(m, 18 H), 0.99 (s, 27 H); ^{13}C NMR ($Me_4Si/CDCl_3$) (**4a**) δ 132.7 (s), 132.5 (s), 44.5 (d), 32.4 (s), 28.7 (t), 28.4 (t), 27.2 (q), 24.4 (t), (**4b**) δ 133.1 (s), 132.9 (s), 132.8 (s), 132.7 (s), 132.6 (s), 132.5 (s), 132.3 (s), 44.5 (d), 44.4 (d), 32.5 (s), 32.4 (s), 28.8 (t), 28.7 (t), 28.4 (t), 28.1 (t), 27.9 (t), 27.7 (t), 27.7 (q), 27.3 (q), 27.2 (q), 24.4 (t), 24.3 (t), 24.2 (t).

Dehydrogenation of Dodecahydro-2,6,10-trimethyltriphenylenes (3a and 3b). The mixture of **3a** and **3b** (0.38 mmol, 108 mg) was heated at 280-300 °C with 5% Pd/C (200 mg) in a 50-mL autoclave for 10 h. The reaction product was extracted with $CHCl_3$. Evaporation of the solvent gave almost pure 2,6,10-trimethyltriphenylene (**10**) (98 mg, 95%) without further purification. The dehydrogenation of **4a** and **4b** was carried out by the same method as above. 2,6,10-Trimethyltriphenylene (**10**): mp 181-182 °C; IR (KBr) 3025, 2917, 2852, 1615, 1503, 1408, 1372, 1262, 816, 765, 593 cm^{-1}; ^1H NMR ($Me_4Si/CDCl_3$) δ 8.33 (d, J = 8.4 Hz, 3 H), 8.22 (s, 3 H), 7.23 (d, J = 6.6 Hz, 3 H), 2.43 (s, 9 H); ^{13}C NMR ($Me_4Si/CDCl_3$) δ 136.5 (s), 129.9 (s), 128.0 (d), 126.9 (s), 123.1 (d), 123.0 (d), 21.8 (q). Anal. Calcd for $C_{21}H_{18}$: H, 6.71; C, 93.29. Found: H, 6.57, C, 93.18. 2,6,10-Tri-*tert*-butyltriphenylene (**11**): 135 mg, 90%; mp 293-294 °C; IR (KBr) 2963, 2902, 2866, 1618, 1502, 1479, 1458, 1409, 1362, 1264, 824, 652 cm^{-1}; ^1H NMR ($Me_4Si/CDCl_3$) δ 8.6 (s, 3 H), 8.6 (d, J = 11.7 Hz, 3 H), 7.70 (d, J = 8.4 Hz, 3 H), 1.50 (s, 27 H); ^{13}C NMR ($Me_4Si/CDCl_3$) δ 149.6 (s), 129.5 (s), 127.5 (s), 124.6 (d), 122.9 (d), 119.1 (d), 35.0 (s), 31.5 (q). Anal. Calcd for $C_{30}H_{36}$: H, 9.15, C, 90.85. Found: H, 9.21, C, 90.78.

Highly Regioselective Functionalization of 2,3-Dialkyl Substituents on Indoles

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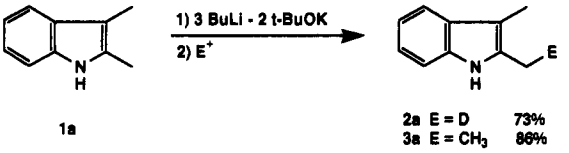
Direct functionalization of the side chains of heteroaromatic nuclei continues to be a significant challenge for the construction of complex alkaloids.[1] The α-metalation of alkyl substituents is one of the most attractive routes for this modification.[2] Although the indole and pyrrole rings are widely found in bioactive compounds, little attention has been paid to the deprotonation of the alkyl side chains on these π-excessive heteroaromatics. During the course of our study of the stabilization of cross-conjugated [6 electrons/4 p orbitals] system,[3,4] we have succeeded in generating a C,N-dianion of 2-methylindole by a particular sequence of base treatments and in introducing some functional groups into the side chains.[5,6] The successful transformation might be due to the stability of the benzene ring and the cross [6e/4p] conjugation in the dianion intermediate.[6] This assumption led us to explore the deprotonation of 2,3-dialkylated indoles. The reaction would predominantly occur at the 2-alkyl side chain.[3] Here we report that the direct metalation of polysubstituted indoles proceed in a highly regioselective manner.

Our first choice for the reaction was 2,3-dimethylindole (**1a**). Treatment of **1a** with butyllithium (3 equiv) followed by addition of potassium *tert*-butoxide (2 equiv)[15] in ether at ambient temperature afforded a bright yellow suspension of the dianion. Quenching by methanol-d_1 (10 equiv) gave 2-(deuteriomethyl)-3-methylindole (**2a**) in 73% yield. The ^{13}C NMR spectra of the N-methylated product showed that the reaction proceeded only at the α-position of 2-methyl group.



The methylation with methyl halides occurred in a similar manner (Table I). A sole product, 2-ethyl-3-methylindole (**3a**) was obtained. The regioselectivity was determined by the differential NOE experiment. Interestingly, methyl bromide was found to be superior as an electrophile to methyl iodide. The usual S_N2 reactivity of alkyl halides is R-I > R-Br > R-Cl > R-F.[7]

Deprotonation of 1,2,3,4-tetrahydrocarbazole (**1c**)[8] also proceeded exclusively at the 1-position (runs 7, 8). No ortho-metalation on the benzene ring occurred. The results form a striking contrast to that observed by Katritzky et al. when the protecting groups of chelating capability were attached to the N atom. Their procedures failed in case of the carboxylate group[9] and led to the ortho-metalation in case of the 1-pyrrolidinomethyl group.[10]

Herein a novel method for the highly regioselective deprotonation of the indole alkyl substituents has been established by the particular sequence of base treatments. This success may be due to the aromatic stabilization of cross [6e/4p] conjugated systems. We are presently pursuing further application revolving around this methodology.

Experimental Section

General. All experiments were performed under Ar atmosphere. Diethyl ether as solvent was distilled from sodium benzophenone ketyl. The reagents are commercial products and used without further purification, unless literature sources or details for the preparation are given. 1,2,3,4-Tetrahydrocyclopent[*b*]-indole (**1d**) and the authentic samples of 2-ethyl-3-methylindole (**3a**) and 1-deuterio-1,2,3,4-tetrahydrocarbazole (**2c**) were prepared in the analogous fashion of 1,2,3,4-tetrahydrocarbazole.[8] Thin-layer chromatography (TLC) analyses were performed with Merck 5715 precoated plate. NMR spectra of ^1H nuclei at 270 MHz and of ^{13}C nuclei at 60 MHz were recorded by a JEOL GX-270 spectrometer. Melting points were measured by a Yanagimoto MP-J3 and are uncorrected. IR spectra were recorded by a JASCO A-100 or a Perkin-Elmer 1640SF spectrometer. Mass spectra (MS) were obtained on a Shimadzu GCMS 9020-DF instrument. Yields of the deuterized products were obtained by the decrease of ^1H NMR integration. The elemental analysis was performed at the

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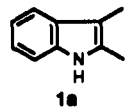
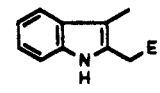
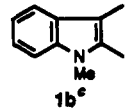
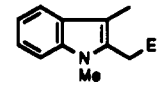
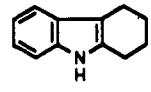
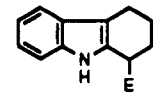
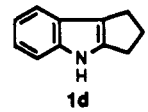
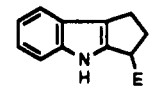
Table I. Reaction of 2,3-Dialkylated Indoles with Electrophiles

run	substrate	electrophile	product	yield (%)
1	 1a	D_2O	 **2a**: E = D[a]	73
2		CH_3I	**3a**: E = CH_3[a]	53
3		CH_3Br	E = CH_3[a]	86
4	 1b[c]	D_2O	 **2b**: E = D[a,b]	66
5		CH_3I	**3b**: E = CH_3[a,b]	83
6		CH_3Br	E = CH_3	97
7	 1c	D_2O	 **2c**: E = D[b]	70
8		CH_3Br	**3c**: E = CH_3[a]	50
9	 1d	CH_3Br	 **3d**: E = CH_3[a]	37

[a] Regioselectivities determined by differential NOE experiments. [b] Regioselectivities determined by comparing with ^{13}C NMR of the authentic samples. [c] Use of 2 equiv each of BuLi and tBuOK.[7]

Laboratory for Organic Elemental Microanalysis of Kyoto University. The purity of all title compounds was judged to be >95% by ^1H and ^{13}C NMR spectral determinations.

Functionalization of Substituted Indoles. General Procedure. To a stirred solution of indole (2.0 mmol) in Et_2O (20 mL) was added BuLi (1.5 M in hexane, 4.0 mL, 6.0 mmol) and then *t*-BuOK (450 mg, 4.0 mmol) at −78 °C. The resulting suspension was gradually warmed to room temperature. When the mixture turned bright orange (ca. 5 min), it was recooled to −78 °C immediately. The electrophile (20 mmol) was added dropwise and quenched by water after 2 h. The mixture was warmed to room temperature, poured into aqueous $NaHCO_3$, and extracted with ether. Dryness over $MgSO_4$, removal of solvents in vacuo, and purification by column chromatography on silica gel (eluant: hexane–ether, 5:1) afforded the corresponding product.

2-(Deuteriomethyl)-3-methylindole (2a): 73%; ^1H NMR ($CDCl_3$) δ 2.19 (s, 3 H, CH_3), 2.22 (s, 2 H, CH_2D), 7.03–7.47 (m, 5 H, Ar and NH); (DMSO-d_6)[10] δ 2.15 (s, 3 H, Me), 2.28 (br s, 2 H, CH_2D), 6.94 (m, 2 H, Ar), 7.22 (d, J = 7.8 Hz, 1 H, Ar), 7.34 (d, J = 7.3 Hz, 1 H, Ar), 10.61 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 8.4, 10.9 (t, CH_2D), 106.8, 110.2, 117.9, 118.9, 120.7, 129.3, 130.7, 135.1; (DMSO-d_6) δ 8.2, 10.9 (t, CH_2D), 105.0, 110.2, 117.2, 117.9, 119.8, 128.9, 131.2, 135.2.

2-Ethyl-3-methylindole (3a): 53 and 86% with MeI and MeBr; mp 64.0–64.5 °C (lit.[7] mp 65–66 °C); TLC R_f 0.50 (hexane–ether, 5:1); IR (neat) 3410, 2975, 1620, 1470, 1325, 1240, 1020, 750; ^1H NMR ($CDCl_3$) δ 1.25 (t, J = 7.6 Hz, 3 H, CH_2CH_3), 2.23 (s, 3 H, Me), 2.72 (q, J = 7.6 Hz, 2 H, CH_2), 7.05–7.13 (m, 2 H, Ar), 7.21–7.26 (m, 1 H, Ar), 7.46–7.49 (m, 1 H, Ar), 7.65 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 8.3, 14.0, 19.4, 106.1, 110.2, 118.0, 119.0, 120.9, 129.5, 135.1, 136.5; MS (EI) 159, 158, 144. These spectral data are identical with those of the authentic sample.[8]

2-(Deuteriomethyl)-1,3-dimethylindole (2b): 66%, ^1H NMR ($CDCl_3$) δ 2.24 (s, 2 H, CH_2D), 2.26 (s, 3 H, Me), 3.57 (s, 3 H, NMe), 7.04–7.17 (m, 3 H, Ar), 7.46 (m, 1 H, Ar); ^{13}C NMR ($CDCl_3$) δ 8.8, 9.8 (t, CH_2D), 29.4, 106.2, 108.4, 117.9, 118.6, 120.5, 128.4, 132.6, 136.5.

2-Ethyl-1,3-dimethylindole (3b): 83 and 97% with MeI and MeBr; picrate mp 88–89 °C (lit.[11] mp 91–92 °C); TLC R_f 0.44 (hexane–ether, 10:1); IR (neat) 2980, 1480, 1380, 1330, 1245, 1200, 1075, 740; ^1H NMR ($CDCl_3$) δ 1.16 (t, J = 7.3 Hz, 3 H, CH_2CH_3), 2.25 (s, 3 H, Me), 2.73 (q, J = 7.3 Hz, 2 H, CH_2CH_3), 3.60 (s, 3 H, NMe), 7.03–7.21 (m, 3 H, Ar), 7.47 (m, 1 H, Ar); ^{13}C NMR ($CDCl_3$) δ 8.6, 14.3, 17.7, 29.3, 105.6, 108.5, 118.0, 118.6, 120.5, 128.4, 136.6, 138.4; MS (EI) 173, 158.

1-Deuterio-1,2,3,4-tetrahydrocarbazole (2c): 70%; ^1H NMR ($CDCl_3$) δ 1.83 (m, 4 H, 2,3-CH_2), 2.67 (m, 3 H, CDH and 4-CH_2), 7.05–7.16 (m, 3 H, Ar), 7.33 (br s, 1 H, NH), 7.44 (d, J = 7.0 Hz, 1 H, Ar); ^{13}C NMR (acetone-d_6) δ 21.6, 23.4 (t, C-1), 23.9, 24.2, 109.6, 111.1, 117.9, 119.0, 121.0, 128.7, 134.9, 137.0. The spectral data are identical with the authentic sample prepared from 2,2,6,6-tetradeuteriocyclohexanone[12] and phenylhydrazinium chloride.[7]

1-Methyl-1,2,3,4-tetrahydrocarbazole (3c): 50%; mp 63–65 °C (lit. mp 69 °C,[13] 66–68 °C[14]); TLC R_f 0.33 (hexane–ether, 5:1); IR (neat) 3400, 3020, 2920, 1462, 1317, 1295, 1224, 1140, 1000, 730; ^1H NMR ($CDCl_3$) δ 1.25 (d, J = 7.0 Hz, 3 H, Me), 1.49–1.56 (m, 1 H, 2-CH_2), 1.75–1.78 (m, 1 H, 2-CH_2), 1.96–2.00 (m, 2 H, 3-CH_2), 2.67–2.69 (m, 2 H, 4-CH_2), 2.92 (m, 1 H, CH), 7.04–7.13 (m, 2 H, Ar), 7.24 (d, J = 7.3 Hz, 1 H, Ar), 7.45 (d J = 6.6 Hz, 1 H, Ar), 7.65 (br s, 1 H NH); ^{13}C NMR ($CDCl_3$) δ 20.2, 21.2, 21.9, 28.7, 32.3, 109.7, 110.5, 118.0, 119.1, 121.0, 127.8, 135.7, 138.6.

3-Methyl-1,2,3,4-tetrahydrocyclopent[*b*]indole (3d): 37%; mp 67–68 °C, picrate 133–134 °C (lit.[14] mp 133–134 °C); TLC R_f 0.37 (hexane–ether, 5:1); IR (neat) 3406.7, 2955.9, 1450.2, 1370.6, 1316.2, 1122.8, 740.8; ^1H NMR ($CDCl_3$) δ 1.24 (d, J = 6.8 Hz, 3 H, Me), 1.99–2.08 (m, 1 H, CH_2), 2.68–2.84 (m, 3 H, CH_2), 3.23 (m, 1 H, CH), 7.06–7.09 (m, 2 H, Ar), 7.20–7.24 (m, 1 H, Ar), 7.42–7.45 (m, 1 H, Ar), 7.59 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 20.2, 23.7, 33.5, 38.2, 111.5, 118.6, 119.5, 120.5, 124.9, 140.9, 148.1. Anal. Calcd for $C_{11}H_{11}N$: C, 84.17; H, 7.65; N, 8.18. Found: C, 83.83; H, 7.65; N, 8.08.

N-Methylation for the Differential NOE Experiments. Typical Procedure. 2-(Deuteriomethyl)-1,3-dimethylindole 2b from 2a. To a stirred solution of 2-(deuteriomethyl)-3-methylindole[10] (290 mg, 2.0 mmol) in ether (20 mL) was added *t*-BuOK (450 mg, 4.0 mmol) and MeI (620 μL, 10 mmol) at 0 °C. After 2 h the mixture was poured into saturated aqueous $NaHCO_3$ and extracted with ether. The combined extracts were dried over $MgSO_4$ and concentrated in vacuo. Purification by column chromatography on silica gel afforded a colorless oil (280 mg, 1.7 mmol, 86%). Spectral data are identical with those indicated above for **2b**.

2-Ethyl-1,3-dimethylindole 3b from 3a: 77%. The spectral data are identical with those indicated above for **3b**.

1,*N*-Dimethyl-1,2,3,4-tetrahydrocarbazole: 78%; TLC R_f 0.50 (hexane–ether, 10:1); ^1H NMR ($CDCl_3$) δ 1.27 (d, J = 7.0 Hz, 3 H, Me), 1.86–1.90 (m, 4 H, CH_2), 2.64–2.75 (m, 2 H, CH_2), 3.02 (m, 1 H, CH), 3.62 (s, 3 H, NMe), 7.02–7.17 (m, 2 H, Ar), 7.23

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(15) (a) We assume that the N-lithiated indoles are first generated by BuLi and that the excess of BuLi and *t*-BuOK form the super basic reagent[7b] in situ. (b) Schlosser, M. *J. Organomet. Chem.* **1967**, *8*, 9. Lochmann, L.; Pospisil, J.; Lim, D. *Tetrahedron Lett.* **1966**, 257. For recent examples, see: Schlosser, M.; Choi, J. H.; Takagishi, S. *Tetrahedron* **1990**, *46*, 5633–5648. Schlosser, M.; Katoulos, G.; Takagishi, S. *Synlett* **1990**, 747–748.

(d, J = 7.7 Hz, 1 H, Ar), 7.46 (d, J = 7.7 Hz, 1 H, Ar); ^{13}C NMR ($CDCl_3$) δ 19.6, 21.2, 28.9, 29.6, 38.5, 53.6, 120.0, 121.2, 124.6, 127.3, 146.7, 154.2, 189.9. One of the peaks of saturated carbons was not separated from another.

***N*,3-Dimethyl-1,2,3,4-tetrahydrocyclopent[*b*]indole:** 94%; TLC R_f 0.50 (hexane–ether, 10:1); ^{1}H NMR ($CDCl_3$) δ 1.30 (d, J = 7.0 Hz, 3 H, Me), 2.06–2.08 (m, 1 H, CH_2), 2.72–2.89 (m, 3 H, CH_2), 3.32 (m, 1 H, CH), 3.68 (s, 3 H, NMe), 7.03–7.14 (m, 2 H, Ar), 7.27 (d, J = 6.2 Hz, 1 H, Ar), 7.43 (d, J = 7.1 Hz, 1 H, Ar); ^{13}C NMR ($CDCl_3$) δ 20.4, 23.3, 30.5, 32.9, 38.2, 109.3, 116.9, 118.7, 119.0, 120.0, 124.2, 141.6, 149.9.

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Supplementary Material Available: ^{1}H and ^{13}C NMR spectral data and the differential NOE experiments after N-methylation (22 pages). Ordering information is given on any current masthead page.

Synthesis of 3-Nitrocyclopropenes

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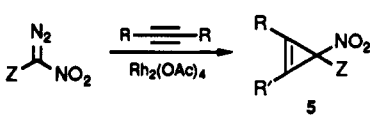
Recently there has been considerable interest in strained-ring nitro compounds as high-energy density materials.[1] Our work in this area has focused on nitrocyclopropanes. While there are several methods for nitrocyclopropane formation,[2] the addition of a nitrocarbene to an alkene has only recently been described by us.[3] In this reaction pioneered by Doyle, rhodium(II) acetate catalyzes the cyclopropanation of alkenes[4] by nitrodiazo compounds.[5] Detailed studies have shown that the success of the reaction is dependent on both the alkene and the nitrodiazo precursor.

Here, we describe the extension of this method to the formation of nitrocyclopropenes **5** from nitrodiazo compounds **1**–**3** and alkynes (Scheme I). These results are presented in Table I along with the corresponding data for ethyl diazoacetate (**4**).[6]

It is apparent from these data that terminal acetylenes are the best substrates for this reaction and that diazo compounds **1** and **2** cyclopropanate a wider range of alkynes than **3**. Very hindered internal alkynes (diphenylacetylene, bis(trimethylsilyl)acetylene) are not cyclopropanated. These observations are consistent with results from the cyclopropanation of alkenes with diazo compounds **1**–**3**. The cyclopropene derived from styrene and

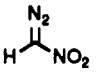
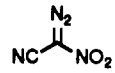
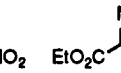
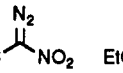
Scheme I



Z = H, EtO_2C, CN

	R	R′	Z
5a	Ph	H	H
5b	*n*-pentyl	H	H
5c	Me	Me	H
5d	TMS	H	H
5e	Ph	H	CN
5f	*n*-Bu	H	CN
5g	Et	Et	CN
5h	TMS	H	CN
5i	Ph	H	CO_2Et
5j	*n*-Bu	H	CO_2Et

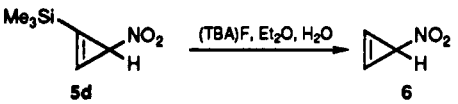
Table I. Yields of Cyclopropenes from Alkynes and Diazo Compounds with Use of $Rh_2(OAc)_4$

	 **1**	 **2**	 **3**	 **4**[a]
PhCCH	60	65	*b*	0
n-BuCCH	33[c]	35	84	84
RCCR	35[d]	35[e]	0	68[d]
(TMS)CCH	30	28[f]	0	86
PhCCPh	0	0	0	

[a] Taken from ref 6. [b] Product was formed but could not be purified beyong 60% purity. [c] Reaction was carried out with 1-heptyne. [d] Reaction was carried out with 2-butyne. [e] Reaction carried out with 2-hexyne. [f] This compound was not purified but was converted directly to 3-cyano-3-nitrocyclopropene in 28% overall yield.

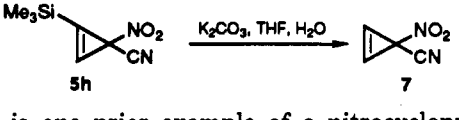
diazo compound **3** could not be purified beyond 60%. It is curious that the nitrodiazo compounds cyclopropanate phenylacetylene and ethyl diazoacetate does not. We have reinvestigated this reaction with ethyl diazoacetate and find no evidence of cyclopropene. The phenyl-substituted nitrocyclopropenes must not be as susceptible to polymerization by the rhodium catalyst as ethyl phenylcyclopropenecarboxylate.[6]

The parent 3-nitrocyclopropene (**6**) and 3-cyano-3-nitrocyclopropene (**7**) can be obtained from the corresponding trimethylsilyl-substituted cyclopropenes **5d** and **5h**. In the case of nitrocyclopropene, deprotection with (TBA)F in wet diethyl ether affords a ca. 5% solution of nitrocyclopropene (eq 1). This material can be detected by NMR and by TLC. Our attempts to isolate **6** have been unsuccessful.



5d **6** (1)

3-Cyano-3-nitrocyclopropene (**7**), on the other hand, is a relatively stable compound as a neat liquid at room temperature. It is prepared by potassium carbonate hydrolysis of the trimethylsilyl derivative **5h** (eq 2).



5h **7** (2)

There is one prior example of a nitrocyclopropene. 1,2-Diphenyl-3-nitrocyclopropene was prepared by Jones and Kobzina in 1965.[7] In 1988 Cheer, Greenberg, and

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