

Synthesis of 2*H*-Indazole-4,7-dione Derivatives from
3-Phenylsydnone and *p*-Toluquinone. The Crystal and
Molecular Structure of 6-Bromo-5-methyl-2-phenyl-2*H*-indazole-4,7-dione

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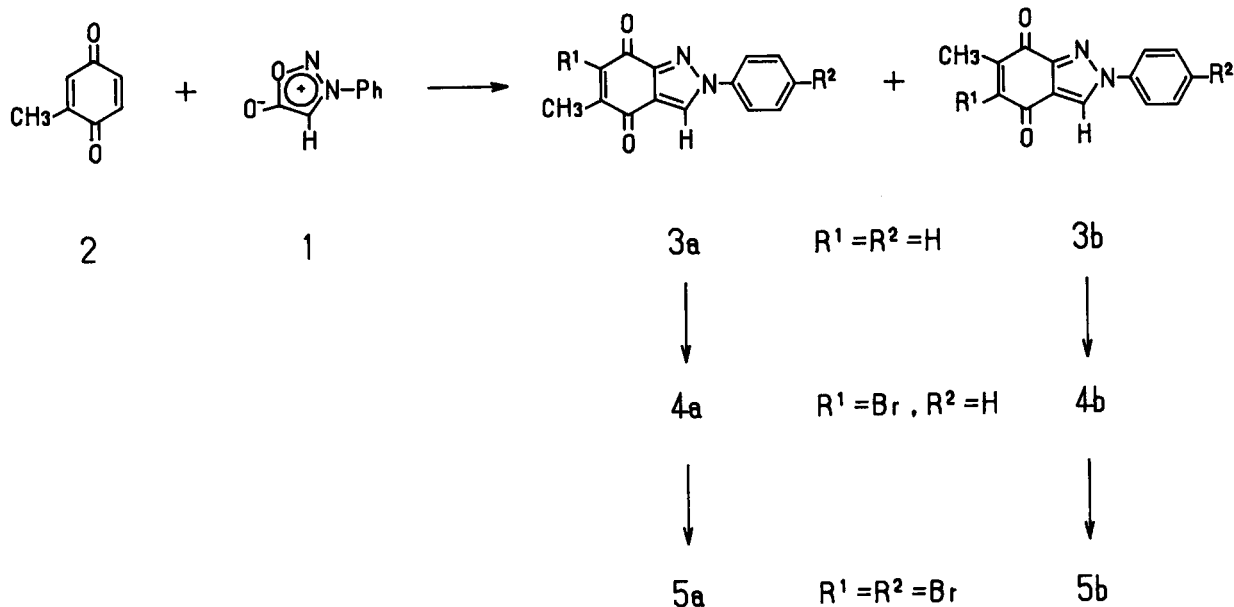
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The 1,3-dipolar cycloaddition of 3-phenylsydnone with *p*-toluquinone afforded 5-methyl- and 6-methyl-2-phenyl-2*H*-indazole-4,7-diones **3a** and **3b**. No regioselectivity was observed in this cycloaddition yielding an equimolar amount of the regioisomers. Reactions of **3a** and **3b** with bromine gave the corresponding mono-**4a** and **4b** and dibromo derivatives **5a** and **5b**, respectively. The crystal structure of 6-bromo-5-methyl-2-phenyl-2*H*-indazole-4,7-dione (**4a**) has been determined by the single crystal X-ray method. The crystals are monoclinic, space group *P*1 with two molecules in a unit cell of dimensions *a* = 8.029(1), *b* = 14.309(1), *c* = 5.895(1) Å, β = 90.24(1)° and *V* = 621 Å³. The structure has been solved by the direct method using 1827 reflections and refined by full-matrix least-squares calculations to *R* = 0.0739.

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Our interest in the 1,3-dipolar cycloaddition reactions of meso-ionic heterocycles to *p*-benzoquinone derivatives led us to synthesize some 2*H*-isoindole-4,7-dione derivatives as a useful precursor of phenothiazone derivatives [1]. In this paper, preparations of 5-methyl-**3a** and 6-methyl-2-phenyl-2*H*-indazole-4,7-diones **3b** via the 1,3-dipolar cycloaddition reaction of 3-phenylsydnone (**1**) with *p*-toluquinone (**2**), and their brominated derivatives, **4a**, **4b**, **5a** and **5b**, as well as an X-ray crystallographic analysis of the product **4a** were reported.

An equimolar mixture of **1** and **2** in xylene was heated to reflux for 10 hours to afford a yellowish crystalline product (42% yield) after usual work up. The examination of proton nmr spectrum indicated this product to be a 1:1 mixture of two possible regioisomers **3a** and **3b** of the corresponding cycloadducts. Attempted separations of the regioisomers by preparative tlc or column chromatography on silica gel or aluminium oxide were unsuccessful. However, repeated recrystallizations from ethanol gave finally pure **3a** as yellow needles that showed, in the nmr



spectrum, a characteristic singlet signal at δ 8.45 ppm assignable to hydrogen at the 3-position, a quartet at δ 6.77 ppm due to the vinylic hydrogen of the quinone ring and a doublet at δ 2.19 ppm for the vicinal methyl hydrogens. From the mother liquor, another regioisomer **3b** was also obtained pure as yellow needles that exhibited a characteristic singlet at δ 8.42, a quartet at δ 6.71 and a doublet at δ 2.21 ppm in the nmr spectrum. The analytical and other spectral data (ir, mass, uv) were compatible with the given cycloadduct-structures, however the regiochemical assignment was not possible.

The reaction of **3a** and **3b** with bromine in acetic acid afforded 6-bromo-5-methyl- and 5-bromo-6-methyl-2-phenyl-2*H*-indazole-4,7-diones, **4a** and **4b**, respectively in good yields. By use of a large excess of bromine, the *N*-phenyl group of **4a** and **4b** was brominated also, affording the *N*-(*p*-bromo)phenyl derivatives, **5a** and **5b**, respectively.

The structure of the cycloadducts was fully characterized from the X-ray crystallographic analysis carried out on the monobrominated product **4a**. The bromo group of **4a** attaches at the 6-position, consequently, the structures of **3a** and **3b** are 5-methyl- and 6-methyl-2-phenyl-2*H*-indazole-4,7-dione respectively. The structures of the dibrominated products **5a** and **5b** were also determined as shown.

X-Ray Crystallographic Results for **4a**.

Atomic coordinates and isotropic thermal parameters

Table I
Final Positional Parameters in Crystal Structure of **4a** [a]

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	Beq, Å ²
N(1)	0.2708(7)	0.0889(4)	-0.0966(8)	3.3(2)
N(2)	0.2520(7)	0.0035(3)	-0.0051(8)	2.9(1)
C(3)	0.3570(9)	0.0240(4)	0.1920(11)	3.2(2)
C(4)	0.5744(9)	0.1963(4)	0.4149(11)	3.4(2)
C(5)	0.6405(9)	0.3081(4)	0.3988(11)	3.2(2)
C(6)	0.5795(10)	0.3398(4)	0.2244(11)	3.5(2)
C(7)	0.4527(9)	0.2725(5)	0.0280(11)	3.6(2)
C(8)	0.3890(8)	0.1640(4)	0.0500(11)	3.2(2)
C(9)	0.4466(8)	0.1271(4)	0.2311(10)	3.0(2)
C(10)	0.1295(8)	-0.0938(4)	-0.1196(10)	2.9(2)
C(11)	0.0417(10)	-0.0974(5)	-0.3270(12)	4.0(2)
C(12)	-0.0780(10)	-0.1911(6)	-0.4331(13)	4.5(2)
C(13)	-0.1072(11)	-0.2789(6)	-0.3430(15)	4.9(2)
C(14)	-0.0189(11)	-0.2731(5)	-0.1371(15)	5.0(2)
C(15)	0.1016(10)	-0.1814(5)	-0.0249(12)	4.0(2)
O(16)	0.6259(7)	0.1660(3)	0.5746(8)	4.5(2)
O(17)	0.4048(7)	0.3056(3)	-0.1291(8)	4.7(2)
C(18)	0.7772(10)	0.3802(5)	0.5909(12)	4.2(2)
Br(19)	0.65445(15)	0.47933(5)	0.20217(15)	5.79(4)
H(3A)	0.359	-0.028(6)	0.280	3.0
H(11A)	0.081	-0.042(7)	-0.395	3.9
H(12A)	-0.099	-0.203(7)	-0.576	4.3
H(13A)	-0.172	-0.348(7)	-0.430	4.9
H(14A)	-0.032	-0.331(7)	-0.090	4.9
H(15A)	0.152	-0.176(6)	0.135	3.8

[a] Atoms are labeled as shown in Figure 1 and H atoms are labeled by the corresponding non-H atoms. Estimated standard deviations, in parenthesis, occur in the last figures for each parameter. H(18A), H(18B), and H(18C) were not detected. $Beq = (8\pi^2/3)\sum_i U_{ij}^2 a_i^* a_j^*$.

Table II
Anisotropic Temperature Factors for Non-H atoms of **4a** [a]

	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
N(1)	0.049(3)	0.034(2)	0.033(3)	0.012(2)	-0.012(2)	0.011(2)
N(2)	0.039(3)	0.027(2)	0.037(3)	0.007(2)	-0.016(2)	0.006(2)
C(3)	0.046(4)	0.032(3)	0.035(3)	0.012(3)	-0.016(3)	0.011(2)
C(4)	0.046(4)	0.036(3)	0.037(4)	0.012(3)	-0.015(3)	0.007(3)
C(5)	0.041(4)	0.036(3)	0.036(4)	0.012(3)	-0.012(3)	0.001(2)
C(6)	0.057(4)	0.033(3)	0.033(4)	0.011(3)	-0.005(3)	0.005(2)
C(7)	0.053(4)	0.038(3)	0.038(4)	0.014(3)	-0.009(3)	0.016(3)
C(8)	0.043(4)	0.032(3)	0.039(4)	0.009(3)	-0.014(3)	0.011(2)
C(9)	0.041(4)	0.032(3)	0.035(3)	0.013(3)	-0.013(3)	0.007(2)
C(10)	0.037(3)	0.031(3)	0.036(3)	0.010(2)	-0.012(3)	0.003(2)
C(11)	0.053(4)	0.049(3)	0.038(4)	0.012(3)	-0.020(3)	0.006(3)
C(12)	0.046(4)	0.065(4)	0.042(4)	0.014(4)	-0.016(4)	-0.007(3)
C(13)	0.054(5)	0.047(4)	0.067(5)	0.008(3)	-0.022(4)	-0.014(4)
C(14)	0.065(5)	0.037(3)	0.070(5)	0.004(3)	-0.023(4)	0.006(3)
C(15)	0.054(4)	0.035(3)	0.048(4)	0.005(3)	-0.020(3)	0.011(3)
O(16)	0.069(3)	0.043(2)	0.047(3)	0.018(2)	-0.029(2)	0.011(2)
O(17)	0.076(4)	0.038(2)	0.052(3)	0.010(2)	-0.026(3)	0.018(2)
C(18)	0.064(5)	0.038(3)	0.041(4)	0.004(3)	-0.021(3)	0.003(3)
Br(19)	0.1107(9)	0.0293(3)	0.0596(11)	0.0085(4)	-0.0268(6)	0.0090(3)

[a] The thermal parameters are in units of Å². The temperature factor has the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hlc^*a^* + 2U_{23}klb^*c^*)]$. Estimated standard deviations are indicated in parenthesis.

Table III

Selected bond Lengths and Bond Angles for **4a** [a]

Bond Lengths (Å)			
N(1)-C(8)	1.332(7)	C(6)-Br(19)	1.882(6)
N(1)-N(2)	1.362(8)	C(7)-O(17)	1.219(9)
N(2)-C(3)	1.363(8)	C(7)-C(8)	1.469(9)
N(2)-C(10)	1.439(6)	C(8)-C(9)	1.403(10)
C(3)-C(9)	1.363(7)	C(10)-C(15)	1.385(10)
C(4)-O(16)	1.221(9)	C(10)-C(11)	1.394(10)
C(4)-C(9)	1.462(8)	C(11)-C(12)	1.383(9)
C(4)-C(5)	1.504(9)	C(12)-C(13)	1.372(12)
C(5)-C(6)	1.340(10)	C(13)-C(14)	1.379(13)
C(5)-C(18)	1.539(8)	C(14)-C(15)	1.378(9)
C(6)-C(7)	1.500(8)		

Bond Angles (deg)			
C(8)-N(1)-N(2)	103.8(5)	C(8)-C(7)-C(6)	112.9(6)
N(1)-N(2)-C(3)	112.7(4)	N(1)-C(8)-C(9)	111.8(5)
N(1)-N(2)-C(10)	119.0(5)	N(1)-C(8)-C(7)	124.9(6)
C(3)-N(2)-C(10)	128.3(5)	C(9)-C(8)-C(7)	123.4(5)
C(9)-C(3)-N(2)	106.0(6)	C(3)-C(9)-C(8)	105.8(5)
O(16)-C(4)-C(9)	122.4(6)	C(3)-C(9)-C(4)	132.9(6)
O(16)-C(4)-C(5)	121.0(5)	C(8)-C(9)-C(4)	121.3(5)
C(9)-C(4)-C(5)	116.6(6)	C(15)-C(10)-C(11)	121.3(5)
C(6)-C(5)-C(4)	120.0(5)	C(15)-C(10)-N(2)	120.3(6)
C(6)-C(5)-C(18)	123.8(5)	C(11)-C(10)-N(2)	118.4(6)
C(4)-C(5)-C(18)	116.3(6)	C(12)-C(11)-C(10)	117.8(7)
C(5)-C(6)-C(7)	125.8(6)	C(13)-C(12)-C(11)	121.9(8)
C(5)-C(6)-Br(19)	121.2(4)	C(12)-C(13)-C(14)	119.1(6)
C(7)-C(6)-Br(19)	113.0(5)	C(15)-C(14)-C(13)	121.1(8)
O(17)-C(7)-C(8)	124.1(5)	C(14)-C(15)-C(10)	118.8(7)
O(17)-C(7)-C(6)	123.0(6)		

[a] Labeling corresponds to that indicated in Figure 1. Estimated standard deviations in parenthesis.

are given in Tables I and II respectively. The identification of the atoms is shown in the ORTEP [2] drawing of the molecule of Figure 1. Some selected bond lengths and bond angles are given in Table III. On the other hand, crystal and other related experimental data are given in the Experimental.

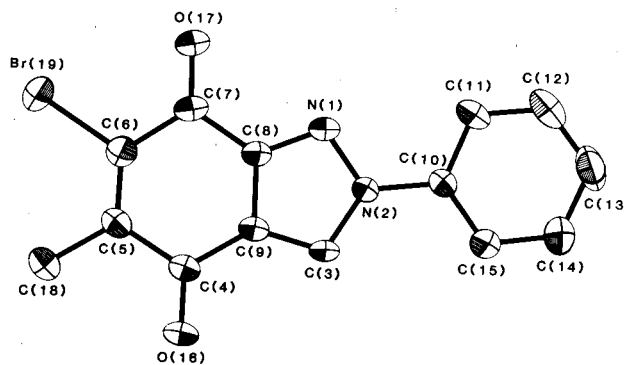
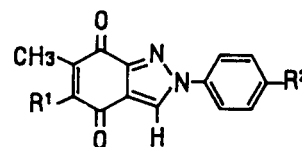
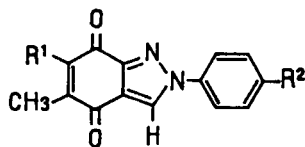


Figure 1. ORTEP drawing of X-ray crystallographically determined structure of **4a**. The carbon, nitrogen and oxygen atoms are drawn as 50% ellipsoids.

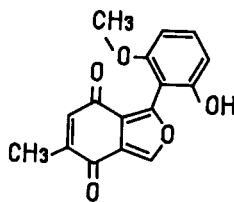
The bond lengths and bond angles of the pyrazole ring moiety are more or less similar to those reported for unsubstituted pyrazole ring [3]. The bonds C(5)-C(6), C(4)-O(16) and C(7)-O(17) of the cyclohexenedione moiety are clearly double bonds and the bonds C(4)-C(5), C(6)-C(7), C(7)-C(8) and C(4)-C(9) are single bonds; slight variations may result from conjugation effects. These values are not much different from those of 1-(2-hydroxy-6-

Table IV

Physical and Analytical Data for Compounds **3**, **4** and **5**

Compound	R ¹	R ²	a			b				
			Yield (%)	Mp (°C)	Molecular Formula	Mass (M*) (Relative intensity %)	Elemental Analyses (%) Found/(Calcd.)			
							C	H	N	Br
3a	H	H		220-222	C ₁₄ H ₁₀ N ₂ O ₂ (238.3)	238 (100)	70.33 (70.58)	4.15 (4.23)	11.79 (11.76)	
3b	H	H	42	198-200	C ₁₄ H ₁₀ N ₂ O ₂ (238.3)	238 (100)	70.41 (70.58)	4.12 (4.23)	11.62 (11.76)	
4a	Br	H	80	231-235 dec	C ₁₄ H ₉ BrN ₂ O ₂ (317.1)	316/318 (98)(100)	53.04 (53.02)	2.86 (2.86)	8.69 (8.83)	25.31 (25.19)
4b	Br	H	78	250-257 dec	C ₁₄ H ₉ BrN ₂ O ₂ (317.1)	316/318 (93)(100)	53.26 (53.02)	2.78 (2.86)	8.49 (8.83)	25.02 (25.19)
5a	Br	Br	65	242-246 dec	C ₁₄ H ₈ Br ₂ N ₂ O ₂ (396.0)	394/396/398 (57)(100)(55)	42.55 (42.46)	1.96 (2.04)	6.87 (7.07)	40.20 (40.35)
5b	Br	Br	60	248-252 dec	C ₁₄ H ₈ Br ₂ N ₂ O ₂ (396.0)	394/396/398 (52)(100)(52)	42.37 (42.46)	2.01 (2.04)	6.99 (7.07)	40.45 (40.35)

methoxyphenyl)-5-methyl-4,7-dihydroisobenzofuran (**6**) [4]. The bond angles of the cyclohexenedione moiety are also similar to those of **6**. However, the bond angle C(6)-C(5)-C(18) 123.8 (5) $^\circ$ is slightly larger than 121.4(5) $^\circ$ reported for **6**; this may be due to steric repulsion between the methyl group and the vicinal bromine group.



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The results indicate also that **4a** is essentially a planar molecules. However, the cyclohexenedione ring takes a boat form puckered downward from the plane of the pyrazole ring: the torsion angles between N(2)-N(1)-C(8) and N(1)-C(8)-C(7) planes, N(2)-C(3)-C(9) and C(3)-C(9)-C(4), C(6)-C(7)-C(8) and C(7)-C(8)-N(1), and C(5)-C(4)-C(9) and C(4)-C(9)-C(3) are 0.79, 1.76, 2.51 and 1.79 $^\circ$ respectively. Interestingly, the bromine(19) and O(17) as well as C(18) and O(16) take almost coplanar arrangements, thus the torsion angles between Br(19)-C(6)-C(7) and C(6)-C(7)-O(17), and O(16)-C(4)-C(5) and C(4)-C(5)-C(18) planes are 0.27 and 1.05 $^\circ$ respectively. Only the aromatic ring C(10)-C(11) is rotated at most 3.34 $^\circ$ about the N(2)-C(10) bond out of the plane of the pyrazole ring.

EXPERIMENTAL

Melting points were determined on a Yanaco micromelting point apparatus and are uncorrected. The infrared spectra were taken on a JASCO A-102 spectrometer using potassium bromide disks and the ultraviolet spectra were recorded with a JASCO UVIDE C-505. The nuclear magnetic resonance spectra were measured on a Varian XL-200 spectrometer, using tetramethylsilane as the internal standard. Mass spectra were obtained with a ESCO EMD-05B spectrometer. For column chromatography, silica gel (Kieselgel 60, Merck, 70-230 mesh ASTM) was used. The starting material, *p*-toluquinone purchased from Tokyo Kasei Kogyo Co., Ltd.

5-Methyl-2-phenyl-2*H*-indazole-4,7-dione (**3a**) and 6-Methyl-2-phenyl-2*H*-indazole-4,7-dione (**3b**).

The mixture of 4.1 g (25 mmoles) of 3-phenylsydnone (**1**) [5] and 3.3 g (27 mmoles) of *p*-toluquinone (**2**) in 100 ml of xylene was refluxed for 10 hours. After evaporation of solvent the residue was chromatographed on silica gel using benzene as the eluent. The pure product was recrystallized four times from ethanol, giving **3a** as yellow needles. From mother liquor **3b** was obtained by further recrystallization.

Among the attempted solvents used for the analogous reactions [1,6-8] (dioxane, tetrahydrofuran, benzene, toluene and xylene), xylene was the best under the above condition.

Compound **3a**.

This compound had ir: 1670 and 1655 (C=O) cm $^{-1}$; uv (methanol): λ max, nm (log ϵ), 260 (4.54), 315 sh (3.38); 1 H nmr (deuteriochloroform): δ

8.45 (s, 1H), 7.85 (m, 1H), 7.81 (m, 1H), 7.60-7.42 (m, 3H), 6.77 (q, 1H), 2.19 (d, 3H).

Compound **3b**.

This compound had ir: 1675 and 1655 (C=O) cm $^{-1}$; uv (methanol): λ max, nm (log ϵ), 261 (4.52), 315 sh (3.35); 1 H nmr (deuteriochloroform): δ 8.42 (s, 1H), 7.85 (m, 1H), 7.81 (m, 1H), 7.61-7.44 (m, 3H), 6.71 (q, 1H), 2.21 (d, 3H).

Bromination of **3a** and **3b**.

Method A. 6-Bromo-5-methyl-2-phenyl-2*H*-indazole-4,7-dione (**4a**) and 5-Bromo-6-methyl-2-phenyl-2*H*-indazole-4,7-dione (**4b**).

To a suspension of 1 mmole of **3a** in 4 ml of acetic acid were added 2 mmoles of bromine and 4 mmoles of sodium acetate. The mixture was allowed to stand in the dark at room temperature for a few days. The product was filtered and recrystallized or column chromatographed (eluent: benzene-chloroform, 7:1), giving **4a** as yellow needles.

From **3b** with bromine by the same method described above **4b** was produced.

Compound **4a**.

This compound had ir: 1680 and 1658 (C=O) cm $^{-1}$; uv (methanol): λ max, nm (log ϵ), 264 (4.45); 1 H nmr (deuteriochloroform): δ 8.48 (s, 1H), 7.86 (m, 1H), 7.82 (m, 1H), 7.62-7.48 (m, 3H), 2.39 (s, 3H).

Compound **4b**.

This compound had ir: 1670 (C=O) cm $^{-1}$; uv (methanol): λ max, nm (log ϵ), 257 (4.63); 1 H nmr (deuteriochloroform): δ 8.52 (s, 1H), 7.83 (m, 2H), 7.56 (m, 3H), 2.42 (s, 3H).

Method B. 6-Bromo-5-methyl-2-(*p*-bromophenyl)-2*H*-indazole-4,7-dione (**5a**) and 5-Bromo-6-methyl-2-(*p*-bromophenyl)-2*H*-indazole-4,7-dione (**5b**).

Treating **3a** or **3b** with 50 mmoles of bromine in a similar manner for the preparation of **4a**, dibromo derivatives **5a** or **5b** were produced respectively. The mixture was chromatographed on silica gel column using benzene-chloroform (7:1) as the eluent. From the first fraction **5a** or **5b** in good yield and from the second fraction a small amount of **4a** or **4b** were obtained.

Compound **5a**.

This compound had ir: 1690 and 1658 (C=O) cm $^{-1}$; uv (methanol): λ max, nm (log ϵ), 268 (4.66); 1 H nmr (deuteriochloroform): δ 8.46 (s, 1H), 7.73 (s, 4H), 2.38 (s, 3H).

Compound **5b**.

This compound had ir: 1685 and 1670 (C=O) cm $^{-1}$; uv (methanol): λ max, nm (log ϵ), 272 (4.60); 1 H nmr (deuteriochloroform): δ 8.50 (s, 1H), 7.72 (s, 4H), 2.42 (s, 3H).

Bromination of **4a** and **4b**.

From **4a** or **4b** by treatment similar to that described above (Method B), **5a** or **5b** was obtained.

Crystallographic Study.

The crystal was obtained by slow crystallization from ethanol. D_m was measured by flotation. A Rigaku automated four-circles diffractometer, AFC-5 was used with graphite monochromated Cu radiation (CuK α = 1.5418 Å). C $_{14}$ H $_9$ N $_2$ O $_2$ Br, M_r = 317.14; monoclinic, P1, a = 8.029(1) Å, b = 14.309(1) Å, c = 5.895(1) Å, α = 98.10(1) $^\circ$, β = 90.24(1) $^\circ$, γ = 111.86(1) $^\circ$, V = 621 Å 3 , D_x = 1.696 g/cm 3 , D_m = 1.688 gm/cm 3 ; Z = 2; Crystal size, 0.10 x 0.07 x 0.30 mm; 2300 intensities were collected, 2θ max = 126 $^\circ$.

Structures were solved by the Monte-Carlo direct method [9] with the aid of MULTAN78 program system [10] using 1827 non-zero unique reflections, and refined by the full-matrix least-squares program with the analytical absorption correction [11]. Non-H atoms were assigned anisotropic temperature factors, except for some H atoms located from

the difference Fourier map and refined with the equivalent isotropic temperature factor to that for the bonded carbon atoms. $R = 0.0739$, $S = [\sum W(|F_o|^2 - |F_c|^2)^2 / (m-n)]^{1/2} = 1.7$, $w = 1/\sigma^2(F^2)$, $\Delta\rho_{max} = 9.5/e \text{ \AA}^{-3}$. Atomic scattering factors are from the International Tables for X-Ray Crystallography [12]. ORTEP was employed for drawing the molecular structures. All calculations were made on a FACOM M-382 at the computer center of Nagoya University.

Listing of atomic parameters, thermal parameters, selected bond lengths and bond angles are included in the supplementary material.

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REFERENCES AND NOTES

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