STRUCTURE REEXAMINATION OF ALIPHATIC NITRONES AND THEIR DIMERS*

Břetislav PRINC** and Otto EXNER

Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, 166 10 Prague 6

Received January 23th, 1979

The structure of some compounds reported in the literature as nitrones *II* has been reexamined using mainly the ^{1}H-NMR and mass spectroscopies. The nitrone structure has been confirmed for the condensation products of N-alkylhydroxylamines with aldehydes (*IIf*) or ketones (*IIj,l,m*), as well as for the products of alkylation of aldoximes with benzyl chloride (*IId,h*). Other similar alkylation reactions yield generally a mixture of the nitrone and the dimeric oxazolidine derivative (*Va,b,e,*), in addition to the O-alkylated oxime (*VI*). Thé nitrone is assumed to be the primary product in any case, its subsequent dimerization is promoted either by the alkaline medium or by the presence of a phenyl group as in *Vg,k*.

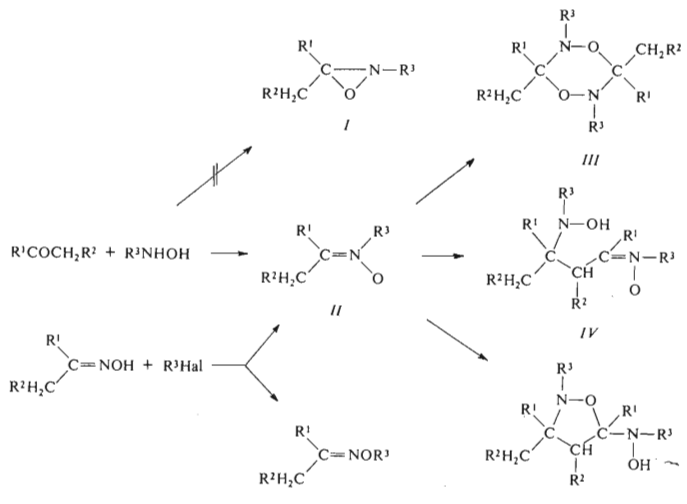
The chemistry of nitrones (N-alkylideneamine N-oxides or N-alkyl oximes) has been developed mainly on aromatic derivatives whose structure is beyond doubt[1,2]. On the contrary, the structure of aliphatic derivatives related to enolizable aldehydes or ketones has been redetermined several times and is not yet proven in all cases. The original oxaziridine formula *I* (disproved ultimately by the synthesis of true oxaziridines[3]) was replaced later by the common nitrone structure *II* but some compounds appeared to be dimeric and were formulated in individual cases as perhydro-1,4,2,5-dioxadiazines[4,5] (*III*), aldol dimers[6,7] (*IV*) or 1,2-oxazolidines[8-10] (*V*). So it happened that one compound, the condensation product of acetone with N-phenylhydroxylamine, was given successively the structures *Ik*, *IIIk*, *IVk*, and *Vk* (ref.[11,4,6,8], respectively) in the course of 60 years; the final proof was furnished by an X-ray analysis[8]. Similarly the product from butanol and N-phenylhydroxylamine was formulated as *IIg* (ref.[12]), *IVg* (ref.[5]), and *Vg* (ref.[9,10]) within 15 years only; the structure *Vg* is now beyond doubt.

The structures of the two N-phenyl derivatives *Vg,k*, firmly established, threw doubts on the nitrone structures *II* of other condensation products of aldehydes and ketones with N-alkylhydroxylamines[13], which were based mostly on elemental analyses and on hydrolytic reactions. In particular it was argued already several

* Part X in the series Oxime Derivatives; Part IX: This Journal *32*, 2096 (1967).

** *Thesis*. Charles University, Prague 1975.

times[5,13–15] that determination of the molecular weight would be necessary in all cases; in addition some liquid products described in the literature could even dimerize during storage and need not be pure individuals. However, the nitrone structure has been unambiguously proven[16,17] for *IIc* and seems to be well evidenced for further more complex derivatives[18–21].



a; $R^1 = R^2 = H$, $R^3 = C_2H_5$
b; $R^1 = R^2 = H$, $R^3 = C_4H_9$
c; $R^1 = R^2 = H$, $R^3 = c\text{-}C_6H_{11}$
d; $R^1 = R^2 = H$, $R^3 = CH_2C_6H_5$
e; $R^1 = H$, $R^2 = R^3 = C_2H_5$
f; $R^1 = H$, $R^2 = C_2H_5$, $R^3 = t\text{-}C_4H_9$
g; $R^1 = H$, $R^2 = C_2H_5$, $R^3 = C_6H_5$
h; $R^1 = H$, $R^2 = C_6H_{13}$, $R^3 = CH_2C_6H_5$
j; $R^1 = CH_3$, $R^2 = H$, $R^3 = CH_3$
k; $R^1 = CH_3$, $R^2 = H$, $R^3 = C_6H_5$
l; $R^1, R^2 = -(CH_2)_3-$, $R^3 = CH_3$
m; $R^1, R^2 = -(CH_2)_4-$, $R^3 = CH_3$

Nitrones can be also prepared by alkylation of aliphatic aldoximes[13], exceptionally also ketoximes. The structure of the products has been dealt with[22–24] only in order to distinguish it from the simultaneously formed O-alkyloximes *VI*. However, the

molecular weight has never been determined, so that the correct structure could be also *V*, or even *IV*, or *III*. The question of the purity is still more important than in the case of the condensation products.

The object of the present reinvestigation are selected products of both the condensation and alkylation reactions, bearing on nitrogen other substituents (R^3 in the formulae *II*–*V*) than phenyl. From the condensation products we were mosty interested in the ketone derivatives *IIj,l,m*, prepared previously by one of us[25], since their nitrone structure was later questioned[13,15]. As representatives of the products from alkylation, we chose the recently described N-alkyl[24] and N-benzyl[22,24] derivatives. Our experimental approach was based mainly on ^{1}H-NMR and mass spectroscopies, the latter method allows to detect even small fractions of dimeric products, on the other hand a partial depolymerization during the evaporation in the ion source cannot be excluded. Our results were consistent with either the structure *II* or *V*; the latter is also closely similar to the products from hydrazobenzene and acetaldehyde investigated by us recently[26,27].

The N-methyl nitrones *IIj,l,m* derived from non-aromatic ketones were prepared as hydrochlorides by the condensation in acidic medium, the bases were liberated by ammonia under anhydrous conditions[25]. The originally proposed[25] structure *II* has been now confirmed both for the hydrochlorides and for freshly prepared bases. In the mass spectrometer the hydrochlorides dissociate completely so that the highest *m/e* found corresponds to the molecular weight of the free monomeric base; the most intensive signal of the spectrum belongs to the $H^{35}Cl$ ion. If the base is freshly prepared, its mass spectrum is very similar to that of the hydrochloride and does not reveal any peak higher than the single m value. However, in an older sample of *IIj* (4 days), the presence of the dimer *Vj* is manifested by a series of less intensive (1 : 20) peaks ending with *m/e* = 174. The structure of this dimer (*Vj*) was deduced from a comparison of the upper part of the mass spectrum with that of *Ve* and of other 1,2-oxazolidines. In order to obtain usable ^{1}H-NMR spectra of the hydrochlorides *IIj,l,m* care must be taken to prevent hydrolysis; even so the signals of N-methylhydroxylamine hydrochloride (δ 2·73) and of the pertinent ketone are always apparent. With this provision the spectra of the hydrochlorides and free bases are very similar. That of *IIj* is the simplest one, consisting of three signals: two sterically non-equivalent C-methyl groups (quadruplets) and a N-methyl group (ill resolved).The latter appears at the same position (δ 3·82) even in the spectra of *III,m*, the remaining part of which is more complex. The IR spectrum of *IIj* does not show any O–H band. The low molar refraction[25] of *IIj,l,m* which casted doubts on their nitrone structure, can be understood[28] referring to isomeric oxaziridines *I*: the increment for the atoms N+O has been found[18,25] between 4·30 and 5·40 cm^3 in nitrones and 4·32–4·41 cm^3 in oxaziridines[18]. The previous value of 6·31 cm^3 for nitrones[29] is clearly in error.

As an example of nitrone derived from an aldehyde we prepared N-butylidene--2-methyl-2-aminopropane N-oxide (*IIf*) by the condensation reaction. In order to search for the presence of dimers, the crude oily product was investigated without purification. The structure *IIf* follows from the ^{1}H-NMR spectrum (signal of the methine proton at δ 6·80 t) and from the mass spectrum (molecular ion $C_8H_{17}NO$). Dimeric molecules were not detected.

We conclude that condensation of N-alkylhydroxylamines with aldehydes or ketones yields actually nitrones *II* which are as a rule sufficiently stable to allow isolation. Under certain conditions, however, particularly in basic medium they can undergo slow dimerization to derivatives of 1,2-oxazolidine *V*. An exception are N-phenyl derivatives which dimerize so fast that true monomeric aliphatic N-phenyl nitrones are not known[7,9,10]. The structure of other nitrones described in the literature[13–21] may be relied upon and the claim of Todd and coworkers[14] that no monomeric aliphatic nitrones were described before 1959 is not substantiated. First such compounds seem to be N-methyl nitrones *IIj,l,m* prepared by us[25]; their originally suggested structure has now been confirmed. The conditions of preparation, in an acidic medium[25], are particularly suitable to avoid dimerization. The configuration of aliphatic aldonitrones has been little investigated, it is believed[16,30] to be *E* like that of aromatic aldonitrones[1].

The alkylation of oximes gives several products which are often difficult to isolate due to their instability. From this point of view the benzylation is most favourable since it yields mostly crystalline and stable N-benzyl nitrones. We were able to reproduce the synthesis of N-octylidenebenzylamine-N-oxide[22] (*IIh*) and N-ethylidenebenzylamine N-oxide[24] (*IId*) and to confirm their supposed structures. The latter is produced in addition to a comparable amount of O-benzylacetaldoxime[24] (*VId*), in the case of the former the minor by-products were not searched for[22]. The monomeric structures follow from the mass spectra, ^{1}H-NMR spectra (the methine proton at δ 6·57 or 6·75, respectively) and IR spectra (absence of any O–H band). No dimeric material was detected even in older samples (after 1 month). From the previous arguments in favour of the nitrone structure of *IIh* and similar N-benzyl derivatives, the high dipole moment[22] is significant even for distinguishing from *III* and *V*.

The reactions of acetaldoxime with ethyl bromide or butyl bromide, and of butyraldoxime with ethyl bromide were reproduced exactly according to the literature[24] and all three gave concordant results. In all the cases the reaction was more complex and the product separation less clean than described[24]. The crude O-alkyloxime fraction, separated by extraction, contained also some nitrone and unreacted oxime (GLC), but it was not further investigated (see[30]). The nitrone fraction consisted of the true nitrone (*IIa,b,e*, respectively) and of the corresponding 1,2-oxazolidine *Va,b,e* in addition to further decomposition products; their ratio changed rapidly with time. The composition of either fractions depends sensitively on the reaction conditions, mainly on the excess of sodium methoxide, and is not exactly reproducible.

The nitrone fraction cannot be purified by distillation since under the conditions described[24] extensive dimerization and decomposition occur. Even the gas–liquid chromatography is not reliable, revealing more compounds than originally present. In one case we isolated the pure nitrone *IIa* by chromatography on silica gel but it dimerized slightly before the mass spectrum was measured, or in the spectrometer. The ^{1}H-NMR spectrum was easily assigned (CH proton δ 6·86) and did not reveal any dimer. We believe that all the liquid products of the alkylation reaction[24] are mainly nitrones *II* contamined with more or less oxazolidine dimer *V*, in particular after a longer storage. This composition agrees also with the cryoscopic molecular weight[24], approximately by 5% higher than calculated for the monomer.

In one case we modified intentionally the reaction conditions by raising the amount of sodium methoxide and obtained pure dimer) 2,4-diethyl-3-propyl-5(N-hydroxy--N-ethylamino)-1,2-oxazolidine (*Ve*) in a 20% yield as a crystalline compound, stable for many days. Its structure follows from the ^{1}H-NMR spectrum revealing the methine proton in the position 5 (δ 4·40) but no methine proton between 6·6 – 7·9δ; this eliminates the possibility *IVb*. The OH proton is perceptible in the ^{1}H-NMR (δ 9·14) as well as in the IR spectrum (3598 cm^{-1} free, 3438 cm^{-1} intramolecularly bonded), the hydrogen bond is also compatible with the assigned structure. The mass spectrum revealed the molecular ion *m/e* 230 and offered the possibility to study once the fragmentation on a pure compound of type *V*. The salient feature is the intensive peak $(mH)^+$ corresponding to the protonated nitrone and few peaks of low abundance between m + 1 and 2 m (m stands for the molecular weight of the monomeric nitrone). Hence the main fragmentation is the reverse of dimerization accompanied with the transfer of one hydrogen. It is promoted by the intramolecular hydrogen bond and can proceed either in two steps or in one step, corresponding to the two possible mechanisms of dimerization. The UV spectrum of *Vb* in ethanol is similar to that observed[7] for a polycyclic dimer of type *V* (231 and 236 nm, respectively) and attributed to partial rearrangement to the isomer *IV* in protic solvents[7]. Such an equilibrium is, however, difficult to prove by other methods.

Concerning the alkylation reaction of oximes we can state that it proceeds in a more complex way than the condensation of N-alkylhydroxylamines but yields essentially the same products in addition to O-alkyl oxime *VI*. For the preparation of nitrones the alkylation is clearly less convenient, exceptionally it can be used to prepare 1,2-oxazolidines. Nitrone *II* seems to be the primary product of either reaction. Its dimerization to *V* is easier with the alkylation due to the alkaline medium, it can proceed either by a one-step 3 + 2 dipolar addition[8,10] or by a two-step mechanism through the intermediate *IV*. Any stereoisomeric forms of *V* have not been isolated. The existence of the two remaining structures, *III* and *IV*, has not been in fact safely proven: *IV* may exist in some cases in equilibrium with *V* under special conditions[7], *III* was mostly evidenced only by the absence of free hydroxyl in the IR spectrum[5]. The less are proven other, a priori improbable isomeric formulae[31].

EXPERIMENTAL

The melting points were determined on a Kofler block and are not corrected. The purity of the products was checked by TLC on silica gel (detection by iodine vapour or UV light) or by GLC. The IR absorption spectra were recorded on a Zeiss UR-20 instrument (wavenumbers in cm^{-1}), the UV spectra on a Jasco spectrometer model ORD/UV-5 (concentration 10^{-3}—10^{-4}M), the ^{1}H-NMR spectra on a Varian HA-100 spectrometer at 100 MHz (30°C, concentration about 0·1M, tetramethylsilane as internal reference, shifts given in the δ-scale), the mass spectra on a JEOL-D-100 spectrometer (75 eV, temperature of the ionization chamber 90°C).

N-Isopropylidenemethylamine N-oxide (*IIj*)

Hydrochloride[25], m.p. 124°C (literature[25] m.p. 126°C corr.); ^{1}H-NMR spectrum in $CDCl_3$ + + CD_3SOCD_3 (2·34 (q, J = 1·3 Hz, 3 H, C—CH_3, probably *cis* to OH), 2·46 (q, J = 0·9 Hz, 3 H, C—CH_3, probably *cis* to CH_3), 3·82 (splitting not well developed, 3 H, N—CH_3), in addition 2·04 (s, CH_3COCH_3), 2·73 (s, $CH_3NHOH.HCl$); mass spectrum: 87 (100), 71 (25), 70 (66), 69 (15), 57 (25), 56 (90), 55 (37), 47 (78), 46 (86), 45 (27), 43 (30), 42 (50), 41 (93), 39 (43), 38 (60, $H^{37}Cl$), 36 (183, $H^{35}Cl$).

Base, freshly prepared[25], not distilled: IR spectrum in chloroform: 1226 (N—O), 1380 (CH_3), 1603 (C=N, 1719, 2972 (CH_3); ^{1}H-NMR spectrum in $CDCl_3$: 2·11 (q, J = 0·8 Hz, 3 H, C—CH_3, 2·15 (q, J = 0·7 Hz, 3 H, C—CH_3, 3·67 (not well resolved multiplet, 3 H, N—CH_3); mass spectrum: 174 (4·2), 128 (5·6), 112 (3), 88 (45), 87 (73), 78 (25), 73 (20), 71 (22), 70 (39), 58 (34), 57 (17), 56 (79), 55 (25), 47 (65), 46 (81), 45 (34), 43 (100), 42 (43), 41 (69), exact *m/e* values of important fragments: 88·0759 — $C_4H_{10}NO$, 87·0685 — C_4H_9NO, 70·0660 — C_4H_8N.

N-Cyclopentylidenemethylamine N-Oxide (*IIl*)

Hydrochloride[25], m.p. 135°C (literature[25] m.p. 137°C corr.); ^{1}H-NMR spectrum in $CDCl_3$ + + CD_3SOCD_3: 1·82—2·07 (m, 4 H, 3,4-CH_2), 2·76—3·01 (m, 4 H, 2,5-CH_2), 3·82 (~s, 3 H, CH_3), in addition 2·74 (s, $CH_3NHOH.HCl$).

Base, freshly prepared[25], not distilled; mass spectrum 114 (5·7), 113 (44), 112 (46), 97 (12), 96 (9·3), 95 (13), 84 (40), 78 (35), 68 (53), 67 (50), 56 (27), 55 (100), 47 (33), 46 (41), 45 (22), 42 (28), 41 (65), 39 (49), 32 (17), 31 (22).

N-Cyclohexylidenemethylamine N-Oxide (*IIm*)

Hydrochloride[25] m.p. 138°C in agreement with the literature[25] (corr.), IR spectrum in Nujol: 784, 874, 915, 1000, 1116, 1156, 1186, 1267, 1341, 1417, 1520, 1688, 1735, 2973. ^{1}H-NMR spectrum in $CDCl_3$ + CD_3SOCD_3: 1·50—1·87 (m, 6 H, 3,4,5-CH_2), 2·12—2·31 (m, 4 H, 2,6-CH_2), 3·83 (s, 3 H, CH_3), in addition 2·73 (s, CH_3NHOH—HCl); mass spectrum: 127 (4·2), 126 (40), 111 (28), 110 (30), 99 (24), 98 (51), 83 (22), 82 (38), 81 (54), 69 (19), 68 (100), 67 (30), 57 (19), 56 (19), 55 (84), 54 (24), 53 (19), 42 (58), 41 (65), 39 (19), 38 (31, $H^{37}Cl$), 36 (100, $H^{35}Cl$).

N-Butylidene-2-methyl-2-aminopropane N-Oxide (*IIf*)

2-Hydroxylamino-2-methylpropane[32] (0·80 g) and butanal (1·1 g, 150%) were left one hour at the room temperature, the excess butanol and water were removed *in vacuo* and the resulting oil investigated immediately; IR spectrum in chloroform: 1206, 1250 (N—O), 1588 (C=N) 2880, 2980; ^{1}H-NMR spectrum in $CDCl_3$: 0·98 (t, J = 7 Hz, 3 H, CH_3—CH_2), 1·40—1·70, (m, 11 H), 2·47 (q, J = 7 Hz, 2 H, CH_2—CH_3), 6·80 (t, J = 6 Hz, 1 H, CH); mass spectrum:

143 (6·5), 112 (7), 72 (4·5), 57 (100), 43 (11), important fragments: 143·1314 — $C_8H_{17}NO$, 112·1112 — $C_7H_{14}N$, 72·0451 — C_3H_6NO.

N-Octylidenebenzylamine N-Oxide[22] (*IIh*)

M.p. 87°C (literature[22] m.p. 88°C); for $C_{15}H_{23}NO$ (233·4) calculated: 77·21% C, 9·93% H, 6·00% N; found: 77·46% C, 9·95% H, 6·19% N. IR spectrum in KBr: 1 296, 1 430, 1 500, 1 600; ^{1}H-NMR spectrum in $CDCl_3$: 0·80 (t, J = 6·5 Hz, 3 H; C$\underline{H}_3$—CH_2), 1·10—1·50 (m, 10 H, CH_2), 2·40 (q, J = 6·5 Hz, 2 H, C$\underline{H}_2$—CH_3), 4·80 (s, 2 H, CH_2—C_6H_5), 6·57 (t, J = 6·5 Hz, 1 H, CH), 7·25—7·40 (m, 5 H, C_6H_5); mass spectrum 233 (3), 217 (1·4), 216 (2·2), 162 (2·6), 149 (11), 146 (9·3), 134 (6), 133 (53), 132 (15), 92 (11), 91 (100), 55 (6·2), 44 (15), 43 (7·4), 41 (12), important fragments: 216·1753 — $C_{15}H_{22}N$, 162·0917 — $C_{10}H_{12}NO$, 149·0835 — $C_9H_{11}NO$.

N-Ethylidenebenzylamine N-Oxide (*IId*)

Was prepared according to the literature[24]. Without cooling, the temperature reached the boiling point of methanol. After stirring 4 h and standing overnight the reaction mixture was diluted with water and extracted with ether (4×), yield 20% of crude *VId*, n_D^{20} 1·5070 (literature[24] gives n_D^{20} 1·5172 for the pure compound). A subsequent extraction of the water layer with chloroform (5×) yielded 15% of *IId*, m.p. 78°C (cyclohexane), in agreement with the literature[24]; IR spectrum in Nujol: 1 244, 1 308, 1 500, 1 586, 1 605, 2 985; ^{1}H-NMR spectrum in $CDCl_3$: 1·96 (d, J = 6 Hz, 3 H, CH_3), 4·85 (s, 2 H, CH_2), 6·75 (q, J = 6 Hz, 1 H, CH), 7·28—7·45 (m, 5 H, C_6H_5); mass spectrum: 149 (8·3), 133 (1·1), 119 (4·2), 91 (100), 77 (1·3), 65 (8·6).

N-Ethylideneethylamine N-Oxide (*IIa*) and Its Dimer (*Va*)

The ethylation of acetaldoxime was carried out in the same way as described in the preceding experiment, yield 18% of crude *VIa*, n_D^{20} 1·3985, 16% of crude *IIa* + *Va*, n_D^{20} 1·4709; mass spectrum of the latter fraction 174 (6·2), 114 (37), 98 (11), 88 (100), 87 (30), 72 (20), 71 (45), 70 (21), 60 (15), 59 (20), 56 (26), 46 (20), 44 (18), 42 (52), 41 (35). The crude fraction was purified by column chromatography on silica gel, carried out as quickly as possible; pure *IIa* was eluted with methanol and the spectra were measured immediately. IR spectrum in chloroform: 1 269, 1 612, 3 350, 3 570, 3 675; ^{1}H-NMR spectrum in $CDCl_3$: 1·46 (t, J = 7 Hz, 3 H, C$\underline{H}_3$—CH_2), 2·02 (d, J = 6 Hz, 3 H, C$\underline{H}_3$—CH), 3·85 (q, J = 7 Hz, 2 H, CH_2), 6·86 (q, J = 6 Hz, 1 H, CH); mass spectrum: 174 (1·4), 114 (10), 98 (4·2), 88 (32), 87 (100), 72 (27), 71 (8·3), 70 (19), 59 (47), 56 (26), 55 (16), 44 (24), 42 (79), 41 (84), important fragments: 174·1373 — $C_8H_{18}N_2O_2$, 114·0914 — $C_6H_{12}NO$, 87·0677 — C_4H_9NO. The ratio of *IIa* and *Va* in the crude fraction may be estimated to 5 : 1.

N-Ethylidenebutylamine N-Oxide (*IIb*) and Its Dimer (*Vb*)

Were prepared[24] as above, yield 20% of crude *VIb*, n_D^{20} 1·4010 literature[24] n_D^{20} 1·4120) and 16% of crude *IIb* + *Vb*, n_D^{20} 1·4550 (literature[24] n_D^{20} 1·4598). Mass spectrum of the latter fraction: 230 (1), 142 (4·7), 116 (9·2), 115 (6·3), 100 (41), 85 (23), 83 (35), 60 (16), 59 (15), 57 (23), 56 (100), 55 (23), 46 (20), 42 (26), 41 (61).

2,4-Diethyl-3-propyl-5-(N-hydroxy-N-ethylamino)-1,2-oxazolidine (*Ve*)

The ethylation of butanaldoxime described in the literature[24] was modified by raising the amount of sodium methoxide to 1·1 mol, yield 14% of crude *VIe*, n_D^{20} 1·4220 (literature[24] n_D^{20} 1·4118

for pure *VIe*) and 25% of crude mixture *IIe* + *Ve*, n_D^{20} 1·4530 (literature n_D^{20} 1·4613). By cooling either fraction deposited crystals of *Ve* which were combined, total yield 20%, m.p. 102°C (ethyl acetate); for $C_{12}H_{26}N_2O_2$ (230·4) calculated: 62·57% C, 11·38% H, 12·16% N; found: 62·83% C, 11·43% H, 11·76% N. IR spectrum in chloroform (*c.* 10^{-1}M): 1 245, 1 383. 1 468, 1 606, 2 882, 2 946, 2 962, 3 440, 3 592 (O—H), *c.* 3 . 10^{-3}M: 3 439, 3 590, UV spectrum in ethanol: λ 231 nm, log ε 3·20; ^{1}H-NMR spectrum in C_5D_5N: 0·72 (t, J = 7 Hz, 3 H, C—CH_2—$C\underline{H}_3$), 0·76 (t, J = 7 Hz, 3 H, C—CH_2—$C\underline{H}_3$), 1·09 (t, J = 7 Hz, 3 H, N—CH_2—$C\underline{H}_3$), 1·11 (t, J = 7 Hz, 3 H, N—CH_2—$C\underline{H}_3$), 0·97—1·45 (m, 6 H, the three CH_2—C groups), 2·48—3·25 (m, 6 H, 3-CH + 4-CH + + CH_2N), 4·40 (d, J = 5 Hz, 1 H, 5-CH), 9·14 (s, 1 H, OH), the assignment was proven by decoupling experiments. Mass spectrum: 230 (2·3), 170 (3·5), 154 (3·5), 116 (100), 115 (13), 100 (28), 98 (28), 84 (18), 71 (28), 69 (16), 57 (21), 56 (46), 55 (32), 43 (38), 42 (25), 41 (45), important fragments: 116·1073 — $C_6H_{14}NO$.

We are much indebted to Dr V. Hanuš, J. Heyrovský Institute of Physical Chemistry and Electrochemistry, for measurement and interpretation of mass spectra. Thanks are also due to Dr M. Buděšínský and Dr M. Masojídková for measuring the ^{1}H-NMR *spectra, Mr P. Formánek for the* IR *and* UV *spectra, and Mr J. Krahulec for GLC analyses; elemental analyses were carried out in the Analytical Department of this Institute (head Dr J. Horáček).*

REFERENCES

1. Hamer J., Macaluso A.: Chem. Rev. *64*, 473 (1964).
2. Delpierre G. R., Lamchen M.: Quart. Rev., Chem. Soc. *19*, 329 (1965).
3. Emmons W. D.: J. Amer. Chem. Soc. *79*, 5739 (1957).
4. Scheiber J., Wolf H.: Justus Liebigs Ann. Chem. *357*, 25 (1907).
5. Thesing J., Mayer H.: Chem. Ber. *89*, 2159 (1956).
6. Banfield F. H., Kenyon J.: J. Chem. Soc. *1926*, 1612.
7. Brown R. F. C., Clark V. M., Sutherland I. O., Todd A.: J. Chem. Soc. *1959*, 2109.
8. Foster R., Iball J., Nash R.: Chem. Commun. *1968*, 1414; J. Chem. Soc., Perkin Trans. 2 *1974*, 1210.
9. Baker A. D., Baldwin J. E., Kelly D. P., DeBernardis J.: Chem. Commun. *1969*, 344.
10. Kliegel W.: Tetrahedron Lett. *1969*, 2627.
11. Bamberger E., Rudolf L.: Ber. Deut. Chem. Ges. *40*, 2236 (1907).
12. Utzinger G. E., Regenass F. A.: Helv. Chim. Acta *37*, 1892 (1954).
13. Rundel W. in the book: *Houben-Weyl: Methoden der Organischen Chemie* (E. Müller, Ed.), Vol. X/4, p. 309. Thieme, Stuttgart 1968.
14. Bonnett R., Brown R. F. C., Clark V. M., Sutherland I. O., Todd A.: J. Chem. Soc. *1959*, 2094.
15. Smith P. A. S.: *The Chemistry of Open-Chain Organic Nitrogen Compounds*, Vol. II, p. 30. Benjamin, New York 1966.
16. Koyano K., Suzuki H.: Tetrahedron Lett. *1968*, 1859.
17. Masui M., Yijima C.: Chem. Pharm. Bull. *17*, 1517 (1969).
18. Krimm H.: Chem. Ber. *91*, 1057 (1958).
19. LeBel N. A., Slusarczuk G. M. J., Spurlock L. A.: J. Amer. Chem. Soc. *84*, 4360 (1962).
20. Baldwin J. E., Bhatnagar A. K., Choi S. C., Shortridge T. J.: J. Amer. Chem. Soc. *93*, 4082 (1971).
21. Kempe U. M., Das Gupta T. K., Blatt K., Gygax P., Felix D., Eschenmoser A.: Helv. Chim. Acta *55*, 2187 (1972).
22. Nerdel F., Huldschinsky I.: Chem. Ber. *86*, 1005 (1953).

23. Exner O.: This Journal *20*, 202 (1955).
24. Kamai G. Kh., Nikolaeva A. D., Perekhodko V. S.: Zh. Org. Khim. *4*, 567 (1968).
25. Exner O.: This Journal *16*, 258 (1951).
26. Hrazdira M.: *Thesis*. Institute of Chemical Technology, Pardubice 1969.
27. Hanuš V., Hrazdira M., Exner O.: This Journal, in press.
28. Exner O.: *Thesis*. Czechoslovak Academy of Sciences, Prague 1960.
29. Auwers K. v., Ottens Ber.: B. Deut. Chem. Ges. *57*, 446 (1924).
30. Kamai G. Kh., Nikolaeva A. D., Perekhodko V. S., Zykova T. V.: Zh. Org. Khim. *6*, 394 (1970).
31. Alford E. J., Hall J. A., Rogers M. A. T.: J. Chem. Soc. (C) *1966*, 1103.
32. Exner O., Kakáč B.: This Journal *28*, 1656 (1963).

Translated by the author (O. E.).