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Phase transfer catalyzed reductive acylation of nitrogen-containing heteroaromatics with acetylcobalt tetracarbonyl *

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Abstract

Phase transfer catalyzed reductive ring-cleavage acylation of isoxazoles or isothiazoles with acetylcobalt tetracarbonyl gives N-acylated 1-amino-2-alkene-3-ones or thiones. Under the same conditions phthalazine, quinoline and isoquinoline react with acetylcobalt tetracarbonyl to give N-acylated dimers. The reactivity of several other nitrogen-containing heterocycles was also investigated.

1. Introduction

Phase transfer catalysis (PTC) is widely used for the *in situ* generation of anionic metal carbonyl complexes under mild conditions [1–3]. One of the more valuable phase transfer processes is the conversion of cobalt carbonyl to the mononuclear cobalt tetracarbonyl anion using aqueous alkali, benzene or toluene as the organic phase and a quaternary ammonium halide (Cl^-, Br^-) as the phase transfer agent. The subsequent reaction of cobalt tetracarbonyl anion with methyl iodide and carbon monoxide gives acetylcobalt tetracarbonyl. A variety of unsaturated substrates, *e.g.*, dienes [4], trienes [5], fulvenes [6] and azadienes [7], react with acetylcobalt tetracarbonyl under mild conditions to form the acetylated products in a regioselective manner. An interesting direct diacylation of Schiff bases (**1**) using catalytic quantities of $Co_2(CO)_8$ under PTC conditions has also been reported [8]. Keto-amides (**2**) are formed as major products in fair to good yields, with the monoamides (**3**) as a reaction by-product.

$$\underset{\mathbf{1}}{R-CH=N-R'} + CO + CH_3I \xrightarrow[CH_2Cl_2,\ PEG\text{-}400]{Co_2(CO)_8,\ base} \underset{60°C,\ 1\ atm}{}$$

$$R-\underset{\displaystyle COCH_3}{\underset{|}{CHN}}-R' \quad \underset{\mathbf{2}}{} \qquad + R-CH_2N-\underset{\displaystyle COCH_3}{\underset{|}{}} \quad \underset{\mathbf{3}}{}$$

Transition metal carbonyls such as $[Fe_2(CO)_9]$ [9], $Co_2(CO)_8$ [10] and $M(CO)_6$ (M = Mo [11–13], Cr [12] and W [13]) have been used for the reductive cleavage of heterocycles, including isoxazoles [11c], isoxazolines [14], isoxazolidines [15], 1,2-oxazines [16] and azirines [17]. The highly functionalized products of these reactions such as β-amino enones and γ-amino alcohols can be used in subsequent transformations [15].

It seemed conceivable to us that nitrogen-containing heteroaromatics would undergo reductive acylation with acetylcobalt tetracarbonyl under mild PTC conditions. We now describe the reactions of isoxazoles, isothiazoles and other five and six-membered ring nitrogen heterocycles with acetylcobalt tetracarbonyl,

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* Dedicated to Professor Paolo Chiusoli, a splendid individual who has made pioneering contributions to organometallic and organic chemistry. We have learned so much from him.

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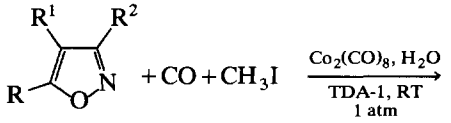
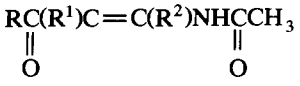
generated *in situ* from CO, CH_3I and dicobalt octacarbonyl.

2. Results and discussion

Treatment of 3,5-dimethylisoxazole (**4a**) with carbon monoxide, benzene, water, TDA-1 [tris(2,6-dioxaheptyl)amine] as the phase transfer catalyst, methyl iodide and cobalt carbonyl (4:1 ratio of **4a**:$Co_2(CO)_8$) at room temperature for 60 h gives 1-methyl-1-(N-acetyl)amino-2-acetylethylene (**5a**) in 45% yield by gas chromatography (36% isolated yield), the remainder being recovered starting material. When the ratio of $Co_2(CO)_8$ to **4** was increased to 1:1, the reaction time decreased to 48 h. In this case, the 1,2-disubstituted ethylene **5a** is formed in 79% GC yield (61% isolated yield of analytically pure material). Similar treatment of 5-methylisoxazole (**4b**) afforded **5b** after 48 h in 42% isolated yield, the remainder being unreacted **4b**. In the case of **4c**, the yield of the corresponding acylation product **5c** was substantially lower. In all cases, a mixture of (*Z*) and (*E*) products is formed (Table 1).



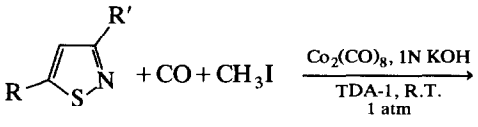
4a–c



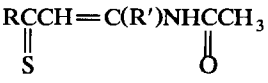
5a–c

4, 5a: R = R^2 = Me, R^1 = H
b: R = Me, R^1 = R^2 = H
c: R = R^2 = Me, R^1 = $CH_2OC_2H_5$

Isothiazoles (**6**) are cleaved in the same manner as isoxazoles to give **7**, which are thia-analogues of **5**. Isothiazoles **6a,b** are less reactive than the corresponding isoxazoles **4a,b** resulting in lower yields of (*E*) and (*Z*)-**7a,b** as compared to **5a,b**. In the case of **7a**, the stereoselectivity of the acylation (*Z*:*E* = 3.1:1) is appreciably lower when compared with that of the isostructural **5a** (*Z*:*E* = 10:1). The structures of **5a–c** and **7a–b** were assigned on the basis of analytical and spectral data. The *Z*:*E* ratio was determined by ^1H NMR spectroscopy (see Experimental section).



6a,b



7a,b

6, 7a: R = R' = CH_3
b: R = CH_3, R' = H

A variety of reaction conditions was used in order to investigate the influence of the phase transfer catalyst, base concentration and reaction time on the yield and the *E*:*Z* ratio of the functionally substituted α-amido ethylenes (*i.e.*, enamides–Table 1).

The experimental findings revealed that the yield of **5** was higher when water was used as the aqueous phase rather than 3 N KOH (runs 3 and 4). The substitution of PEG-400 for TDA-1 as the phase transfer catalyst did not influence the *E*:*Z* ratio of **5b** but did affect the yield (runs 3 and 5). Also decreasing the concentration of base increases the *E*:*Z* ratio of **5b** (runs 3 and 4).

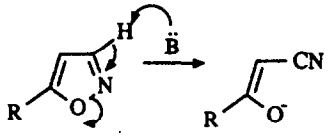
It is well known that isoxazoles unsubstituted at the 3-position (*e.g.*, **8**) are easily cleaved by bases giving (*Z*)-enolates (*e.g.*, **9**), the reaction being stereoselective below −40°C [18]. The reaction of isoxazoles **4a** with CO in the presence of $Co_2(CO)_8$/TDA-1 was also carried out without methyl iodide using water or 3N KOH as the aqueous phase. In both cases, the un-

TABLE 1. PTC reactions of isoxazoles (**4**) and isothiazoles (**6**) with $Co_2(CO)_8$/CO/KOH(H_2O)/C_6H_6/CH_3I/P.T. agent/R.T.

Substrate	Run	Molar ratio sub./$Co_2(CO)_8$	H_2O KOH (N)	Phase transfer agent	Reaction time (h)	Product	*E*:*Z*	Yield [a] %
4a	1	4:1	H_2O	TDA-1	60	**5a**	1:10	36 (46 [b])
4a	2	1:1	H_2O	TDA-1	48	**5a**	1:10	61 (79 [b])
4b	3	2:1	3N	TDA-1	48	**5b**	2.2:1	28
4b	4	2:1	H_2O	TDA-1	48	**5b**	3.4:1	42
4b	5	2:1	3N	PEG-400	48	**5b**	2.2:1	15
4c	6	2:1	3N	PEG-400	54 [c]	**5c**	1.3:1	5
6a	7	2:1	1N	TDA-1	48	**7a**	1:3.1	19
6b	8	2:1	1N	TDA-1	48	**7b**	2.1:1	12

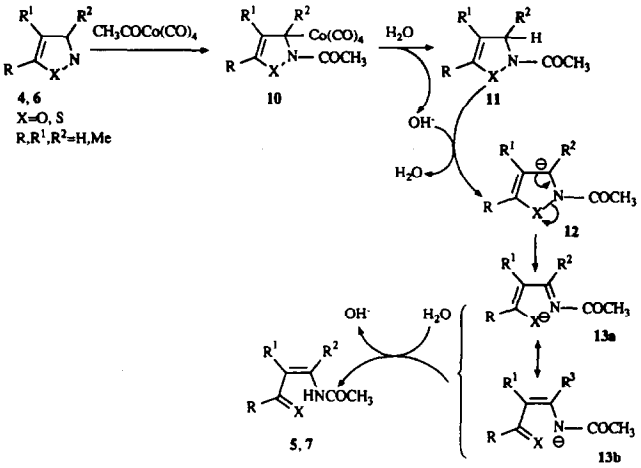
[a] Isolated yield. [b] GC yield. [c] 45–50°C.

changed starting material was recovered quantitatively after reaction for three days. Therefore, the reaction mechanism differs significantly from the aforementioned base-induced cleavage of isoxazoles. A possible mechanism for the reductive ring-cleavage acylation reaction is outlined in Scheme 1. 1,2-Addition of the organocobalt compound to **4** or **6** would generate **10**. The latter can experience C–Co bond cleavage by water to give **11**. Deprotonation of **11** can give **12** which, on N–X bond rupture, affords **13a**, which is in tautomeric equilibrium with **13b**. The product can then arise by protonation of **13**. The formation of the (Z)-isomer as the main product in reactions involving **4a** and **6a** is probably due to the methyl group (R^2) in the intermediate ambident open-chain anion **13**.



(8) (9)

Benz[*d*]isoxazole, under the same phase transfer conditions, is transformed to 2-hydroxybenzonitrile in 71% isolated yield. No acylation occurred in this case, possibly due to the presence of an electron withdrawing benzene substituent which decreases the nucleophilicity of the C=N bond and, at the same time, increases the acidity of the proton in the heterocyclic ring. Thus, the addition of $CH_3COCo(CO)_4$ does not take place at the C=N bond and base-induced ring cleavage is the only reaction [18]. As expected, this

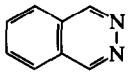
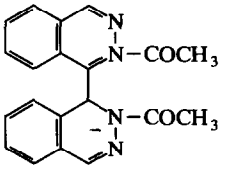
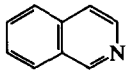
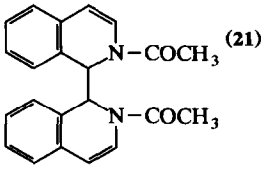
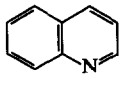
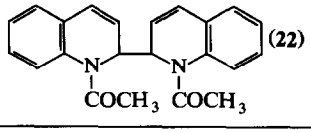


Scheme 1.

transformation does not occur under neutral (H_2O) conditions.

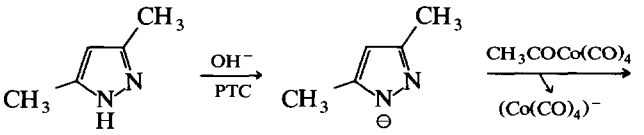
In the case of other five-membered ring nitrogen-containing heterocycles, *viz.* pyrazoles, only 3,5-dimethylpyrazole (**14**) reacts with acetylcobalt tetracarbonyl under PTC conditions to give 1-acetyl-3,5-dimethyl pyrazole (**16**) in 30% yield. Unlike isoxazoles and isothiazoles, pyrazole **14** reacts with $CH_3COCo(CO)_4$ only when 3N KOH is used as the aqueous phase. No reaction occurs by the use of 1N KOH or water. Therefore, the reaction most probably proceeds by deprotonation of **14** to **15** at the interface, followed by reaction with $CH_3COCo(CO)_4$ to form **16**. N-Phenylpyrazole, 3-methyl-1-phenylpyrazole and 1,3,5-tri-

TABLE 2. Reaction of bicyclic heterocycles with $Co_2(CO)_8/CO/KOH(H_2O)/C_6H_6/CH_3I/TDA\text{-}1/R.T.$

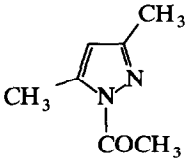
Substrate	Molar ratio sub./$Co_2(CO)_8$	KOH (N_{conc})	Reaction time	Product	Isolated Yield
 (17)	2:1	3N	72	 (20)	54
	2:1	H_2O	48		45
 (18)	2:1	3N	48	 (21)	27
	2:1	H_2O	48		27
 (19)	2:1	H_2O	84	 (22)	traces [a]

[a] Tentative structure. It is conceivable that the structure of **22** is the 4,4'-isomer, although the chemical shift of methine proton would be quite different.

methylpyrazole, all of which are already substituted at the 1-position do not react with acetylcobalt carbonyl under the same PTC conditions even under prolonged heating.



14 15



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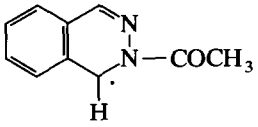
The reaction of phthalazine (**17**), isoquinoline (**18**) and quinoline (**19**) with acetylcobalt tetracarbonyl under the same PTC conditions, results in the formation of acylated dimeric products **20–22** in low to moderate yields (Table 2). The structure of these products was established by analytical and spectral data, including COSY and HETCOR NMR methods (see Experimental section). These acylation and dimerization reactions may proceed via a radical pathway involving a benzyl radical and then homocoupling. No acetylation–dimerization occurs in the case of 1,4-diethoxyphthalazine, probably for steric reasons.



3. Experimental section

3.1. General

Spectral data were obtained with Perkin-Elmer 783 (IR), Varian XL 300 and VG 7070E (MS) spectrometers. Elemental analyses were carried out by MHW Laboratories, Phoenix, AZ, USA. Cobalt carbonyl and most of the organic reactants were purchased from commercial sources and were used as received.

The following were synthesized: **4c** was prepared in 80% yield by reacting 3.5-dimethyl-4-chloromethyl isoxazole and $NaOC_2H_5/C_2H_5OH$ at 45°C for 12 h. ^1H NMR ($CDCl_3$) δ 1.19 (t, 3H, $-OCH_2CH_3$), 2.24 (s, 3H, CH_3C^3), 2.35 (s, 3H, CH_3C^5), 3.45 (q, 2H, $-OCH_2CH_3$), 4.23 (s, 2H, $-OCH_2$–ring); MS *m/e* 112 $[M - CH_3CO]^+$. **6b** was prepared in 35% yield from 3,5-dimethylisoxazole [19].

1,4-Diethoxyphthalazine was prepared in 60% yield by reacting 1,4-dichlorophthalazine and $NaOC_2H_5/C_2H_5OH$ at 45°C for 12 h. ^1H NMR($CDCl_3$) δ 1.45 (t, 6H, $2 \times CH_3$), 4.40 (q, 4H, $2 \times OCH_2$), 7.50–8.11 (m, 4H, aromatic protons); MS *m/e* 218 $[M]^+$, 203 $[M - CH_3]^+$.

1,3,5-Trimethylpyrazole was prepared in 66% yield by deprotonation of 3,5-dimethylpyrazole with ^{n}BuLi in THF, followed by methylation with CH_3I at 0°C–R.T., for 20 h, and workup by TLC.

3.2. General procedure for the reaction of isoxazoles, isothiazoles, benz[d]isoxazole, phthalazine, quinoline, isoquinoline and pyrazoles with acetylcobalt tetracarbonyl

Carbon monoxide was bubbled through a solution of 3N KOH (or 1N KOH or H_2O–15 ml) containing 0.6 mmol (180 mg) of TDA-1. After stirring for 30 minutes, a degassed solution of $Co_2(CO)_8$ [171 mg, 0.5 mol.] in benzene (20 ml) was added, and the mixture was heated at 35–40°C for 20–40 minutes (or overnight at R.T. in H_2O) to generate $[Co(CO)_4]^-$. After cooling to R.T., methyl iodide (2 ml) was added, followed 30 minutes later by the starting material (1 mmol) in benzene (5 ml). The reaction mixture was stirred under CO at R.T. and 1 atm for 2 or 3 days (monitored by GC). After reaction was complete, the phases were separated. The aqueous phase was neutralized (1N HCl), and extracted with ether (4×25 ml). The combined organic layer was dried ($MgSO_4$) and concentrated by rotary evaporation. Pure products were isolated by preparative TLC using hexane-CH_2Cl_2 (4:1) as eluent.

3.3. Characterization data for products

5a: IR (neat): ν(NH) 3500 cm^{-1}, ν(CO) 1720 cm^{-1}, 1655 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.09 (s, 3H, $=C^1-CH_3$ (Z)), 2.10 (s, 3H, $CH_3COC^2H=$), 2.19 (s, 3H, $=C^1CH_3$ (E)), 2.31 (s, 3H, CH_3CONH), 5.27 (s, 1H, C^2H_z), 5.72 (s, 1H, C^2H_E); ^{13}C NMR ($CDCl_3$) δ 21.80 ($CH_3COC^2H=$), 25.39 (CH_3CONH), 30.47 ($CHC^1H=$), 105.20 ($=C^2H$), 155.09 ($=C^1CH_3NH$), 169.48 ($CONH$), 199.34 ($COC^2H=$); MS (*m/e*) 141 $[M]^+$. Anal. calcd. for $C_7H_{11}NO_2$: C, 59.56; H, 7.85. Found: C, 59.66; H, 8.61%.

5b: IR (neat): ν(NH) 3360 cm^{-1}, ν(CO) 1710 cm^{-1}, 1665 cm^{-1}; ^1H NMR ($CDCl_3$ δ 2.11 (s, 3H, $CH_3COC^2H=$), 2.22 (s, 3H, CH_3CONH), 5.49 [d(^3J(*cis* H^2-H^1) = 8.7 Hz), 1H, H_Z^2], 5.71 [d(^3J(*trans* $^2H-^1H$) = 14.6 Hz), 1H, H_E^2], 7.34 [dd(^3J(*cis* $^1H-^2H$) = 8.7 Hz, $^3J(H^1-NH)$ = 11.0 Hz), 1H, H_Z^1], 7.91 [dd(^3J(*trans* H^1-H^2) = 14.6 Hz, ($^3J(H^1-NH)$ = 9.3 Hz), 1H, H_E^1], 8.55 (S(br), 1H exchangeable with D_2O); ^{13}C NMR 23.29 ($CH_3COC^2H=$), 26.15 (CH_3CONH), 104.02 ($=C^2HCO$), 111.64 ($=C^1HNH$), 168.94 ($CONH$), 198.99 ($COC^2H=$), MS (*m/e*) 127 $[M]^+$. Anal. Calcd. for $C_6H_9NO_2$: C, 56.68; H, 7.14. Found: C, 56.32; H, 7.22%.

5c: IR (neat): ν(NH) 3410 cm^{-1}, ν(CO) 1718 cm^{-1}, 1680 cm^{-1}, ^1H NMR ($CDCl_3$) δ 1.09 (t, 3H, OCH_2CH_3 (*E*)), 1.14 (t, 3H, OCH_2CH_3 (*Z*)), 2.03 (s, 3H, CH_3C^1H= (*E*)), 2.15 (s, 3H, CH_3C^1= (*Z*)), 2.23 (s, 3H, CH_3COC^2= (*E*), 2.40 (s, 3H, CH_3COC^2= (*Z*)), 2.52 (s, 3H, CH_3CONH (*E*)), 2.66 (s, 3H, CH_3CONH (*Z*)), 3.355 (q, 2H, OCH_2CH_3 (*Z*)), 3.425 (q, 2H, OCH_2CH_3 (*E*)), 4.08 (s, 2H, OCH_2C^2= (*Z*)), 4.14 (s, 2H, OCH_2C^2= (*E*)), MS (*m/e*) 156 $[M - CH_3CO]^+$, 43 $[CH_3CO]^+$ base peak. Anal. Calcd. for $C_{10}H_{17}NO_3$: C, 60.28; H, 8.60. Found: C, 59.99; H, 8.47%.

7a IR (neat): ν(NH) 3415 cm^{-1}, ν(CO) 1719 cm^{-1}, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.12 (s, 3H, $CH_3C(S)$], 2.11 (s, 3H, CH_3C^1= (*Z*)), 2.22 (s, 3H, CH_3C^1= (*E*)), 2.33 (s, 3H, CH_3CONH), 5.29 (s, 1H, C^2H_z), 5.77 (s, 1H, C^2H_E), 8.20 (s(br), 1H, NH exchangeable with D_2O), MS (*m/e*) 142 $[M - CH_3]^+$. Anal. Calcd. for $C_7H_{11}NOS$: C, 53.47; H, 7.05. Found: C, 53.56; H, 7.00%.

19 IR (neat) ν(NH) 3410 cm^{-1}, ν(CO) 1720 cm^{-1}, 1665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.00 (s, 3H, CH_3COC^2H=), 2.24 (s, 3H, CH_3CONH), 5.36 [d (^3J(*cis* H^2–H^1) = 8.5 Hz), 1H, H^2_Z], 5.71 [d(^3J(*trans* H^2–H^1) = 14.5 Hz), 1H, H^2_E], 7.34 [dd (^3J(*cis* H^1–H^2) = 8.5 Hz, (^3J(^{1}H–NH) = 10.9 Hz), 1H, H^1_Z], 7.88 [dd, (^3J(*trans* H^1–H^2) = 14.5 Hz, ^3J(^{1}H–NH) = 9.0 Hz, 1H, H^1_E], 8.24 (s(br), 1H, NH exchangeable with D_2O); MS (*m/e*) 143 $[M]^+$. Anal. Calcd. for C_6H_9NOS. C, 50.32; H, 6.33. Found: C, 50.52; H, 6.61%.

20 M.p.: 194–196°C; IR (KBr) ν(CO) 1675 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.32 (s, 3H, CH_3), 5.79 (s, 1H, H^1), 6.16 [d(J = 7.4 Hz), 1H, H^8], 7.11 (m, 1H, H^7), 7.35 (m, 2H, H^5, H^6), 7.79 (s, 1H, H^4); ^{13}C NMR ($CDCl_3$) 21.29 (CH_3), 50.09 (C^1), 124.82 (C^{4a}), 128.18 ($C^{6 \text{ or } 5}$), 128.70 (C^8), 128.81 ($C^{5 \text{ or } 6}$), 130.08 (C7), 131.42 (C^{8a}), 142.00 (C^4), 171.73 (CO); MS (EI) (*m/e*) 173 $[M/2]^+$. MS (CI) (*m/e*) 347 $[M + 1]^+$. Anal. Calcd. for $C_{20}H_{18}N_4O_2$: C, 69.35; H, 5.24. Found, C, 69.47; H, 5.18%.

21 M.p. 190–192°C; IR (KBr) ν(CO) 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.14 (s, 3H, CH_3), 5.79 (s, 1H, H^1), 5.93 [d (J = 7.6 Hz), 1H, H^8], 6.18 [d (J = 7.8 Hz), 1H, H^4], 6.63 [d (J = 7.8 Hz), 1H, H^3], 6.74 (m, 1H, H^7), 7.13 (m, 2H, H^5, H^6); ^{13}C NMR ($CDCl_3$) 21.62 (CH_3), 52.58 (C^1), 110.99 (C^3), 124.07 (C^4), 125.73 (C^{4a}), 127.91, 125.75 (C^5, C^6), 128.74 (C^8), 128.82 (C^7), 130.60 (C^{8a}), 168.58 (CO); MS (EI) (*m/e*) 172 $[M/2]^+$, MS (CI) (*m/e*) 345 $[M + 1]^+$. Anal. Calcd. for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85. Found: C, 77.00; H, 5.88%.

22 M.p. 184–187°C. IR (KBr) ν(CO) 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.12 (s, 3H, CH_3), 5.70 (s, 1H, H^2), 5.91 [d (J = 7.0 Hz), 1H, $H^{4 \text{ or } 3}$], 6.17 [d (J = 7.0 Hz), 1H, $H^{3 \text{ or } 4}$], 6.31 [d (J = 7.7 Hz), 1H, H^7]. 6.70 [d (J = 9.4 Hz), 1H, H^8], 7.18 (m, 2H, H^5, H^6); MS (CI) (*m/e*) 345 $[M + 1]^+$. Anal. Calcd. for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85. Found: C 76.64; H, 5.82%.

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