz, H^2 in indoline), 6.92 (1H, dt, *J* = 7.3, 1.2 Hz, aromatic H), 6.98 (1H, d, *J* = 12.4 Hz, olefinic H), 7.07 (1H, dt, *J* = 7.3, 1.2 Hz, aromatic H), 7.10 (1H, dt, *J* = 7.3, 1.2 Hz, aromatic H), 7.19 (1H, d, *J* = 7.9 Hz, aromatic H), 7.30 (1H, d, *J* = 7.3 Hz, aromatic H), 7.34 (1H, t, *J* = 7.3 Hz, aromatic H), 7.38 (1H, s, H^2 in indole), 7.39 (1H, d, *J* = 7.3 Hz, aromatic H), 7.42 (1H, d, *J* = 7.3 Hz, aromatic H), 7.82 (1H, t, *J* = 7.3 Hz, olefinic H), 8.03 (1H, d, *J* = 12.4 Hz, olefinic H), 10.25 (1H, s(br), N-H in indole). High ms m/z: Calcd for $C_{20}H_{17}N_3O_2$ (M^+): 331.1321. Found: 331.1332. Anal. Calcd for $C_{20}H_{17}N_3O_2$: C, 72.49; H, 5.17; N, 12.68. Found: C, 72.54; H, 5.28; N, 12.44. The second eluate gave 46.7 mg (21.8%) of 9'-nitro-8'β-nitromethyl[spiro[3*H*-indole-3,6'-5'*H*,5'aβ*H*,6'*H*,6'aβ*H*,7'*H*,8'α*H*-indolo[1,2-*b*]-isoquinoline]](**4**) as dark violet flaky crystals (ethyl acetate), mp 238-240 °C. Ir (KBr) cm^{-1}: 1566, 1560. ^1H- and ^{13}C-Nmr : see Table 1. High ms m/z: Calcd for $C_{24}H_{20}N_4O_4$ (M^+): 428.1484. Found: 428.1500. Anal. Calcd for $C_{24}H_{20}N_4O_4$: C, 67.28; H, 4.71; N, 13.08. Found: C, 67.15; H, 4.93; N, 12.86. The third eluate gave 42.6 mg (19.9%) of 9'-nitro-8'α-nitromethyl[spiro[3*H*-indole-3,6'-5'*H*,5'aβ*H*,6'*H*,6'aβ*H*,7'*H*,8'β*H*-indolo[1,2-*b*]isoquinoline]] (**5**) as red violet prisms (ethyl acetate), mp 229-231 °C. Ir (KBr) cm^{-1}: 1580, 1536. ^1H- and ^{13}C-Nmr : see Table 2. High ms m/z: Calcd for $C_{24}H_{20}N_4O_4$ (M^+): 428.1485. Found: 428.1521. Anal. Calcd for $C_{24}H_{20}N_4O_4$: C, 67.28; H, 4.71; N, 13.08. Found: C, 67.11; H, 4.73; N, 12.81.

Reaction with *N*-Methylindole (6)

Reaction period at room temperature: 12 h. Solvent for chromatography: 50% hexane in chloroform. The first eluate gave 19 mg (11.0%) of *N*-methyl-3-trifluoroacetylindole (**10**), as colorless needless (ether - hexane), mp 104-105 °C (lit.,[4] mp 105 °C). The second eluate afforded 36.1 mg (19.2%) of 3-(*N*-methylindolyl)-4-nitrobutanal (**9**) as light brown oil. Ir (neat) cm^{-1}: 1722, 1550. ^1H-Nmr (acetone-d_6) δ: 3.06 (2H, dd, J = 7.1, 1.5 Hz, methylene H), 3.77 (3H, s, N-Me), 4.42 (1H, quint, J = 7.1 Hz, methine H), 4.91 (2H, d, J = 7.1 Hz, methylene H), 6.99-7.43 (4H, m, aromatic H), 7.70 (1H, d, J = 7.7 Hz, H^2 in indole), 9.71 (1H, t, J = 1.5 Hz, -CHO). High ms m/z: Calcd for $C_{13}H_{14}N_2O_3$ (M^+): 246.1015. Found: 246.1026.

Reaction with 3-Methylindole (8)

Reaction period at 0 °C: 1 h. Solvent for chromatography: 5% ethyl acetate in chloroform. The first eluate gave 28 mg (15.5%) of 1-(4'-nitro-1',3'-butadienyl)-2α-[2"-(3"-methylindolyl)]-3β-methylindoline (**11**), as orange-red prisms (ethyl acetate), mp 128-131 °C (dec.). Ir (KBr) cm^{-1}: 3387, 1614, 1583. ^1H-Nmr (acetone-d_6) δ: 1.52 (3H, d, J = 6.5 Hz, -Me), 2.42 (3H, s, -Me), 3.53 (1H, quint, J = 6.5 Hz, methine H), 5.26 (1H, d, J = 6.5 Hz, methine H), 5.50 (1H, dd, J = 12.7, 12.1 Hz, olefinic H), 6.91 (1H, d, J = 12.1 Hz, olefinic H), 7.00-7.51 (8H, m, aromatic H), 7.81 (1H, t, J = 12.1 Hz, olefinic H), 8.03 (1H, d, J = 12.7 Hz, olefinic H), 10.05 (1H, br, N-H in indole). High ms m/z: Calcd for $C_{22}H_{21}N_3O_2$ (M^+): 359.1634. Found: 359.1684. The second eluate afforded 72.5 mg (31.8%) of 5'β-methyl-3-methylene-9'-nitro-8'β-nitromethyl[spiro[2*H*,3*H*-indole-2,6'-5'α*H*,5'aβ*H*,6'aβ*H*,7'*H*,8'α*H*-indolo[1,2-*b*]isoquinoline]](**12**), as red violet prisms (ethyl acetate), mp 264-266 °C. Ir (KBr) cm^{-1}: 3379, 1608, 1568, 1550. ^1H- and ^{13}C-Nmr: see Table 3. High ms m/z: Calcd for $C_{26}H_{24}N_4O_4$ (M^+): 456.1797. Found:

456.1842. Anal. Calcd for $C_{26}H_{24}N_4O_4$: C, 68.41; H, 5.30; N, 12.27. Found: C, 68.46; H, 5.31; N, 11.98.

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Received, 20th October, 1993