ACID-INDUCED CYCLIZATION OF 3-BENZYL-3,4-DIHYDRO-2-PYRAZINONES: SYNTHESIS OF 1,2,3,4,5,6-HEXAHYDRO-1,5-IMINO-3-BENZAZOCINE DERIVATIVES

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Abstract - 3,4-Dihydro-4-ethoxycarbonyl-2-pyrazinones(3), which can be prepared by cyclization of dipeptide aldehyde acetals(2) in the presence of a catalytic amount of proton acid, were shown to be useful intermediates for the preparation of complex heterocycles by acid-induced C-C bond formation. The acid-induced intramolecular cyclization of the intermediates(3) afforded regioselectively 1,5-ethoxycarbonylimino-3-methyl-1,2,5,6-tetrahydro-3-benzazocin-4(3H)-one(4) in quantitative yield. The structural characterization of the cyclization product(4) and its derivatives(6 and 7) was carried out mainly by the analysis of the NMR spectra.

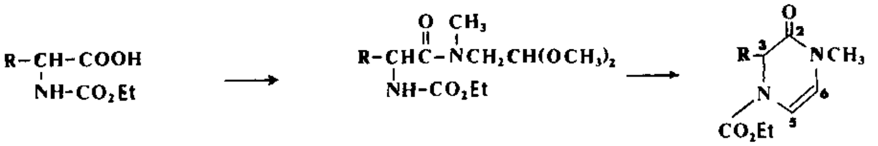
Piperazine, 1,2,3,4-tetrahydroisoquinoline and their derivatives are biologically interesting compounds, because of their diverse pharmacological properties. A great number of reports dealing with the synthesis of these compounds have been published. However, the 1,2,3,4,5,6-hexahydro-1,5-imino-3-benzazocines, possessing both of a tetrahydroisoquinoline and a piperazine ring as a common part, have not been widely investigated. On the basis of these observations and in continuation to our studies of structure-activity relationship, a facile route was sought to prepare some 1,5-imino-3-benzazocine derivatives.

The only known synthetic method[1] for the preparation of 1,2,3,4,5,6-hexahydro-1,5-imino-3-benzazocines has involved the hydrolysis and cyclization of methyl 1-phthalimidomethyl-1,2,3,4-tetrahydroisoquinoline-3-carboxylate, which was synthesized by Bischler-Napieralski reaction of N-phthalimidoacetylphenylalanine followed by reduction.

The N-ethoxycarbonylphenylalanines(1) were condensed with sarcocinal dimethyl acetal to provide amides(2) in excellent yield via the mixed anhydrides derived from isobutyl chloroformate in the presence of triethylamine.

Cyclization of phenylalanylsarcocinal dimethyl acetals(2) occurred smoothly at room temperature by stirring in acetonitrile containing a catalytic amount of proton acid, such as hydrochloric acid, for an hour to yield reaction products(3) in almost quantitative yield.

The facile availability of various starting compounds of type 2 led us to consider that this reaction would provided a general procedure to obtain the 3,4-dihydro-4-ethoxycarbonyl-2-pyrazinone having a variety of substituents at N-1 and C-3 positions. Actually, 3,4-dihydro-4-ethoxycarbonyl-1-methyl-2-pyrazinone(3d), the first and still most simple member of this series was prepared in a similar way from N-ethoxycarbonylglycylsarcosinal dimethyl acetal(2d) in quantitative yield.



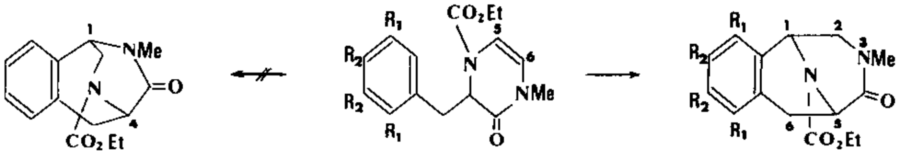
1a b c d　　2a b c d　　3a b c d

a　R = $C_6H_5CH_2-$
b　= 2,5-$(CH_3O)_2C_6H_3CH_2-$
c　= 3,4-$(CH_3O)_2C_6H_3CH_2-$
d　= H

The structure of the cyclization products(3) was fully supported by microanalytical results and spectral data, and by molecular weights determined by mass spectrometry. The IR spectrum of 3d exhibited two strong absorption bands at 1680 and 1715 cm^{-1} due to amide and carbamoyl carbonyl group, respectively. The NMR spectrum of 3d, showing the signals of vicinal olefinic protons at δ 6.39(1H, br. d, J=5.8 Hz) and 5.48 ppm (1H, d, J=5.8 Hz), proved beyond all doubt that 3 indeed had been formed as shown above. The literature reveals that 1,3,4,5,6-alkyl or aryl substituted 3,4-dihydro-2-pyrazinones have been synthesized from dianil and ketene by intermolecular cycloaddition.[2]

Compound 3 seems to be a suitable intermediate to construct 1,5-imino-3-

benzazocine by Grewe cyclization method.[3] Under acid conditions a competition between cyclization at C-5 and C-6 positions of pyrazinone upon benzene ring is obviously possible and might be expected to depend upon such factors as the nitrogen substituents and steric environment of the substrate. Surprisingly, heating a solution of 3-benzyl-3,4-dihydro-2-pyrazinone(3) in trifluoroacetic acid afforded a cyclization product, 1,5-imino-3-benzazocin-4-one(4), regioselectively as a single product in almost quantitative yield. The structure of 4 was based on the correct elemental analysis and spectral data. The IR spectrum of 4a showed the characteristic stretching at 1705 and 1645 cm^{-1} for two carbonyl groups. The more significant feature of the NMR spectrum of 4a was the appearance of the signals due to two methine protons at δ 5.01 and 5.43 ppm and two methylene protons centered at δ 3.21 and 3.61 ppm and the disappearance of the signals due to one aromatic proton and two olefinic protons. However, it is difficult to rule out completely the possibility that the structure of the product is not 1,2,5,6-tetrahydro-1,5-imino-3-benzazocin-4(3H)-one(4) (cyclization at C-5) but 4,5-dihydro-4,1-iminomethano-1H-2-benzazepin-3(2H)-one(5) (cyclization at C-6). From the first order analysis of spectral data, it is difficult to recognize the distinction between structures 4 and 5.



5

3a b

4a b c

a $R_1=R_2=H$
b $R_1=OCH_3, R_2=H$
c $R_1=H, R_2=OCH_3$

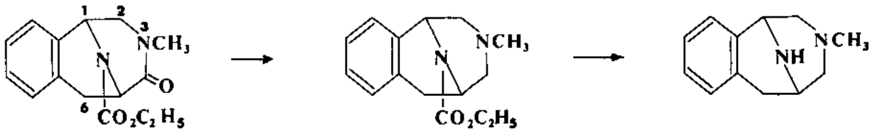
For the final confirmation of the structure(4), lactam(4a) was reduced with sodium borohydride to provide amine(6) whose NMR spectrum indicated a high-field shift of the signals of N-methyl and methylene at C-2 position, both of which were adjacent to 3-nitrogen. Hydrolysis and decarboxylation of 6 with concd. hydrochloric acid gave rise to 7 and in its NMR spectrum, a high-field shift of signals assignable to two methine protons was observed. The chemical shift of compounds 4a, 6 and 7 are summarized in Table 1. In addition to the above

Table 1

Compounds	H-1	H-5	H-2a	H-2b	N-Me
4a	5.43	5.01	4.00	3.22	2.85
6	5.08(-0.35)	4.55(-0.46)	2.73(-1.27)	2.30(-0.92)	2.11(-0.74)
7	3.94(-1.14)	3.44(-1.11)	2.74(+0.01)	2.35(+0.05)	2.11

Numerals in parenthesis are quoted the difference ($\Delta\delta_{6-4a}$ and $\Delta\delta_{7-6}$) in each lines.

findings, an alternative possible structure(5) was rejected for two reasons: (i) the 400 Mc spectrum[4] of 7 exhibits evidence of a typical W-type coupling (ca. 1.5 Hz) of two methine protons across four bonds $\left(H\text{-}\underset{|}{\overset{|}{C}}_{(1)}\text{-}\underset{H}{N}\text{-}\underset{|}{\overset{|}{C}}_{(5)}\text{-}H\right)$ and (ii) the mass spectrum of 7 shows characteristic fragment pattern of 1,2,3,4,5,6-hexahydro-1,5-imino-3-benzazocines.[5]



4a 6 7

In addition, it is noteworthy that the reaction of 2c with a catalytic amount of proton acid, such as hydrochloric acid, proceeded even at cold temperature to provide a cyclization product(4c) and the reaction of compounds(2) with trifluoroacetic acid under refluxing for few hours proceeded to afford directly 1,5-imino-3-benzazocines(4).

The straight forward nature of this work, beginning with readily available amino acid, is of choice to prepare useful quantities of 3,4-dihydro-2-pyrazinones. We emphasise the overall simplicity of the operations involved and the excellence of overall yield. Studies on related pyrazinones and their application to the synthesis of alkaloids with medicinal interest currently are in progress and will be reported separately.

Experimental

Melting points were determined using a Yanaco micro-melting point apparatus and are uncorrected. NMR spectra were recorded on a Varian EM-390 spectrometer (using TMS as an internal standard). IR spectra were obtained in potassium bromide, unless otherwise specified, using a JASCO IRA-2 spectrometer. Mass spectra were recorded on a JEOL JMS-01SG at 75 ev using a direct inlet system.

N-Ethoxycarbonyl amino acids(1a, b, c, d) were prepared from the requisite amino acids and ethyl chloroformate by standard procedure.[6]

dl-N-Ethoxycarbonylphenylalanine(1a), mp 92-94°.[6]

dl-N-Ethoxycarbonyl-2,5-dimethoxyphenylalanine(1b), mp 115-116°; ν_{max} cm^{-1}: 3340, 1710, 1692; m/e(%): 297(M$^+$, 20), 208(18), 151(base peak); δ($CDCl_3$): 1.19(3H, t, J=7.3), 3.11(2H, m), 3.73, 3.78(each 3H, s), 4.06(2H, q, J=7.3), 4.54(1H, m), 5.53(1H, br. d, J=6.7, NH), 6.79(3H, br. s), 8.70(1H, br. s, CO_2H).

Anal. Calcd for $C_{14}H_{19}NO_6$: C, 56.56: H, 6.44: N, 4.71. Found: C, 56.26: H, 6.41: N, 4.49.

dl-N-Ethoxycarbonyl-3,4-dimethoxyphenylalanine(1c), mp 112-114°; ν_{max} cm^{-1}: 3340, 1760, 1733, 1708, 1682; m/e(%): 297(M$^+$, 23), 208(23), 152(33), 151(base peak); δ($CDCl_3$): 1.20(3H, t, J=7.2), 3.09(2H, m), 3.86(6H, s), 4.10(2H, q, J=7.2), 4.64 (1H, m), 5.15(1H, br., NH), 6.77(3H, m), 9.18(1H, br. s, CO_2H).

Anal. Calcd for $C_{14}H_{19}NO_6$: C, 56.56: H, 6.44: N, 4.71. Found: C, 56.40: H, 6.39: N, 4.75.

N-Ethoxycarbonylglycine(1d), mp 73-74°.[6]

N-Ethoxycarbonylphenylalanylsarcosinal dimethyl acetals(2a, b, c).

To a solution of 20 mM of N-ethoxycarbonylphenylalanine(1) in 150 ml of CH_2Cl_2 at -15° was added 3.1 ml (22 mM) of Et_3N and 3.0 g (22 mM) of isobutyl chloroformate.[5] After stirring at -15° for 1 hr, a solution of 22 mM of aminoacetaldehyde dimethyl acetal in 10 ml of CH_2Cl_2 was added at the same temperature. The mixture was allowed to warm to room temperature. The reaction mixture was washed with aq. $NaHCO_3$, 5% aq. tartaric acid, and water, successively, and dried over Na_2SO_4. Filtration of the drying agent and evaporation of the filtrate afforded acetal(2) (80-90% yield).

N-Ethoxycarbonylphenylalanylsarcosinal dimethyl acetal(2a), liquid; $\nu_{max}^{liq.}$cm^{-1}: 3400, 1713, 1640, 700; m/e(%): 338(M$^+$, 23), 323(50), 307(40), 192(base peak);

δ(CDCl$_3$): 1.20(3H, t, J=7.3), 2.80(3H, s), 3.34, 3.36(each 3H, s), 4.09(2H, q, J=7.3), 4.39(1H, t, J=5.1), 4.90(1H, m), 5.56(1H, br. d, J=7.5, NH), 7.27(5H, br. s).

Anal. Calcd for $C_{17}H_{26}N_2O_5$: C, 60.34: H, 7.74: N, 8.28. Found: C, 60.22: H, 7.87: N, 8.46.

N-Ethoxycarbonyl-2,5-dimethoxyphenylalanylsarcosinal dimethyl acetal(2b), mp 97-98°; ν_{max} cm^{-1}: 3400, 1705, 1635; m/e(%): 398(M$^+$, 16), 309(40), 252(base peak), 161(65); δ(CDCl$_3$): 1.14(3H, t, J=7.2), 3.04(3H, s), 3.34, 3.38(each 3H, s), 3.73 (3H, s), 3.82(3H, s), 3.99(2H, q, J=7.2), 4.41(1H, t, J=5.4), 4.99(1H, m), 5.52(1H, br. d, J=8.2), 6.75(3H, m).

Anal. Calcd for $C_{19}H_{30}N_2O_7$: C, 57.27: H, 7.59: N, 7.03. Found: C, 56.91: H, 7.43: N, 6.87.

N-Ethoxycarbonyl-3,4-dimethoxyphenylalanylsarcosinal dimethyl acetal(2c), mp 98-99°; ν_{max} cm^{-1}: 3250, 1712, 1633; m/e(%): 398(M$^+$, 30), 309(base peak), 151(96); δ(CDCl$_3$): 1.20(3H, t, J=7.1), 2.82(3H, s), 3.31(3H, s), 3.36(3H, s), 3.84(6H, s), 4.09(2H, q, J=7.1), 4.36(1H, t, J=5.4), 4.84(1H, q, J=7.8), 5.60(1H, br. d, J=7.8, NH), 6.78(3H, s).

Anal. Calcd for $C_{19}H_{30}N_2O_7$: C, 57.27: H, 7.59: N, 7.03. Found: C, 57.08: H, 7.50: N, 7.00.

N-Ethoxycarbonylglycylsarcosinal dimethyl acetal(2d), bp$_{0.01}$ 130-135° (bath temp); $\nu_{max}^{liq.}$ cm^{-1}: 3450, 1717, 1653; m/e(%): 248(M$^+$, 20), 233(26), 217(30), 102(base peak); δ(CDCl$_3$): 1.26(3H, t, J=7.2), 3.03(3H, s), 3.49(6H, s), 3.48(2H, d, J=5.2), 4.02 (2H, m), 4.13(2H, q, J=7.2), 4.48(1H, t, J=5.2), 5.66(1H, br. s, NH).

Anal. Calcd for $C_{10}H_{20}N_2O_5$: C, 48.38: H, 8.12: N, 11.28. Found:C, 48.23: H, 8.25: N, 11.09.

3,4-Dihydro-4-ethoxycarbonyl-1-methyl-2-pyrazinones(3a, b, d).

To a solution of 10 mM of acetal(2) in 30 ml of CH$_3$CN was added 0.5 ml of c.HCl in 10 ml of CH$_3$CN. After stirring at ambient temperature for 1 hr, the reaction mixture was diluted with 200 ml of water and extracted with CH$_2$Cl$_2$. The CH$_2$Cl$_2$ extract was washed with water and dried over Na$_2$SO$_4$. Usual work-up gave pyrazinone(3).

3-Benzyl-3,4-dihydro-4-ethoxycarbonyl-1-methyl-2-pyrazinone(3a): mp 63-65°; ν_{max} cm^{-1}: 1712, 1670, 740, 692; m/e(%): 274(M$^+$, 48), 183(base peak), 111(76). In the NMR spectrum, a set of signals due to rotamers was observed.[8] For one rotamer δ($CDCl_3$): 0.93(3H, t, J=7.3), 3.08(3H, s), 3.77(2H, q, J=7.3), 4.95(1H, br. t, J=7.2), 5.53(1H, d, J=6.0), 6.39(1H, br. d, J=6.0), 7.23(5H, m), and the other: 1.20(3H, t, J=7.3), 3.08(3H, s), 4.12(2H, q, J=7.3), 5.09(1H, br. t, J=7.1), 5.25(1H, d, J=6.0), 6.13(1H, br. d, J=6.0), 7.23(5H, s). The ratio of the former to the latter is about 5:3.

Anal. Calcd for $C_{15}H_{18}N_2O_3$: C, 65.68: H, 6.61: N, 10.21. Found: C, 65.51: H, 6.48: N, 10.20.

3-(2,5-Dimethoxybenzyl)-3,4-dihydro-4-ethoxycarbonyl-1-methyl-2-pyrazinone(3b): mp 82-83°; $\nu_{max}^{liq.}$ cm^{-1}: 1712, 1678; m/e(%): 334(M^+, 27), 183(72), 111(base peak); a pair of rotamers was also existed: the spectrum of the major one shows at δ($CDCl_3$): 1.01(3H, t, J=7.2), 3.08(3H, s), 3.72 and 3.78 (each 3H, s), 3.81(2H, q, J=7.2), 4.98(1H, br. t, J=5.1), 5.50(1H, d, J=5.6), 6.33(1H, dd, J=5.6, 1.8), 6.71(3H, m); the other shows at δ: 1.18(3H, t, J=7.2), 4.09(2H, q, J=7.2), 5.13(1H, br. t, J=6.0), 5.31(1H, d, J=6.1), 6.15(1H, dd, J=6.1, small).

Anal. Calcd for $C_{17}H_{22}N_2O_5$: C, 61.07: H, 6.63: N, 8.38. Found: C, 60.68: H, 6.69: N, 8.38.

3,4-Dihydro-4-ethoxycarbonyl-1-methyl-2-pyrazinone(3d): $bp_{0.05}$ 95-98° (bath temp.); $\nu_{max}^{liq.}$ cm^{-1}: 1710, 1680, 1658, 760; m/e(%): 184(M^+, 45), 156(17), 111(33), 93(base peak); δ($CDCl_3$): 1.30(3H, t, J=7.1), 3.09(3H, s), 4.23(2H, q, J=7.1), 4.29(2H, s), 5.48(1H, d, J=5.8), 6.39(1H, br. s).

Anal. Calcd for $C_8H_{12}N_2O_3$: C, 52.16: H, 6.57: N, 15.21. Found: C, 51.54: H, 6.76: N, 15.61.

1,5-Ethoxycarbonylimino-3-methyl-1,2,5,6-tetrahydro-3-benzazocin-4(3H)-ones (4a, b, c).

A solution of 5 mM of pyrazinone(3) in 8 ml of CF_3CO_2H was refluxed for several hours until TLC indicated complete conversion. The mixture was concentrated to afford an oil, which was dissolved in CH_2Cl_2 and washed with aq. $NaHCO_3$ solution and water, and dried over Na_2SO_4. Usual work-up gave benzazocinone (4a, b).

Treatment of 2c with HCl in CH_3CN, as mentioned in procedure of 3a, b, d, provided directly 4a.

1,5-Ethoxycarbonylimino-3-methyl-1,2,5,6-tetrahydro-3-benzazocin-4(3H)-one(4a); mp 121-123°; ν_{max} cm^{-1}: 1705, 1645, 755; m/e(%): 274(M^+, 70), 203(98), 202(base peak), 130(95); δ($CDCl_3$): 1.29(3H, t, J=7.1), 2.85(3H, s), 3.10(1H, dd, J=16.8 and 2.1), 3.22(1H, dd, J=11.8 and 1.1), 3.33(1H, dd, J=16.8 and 5.3), 4.00(1H, dd, J=11.8 and 4.5), 4.22(2H, q, J=7.1), 5.01(1H, br. m), 5.43(1H, br. m), 7.25(4H, m, AA'BB').

Anal. Calcd for $C_{15}H_{18}N_2O_3$: C, 65.68: H, 6.61: N, 10.21. Found: C, 65.66: H, 6.59: N, 10.01.

7,10-Dimethoxy-1,5-ethoxycarbonylimino-3-methyl-1,2,5,6-tetrahydro-3-benzazocin-4(3H)-one(4b); amorph; $\nu_{max}^{CHCl_3}$ cm^{-1}: 1695, 1643; m/e(%): 334(M^+, 59), 263(80), 262(base peak), 190(65); δ($CDCl_3$): 1.25(3H, t, J=7.2), 2.83(3H, s), 2.92(1H, dd, J=17.7 and 5.6), 3.17(1H, dd, J=17.7 and 2.0), 3.25(1H, dd, J=12.0 and 1.3), 3.75 and 3.82(each 3H, s), 3.82(1H, dd, J=12.0 and 4.6), 4.16(2H, q, J=7.2), 4.98(1H, m), 5.61(1H, m), 6.70(2H, s).

Anal. Calcd for $C_{17}H_{22}N_2O_5$: C, 61.07: H, 6.63: N, 8.38. Found: C, 61.01: H, 6.82: N, 8.12.

8,9-Dimethoxy-1,5-ethoxycarbonylimino-3-methyl-1,2,5,6-tetrahydro-3-benzazocin-4(3H)-one(4c); mp 197-198°; ν_{max} cm^{-1}: 1695, 1641; m/e(%): 334(M^+, 29), 263(39), 262(base peak), 190(34); δ($CDCl_3$): 1.29(3H, t, J=7.3), 2.76(3H, s), 3.01(1H, dd, J=15.9 and 2.7), 3.21(1H, dd, J=11.8 and 1.4), 3.24(1H, dd, J=15.9 and 6.7), 3.87 and 3.89(each 3H, s), 3.97(1H, dd, J=11.8 and 4.6), 4.22(2H, q, J=7.3), 4.99(1H, br. m), 5.35(1H, br. m), 6.60(1H, s), 6.65(1H, s).

Anal. Calcd for $C_{17}H_{22}N_2O_5$: C, 61.07: H, 6.63: N, 8.38. Found: C, 60.96: H, 6.50: N, 8.39.

1,5-Ethoxycarbonylimino-1,2,3,4,5,6-hexahydro-3-methyl-3-benzazocine(6).

To a solution of 2.00 g of 4a in 20 ml of MeOH was added in small portions 2.0 g of $NaBH_4$ below 20°. After vigorous stirring for 20 hr at room temperature, the mixture was made acidic with 6N HCl and concentrated under reduced pressure. The residue was made alkaline with 3N NaOH and extracted with CH_2Cl_2. The extract was worked up as usual and chromatographed on SiO_2 using AcOEt as an eluent to afford 6(1.65 g, 80%): $bp_{0.004}$ 122-125° (bath temp.); $\nu_{max}^{liq.}$ cm^{-1}: 2820, 1708; m/e(%): 260(M^+, 65), 202(base peak), 130(65); δ($CDCl_3$): 1.21(3H, t, J=7.2), 2.11 (3H, s), 2.30(2H, dd, J=11.4 and 3.5), 2.6-2.9(centered at 2.73) (2H, m), 2.79 (1H, dd, J=17.8 and 1.2), 3.28(1H, dd, J=17.8, and 7.5), 4.12(2H, q, J=7.2), 4.55(1H, m), 5.08(1H, m), 7.12(4H, m).

Anal. Calcd for $C_{15}H_{20}N_2O_2$: C, 69.21: H, 7.74: N, 10.76. Found: C, 69.57: H, 7.56: N, 10.57.

1,2,3,4,5,6-Hexahydro-1,5-imino-3-methyl-3-benzazocine(7).

A suspension of 0.46 g of 6 in 5 ml of 35% HCl was refluxed for 40 hr. The reaction mixture, was made alkaline with 3N NaOH, extracted with CH_2Cl_2. The CH_2Cl_2 extract was worked up as usual to yield 7(0.33 g, 100%): mp 71-72°; ν_{max} cm^{-1}: 3250, 2770, 763, 730; m/e(%): 188(M^+, 6), 144(15), 130(29), 58(base peak); δ($CDCl_3$): (400 MHz): 1.82(1H, br. s, NH), 2.09(3H, s, NMe), 2.35(1H, dd, J=10.3 and 3.0, H-2 axial), 2.36(1H, dd, J=10.3 and 3.0, H-4 axial), 2.74(1H, dt, J=10.3 and 3.0, H-2 equatorial), 2.81(1H, dt, J=10.3 and 3.0, H-4 equatorial), 2.80(1H, d, J=17.1, H-6 axial), 3.12(1H, dd, J=17.1 and 7.8, H-6 equatorial), 3.44(1H, dt, J=7.8 and 3.0, H-5), 3.94(1H, br. t, J=3.0, H-1), 7.10(4H, aromatic).

Anal. Calcd for $C_{12}H_{16}N_2$: C, 76.56: H, 8.57: N, 14.88. Found: C, 76.53: H, 8.63: N, 14.71.

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