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

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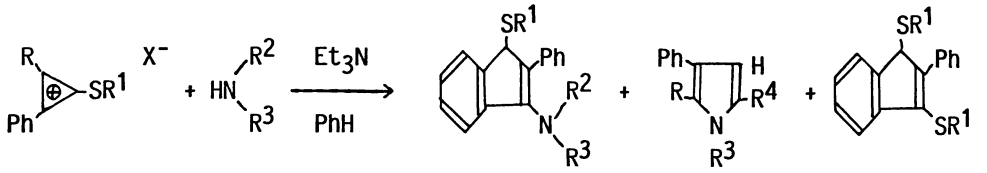
The reactions of monoalkylthio- or monoarylthio-substituted cyclopropenium salt (**1**) with a number of secondary amines were studied. The amines, such as *N*-methylaniline, yielded indenes, whereas *N*-alkyl- or *N*-arylbenzylamines gave 1-alkyl- or 1-aryl-2-phenylpyrroles in low-to-moderate yields, depending on the kinds of substituents of the amines and **1**. The reaction with *N*-isopropylbenzylamine-α,α-d_2 (*i*-PrNHCD$_2$Ph) 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 opend 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 possesing 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 acyclic[2] 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 alcohols[1] gave polyfunctionally substituted indenes 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



1 **2** **3** **4** **5**

1	R	R[1]	X
a	Ph	Me	Br
b	Ph	4-MeC$_6$H$_4$	BF$_4$
c	Ph	*t*-Bu	BF$_4$
d	Me	Me	Br
e	Me	*t*-Bu	BF$_4$

2	R[2]	R[3]
a	Me	Ph
b	Ph	Ph
c	PhCH$_2$	Me
d	PhCH$_2$	Et
e	PhCH$_2$	*i*-Pr
c-d_2	PhCD$_2$	*i*-Pr
f	PhCH$_2$	*t*-Bu
g	PhCH$_2$	Ph
h	PhCH$_2$	PhCH$_2$
i	PhCH$_2$	PhCH$_2$CH$_2$
j	4-NO$_2$C$_6$H$_4$CH$_2$	Me
k	4-NO$_2$C$_6$H$_4$CH$_2$	PhCH$_2$
l	2-NO$_2$C$_6$H$_4$CH$_2$	PhCH$_2$

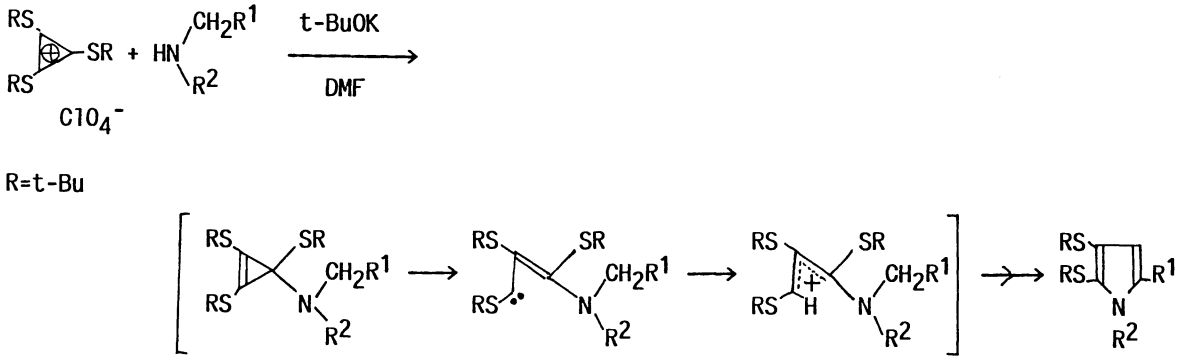
6

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*-Pr, Ph)	64
	2e-*d*$_2$	**4ae-*d*** (Ph, *i*-Pr, Ph)[a]	61
	2f	**4af** (Ph, *t*-Bu, Ph)	16
	2g	**4ag** (Ph, Ph, Ph)	33
	2h	**4ah** (Ph, $PhCH_2$, Ph)	63, 64,[b] 28[c]
	2i	**4ai** (Ph, $PhCH_2CH_2$, Ph)	15
	2j	**4aj** (Ph, Me, 4-$NO_2C_6H_4$)	17
	2k	**4ak** (Ph, $PhCH_2$, 4-$NO_2C_6H_4$)	47
	2l	**4al** (Ph, $PhCH_2$, 2-$NO_2C_6H_4$)	39
1b	**2a**	**3ba** (4-MeC_6H_4, Me, Ph)	52
	2b	**3bb** (4-MeC_6H_4, Ph, Ph)	33[d]
	2c	**4ac** (Ph, Me, Ph)	34
	2e	**4ae** (Ph, *i*-Pr, Ph)	52
	2f	**4af** (Ph, *t*-Bu, Ph)	16
	2g	**4ag** (Ph, Ph, Ph)	34[e]
	2h	**4ah** (Ph, $PhCH_2$, Ph)	51
1c	**2c**	**4ac** (Ph, Me, Ph)	55
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-$NO_2C_6H_4$)	11
	2k	**4dk** (Me, $PhCH_2$, 4-$NO_2C_6H_4$)	12
1e	**2c**	**4dc** (Me, Me, Ph)	18

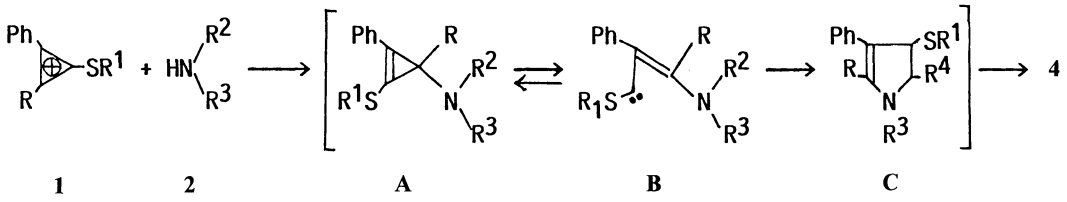
a) The product was pyrrole-3-*d*. b) $EtN(i\text{-}Pr)_2$ was used. c) Pyridine was used as a base. d) The by-product **5** (R^1=4-MeC_6H_4) was obtained in 20% yield. e) **5** (R^1=MeC_6H_4) was separated in 7%.



Scheme 2.

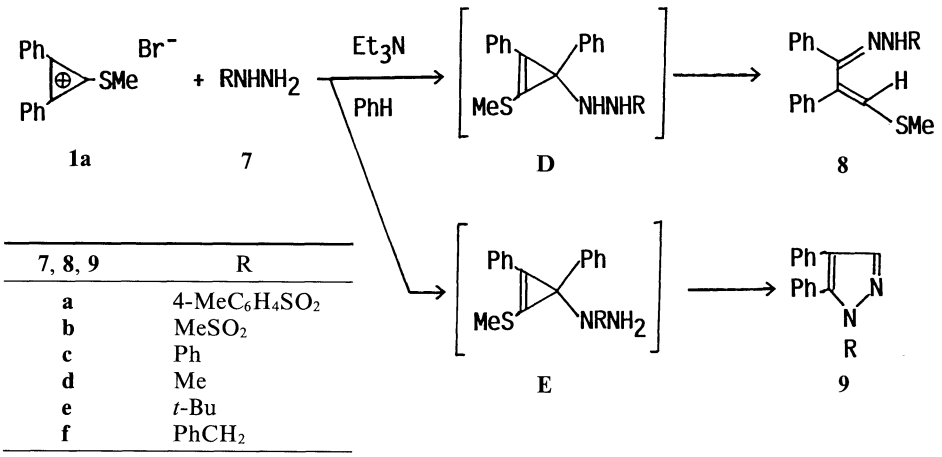
1). The reaction of **1** with secondary amines having no benzyl substituents offered indenes in moderate yields. The secondary benzylamines provided pyrroles in various yields. Interestingly, 2- and 4-nitrobenzyl groups were selectively incorporated into the pyrrole rings, even in the presence of the unsubstituted benzyl group. The yield of the pyrroles **4** were highly affected by the bulkiness of the substituents of **1** and secondary amines **2**(R^3). 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



1 2 A B C

Scheme 3.



7, 8, 9	R
a	4-$MeC_6H_4SO_2$
b	$MeSO_2$
c	Ph
d	Me
e	*t*-Bu
f	$PhCH_2$

1a 7 D 8 E 9

Scheme 4.

brown mass.

In a former paper we have reported that the reaction of **1** with Grignard reagents,[4] thiols, and alcohols[1] 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-*d*$_2$** (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** (R^1=4-MeC_6H_4) as a by-product (Table 1). The reaction of **1** with thiol is known to give the thio-substituted indenes.[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 product was separated upon chromatographic separation. Tosylhydrazone **7a** with **1a** yielded an unsaturated tosylhydrazide **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**.

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	—

Experimental

General. The melting points were uncorrected. The ^{1}H NMR spectra were recorded on a Hitachi R-24B (60 MHz) and ^{13}C NMR spectra on a JEOL JNM FX-90Q (22.40 MHz). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ 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 cm^3) was stirred at room temperature for 1 h. The solution was washed with water, dried over Na_2SO_4, 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; ^{1}H 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 $C_{23}H_{21}NS$: C, 80.42; H, 6.16; N, 4.07%. **3ab**: Mp 159—161 °C; ^{1}H 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 $C_{28}H_{23}NS$: C, 82.92; H, 5.71; N, 3.45%. **4ac**: Mp 179—183 °C (lit,[7] 178—179 °C); ^{1}H 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; ^{1}H NMR δ=1.30 (t, *J*=7 Hz, 3H, Me), 3.90 (q, *J*=7 Hz, 2H, CH_2), 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 $C_{24}H_{21}N$: C, 89.12; H, 6.54; N, 4.33%. **4ae**: Mp 196—198 °C; ^{1}H NMR δ=1.25 (d, *J*=7.5 Hz, 6H, 2Me), 4.45 (sept, *J*=7.5 Hz, 1H, C<u>H</u>Me), 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 $C_{25}H_{23}N$: C, 88.98; H, 6.86; N, 4.15%. **4af**: Mp 175—177 °C; ^{1}H 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 $C_{26}H_{25}N$: C, 88.84; H, 7.16; N, 3.98%. **4ag**: Mp 200—203 °C (lit,[11] 197 °C); ^{1}H 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; ^{1}H NMR δ=5.05 (s, 2H, CH_2), 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 $C_{29}H_{23}N$: C, 90.35; H, 6.01; N, 3.63%. **4ai**: Mp 129—131 °C; IR(KBr) 1600 and 1340 cm^{-1}; ^{1}H NMR δ=2.2—2.7 (m, 2H, NCH_2), 3.9—4.4 (m, 2H, Ph<u>C</u>H_2), 6.50 (s, 1H, C4-H), and 6.5—7.6 (m, 20H, 4Ph); ^{13}C 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 $C_{30}H_{25}N$: C, 90.18; H, 6.31; N, 3.51%. **4aj**: Mp 210—214 °C; IR(KBr) 1590, 1505, and 1335 cm^{-1}; ^{1}H 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); ^{13}C 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 $C_{23}H_{18}N_2O_2$: C, 77.94; H, 5.11; N, 7.92%. **4ak**: Mp 163—165 °C; IR(KBr) 1590, 1505, and 1335 cm^{-1}; ^{1}H NMR δ=5.10 (s, 2H, CH_2), 6.70 (s, 1H, C4-H), and 7.0—8.3 (m, 19H, Ar); ^{13}C 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 $C_{29}H_{22}N_2O_2$: C, 80.91; H, 5.15; N, 6.51%. **4al**: Mp 146—148 °C; ^{1}H NMR δ=4.82 (s, 2H, CH_2), 6.42 (s, 1H, C4-H), and 6.4—8.0 (m, 19H, Ar); ^{13}C 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 $C_{29}H_{22}N_2O_2$: C, 80.91; H, 5.15; N, 6.51%. **3ba**: Mp 139—142 °C; ^{1}H 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 $C_{29}H_{25}NS$: C, 83.01; H, 6.01; N, 3.33%. **3bb**: Mp 186—189 °C: ^{1}H 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 $C_{34}H_{27}NS$: C, 84.78; H, 5.64; N, 2.92%. **4dc**: Mp 159—162 °C (lit,[12] 160—162 °C); ^{1}H 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}; ^{1}H NMR δ=2.34 (s, 3H, Me), 6.52 (s, 1H, C4-H), and 6.9—7.6 (m, 15H, 3Ph); ^{13}C 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 $C_{23}H_{19}N$: C, 89.28; H, 6.18; N, 4.52%. **4dh**: Mp 130—133 °C; IR(KBr) 1490 and 1450 cm^{-1}; ^{1}H NMR δ=2.25 (s, 3H, Me), 5.15 (s, 2H, NCH_2), 6.40 (s, 1H, C4-H), and 6.8—7.6 (m, 15H, 3Ph); ^{13}C 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 $C_{24}H_{21}N$: C, 89.12; H, 6.54; N, 4.33%. **4dj**: Mp 149—150 °C; IR(KBr) 1590, 1520, and 1350 cm^{-1}; ^{1}H 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 $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.51; N, 9.58%. **4dk**: Mp 121—123 °C; ^{1}H NMR δ=2.28 (s, 3H, Me), 5.18 (s, 2H, NCH_2), 6.06 (s, 1H, C4-H), and 6.8—8.3 (m, 14H, Ar); ^{13}C 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 $C_{24}H_{20}N_2O_2$: C, 78.24; H, 5.57; N, 7.60%. **5**(R^1=4-MeC_6H_4): Mp 176—179 °C (lit,[1] 177—178 °C).

The Reaction of *N*-Isopropylbenzylamine-*α*,*α*-d_2 (2e-d_2). The amine **2e-d_2** was prepared from the reduction of *N*-isopropylbenzamide with $LiAlD_4$ in 72% yield according to a similar procedure as described in the literature.[13] **2e-d_2**: Oil; ^{1}H NMR δ=1.08 (d, *J*=6.5 Hz, 7H, 2Me+NH), 2.86 (sept, *J*=6.5 Hz, 1H, C<u>H</u>Me_2), 3.78 (s, small, CH_2), and 6.8—7.9 (m, 5H, Ph). The content of deuterium was determined to be 98% by the use of CH_2 signal integration. A similar reaction of **1a** with **2e-d_2**, 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 ^{1}H NMR spectrum of the product. **4ae-*d***: Mp 192—193 °C; ^{1}H NMR δ=1.20 (d, *J*=7.5 Hz, 6H, 2Me), 4.42 (sept, *J*=7.5 Hz, 1H, C<u>H</u>), 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 cm^3) and aqueous HCl (3 mol dm^{-3}, 10 cm^3) was heated at reflux for 4 h. Dilution with water and extruction by CH_2Cl_2 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 cm^3) was stirred for an appropiriate

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 $C_{23}H_{22}N_2O_2S_2$: 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 $C_{16}H_{14}N_2$: 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 $C_{19}H_{20}N_2$: C, 82.57; H, 7.29; N, 10.13%.

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