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Cathodic Reduction of Benzoyl Cyanides

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Introduction

The chemical reduction of acyl cyanides has been studied extensively. The products of such reactions are highly dependent on the reaction conditions and particularly on the reducing agents used. For example, reduction with Zn/HCl or hydrogen in the presence of a Ni catalyst yields cyanohydrins, whereas reduction with $LiAlH_4$ or hydrogen in the presence of a Pd catalyst in acetic acid yields α-amino alcohols.[1] Selective reduction leading to α-amino ketones is accomplished using the Stephen reaction.[2] Recently, it has been reported that the action of titanous chloride on benzoyl cyanides produces hydrodimerization to give benzil dicyanohydrins.[3] Furthermore, the photoreduction of benzoyl cyanides to benzil dicyanohydrins has also been investigated.[4]

However, the electrochemical reduction of acyl cyanides has not been studied thoroughly. We report here the macroscale cathodic reduction of benzoyl cyanides **1** in acetonitrile at a platinum cathode. We found that the electrochemical reduction of **1** provides different products depending upon whether water is present in the electrolyte system. When the electrolysis is conducted in aqueous acetonitrile, the corresponding benzil **2** is formed as the final product *via* the benzyl dicyanohydrin, whereas, only mandelonitrile benzoate (**3**) is produced in absolute acetonitrile. In each case, reduction most likely proceeds *via* a one-electron process.

Results and Discussion

Preparative electrolyses were performed in an undivided cell by passing a constant current at rt. Tetraethylammonium *p*-toluenesulfonate (Et_4NOTs) was used as the supporting electrolyte. The results are summarized in Table 1. In most cases, the starting benzoyl cyanides **1** were almost totally consumed by the time approximately 1.2 F/mol had passed through the electrolyte.

In aqueous acetonitrile, a precipitate of benzyl dicyanohydrins was often observed during electrolysis. However, during the final stage, a considerable amount of the benzyl dicyanohydrins was converted into benzils **2**, thus liberating hydrogen cyanide, due to their instability.[4] Consequently, the product yields were determined such that the remaining dicyanohydrins were completely converted into **2** by heating the mixture of products, although the actual electrolysis products were the benzyl dicyanohydrins.

As shown in Table 1, the yields of **2** were not significantly influenced by the nature or position of the substituent on the benzene ring. This method may be convenient for preparing symmetrical benzils, such as 2,2′- or 4,4′-dichlorobenzils, or methyl-substituted benzils, which are not readily obtained by the usual route through benzoin condensation.[5] Replacement of acetonitrile with another polar aprotic solvent, such as acetone, dioxane, or DMF, gave lower yields of **2**. The use of alkaline metal salts, like $NaClO_4$, as the supporting electrolyte drastically decreased the yields. Moreover, electrolysis in a divided cell caused the hydrolysis of **1** to benzoic acids, probably *via* electrogenerated base catalysis.

Table 1. Electrolytic Reduction of Benzoyl Cyanides 1a−h[a]

benzoyl cyanide **1**	Ar	% yield of products[b]			
		benzil **2**[c]		maldelonitrile benzoate **3**[d]	
1a	C_6H_5	**2a**	67 (75)	**3a**	63 (74)
1b	2-MeC_6H_4	**2b**	63	**3b**	53
1c	4-MeC_6H_4	**2c**	63 (68)	**3c**	65 (76)
1d	2-$MeOC_6H_4$	**2d**	56	**3d**	0[e]
1e	4-$MeOC_6H_4$	**2e**	63 (70)	**3e**	43 (57)
1f	2-ClC_6H_4	**2f**	64	**3f**	65
1g	4-ClC_6H_4	**2g**	62	**3g**	61
1h	4-*t*-BuC_6H_4	**2h**	59 (64)	**3h**	65 (69)

[a] Benzoyl cyanide **1** (25 mmol) and Et_4NOTs (10 mmol) were used. Strength of constant current: 0.4 A. Current passed: 1.2 F/mol. [b] Isolated yield by distillation or recrystallization. Values in parentheses are GLC yield. [c] In MeCN−H_2O (70−10 mL). [d] In 80 mL of MeCN. [e] **2d** was formed in a yield of 55%.

On the other hand, the electrolysis of **1** in absolute acetonitrile gave the corresponding mandelonitrile benzoates **3** instead of benzils **2**, except for 2-methoxybenzoyl cyanide (**1d**). The same products are produced when **1** is treated with $NaBH_4$ in a two-phase system consisting of CH_2Cl_2 and water in the presence of Bu_4NBr, where it is postulated that the benzaldehyde cyanohydrin anion which is formed as the primary reduction product is acylated with an unreacted molecule of benzoyl cyanide.[6] Indeed, benzoyl cyanides react very readily with aldehydes in the presence of cyanide ion to give **3**.[7] However, such intermediates were not detected during the present electrolyses. Instead, benzil **2** was observed during the initial stage, and was then transformed into mandelonitrile benzoate **3** as the electrolysis proceeded.

Figure 1 shows the product distributions of the electrolysis of **1a** based on GLC analysis of the electrolyte as a function of the applied charge. The total yields of **2a** and **3a** increased almost linearly with an increase in the applied charge. Using the slope of the line, we can estimate that the 1 F is consumed per mole of **1a** for the formation of **2a** and **3a**. This suggests that the transformation of **2a** into **3a** does not involve electron transfer between the cathode and **2a**.

A simple mechanism for the present reaction is shown in Scheme 1. Benzoyl cyanides undergo one-electron reduction to form radical anions, followed by dimerization to give benzil dicyanohydrin dianions **A**. In aqueous acetonitrile, the resulting dianion is immediately protonated to give benzil dicyanohydrin, which slowly decomposes to benzil **2**. On the other hand, in absolute acetonitrile, a proton is not readily available, and dianions **A** eject a cyanide ion to form epoxide, which undergoes displacement and subsequent protonation to give the corresponding mandelonitrile benzoate **3**.[8]

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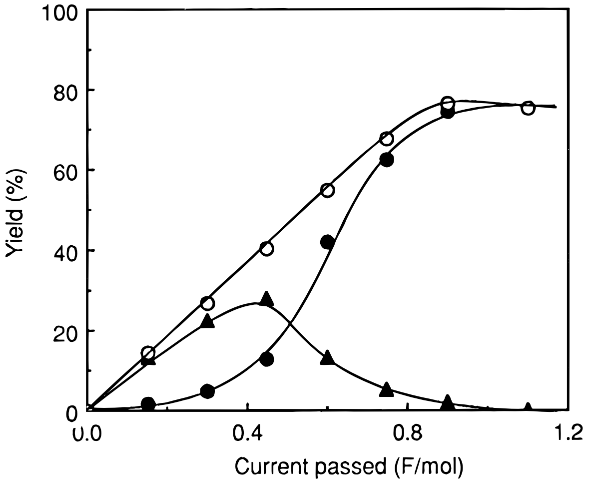
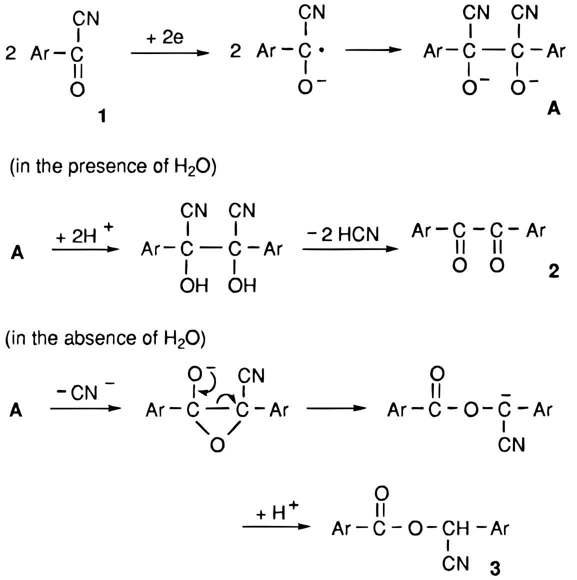


Figure 1. Relationships between the product yields and consumed current in the electrolysis of benzoyl cyanide **1a** (25 mmol) in 0.125 M Et_4NOTs−MeCN (80 mL). ▲, benzil **2a**; ●, mandelonitrile benzoate **3a**; ○, total yield.

Scheme 1



A similar displacement has been found to take place in the reaction of **2a** with sodium cyanide in aprotic solvents, such as DMSO or DMF, in which the carbanion of **3a** is formed as an intermediate, although **3a** itself has not been isolated.[9] The failure of **1d** to provide the corresponding **3d** may be due to the electrometric effect of the methoxy group at the ortho position, which hinders the intramolecular nucleophilic attack of the cyanohydrin carbon center by the oxyanion to give the epoxide.

Experimental Section

Melting and boiling points are uncorrected. The ^1H NMR and ^{13}C NMR spectra were measured at 90 and 22.4 MHz, respectively, in $CDCl_3$, unless otherwise noted. Chemical shifts are given in ppm downfield (δ) from Me_4Si as an internal standard. GC/MS analyses were performed using a 30-m capillary column (0.25 mm diameter; liquid phase, SPB-1) with an ionization potential of 70 eV. Gas-liquid chromatography (GLC) was performed using a 2.0-m glass column packed with FFAP on Chromosorb W AW and a 1-m stainless steel column packed with Silicone SE-30 on Uniport B. The carrier gas for each column was N_2 and the detector was FID. Elemental analyses were performed by the Instrumental Analyses Laboratories at Hokkaido University.

Benzoyl cyanides **1a**−**h** were prepared from the corresponding benzoyl chlorides and CuCN as reported elsewhere.[10] Et_4NOTs was prepared by refluxing an ethanol solution of triethylamine and ethyl *p*-toluenesulfonate according to the method in the literature.[11] Anhydrous acetonitrile was obtained by refluxing with P_2O_5, followed by distillation under dry nitrogen.

Preparative-Scale Electrolyses. Electrolyses were performed in a 100-mL beaker. A platinum gauze cylinder (33 mm diameter, 40 mm high) served as the cathode, and a cylindrical platinum gauze anode (25 mm diameter, 40 mm high) was concentrically placed inside the cathode.

The electrodes were connected to an adjustable DC power supply. The power source was a Torio Model PR-653 regulated DC supply (35 V, 3 A). For electrolysis in anhydrous acetonitrile, a calcium chloride tube was connected to the equipment. The cell was cooled with running water and the electrolyte was magnetically stirred. The progress of the reaction was monitored by either GLC or TLC.

Cathodic Reduction of Benzoyl Cyanides (1a−**h). General Procedure in aqueous MeCN.** A mixture of benzoyl cyanide **1** (25 mmol), Et_4NOTs (10 mmol), MeCN (70 mL), and H_2O (10 mL) was electrolyzed at a constant current of 0.4 A. The terminal voltage ranged from 5 to 7 V. After 1.2 F/mol of charge had been passed, the catholyte was evaporated *in vacuo* at rt. The residue was treated with brine (70 mL), and the liberated oily layer was extracted with Et_2O (50 mL × 3). The ether extracts were washed with brine (30 mL), dried ($MgSO_4$), and concentrated. The crude products that were obtained from three such electrolyses were combined and slowly heated in an oil bath. At about 150 °C, the evolution of hydrogen cyanide was observed. The oil bath temperature was then maintained at 210 °C for 40 min, and the hot reaction mixture was distilled *in vacuo*. The isolated yields of **2** are given in Table 1. Analytical samples were obtained by recrystallization from EtOH.

Benzil (2a): mp 96−97 °C, yellowish rodlike crystals from EtOH (lit.[12] mp 95 °C); bp 154−156 °C/3 Torr (lit.[12] bp 188 °C/12 Torr); IR (KBr) 1661 cm^{-1}; ^1H NMR δ 7.4−7.8 (m, 6H), 7.9−8.2 (m, 4H); ^{13}C NMR δ 129.0 (CH), 129.9 (CH), 133.1 (C), 134.9 (CH), 194.5 (CO); MS *m/z* (rel intensity) 210 (M^+, 6), 105 (100), 77 (37).

2,2′-Dimethylbenzil (2b): mp 92−95 °C, yellow needles from EtOH (lit.[12] mp 92−94 °C); bp 164−167 °C/3 Torr; IR (KBr) 1672 cm^{-1}; ^1H NMR δ 2.70 (s, 6H), 7.1−7.8 (m, 8H); ^{13}C NMR δ 21.8 (CH_3), 126.0 (CH), 131.9 (C), 132.6 (CH), 133.0 (CH), 133.6 (CH), 141.5 (C), 196.9 (CO); MS *m/z* (rel intensity) 238 (M^+, 1), 119 (100), 91 (31).

4,4′-Dimethylbenzil (2c): mp 104−105 °C, yellow plates from EtOH, (lit.[12] mp 104−105 °C); bp 209−211 °C/7 Torr; IR (KBr) 1661 cm^{-1}; ^1H NMR δ 2.41 (s, 6H), 7.28 (d, $J = 8$ Hz, 4H), 7.86 (d, $J = 8$ Hz, 4H); ^{13}C NMR δ 21.9 (CH_3), 129.7 (CH), 130.0 (CH), 130.8 (C), 146.0 (C), 194.4 (CO); MS *m/z* (rel intensity) 238 (M^+, 4), 119 (100), 91 (27).

2,2′-Dimethoxybenzil (2d): mp 131−132 °C, colorless needles from EtOH (lit.[13] mp 128−129 °C); bp 201−204 °C/3 Torr; IR (KBr) 1655 cm^{-1}; ^1H NMR δ 3.55 (s, 6H), 6.8−7.3 (m, 4H), 7.4−7.7 (m, 2H), 8.0−8.3 (m, 2H); ^{13}C NMR δ 55.8 (CH_3), 112.6 (CH), 121.4 (CH), 123.5 (C), 130.4 (CH), 135.6 (CH), 160.4 (C), 192.5 (CO); MS *m/z* (rel intensity) 270 (M^+, 5), 135 (100).

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4,4′-Dimethoxybenzil (2e): mp 133−134 °C, golden yellow needles from EtOH (lit.[12] mp 133 °C); bp 215−219 °C/3 Torr; IR (KBr) 1655 cm^{-1}; ^{1}H NMR δ 3.86 (s, 6H), 6.95 (d, $J = 9$ Hz, 4H), 7.94 (d, $J = 9$ Hz, 4H); ^{13}C NMR δ 55.6 (CH$_3$), 114.3 (CH), 126.4 (C), 132.3 (CH), 164.9 (C), 193.5 (CO); MS m/z (rel intensity) 270 (M$^+$, 2), 135 (100).

2,2′-Dichlorobenzil (2f): mp 134−135 °C, golden yellow needles from EtOH (lit.[12] mp 133 °C); bp 186−188 °C/3 Torr; IR (KBr) 1684 cm^{-1}; ^{1}H NMR δ 7.2−7.8 (m, 6H), 7.9−8.2 (m, 6H); ^{13}C NMR δ 127.3 (CH), 130.9 (CH), 132.2 (C), 132.7 (CH), 134.8 (CH), 135.0 (C), 191.0 (CO); MS m/z (rel intensity) 278 (M$^+$, trace), 139 (100), 111 (24).

4,4′-Dichlorobenzil (2g): mp 197−199 °C yellow needles from EtOH, (lit.[12] mp 199 °C); bp 216−220 °C/3 Torr; IR (KBr) 1659 cm^{-1}; ^{1}H NMR δ 7.43 (d, $J = 9$ Hz, 4H), 7.92 (d, $J = 9$ Hz, 4H); ^{13}C NMR δ 129.5 (CH), 131.3 (CH), 141.8 (C), 159.7 (C), 192.4 (CO); MS m/z (rel intensity) 278 (M$^+$, 1), 139 (100), 111 (27).

4,4′-Di-*tert*-Butylbenzil (2h): mp 103−104 °C, fine powder crystals from EtOH (lit.[9a] mp 104−104.5 °C); bp 235−240 °C/6 Torr; IR (KBr) 1682 cm^{-1}; ^{1}H NMR δ 1.33 (s, 18H), 7.51 (d, $J = 9$ Hz, 4H), 7.92 (d, $J = 9$ Hz, 4H); ^{13}C NMR δ 31.0 (CH$_3$), 35.2 (C), 126.0 (CH), 129.9 (CH), 130.7 (C), 158.8 (C), 194.5 (CO); MS m/z (rel intensity) 322 (M$^+$, 1), 161 (100). Anal. Calcd for $C_{22}H_{26}O_2$: C, 81.95; H, 8.13. Found: C, 82.08; H, 8.34.

Isolation of Benzil Dicyanohydrin. The electrolysis of **1a** (25 mmol) was repeated by passing a current of 30 mF. After the usual workup, the residue of the ether extracts was suspended in benzene (15 mL), and insoluble materials were collected by filtration and washed with small amounts of benzene. The crude product was recrystallized from acetone−hexane (1:2) to which a few drops of acetic acid had been added (0.73 g, 22%). **Benzil dicyanohydrin:** mp 177−180 °C dec white powder crystals (lit.[3b] mp 175−176 °C dec). The IR and ^{1}H NMR spectra were in agreement with those reported.[3b] IR (KBr) 3368, 2255(vw) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 7.05 (s, 2H), 7.24−7.74 (m, 10H); ^{13}C NMR (acetone-d_6) δ 79.8 (C), 119.4 (CN), 128.3 (CH), 128.4 (CH), 130.5 (CH), 136.0 (C). It has been reported that dicyanohydrins are unstable, even at rt, and therefore the results of elementary analyses do not always agree with the calculated values.[4]

General Procedure in Anhydrous MeCN. Using a procedure similar to that in aqueous MeCN, benzoyl cyanide **1** (25 mmol) was electrolyzed without the addition of water. The termimal voltage ranged from 7 to 12 V. After the usual workup, the residue of the ether extracts was passed through a short column (25 mm diameter, 15 cm high) of silica gel by eluting with ether. The eluate was evaporated to dryness, and the residue was recrystallized from EtOH. The yields of the purified products are given in Table 1.

α-Cyanobenzyl benzoate (3a): mp 60−62 °C, leaflets from EtOH (lit.[14] mp 63−64 °C); bp 176−177 °C/3 Torr. The IR and NMR spectra were in agreement with those reported:[15] IR (KBr) 2249 (vw), 1732, 1248 cm^{-1}; ^{1}H NMR δ 6.67 (s, 1H), 7.3−7.8 (m, 8H), 8.0−8.2 (m, 2H); ^{13}C NMR δ 63.4 (CH), 116.2 (CN), 127.8 (CH), 128.2 (C), 128.6 (CH), 129.3 (CH), 130.1 (CH), 130.4 (CH), 132.0 (C), 134.1 (CH), 164.6 (CO); MS m/z (rel intensity) 237 (M$^+$, 36), 116 (69), 105 (100), 77 (41).

α-Cyano-2-methylbenzyl *o*-methylbenzoate (3b): mp 50−52 °C, prisms from EtOH; IR (KBr) 2243 (vw), 1734, 1238 cm^{-1}; ^{1}H NMR δ 2.49 (s, 3H), 2,61 (S, 3H), 6.74 (S, 1H), 7.1−8.1 (m, 8H); ^{13}C NMR δ 19.0 (CH$_3$), 21.8 (CH$_3$), 61.3 (CH), 116.2 (CN), 126.0 (CH), 126.8 (CH), 127.2 (C), 128.6 (CH), 130.2 (C), 130.5 (CH), 131.0 (CH), 131.4 (CH), 132.1 (CH), 133.2 (CH), 136.7 (C), 141.5 (C), 165.0 (CO); MS m/z (rel intensity) 265 (M$^+$, 28), 135 (42), 130 (78), 119 (100). Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 77.08; H, 5.85; N, 5.26.

α-Cyano-4-methylbenzyl *p*-methylbenzoate (3c): mp 50−52 °C, fine powder cryatals from EtOH; IR (KBr) 2253 (vw), 1722, 1088 cm^{-1}; ^{1}H NMR δ 2.38 (s, 3H), 2.40 (s, 3H), 6.62 (s, 1H), 7.2−8.1 (m, 8H); ^{13}C NMR δ 21.3 (CH$_3$), 21.7 (CH$_3$), 63.1 (CH), 116.4 (CN), 125.5 (C), 127.9 (CH), 129.2 (C), 129.3 (CH), 129.9 (CH), 130.1 (CH), 140.6 (C), 145.0 (C), 164.7 (CO); MS m/z (rel intensity) 265 (M$^+$, 22), 130 (53), 119 (100), 91 (30). Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.97; H, 5.76; N, 5.24.

α-Cyano-4-methoxybenzyl *p*-methoxybenzoate (3e): mp 64−66 °C, leaflets from EtOH (lit.[14] mp 69−70 °C); IR (KBr) 2268 (vw), 1711, 1255 cm^{-1}; ^{1}H NMR δ 3.81 (s, 3H), 3.84 (s, 3H), 6.59 (s, 1H), 6.8−7.1 (m, 4H), 7.4−8.2 (m, 4H); ^{13}C NMR δ 55.4 (CH$_3$), 55.5 (CH$_3$), 62.8 (CH), 113.9 (CH), 114.6 (CH), 116.6 (CN), 120.6 (C), 124.3 (C), 129.6 (CH), 132.2 (CH), 161.1 (C), 164.2 (C), 164.3 (CO); MS m/z (rel intensity) 297 (M$^+$,18), 146 (100), 135 (44). Anal. Calcd for $C_{17}H_{15}NO_4$: C, 68.67; H, 5.08; N, 4.71. Found: C, 68.72; H, 5.16; N, 4.67.

α-Cyano-2-chlorobenzyl *o*-chlorobenzoate (3f): mp 49−51 °C fine powder crystals from EtOH; IR (KBr) 2257 (vw), 1742, 1234 cm^{-1}; ^{1}H NMR δ 6.94 (s, 1H), 7.1−8.0 (m, 8H); ^{13}C NMR δ 61.2 (CH), 115.1 (CN), 126.8 (CH), 127.5 (C), 127.7 (CH), 129.2 (C), 129.7 (CH), 130.3 (CH), 131.4 (CH), 131.9 (CH), 132.0 (CH), 133.5 (C), 133.8 (CH), 134.6 (C), 163.1 (CO); MS m/z (rel intensity) 305 (M$^+$, 15), 150 (53), 139 (100). Anal. Calcd for $C_{15}H_9NO_2Cl_2$: C, 58.85; H, 2.96; N, 4.58; Cl, 23.16. Found: C, 58.89; H, 3.08; N, 4.52; Cl, 22.91.

α-Cyano-4-chlorobenzyl *p*-chlorobenzoate (3g): mp 77−78 °C, fine powder crystals from EtOH; IR (KBr) 2262 (vw), 1728, 1094 cm^{-1}; ^{1}H NMR δ 6.63 (s, 1H), 7.3−7.7 (m, 6H), 7.9−8.1 (m, 2H); ^{13}C NMR δ 62.9 (CH), 115.7 (CN), 126.4 (C), 129.1 (CH), 129.3 (CH), 129.7 (CH), 130.3 (C), 131.4 (CH), 136.9 (C), 140.9 (C), 163.7 (CO); MS m/z (rel intensity) 305 (M$^+$,17), 150 (59), 139 (100). Anal. Calcd for $C_{15}H_9NO_2Cl_2$: C, 58.85; H, 2.96; N, 4.58; Cl, 23.16. Found: C, 58.91; H, 3.09; N, 4.53; Cl, 23.12.

α-Cyano-4-*tert*-butylbenzyl *p*-*tert*-butylbenzoate (3h): mp 107−109 °C fine powder crystals from EtOH; IR (KBr) 2245 (vw), 1720, 1263 cm^{-1}; ^{1}H NMR δ 1.32 (s, 18H), 6.67 (s, 1H), 7.4−7.6 (m, 6H), 7.9−8.1 (m, 2H); ^{13}C NMR δ 31.0 (CH$_3$), 31.2 (CH$_3$), 34.8 (C), 35.2 (C), 63.0 (CH), 116.4 (CN), 125.6 (CH), 126.2 (CH), 127.7 (CH), 129.2 (C), 130.0 (CH), 153.6 (C), 157.9 (C), 159.6 (C), 164.6 (CO); MS m/z (rel intensity) 349 (M$^+$,14), 334 (15), 172 (14), 161 (100). Anal. Calcd for $C_{23}H_{27}NO_2$: C, 79.05; H, 7.79; N, 4.01. Found: C, 78.88; H, 7.93; N, 3.90.

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