^1H AND ^{13}C NMR SPECTRA OF C- AND N-SUBSTITUTED OXAZOLIDINES

A. V. Germash, V. V. Zorin,
S. S. Zlot-skii, D. L. Rakhmankulov,
and A. B. Terent'ev

UDC 547.787.1:543.422.25

An interrelationship between the structure of oxazolidines and the character of their ^1H and ^{13}C NMR spectra was ascertained, and the most characteristic signals of the individual groups, which make it possible to establish the structure of the investigated compounds, were found.

The radical addition of ethylene to 1,3-diheterocyclopentenes that contain two identical (oxygen) or different (oxygen and nitrogen) heteroatoms and telomerization lead to the formation of several types of telomers with rather complex structures. To prove the structures of these compounds we have successfully used ^1H and ^{13}C NMR spectroscopy [1]. The use of propylene [2] and isobutylene [3] as monomers in the telomerization leads to branching in the alkyl substituent.

The establishment of the structures is a more complex problem when the heteroring includes different heteroatoms, as in the case of 1,3-oxazolidines. 2-Hexyl-N-butyloxazolidine and N-butyl-N-octylformamide are formed under the conditions of radical addition of N-butyl-1,3-oxazolidine to 1-hexene [4]. In the case of telomerization the composition of the reaction mixture and the structure of the telomers are complicated substantially due to both the formation of isomeric homologs and possible intramolecular transformations of the intermediate radicals.

In the present research, on the basis of a series of specially synthesized compounds, we ascertained the effect of changes in the structure of substituted oxazolidines on the peculiarities of their ^1H and ^{13}C NMR spectra and the most characteristic signals of individual groups, which make it possible to assign a given compound to a certain homolytic series. The investigated compounds were characterized by the results of elementary analysis and their physicochemical constants (Table 1). The purity of the samples was monitored by gas–liquid chromatography (GLC).

A singlet of an NCH_2O group with a chemical shift of 4.05 ppm is characteristic for the PMR spectrum of N-butyl-1,3-oxazolidine, which does not have a substituent in the 2 position (Table 1). The introduction of substituent R in the 2 position shifts the C–H signal somewhat to strong field – a triplet (broken down) appears at 3.8-3.9 ppm.

A rigid ring structure leads to nonequivalence of the hydrogen atoms of the $O-CH_2CH_2N$ methylene groups, as a result of which the spectrum of 2-substituted oxazolidines (in which yet another chiral center develops) is a complex system of the ABCD type that comprises a multiplet, which, nevertheless, is extremely characteristic for compounds of this type.

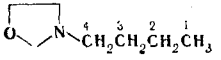
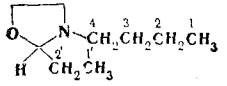
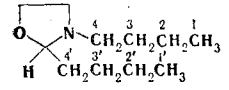
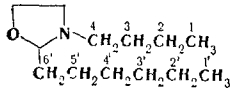
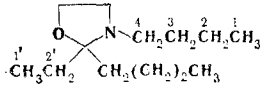
The ring NCH_2 group of N-butyl-1,3-oxazolidine is represented by a triplet with a chemical shift of 2.71 ppm, while a triplet shifted to stronger field (2.39 ppm) corresponds to the CH_2N group in the side chain. The signal of the ring CH_2O group is shifted somewhat to stronger field (triplet at 3.59 ppm) as compared with the CH_2O group in linear structures [2].

In the case of 2-alkyl-1,3-oxazolidines the triplets of the OCH_2 and NCH_2 groups degenerate to multiplets, among which one can isolate the signals of CH_2N groups, the centers of the multiplets of which are found at 2.3-2.5 ppm. In this case also the multiplet centered at stronger field was assigned to a CH_2N group in the side chain. The signal of the CH_2O group evidently consists of two separate multiplets with a common center at 3.4-3.6 ppm; one

Ufa Petroleum Institute 450062. A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow 117813. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 900-903, July, 1982. Original article submitted June 6, 1981.

 0009-3122/82/1807-0680$07.50

TABLE 1. Physicochemical and Spectral (^1H and ^{13}C NMR) Characteristics of 1,3-Oxazolidines

No.	Compound	bp, °C (hPa)	n_D^{20}	d_4^{20}	Type of spectrum	NCHO	CH_2O, CH_2N (ring)	Side chains		
								$-CH_2N<$	$-CH_3$	$-CH_2-$
1		44—45 (8)[a]		0,9025	^1H ^{13}C	4,05 (s) 87,0	3,59 t, 2,71 63,8, 54,1	2,39 (t) 52,7	0,89 m 14,2	1,6—1,24 m 32,2, 20,9
2		55 (9)[b]	1,4370	0,8846	^1H ^{13}C	3,81[c] 97,6	3,44[c], 2,36[c] 64,7, 53,2	2,31[c] 52,7	0,87 t, 0,84 t 8,8, 14,2	1,5—1,25 m 27,4, 31,8, 20,9
3		77—80 (9)[d]	1,4410	0,8779	^1H ^{13}C	3,91[c] 96,8	3,53[c], 2,53[c] 64,4, 53,2	2,42[c] 52,4	0,89 t, 0,87 t 14,2	1,5—1,22 m 34,4, 31,8, 27,4, 23,2, 20,8
4		87/4	1,4491	0,8708	^1H ^{13}C	3,96[c] 96,9	3,58, 2,57 64,8, 53,1	2,47 52,3 (4)	0,91 t, 0,95 t 14 (1,1)	1,56—1,16 m 34,5 (6), 32,4 (3), 31,7 (3), 29,8 (4), 25,0 (5), 22,9 (2), 20,6 (2)
5		—	—	—	^1H	—	3,73[c], 2,93[c]	2,42[c] (4)	0,87 t, 0,87 t	1,47—1,03, 3,44 (2′)

[a]Found: C 65.1; H 12.0; N 10.8%. $C_7H_{25}NO$. Calculated: C 65.2; H 11.9; N 10.7%. [b]Found: C 68.8; H 12.1; N 8.9%. $C_9H_{19}NO$. Calculated: C 68.8; H 12.0; N 8.9%. [c]The complex ABCD system is denoted. [d]Found: C 71.3; H 12.4; N 7.6%. $C_{11}H_{23}NO$. Calculated: C 70.9; H 12.5; N 7.7%.

of the multiplets (the one that does not overlap with the other signals and has an intensity of 1H) occupies the region centered at 3.2 ppm, while the second part is overlapped by the signals of the NCHO group. The appearance of two substituents in the 2 position in oxazolidine does not introduce substantial changes in the structure and the chemical shifts of the signals. A signal of the methylene group in CH_3CH_2—C at rather weak field for groups of this sort — 3.44 ppm — appears in the spectrum of compound No. 5 (Table 1).

The ^{13}C NMR spectra give clearer and more easily interpretable information regarding the structures of substituted oxazolidines (Table 1). The signal of the carbon in the $N^{13}CO$ group is, of course, one of the most characteristic signals here. This signal is found in the most populated part of the spectrum (80-100 ppm), and its chemical shift changes substantially as the hydrogen atoms are replaced by alkyl groups. Thus the chemical shift of the signal of the $N^{13}CH_2O$ group (87.0 ppm) is almost 10 units smaller than in the case of the NCH(R)O group (R = alkyl) (96.8-97.6 ppm). A similar but less clearly expressed regularity was observed for branched monocarboxylic acids and their derivatives that contain a $>C^{13}COOH$ grouping [5]. An increase in the number of substituents attached to the α-carbon atom led to a shift of the ^{13}COO signal to weak field. The signal of the $^{13}CH_2O$ group (in the ring) (63.8-64.7 ppm) is found at weaker field (by 2-3 ppm) than in linear compounds. The same difference also occurs in the chemical shifts of the signals of $^{13}CH_2N$ groups in the ring and in the side chain — two well-resolved signals are observed in the spectrum. These three groups of signals, which have characteristic chemical shifts in the region that is not occupied by the signals of other groups (particularly $^{13}CH_2$), make it possible to sufficiently reliably establish the structures of the investigated oxazolidines and the number and position of the substituents.

Among the remaining signals, the signals of the $^{13}CH_3$ group, the chemical shift of which changes substantially as a function of the length of the substituent chain, are the most informative. In the case of the long-chain butyl radical the $^{13}CH_3$ signal is found in the usual region (~14 ppm), regardless of the position of the substituents (C_4H_9—C or C_4H_9N). At the same time, in the case of the CH_2CH_3 group this signal is shifted substantially to strong field (8.8 ppm) to a region that is free of groups of other signals. In analogy with the available data [5], it might be expected that in the case of 2,2-alkylethyl-substituted oxazolidines this signal is shifted to even stronger field. The assignment of the signals of the $^{13}CH_2$ groups was made in analogy with the data for the structurally corresponding hydrocarbons.

EXPERIMENTAL

The ^1H NMR spectra of 30% solutions of the compounds in CCl_4 were recorded with a Perkin-Elmer P-20 spectrometer with tetramethylsilane (TMS) as the external standard. The ^{13}C NMR spectra of solutions of the compounds in benzene were recorded with a Bruker Physics HX-90 spectrometer (22.635 MHz) with suppression of coupling with the protons. All of the chemical shifts were reckoned from TMS.

The synthesis of 2-alkyl-substituted oxazolidines was realized by the method in [6] by the reaction of aldehydes (ketones) with alkylaminoethanols. The physicochemical characteristics of the compounds obtained are presented in Table 1.

LITERATURE CITED

1. V. P. Nayanov, V. V. Zorin, S. S. Zlot-skii, A. B. Terent'ev, and D. L. Rakhmankulov, Zh. Prikl. Khim., 50, 1418 (1977).
2. O. G. Safiev, Master's Dissertation, Ufa (1980).
3. O. G. Safiev, U. B. Imashev, and A. B. Terent'ev, Izv. Akad. Nauk SSSR, Ser. Khim., No. 7, 1590 (1980).
4. A. A. Lapshova, V. V. Zorin, S. S. Zlot-skii, R. A. Karakhanov, and D. L. Rakhmankulov, Zh. Org. Khim., 16, 2533 (1980).
5. A. B. Terent'ev, V. Y. Dostovalova, and R. Kh. Freidlina, Org. Magn. Reson., 9, 301 (1977).
6. A. A. Lapshova, V. V. Zorin, E. A. Kantor, S. S. Zlot-skii, R. A. Karakhanov, and D. L. Rakhmankulov, Zh. Prikl. Khim., 53, 704 (1980).