

The Reactions of Monoalkylthio- or Monoarylthio-Substituted Cyclopropenium Salt with Nitrogen Nucleophiles: Formation of Polyfunctionally Substituted Pyrroles or Pyrazoles

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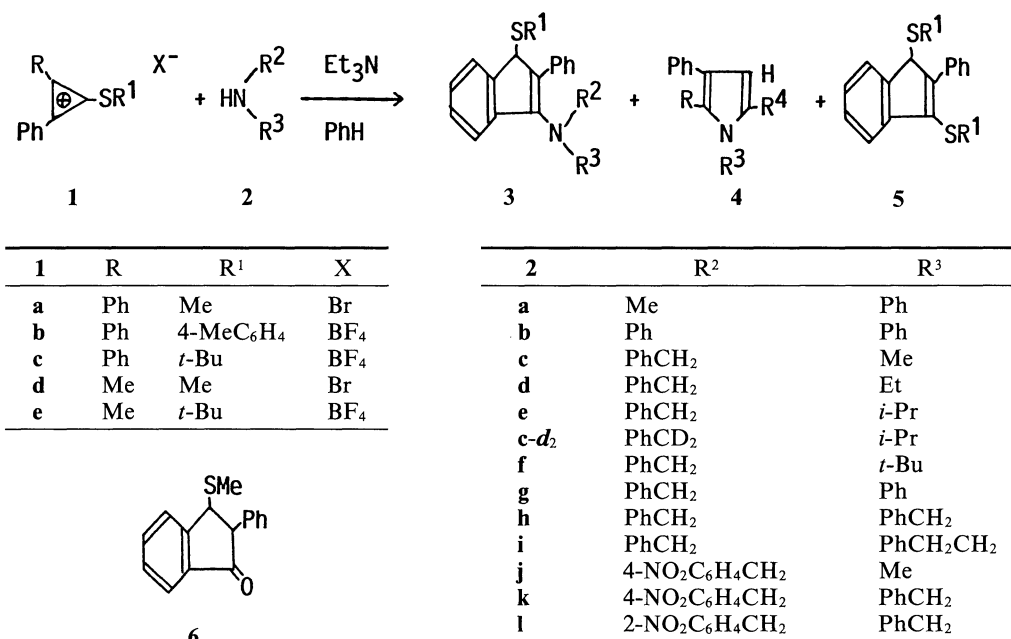
The reactions of monoalkylthio- or monoarylthio-substituted cyclopropenium salt (**1**) with a number of secondary amines were studied. The amines, such as *N*-methylaniline, yielded indenenes, whereas *N*-alkyl- or *N*-arylbenzylamines gave 1-alkyl- or 1-aryl-2-phenylpyrroles in low-to-moderate yields, depending on the kinds of substituents of the amines and **1**. The reaction with *N*-isopropylbenzylamine- α, α - d_2 (*i*-PrNHCD₂Ph) resulted in the formation of the 1-isopropyl-2,3,5-triphenylpyrrole-4- d , clearly indicating the intramolecular H-abstraction mechanism via vinylcarbene intermediates for the formation of pyrroles. The reaction of **1** with tosylhydrazones afforded the ring opened hydrazide, while with phenyl-, methyl-, and *t*-butylhydrazines gave 1,4,5-trisubstituted pyrazoles in small yields.

Our continuing studies are developed to reactions of the cyclopropenium salts and cyclopropenes possessing heteroatom substituents such as sulfur,^{1–4} nitrogen,⁵ or phosphorus.⁶ We have previously reported that the reaction of the monoalkylthio- or monoarylthio-substituted cyclopropenium salts **1**, e.g. 1-methylthio-2,3-diphenylcyclopropenium bromide (**1a**) with acyclic² and cyclic 1,3-diketones,³ afforded the cyclopentadienols and 2*H*-pyran derivatives, respectively. Moreover, the reaction of **1a** with Grignard reagents,⁴ thiols, or alcohols¹ gave polyfunctionally substituted indenenes as final products. These results led us to study the reaction of **1** with nitrogen nucleophiles.

Salts **1a–e** were prepared as previously described.¹⁾ The reactions of **1a** with primary amines, such as

benzylamine, ethylamine, aniline, and allylamine, yielded resinous masses, which are composed of a mixture of a number of products on TLC. On the other hand, the treatment of **1a** with *N*-methylaniline (**2a**), a less basic amine, in the presence of triethylamine in dry benzene at room temperature for 1 h produced 3-(*N*-methylanilino)-1-methylthio-2-phenyl-1*H*-indene (**3aa**) in 45% yield. The structure **3aa** was determined from its spectral data as well as the formation of the indanone **6** in 78% yield by acidic hydrolysis of **3aa**.

The reaction of **1a** with *N*-methylbenzylamine **2c** under similar reaction conditions provided the known 1-methyl-2,3,5-triphenylpyrrole **4ac**,⁷⁾ rather than the corresponding indene. The reactions of **1a–e** with the various secondary amines **2a–l** were also studied (Table

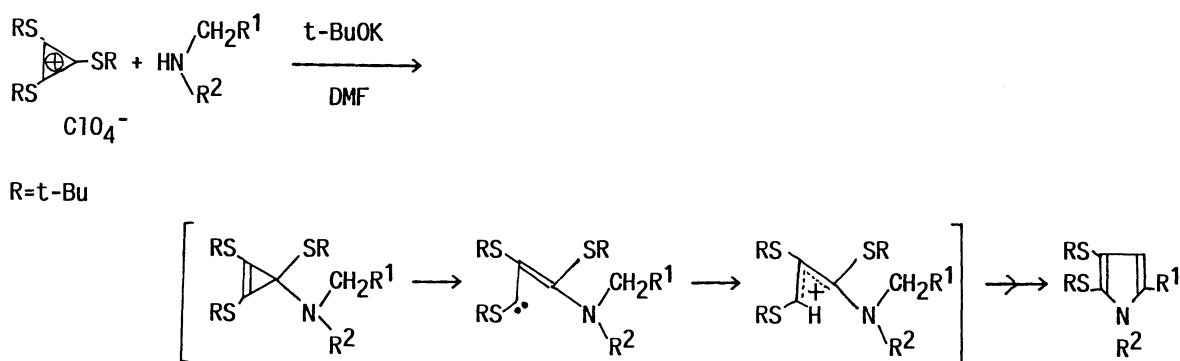


Scheme 1.

Table 1. The Reaction of **1** with **2** in the Presence of Triethylamine

Reactants		Products	Yield
1	2	(Substituents for 3: R ¹ , R ² , R ³ or 4: R, R ³ , R ⁴)	%
1a	2a	3aa (Me, Me, Ph)	45
	2b	3ab (Me, Ph, Ph)	41
	2c	4ac (Ph, Me, Ph)	36
	2d	4ad (Ph, Et, Ph)	31
	2e	4ae (Ph, <i>i</i> -Pr, Ph)	64
	2e- <i>d</i> ₂	4ae- <i>d</i> (Ph, <i>i</i> -Pr, Ph) ^{a)}	61
	2f	4af (Ph, <i>t</i> -Bu, Ph)	16
	2g	4ag (Ph, Ph, Ph)	33
	2h	4ah (Ph, PhCH ₂ , Ph)	63, 64, ^{b)} 28 ^{c)}
	2i	4ai (Ph, PhCH ₂ CH ₂ , Ph)	
	2j	4aj (Ph, Me, 4-NO ₂ C ₆ H ₄)	17
	2k	4ak (Ph, PhCH ₂ , 4-NO ₂ C ₆ H ₄)	47
	2l	4al (Ph, PhCH ₂ , 2-NO ₂ C ₆ H ₄)	39
	1b	2a	3ba (4-MeC ₆ H ₄ , Me, Ph)
2b		3bb (4-MeC ₆ H ₄ , Ph, Ph)	33 ^{d)}
2c		4ac (Ph, Me, Ph)	34
2e		4ae (Ph, <i>i</i> -Pr, Ph)	52
2f		4af (Ph, <i>t</i> -Bu, Ph)	16
2g		4ag (Ph, Ph, Ph)	34 ^{e)}
2h		4ah (Ph, PhCH ₂ , Ph)	51
1c		2c	4ac (Ph, Me, Ph)
1d	2c	4dc (Me, Me, Ph)	15
	2g	4dg (Me, Ph, Ph)	33
	2h	4dh (Me, PhCH ₂ , Ph)	23
	2j	4dj (Me, Me, 4-NO ₂ C ₆ H ₄)	11
	2k	4dk (Me, PhCH ₂ , 4-NO ₂ C ₆ H ₄)	12
	1e	2c	4dc (Me, Me, Ph)

a) The product was pyrrole-3-*d*. b) EtN(*i*-Pr)₂ was used. c) Pyridine was used as a base. d) The by-product **5** (R¹=4-MeC₆H₄) was obtained in 20% yield. e) **5** (R¹=MeC₆H₄) was separated in 7%.

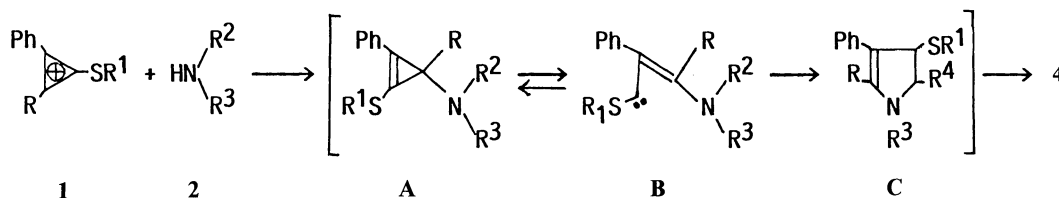


Scheme 2.

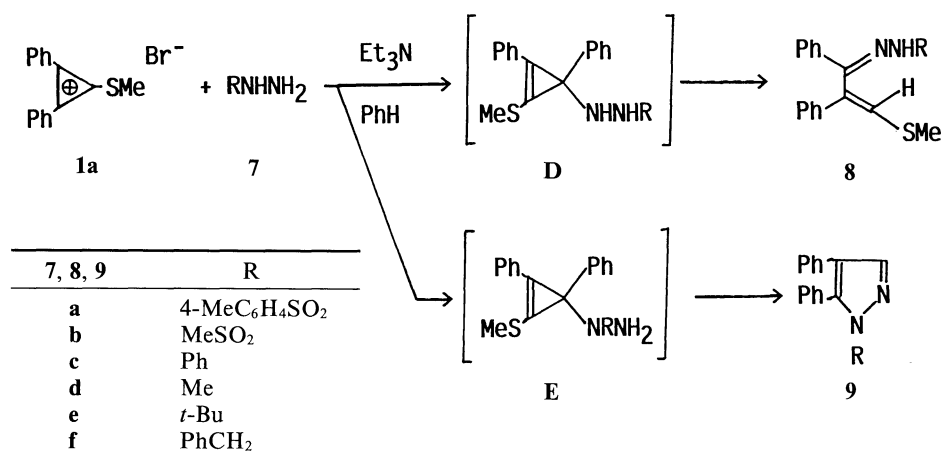
1). The reaction of **1** with secondary amines having no benzyl substituents offered indenenes in moderate yields. The secondary benzylamines provided pyrroles in various yields. Interestingly, 2- and 4-nitrobenzyl groups were selectively incorporated into the pyrrole rings, even in the presence of the unsubstituted benzyl group. The yield of the pyrroles **4** were highly affected by the bulkiness of the substituents of **1** and secondary amines **2**(R³). Moderately bulky *N*-isopropylbenzylamine **2e** resulted in the best yield. A number of chemical and physical interests concerning the pyrroles

have been developed in recent years.⁸⁾

It has been reported that tris(*t*-butylthio)cyclopropenium ions react with secondary amines by the use of *t*-BuOK as a base in DMF to produce pyrroles in moderate yields.^{9,10)} The reaction mechanism is considered to involve the vinylcarbene intermediate followed by an intermolecular protonation, since no distribution of deuterium is observed at the 4-position of the pyrrole in the reaction with dimethylamine-*d*₆ (Scheme 2).⁹⁾ The reaction conditions of *t*-BuOK/DMF were not amenable in our case: the reaction of **1a** with **2c** gave only a tarry



Scheme 3.



Scheme 4.

brown mass.

In a former paper we have reported that the reaction of **1** with Grignard reagents,⁴⁾ thiols, and alcohols¹⁾ offered relatively stable cyclopropenes as intermediates, while some attempts to isolate cyclopropenes failed in reactions with 1,3-diketones.^{2,3)} An attempt to isolate the cyclopropene in the reaction of **1a** with **2e** using triethylamine as a base at lower temperature or shorter reaction time was unsuccessful and only **4ae** was obtained.

In order to clarify the most plausible mechanism, the dideuterated *N*-isopropylbenzylamine **2e-d₂** (D content 98%) was reacted with **1a** under similar conditions to afford the pyrrole-4-*d*, **4ae-d** (D content 96%) in 61% yield. This result indicates proton abstraction of the vinylcarbene via either an intramolecular radical-type process or direct insertion to the C-H bond of the benzyl methylene. A plausible mechanism was described in Scheme 3. An initially formed cyclopropene **A** would produce the vinylcarbene **B** stabilized by the adjacent sulfur group, followed by the formation of the pyrroline **C**. Elimination of a thiol from **C** yields the pyrrole **4**. In the reaction of **1c** with **2b** or **2g**, the thiol could be trapped by **1c** forming the indene **5** (R¹=4-MeC₆H₄) as a by-product (Table 1). The reaction of **1** with thiol is known to give the thio-substituted indenenes.¹⁾

Furthermore reactions of **1a** with hydrazines **7** were also investigated (Scheme 4 and Table 2). Some reaction products were obtained, from which a pure

Table 2. The Reaction of **1a** with **7**

Reactant	Reaction time/h	Product (Yield/%)
7a	48	8a (5.5)
7b	24	—
7c	1	9c (15)
7d	1	9d (32)
7e	12	9e (3.6)
7f	1	—

product was separated upon chromatographic separation. Tosylhydrazone **7a** with **1a** yielded an unsaturated tosylhydrazone **8a**. On the other hand, **7c**—**e** gave the corresponding 1,4,5-trisubstituted pyrazoles **9**. The former product **8a** may arise from a nucleophilic attack of β-nitrogen onto C-2 of **1a** of form the cyclopropene **D**, followed by ring opening and proton transfer, affording **8a**. The formation of pyrazoles **9** could be explained by an initial nucleophilic attack of α-nitrogen followed by ring opening, and again ring closure. Presumably, both routes might proceed via a vinylcarbene intermediates, like **B**.

Experimental

General. The melting points were uncorrected. The ¹H NMR spectra were recorded on a Hitachi R-24B (60 MHz) and ¹³C NMR spectra on a JEOL JNM FX-90Q (22.40 MHz). ¹H and ¹³C NMR spectra were recorded in CDCl₃ unless otherwise stated, using TMS as an internal standard. The IR

spectra were obtained on a JEOL JIR 100.

The Reaction of Cyclopropenium Salt 1 with Secondary Amine 2. General Procedure. A mixture of **1** (2.0 mmol), secondary amine **2** (2.0 mmol), and triethylamine (2.2 mmol) in benzene (15 cm³) was stirred at room temperature for 1 h. The solution was washed with water, dried over Na₂SO₄, and condensed under reduced pressure. The resulting resinous product was purified by column chromatography over silica gel and recrystallized from 2-propanol to yield indene **3** or pyrrole **4**. **3aa**: Mp 139–142 °C; ¹H NMR δ=1.45 (s, 3H, MeS), 3.00 (s, 3H, MeN), 4.80 (s, 1H, CH), and 6.4–7.7 (m, 14H, Arom); MS (*m/z*) 343 (M⁺). Found: C, 80.21; H, 6.22; N, 3.98%. Calcd for C₂₃H₂₁NS: C, 80.42; H, 6.16; N, 4.07%. **3ab**: Mp 159–161 °C; ¹H NMR δ=1.51 (s, 3H, MeS), 4.80 (s, 1H, CH), and 6.6–7.4 (m, 19H, Arom); MS (*m/z*) 405 (M⁺). Found: C, 82.99; H, 6.54; N, 3.36%. Calcd for C₂₈H₂₃NS: C, 82.92; H, 5.71; N, 3.45%. **4ac**: Mp 179–183 °C (lit.⁷) 178–179 °C; ¹H NMR δ=3.40 (s, 3H, Me), 6.40 (s, 1H, C4-H), and 6.7–7.6 (m, 15H, 3Ph); MS (*m/z*) 309 (M⁺). **4ad**: Mp 104–107 °C; ¹H NMR δ=1.30 (t, *J*=7 Hz, 3H, Me), 3.90 (q, *J*=7 Hz, 2H, CH₂), 6.33 (s, 1H, C4-H), and 6.9–7.6 (m, 15H, 3Ph); MS (*m/z*) 323 (M⁺). Found: C, 89.03; H, 6.53; N, 4.43%. Calcd for C₂₄H₂₁N: C, 89.12; H, 6.54; N, 4.33%. **4ae**: Mp 196–198 °C; ¹H NMR δ=1.25 (d, *J*=7.5 Hz, 6H, 2Me), 4.45 (sept, *J*=7.5 Hz, 1H, CHMe), 6.35 (s, 1H, C4-H), and 6.9–7.6 (m, 15H, 3Ph); MS (*m/z*) 337 (M⁺). Found: C, 89.11; H, 6.84; N, 4.04%. Calcd for C₂₅H₂₃N: C, 88.98; H, 6.86; N, 4.15%. **4af**: Mp 175–177 °C; ¹H NMR δ=1.35 (s, 9H, 3Me), 6.20 (s, 1H, C4-H), and 6.8–7.6 (m, 15H, 3Ph). MS (*m/z*) 351 (M⁺). Found: C, 88.76; H, 7.21; N, 4.03%. Calcd for C₂₆H₂₅N: C, 88.84; H, 7.16; N, 3.98%. **4ag**: Mp 200–203 °C (lit.¹¹) 197 °C; ¹H NMR δ=6.65 (s, 1H, C4-H) and 6.7–7.6 (m, 20H, 4Ph); MS (*m/z*) 371 (M⁺). **4ah**: Mp 165–167 °C; ¹H NMR δ=5.05 (s, 2H, CH₂), 6.50 (s, 1H, C4-H), and 6.6–7.5 (m, 20H, 4Ph); MS (*m/z*) 385 (M⁺). Found: C, 90.50; H, 6.04; N, 3.46%. Calcd for C₂₉H₂₃N: C, 90.35; H, 6.01; N, 3.63%. **4ai**: Mp 129–131 °C; IR (KBr) 1600 and 1340 cm⁻¹; ¹H NMR δ=2.2–2.7 (m, 2H, NCH₂), 3.9–4.4 (m, 2H, PhCH₂), 6.50 (s, 1H, C4-H), and 6.5–7.6 (m, 20H, 4Ph); ¹³C NMR δ=37.1 (t), 46.5 (t), 109.5 (d), 123.0 (s), 125.0 (d), 126.2 (d), 127.1 (d), 127.6 (d), 128.0 (d), 128.2 (d), 128.4 (d), 128.5 (d), 129.0 (d), 131.2 (d), 131.7 (s), 133.3 (s), 133.7 (s), 134.9 (s), 136.2 (s), and 138.0 (s); MS (*m/z*) 399 (M⁺). Found: C, 90.21; H, 6.23; N, 3.56%. Calcd for C₃₀H₂₅N: C, 90.18; H, 6.31; N, 3.51%. **4aj**: Mp 210–214 °C; IR (KBr) 1590, 1505, and 1335 cm⁻¹; ¹H NMR δ=3.50 (s, 3H, NMe), 6.58 (s, 1H, C4-H), 7.0–7.7 (m, 12H, Ar), and 8.1–8.3 (m, 2H, Ar); ¹³C NMR δ=37.1 (t), 46.5 (t), 109.5 (d), 123.0 (s), 125.0 (d), 126.2 (d), 127.1 (d), 127.6 (d), 128.0 (d), 128.2 (d), 128.4 (d), 128.5 (d), 129.0 (d), 131.2 (d), 131.7 (s), 133.3 (s), 133.7 (s), 134.9 (s), 136.2 (s), and 138.0 (s); MS (*m/z*) 354 (M⁺). Found: C, 77.81; H, 4.92; N, 7.89%. Calcd for C₂₃H₁₈N₂O₂: C, 77.94; H, 5.11; N, 7.92%. **4ak**: Mp 163–165 °C; IR (KBr) 1590, 1505, and 1335 cm⁻¹; ¹H NMR δ=5.10 (s, 2H, CH₂), 6.70 (s, 1H, C4-H), and 7.0–8.3 (m, 19H, Ar); ¹³C NMR δ=48.9 (t), 112.1 (d), 123.9 (d), 124.4 (d), 125.7 (d), 125.8 (d), 127.2 (d), 127.7 (d), 128.2 (d), 128.5 (d), 131.2 (s), 132.3 (s), 133.3 (s), 135.5 (s), 138.2 (s), 139.8 (s), and 146.2 (s); MS (*m/z*) 430 (M⁺). Found: C, 80.78; H, 5.31; N, 6.61%. Calcd for C₂₉H₂₂N₂O₂: C, 80.91; H, 5.15; N, 6.51%. **4al**: Mp 146–148 °C; ¹H NMR δ=4.82 (s, 2H, CH₂), 6.42 (s, 1H, C4-H), and 6.4–8.0 (m, 19H, Ar); ¹³C NMR δ=48.7 (t), 110.6 (d), 123.1 (d), 125.2 (d), 126.2 (d), 126.9 (d), 127.5 (d), 127.9 (d),

128.0 (d), 128.1 (d), 128.5 (d), 128.7 (d), 128.8 (d), 131.4 (d), 132.0 (d), 132.8 (d), 133.0 (d), 133.6 (d), 135.9 (s), 138.3 (s), and 149.8 (s); MS (*m/z*) 430 (M⁺). Found: C, 80.82; H, 5.22; N, 6.63%. Calcd for C₂₉H₂₂N₂O₂: C, 80.91; H, 5.15; N, 6.51%. **3ba**: Mp 139–142 °C; ¹H NMR δ=2.28 (s, 3H, Me), 2.96 (s, 3H, NMe), 5.00 (s, 1H, CH), and 6.7–7.7 (m, 19H, Ar); MS (*m/z*) 419 (M⁺). Found: C, 83.12; H, 6.04; N, 3.41%. Calcd for C₂₉H₂₅NS: C, 83.01; H, 6.01; N, 3.33%. **3bb**: Mp 186–189 °C; ¹H NMR δ=2.30 (s, 3H, Me), 5.12 (s, 1H, CH), and 6.2–7.6 (m, 19H, Ar); MS (*m/z*) 481 (M⁺). Found: C, 84.83; H, 5.54; N, 2.98%. Calcd for C₃₄H₂₇NS: C, 84.78; H, 5.64; N, 2.92%. **4dc**: Mp 159–162 °C (lit.¹²) 160–162 °C; ¹H NMR δ=2.86 (s, 3H, Me), 3.51 (s, 3H, NMe), 6.21 (s, C4-H), and 7.1–7.5 (m, 10H, 2Ph). **4dg**: Mp 173–175 °C; IR (KBr) 1595 and 1490 cm⁻¹; ¹H NMR δ=2.34 (s, 3H, Me), 6.52 (s, 1H, C4-H), and 6.9–7.6 (m, 15H, 3Ph); ¹³C NMR δ=12.4 (q), 109.3 (d), 122.8 (s), 125.4 (d), 125.9 (d), 127.5 (d), 127.9 (d), 128.0 (d), 128.1 (d), 128.4 (d), 128.6 (d), 129.0 (d), 133.2 (s), 133.9 (s), 136.9 (s), and 139.2 (s); MS (*m/z*) 309 (M⁺). Found: C, 89.34; H, 6.11; N, 4.55%. Calcd for C₂₃H₁₉N: C, 89.28; H, 6.18; N, 4.52%. **4dh**: Mp 130–133 °C; IR (KBr) 1490 and 1450 cm⁻¹; ¹H NMR δ=2.25 (s, 3H, Me), 5.15 (s, 2H, NCH₂), 6.40 (s, 1H, C4-H), and 6.8–7.6 (m, 15H, 3Ph); ¹³C NMR δ=11.4 (q), 48.0 (t), 109.7 (d), 122.5 (s), 125.3 (d), 125.7 (d), 126.7 (d), 126.9 (d), 127.1 (d), 128.1 (d), 128.3 (d), 128.4 (d), 128.8 (d), 133.5 (s), 134.4 (s), 137.2 (s), and 138.9 (s); MS (*m/z*) 323 (M⁺). Found: C, 89.05; H, 6.69; N, 4.26%. Calcd for C₂₄H₂₁N: C, 89.12; H, 6.54; N, 4.33%. **4dj**: Mp 149–150 °C; IR (KBr) 1590, 1520, and 1350 cm⁻¹; ¹H NMR δ=2.48 (s, 3H, Me), 3.72 (s, 3H, NMe), 6.58 (s, 1H, C4-H), and 7.2–8.6 (m, 19H, Ar); MS (*m/z*) 292 (M⁺). Found: C, 74.10; H, 6.43; N, 4.38%. Calcd for C₁₈H₁₆N₂O₂: C, 73.95; H, 5.51; N, 9.58%. **4dk**: Mp 121–123 °C; ¹H NMR δ=2.28 (s, 3H, Me), 5.18 (s, 2H, NCH₂), 6.06 (s, 1H, C4-H), and 6.8–8.3 (m, 14H, Ar); ¹³C NMR δ=11.3 (q), 48.2 (t), 111.3 (d), 123.8 (s), 124.0 (d), 125.4 (d), 125.8 (d), 127.5 (d), 128.0 (d), 128.1 (d), 128.5 (d), 129.1 (d), 129.7 (s), 132.1 (s), 136.4 (s), 137.9 (s), 139.6 (s), and 146.0 (s); MS (*m/z*) 368 (M⁺). Found: C, 78.35; H, 5.31; N, 7.54%. Calcd for C₂₄H₂₀N₂O₂: C, 78.24; H, 5.57; N, 7.60%. **5** (R¹=4-MeC₆H₄): Mp 176–179 °C (lit.¹) 177–178 °C).

The Reaction of *N*-Isopropylbenzylamine- α,α -d₂ (2e-d₂). The amine **2e-d₂** was prepared from the reduction of *N*-isopropylbenzamide with LiAlD₄ in 72% yield according to a similar procedure as described in the literature.¹³ **2e-d₂**: Oil; ¹H NMR δ=1.08 (d, *J*=6.5 Hz, 7H, 2Me+NH), 2.86 (sept, *J*=6.5 Hz, 1H, CHMe₂), 3.78 (s, small, CH₂), and 6.8–7.9 (m, 5H, Ph). The content of deuterium was determined to be 98% by the use of CH₂ signal integration. A similar reaction of **1a** with **2e-d₂**, as above, provided 1-isopropyl-2,3,5-triphenylpyrrole-4-d **4ae-d** in 61% yield. The amount of deuterium was assigned to be 96% by the ¹H NMR spectrum of the product. **4ae-d**: Mp 192–193 °C; ¹H NMR δ=1.20 (d, *J*=7.5 Hz, 6H, 2Me), 4.42 (sept, *J*=7.5 Hz, 1H, CH), 6.36 (s, small, C4-H), and 6.9–7.8 (m, 15H, 3Ph); MS (*m/z*) 338 (M⁺).

Hydrolysis of 3aa. A solution of **3aa** (0.5 mmol) in a mixture of ethanol (15 cm³) and aqueous HCl (3 mol dm⁻³, 10 cm³) was heated at reflux for 4 h. Dilution with water and extraction by CH₂Cl₂ gave 1-indanone **6**¹ in 83% yield. **6**: Mp 76–78 °C (lit.¹) 77–78 °C).

The Reaction of 1a with Hydrazine 7. A mixture of **1a** (1.0 mmol), hydrazine **7** (1.1 mmol), and triethylamine (1.1 mmol) in benzene (10 cm³) was stirred for an appropriate

time until the disappearance of the crystals of **1a**. The solution was, then washed with water and dried over sodium carbonate. Condensation and chromatographic purification (cc, silica gel) produced pure crystals. **8a**: Mp 159–161 °C (ether); IR(KBr) 1380 and 1170 cm^{-1} ; ^1H NMR δ =2.29 (s, 3H, Me), 2.31 (s, 3H, Me), 6.16 (s, 1H, CH=), and 6.8–8.0 (m, 15H, Ar+NH); MS(m/z) 422 (M^+). Found: C, 65.32; H, 5.31; N, 6.65%. Calcd for $\text{C}_{23}\text{H}_{22}\text{N}_2\text{O}_2\text{S}_2$: C, 65.37; H, 5.24; N, 6.61%. **9c**: Mp 213–214 °C (ethanol, lit.¹⁴) 210–211 °C; ^1H NMR δ =7.0–7.5 (m, 15H, 3Ph) and 7.89 (s, 1H, CH); ^{13}C NMR δ =123.8 (s), 126.6 (d), 127.8 (d), 128.6 (d), 129.4 (d), 129.8 (d), 130.0 (d), 130.1 (d), 131.6 (s), 131.9 (d), 134.2 (s), 140.6 (s), 141.1 (d), and 141.4 (s) MS(m/z) 296 (M^+). **9d**: Mp 116–117 °C (ether); IR(KBr) 1590 cm^{-1} ; ^1H NMR δ =3.71 (s, 3H, Me), 6.9–7.5 (m, 10H, 2Ph), and 7.62 (s, 1H, CH); ^{13}C NMR δ =37.1 (q), 120.9 (s), 125.9 (s), 127.2 (d), 128.3 (d), 128.7 (d), 128.8 (d), 130.0 (d), 130.4 (s), 133.0 (s), 137.4 (d), and 139.8 (s); MS(m/z) 234 (M^+). Found: C, 81.92; H, 6.17; N, 11.91%. Calcd for $\text{C}_{16}\text{H}_{14}\text{N}_2$: C, 82.02; H, 6.02; N, 11.95%. **9e**: Mp 220–225 °C (ether); ^1H NMR δ =1.18 (s, 9H, 3Me), 7.25 (s, 1H, CH), and 7.5–8.8 (m, 10H, 2Ph); MS(m/z) 276 (M^+). Found: C, 82.63; H, 7.24; N, 10.13%. Calcd for $\text{C}_{19}\text{H}_{20}\text{N}_2$: C, 82.57; H, 7.29; N, 10.13%.

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