Tautomerism of 9-Formyltetrahydro-4*H*-pyrido[1,2-*a*]pyrimidin-4-ones and their Ring Homologues: a ^{1}H, ^{13}C, and ^{15}N Nuclear Magnetic Resonance Study[1]

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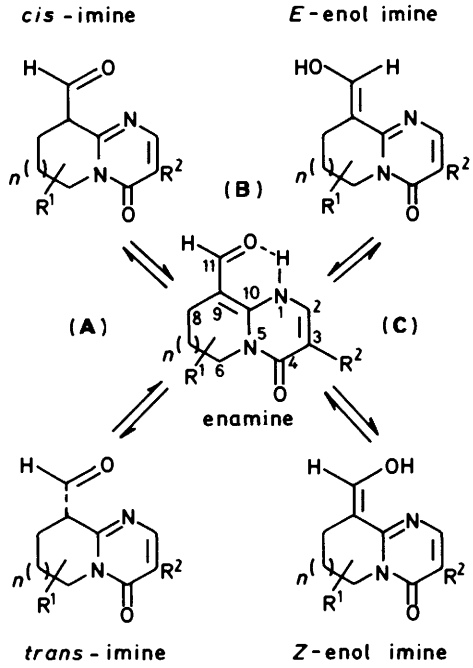
By ^{1}H, ^{13}C and ^{15}N n.m.r. studies we have established that tautomeric equilibria of 9-formyltetrahydro-4*H*-pyrido[1,2-*a*]pyrimidines and their homologues are controlled mainly by the size of the ring containing a single nitrogen atom. Thus in the pyrrolo analogues the enol imine form is predominant, with the azepino homologues the enamine, and with the azocino analogues the imine. The enol imine–enamine interconversion is relatively fast, whereas the imine–enamine interconversion is slow on the n.m.r. time-scale. The relative stabilities of the individual tautomers are explained by stereochemical factors and hydrogen bonding.

In earlier papers we have demonstrated that the 9-formyltetrahydro-4*H*-pyrido[1,2-*a*]pyrimidin-4-ones and their α-formyl-2,3-polymethylene-3,4-dihydroquinazolin-4-one analogues are potentially tautomeric systems which may exist as equilibrium mixtures of imine (**A**), enamine (**B**), and enol imine (C) forms (Scheme 1).[2-6] In addition, enol imines can assume either the *Z*- or the *E*-configuration and, when the piperidine ring has an additional substituent, *cis*- and *trans*-configurations have to be considered too. Characteristic ^{1}H, ^{13}C, and ^{15}N n.m.r. data have enabled the individual tautomers and stereoisomers to be identifed and their approximate ratios to be determined.[2] With the analogous 9-phenylhydrazono,[7,8] 9-arylaminomethylene,[8,9] and 9-dimethylaminomethylene[10] derivatives, in order to establish structure–effect correlations,[11-14] the size of the ring containing a single nitrogen atom was varied, resulting in characteristic changes in the isomeric–tautomeric situation. In the present paper an n.m.r. study of the 9-formyltetrahydro-pyrrolo-, -pyrido-, -azepino-, and -azocino-[1,2-*a*]pyrimidin-4-ones (**1**)—(**8**) and of the corresponding derivatives with fixed enol ether (**9**)—(**12**) or enamine [(**13**) and (**14**)] structure is reported (Scheme 2).



Scheme 1.

Results and Discussion

Formylpyrrolopyrimidines.—In compounds (**1**) and (**2**), in accord with u.v. data,[6] the enol imine tautomer was found to be dominant. This was proved by the presence of a high-field signal (at δ 7.31—7.88) for H-11 (Table 1), which showed allylic coupling of 1—2 Hz with the 8-protons. This coupling was independent of ring size and could be observed in compounds (**9**)—(**12**) too.

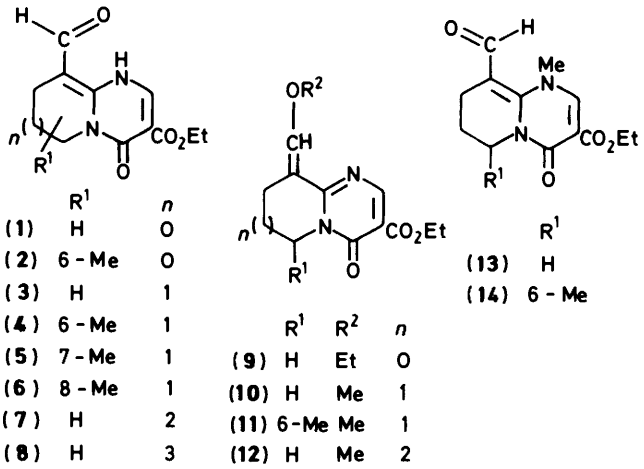
The chemical shift of H-11 is solvent-dependent in (**1**) and (**2**): 7.31 and 7.34 respectively in $CDCl_3$, 7.83 and 7.88 in $(CD_3)_2SO$. On the basis of our earlier observations[7-10] this phenomenon is considered to be mainly due to the fact that in chloroform the *Z*-isomer and in Me_2SO the *E*-isomer is predominant. A further proof of the assigned *Z* and *E* configuration is obtained from nuclear Overhauser effect difference experiments: saturation of H-11 in (**2**) results in a pronounced intensity enhancement of 8-H_2 in $CDCl_3$ solution, whereas in $(CD_3)_2SO$ no effect was observed. The preponderance of the enol imine tautomer (C) is further corroborated by the shift of C(11), which is in good agreement with that observed in the fixed tautomer (**9**) (Table 2). With 9-arylaminomethylene- and 9-phenylhydrazono-tetrahydropyridopyrimidines we have shown that, owing to the difference in conjugation, the C(9) shift differs significantly for the *E*- and *Z*-stereoisomers $\{\delta[C(9)]_Z < \delta[C(9)]_E\}$. Differences for the C(3) signals are also characteristic, though smaller.[7-9] The *E*- and *Z*-isomers of (**1**) and (**2**) were identified by analogy. As expected from the bond angles in the five-membered ring, steric interaction between C(8) and O–C(11) in the *E*-isomer is not very strong and therefore shifts for C(8) scarcely differ between the *Z*- and *E*-isomers of the pyrrolopyrimidines.[8] In the enol ether (**9**) the configuration at C(11) cannot be unambigously defined from the shift of H-11 (δ 7.57). The good agreement of the ^{13}C data for the enol ether (**9**) and for (**1**) and (**2**) measured in $(CD_3)_2SO$ provides evidence for the *E*-configuration of (**9**). The ^{15}N n.m.r. shifts of the sparingly soluble compound (**1**) labelled with ^{15}N at N(1) and of (**9**) were measured (Table 3). Shifts of N(1) for (**9**) (in $CDCl_3$) and (**1**) [in $(CD_3)_2SO$] almost coincided (δ −167.3 and −167.9, respectively). In $CDCl_3$,

however, the N(1) signal of (1) was shifted significantly upfield (δ −181.1). In view of the shielding effect of hydrogen bonds on sp^2-hybridized nitrogen,[15] and concomitant non-bonded interactions between N(1) and O–C(11), the observed upfield shift may be partly caused by the fact that for (1) the *Z*-isomer is preferred in chloroform. However, this upfield shift may be indicative of the appearance of a minor enamine species in a mobile enol imine ⇌ enamine tautomeric equilibrium.[2] The observed shielding of C(9) and deshielding of C(11) in $CDCl_3$ solutions of (1) and (2) comparison with data from solutions in $(CD_3)_2SO$ can be explained in terms of both *E* ⟶ *Z* isomerization and enol imine ⟶ enamine conversion.[2,9] The measured upfield shift of C(2) in $CDCl_3$ indicates the appearance of the tautomer (B).

The ^{15}N n.m.r. studies revealed that the proportion of the potential enamine tautomer (B) could only be low (<15%) in the equilibrium mixture, in contrast to the case of pyridopyrimidines, where (B) is the dominant tautomer.[2] Such a dramatic change in the tautomeric equilibrium may be attributed to a significant increase in bond angles and thereby of the distance between N(1) and O–C(11) in the five-membered ring. As a consequence, the conditions for strong internal hydrogen bonding, stabilizing the enamine form, are lacking.

In the *E*-isomer of the enol imine (2) the OH signal appears at δ 4.9; this value is increased only to δ 6.2 in the *Z*-isomer. In view of this, hydrogen bonding might occur in the latter, but should be weaker than found in the 9-phenylaminomethylene and 9-phenylhydrazone derivatives.[7,9] A weakening of internal hydrogen bonding was also observed with the corresponding 9-phenylaminomethylenepyrrolopyrimidines as compared with the appropriate pyridopyrimidines.[8]

Formylpyridopyrimidines.—We have established earlier that in the tautomeric equilibria (A) ⇌ (B) ⇌ (C) the enamine (B) prevails, but a small amount of (C) is also present (in the fast equilibrium). For the assessment of the (B)/(C) ratio in compound (4) a method based on ^{15}N shifts and $^1J(^{15}NH)$ couplings was worked out.[2] *X*-Ray crystallography demonstrated that in tetrahydropyridopyrimidines Me-6 and C(4)=O are farther apart in the enamine form than in the imine form, and this alleviates steric interactions in the former.[16] With 9-aminotetrahydro-4*H*-pyrido[1,2-*a*]pyrimidines we have found that introduction of a 6-Me group increases the proportion of the enamine form in the enamine ⇌ imine equilibrium.[17] Date in Table 3 demonstrate that again the (B)/(C) ratio is highest for the 6-Me derivatives. A downfield shift of 10 p.p.m. at N(5) caused by 6-Me in the β-position is in good agreement with values measured for analogous 9-substituted derivatives.[10,18] A



	R^1	*n*
(1)	H	0
(2)	6-Me	0
(3)	H	1
(4)	6-Me	1
(5)	7-Me	1
(6)	8-Me	1
(7)	H	2
(8)	H	3

	R^1	R^2	*n*
(9)	H	Et	0
(10)	H	Me	1
(11)	6-Me	Me	1
(12)	H	Me	2

	R^1
(13)	H
(14)	6-Me

Scheme 2.

Table 1. Selected ^1H n.m.r. data of compounds (1)—(10), (12), and (13) in $CDCl_3$

	H-2	H-11	NH or OH
(1*Z*)	8.48s	7.31t	
(1*E*)[a]	8.37s	7.83t	
(2*Z*)	8.46s	7.34t	6.2br
(2*E*)[a]	8.28s	7.88d	4.9br
(3)	8.25d	8.78d	14.39br
(4)	8.23d	8.92d	14.50br
(5)	8.21d	8.71d	14.45br
(6)	8.22d	8.80d	14.64br
(7)	8.18brs	8.72brs	15.15br
	(8.49brs)	(9.90brs)	
(8)	(8.26brs)	(8.76brs)	(16.34br)
	8.59brs	9.88d	
(9)	8.58s	7.57t	
(10)	8.57s	7.96t	
(12)	8.58s	7.15t	
(13)	8.17s	9.74s	

[a] In $(CD_3)_2SO$ (values in parentheses refer to minor component).

Table 2. ^{13}C Chemical shifts of compounds (1)—(3), (7)—(10), (12), and (13) (values in parentheses refer to minor component)

	C(2)	C(3)	C(4)	C(6)	C(7)	C(7a)	C(7b)	C(8)	C(9)	C(10)	C(11)	$CO_2CH_2CH_3$			Others
(1*Z*)	157.4	*b*	*b*	46.0				20.6	*b*	*b*	158.7	163.7	61.2	14.3	
(1*E*)[a]	159.8	110.5	164.7*	45.1				20.6	108.7	157.2	152.7	163.9*	60.1	14.4	
(2*Z*)	156.9	112.8	163.7*	55.9				29.8	102.9	157.2	160.4	162.4*	61.2	14.3	6-Me: 20.9
(2*E*)[a]	159.6[c]	110.8	163.9	54.0				29.4	107.1	156.9	153.5[c]	163.9	60.0	14.3	6-Me: 20.9
(3)[d]	147.5	105.4	157.0	41.4	20.0			22.1	92.8	151.3	184.6	162.9	60.9	14.2	
(7)	147.7	106.0	158.1	42.6	25.5	25.0		25.5	98.8	156.6	187.0	162.9	60.9	14.3	
	(156.6)	*b*	*b*	*b*	(27.8)*	(24.0)		(29.6)*	(55.5)	*b*	(195.4)	*b*	*b*	*b*	
(8)	157.2	115.1	163.5	43.7	28.8	24.6	24.6	31.5	54.5	157.8	195.8	165.6	61.3	14.2	
	(147.2)	(105.7)	(162.6)	(42.0)	(29.6)*	(20.1)	(27.1)	(30.5)*	(96.0)	(158.1)	(188.7)	*b*	(61.0)	*b*	
(9)	161.0[c]	112.2	163.9	45.0				20.9	110.5	158.1	153.3[c]	164.5	60.9	14.3	OEt: 71.1, 15.4
(10)	158.2	110.1	160.7	42.0	20.3			20.3	108.0	158.9	159.6	164.7	60.5	14.4	OMe: 62.2
(12)	156.2	112.7	164.3	42.8	24.4	21.0		20.3[c]	113.7	159.0	158.2	164.9	60.1	14.3	OMe: 61.5
(13)	152.9	102.8	156.1	43.0	20.2			22.8	101.4	152.8	184.5	162.5	60.8	14.3	NMe: 49.6

* Tentative assignment.
[a] In $(CD_3)_2SO$. [b] Could not be assigned owing to low intensity or overlap. [c] Assignment proved by selective $^{13}C\{^1H\}$ decoupling. [d] From ref. 2.

study of proton-coupled ^{13}C spectra demonstrated that, while the shifts of C(2) and C(11) are diagnostic for the enol imine and enamine tautomers respectively, the values of ^{1}J(C,H) are only characteristically different for C(11) (Table 4). An interesting feature of the proton-coupled spectra is that C-3 is coupled with H-2 (^{2}J 5 Hz) only in the fixed enol imine structure, whereas in the enamines ^{2}J < 1 Hz. For the enamine in turn a relatively large coupling of H-11 and C(9) (^{2}J *ca.* 17—23 Hz) is characteristic.

Formyl-azepino-and-azocino-pyrimidines.—In the ^{1}H and ^{13}C spectra of compounds (7) and (8) taken immediately after dissolution, two sets of signals in intensity ratios of 90:10 and 15:85 respectively were observed, and these remained unchanged. Chemical shifts for the major component of (7) and those for the minor component of (8) were in good agreement with values found for the pyridopyrimidine analogues.[2] This indicated that these signals represent a fast (B) ⇌ (C) tautomeric equilibrium in which again the enamine form is in excess. The other set of signals, assigned to tautomer (A), was characterized by a shift of H-11 (formyl proton) to δ 9.90 and 9.88, respectively, and of the H-2 signal from δ 8.18 to 8.49 and from δ 8.26 to 8.59 respectively. Structure (A) was further supported by the shifts of C(9) (δ 55.5 and 54.4) and C(11) (δ 195.4 and 195.8). Deshielding of C(2) and C(3) by *ca.* 10 p.p.m. in this tautomer is also noteworthy.[19]

Further proof for structure (A) was provided by a comparison of the minor signal for N(1) in the spectrum of (7) labelled at N(1) with ^{15}N (δ −158.3) with those observed for other tetrahydropyridopyrimidines having an imine-type structure.[2,18] On the basis of the signal at δ −245.0, the approximation described for the pyridopyrimidine analogues gives a (B):(C) ratio of 83:17. This approach was justified because the N(1) shifts of ethyl 6,7,8,9-tetrahydro-4*H*-4-oxopyrido[1,2-*a*]pyrimidine-3-carboxylate and the seven-membered homologue were almost identical (δ −145.5 and −144.5).

The fact that separate sets of signals exist for compounds (7) and (8) also indicates that on the n.m.r. time-scale the interconversion of (B) and (C) is fast while that of (A) and (B) is relatively slow. In the 9-formylpyrido- (3), -azepino- (7), and -azocino-derivatives (8) the NH proton signals appear at δ 14.39, 15.15, and 16.34, respectively, which corresponds to an increase in the strength of hydrogen bonds in this order. This trend may be rationalized in terms of a gradual decrease of bond angles with increasing ring size resulting in the approach of NH and O=C(11). Another factor contributing to the formation of internal hydrogen bonds is planarity of the O=C(11)–C=C–NH unit. In view of the nature of the chair and boat conformations of the azepino ring (Figure), coplanarity is only possible in the unfavoured boat conformer. A Dreiding model of the chair conformer reveals that here the distance between N*H* and *O*–C(11) is larger, and that a coplanar arrangement of the three atoms would require an angle of 45° between the C=O bond of the formyl group and the plane of the C(9)=C(10) bond. All these factors destabilize this structure. In compound (8) a planar arrangement of the O=C(11)–C=C–NH moiety can only be envisaged in the boat-chair conformation of the eight-membered ring. This is, however, destabilized by the steric interaction between H_{ax}-6 and H_{ax}-8. It can thus be concluded that changes in the tautomeric equilibria of (7) and (8) can be assigned to steric effects associated with increased ring size.

Table 3. ^{15} N N.m.r. data and tautomeric ratios (value in parentheses refers to minor component)

Compound	δ(N-1)	δ(N-5)	^{1}J(^{15}N,H)/ Hz	^{2}J(^{15}N,H-2)/ Hz	Enol imine % *b*	*c*
(1)	−181.1				*ca.* 90	
(3)	−247.1	−231.5	81.2	3	15	12
(4)[a]	−251.6	−221.6	87.4	3	10	5
(5)	−247.6	−231.8	83.6	3	14	9
(6)	−248.5	−231.8	85.4	3	13	7
(7)	−245.0				17	
	(−158.3)					
(9)	−167.3	−197.8				
(10)	−161.8	−204.6				
(11)	−161.2	−193.5				
(13)	−267.3	−232.2				
(14)	−268.3	−222.5				

[a] Unfortunately data obtained for (3) were published earlier for this compound, in error.[2] [b] Calculated from δ(N-1) shifts. [c] Calculated from ^{1}J(^{15}N,H) coupling constants.

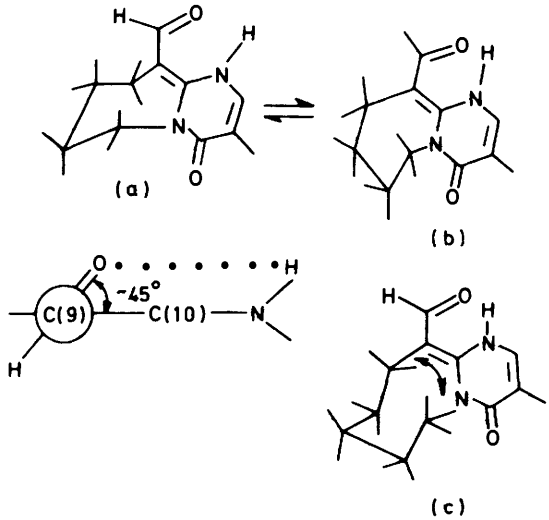
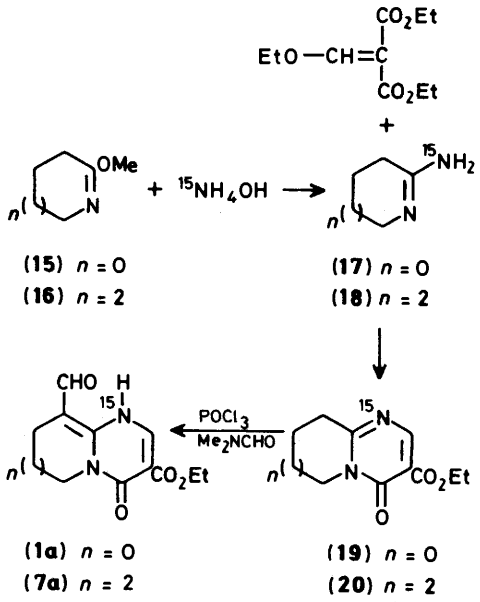


Figure. (a) Chair conformer of (7) projected along the C(9)–C(11) bond; (b) boat conformer of (7); (c) boat-chair conformer of (8) (the arrow indicates the proximity of H_{ax}-6 and H_{ax}-8)

Table 4. Significant ^{13}C–^{1}H couplings (Hz)

Compound	^{1}J C(2)	C(6)	C(7)	C(8)	C(11)	OCH_2	CH_3	NMe	OR	^{2}J(C,H) C(9)(H-11)	C(3)(H-2)
(3)	183	144	127	130	171	148	127			17	2
(9)	181	147		130	180	148	127		146, 127	< 6	5
(10)	180	143	130	130	184	147	127		146	< 6	5
(13)	178	144	127	127	171	148	127	143		23	< 1



Scheme 3.

Experimental

N.m.r. Measurements.—The ^1H, ^{13}C, and ^{15}N n.m.r. spectra were recorded in the pulsed Fourier transform mode (16K data points for the FID) at 99.54, 25.00, and 10.04 MHz, respectively, with a JEOL FX-100 instrument. The ^1H and ^{13}C chemical shifts were determined on the δ scale using tetramethylsilane as internal standard. For the ^{13}C measurements a spectral width of 5 000 Hz, a flip angle of 30°, and a pulse delay of 1.6 s were used. Broad-band-decoupled and in some cases single-frequency off-resonance, attached proton test, or gated decoupled spectra were recorded. The ^{15}N chemical shifts were determined relative to the signal of external $K^{15}NO_3$ (δ −3.55) and then converted to relate to that of external neat nitromethane (δ 0.0). Chemical shifts upfield from the reference are negative. Typical acquisition parameters are: spectral width 5 000 Hz, flip angle 30°, pulse delays up to 5 s. The INEPT method was also used, with the $^1J(^{15}N,H)$(80—85 Hz) and $^2J(^{15}N,H\text{-}2)$ couplings of N-1. [The latter coupling for compound (**1a**) was determined from the ^1H n.m.r. spectrum and a value of 10.9 Hz was found.] The tautomer ratios were obtained by integration of the ^1H n.m.r. spectra and from the peak heights of the corresponding signals in the ^{13}C n.m.r. spectra, by averaging the values of 5—8 signals.

Synthesis of ^{15}N*-Labelled Compounds.*—Each of the imino ethers (**15**) and (**16**) was treated with a 20% solution of $^{15}NH_4OH$ enriched in ^{15}N to 50% (Isocommerz GmbH, G.D.R.) to give the ^{15}N-labelled amidines (**17**) and (**18**). These were condensed[20] with ethoxymethylenemalonate to give the pyrrolo- (**19**) and azepino-pyrimidine (**20**) derivatives, which afforded, on Vilsmeier-Haack formylation[6], (**1a**) and (**7a**) respectively (Scheme 3).

Ethyl 9-(*Methoxymethylene*)-4-*oxo*-6,7,8,9-*tetrahydro*-4H-*pyrido*[1,2-a]*pyrimidine*-3-*carboxylate* (**10**).—To a cooled, stirred solution of compound (**3**) (5 mmol) in chloroform (25 ml) was added dropwise a solution of diazomethane prepared from *N*-nitrosomethylurea[21] (10 mmol) in diethyl ether (15 ml) at 0 °C, then the mixture was stirred for 2 h at 15 °C. Glacial acetic acid (0.1 ml) was added, the reaction mixture was evaporated to dryness, and the oily residue was treated with a mixture of diethyl ether and methanol. The crystalline *product* was filtered off and washed with diethyl ether; m.p. 168 °C (yield 0.8 g, 61%) (Found: C, 58.9; H, 6.0; N, 10.6. $C_{13}H_{16}N_2O_4$ requires C, 59.1; H, 6.1; N, 10.6%).

Ethyl 9-*Formyl*-1-*methyl*-4-*oxo*-1,6,7,8-*tetrahydro*-4H-*pyrido*[1,2-a]*pyrimidine*-3-*carboxylate* (**13**).—To a cooled solution of 3-ethoxycarbonyl-1-methyl-4-oxo-6,7,8,9-tetrahydro-4*H*-pyrido[1,2-*a*]pyrimidinium methyl sulphate (10 mmol) in dimethylformamide (100 ml), $POCl_3$ (20 mmol) was added dropwise at 15—20 °C, and the mixture was stirred for 1 h at room temperature, then for 2 h at 60 °C. The mixture was then cooled and poured onto crushed ice (40 g), and the pH was adjusted to neutral with aqueous 20% Na_2CO_3. The aqueous mixture was extracted with benzene (2 × 20 ml), the pH of the aqueous phase was adjusted to 8.5, and sodium chloride (6 g) was added. The aqueous phase was stirred with a mixture of chloroform (60 ml) and ethanol (12 ml) for 30 min. The combined organic phases were dried (Na_2SO_4) and evaporated to dryness to obtain *compound* (**13**), which was crystallized from ethyl acetate; m.p. 162—163 °C (yield 1.4 g, 53%) (Found: C, 58.9; H, 6.1; N, 10.5. $C_{13}H_{16}N_2O_2$ requires C, 59.1; H, 6.1; N, 10.6%).

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