CONCLUSIONS

1. The formation of three isomeric tetra-substituted disiloxydiphenyls in the dimerization—rearrangement of 2-trimethylsilyl-4-tert-butyl-6-triethylsilylphenoxyl is attributed to presence of two reaction sites which determine the ability of both the trimethylsilyl and triethylsilyl groups to undergo dimerization with migration.

2. The steric interaction of the ortho-organosilyl substituents in 2-trimethylsilyl-4-tert-butyl-6-triethylsilylphenoxyl alters the relative migratory capacity of these substituents relative to that in 2-trimethylsilyl- and 2-triethylsilyl-4,6-di-tert-butylphenoxyls.

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INVESTIGATION OF THE STRUCTURE OF THE PRODUCTS FROM TELOMERIZATION OF ETHYLENE WITH 1,3-DIHETEROCYCLOPENTANES BY THE ^{13}C NMR METHOD

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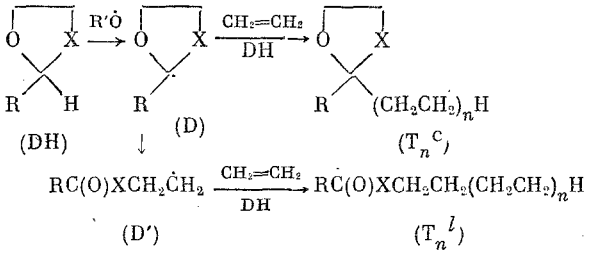
Investigation of radical isomerization and addition in 1,3-diheterocyclopentanes $\overset{1}{X}CH_2CH_2O\overset{1}{C}HR$ (DH) (X = O, NC_4H_9, S; R = H, CH_3) in the presence of tert-butyl peroxide (TBP) (130-150°C) showed that the R'O· radicals mainly abstract a hydrogen atom from the —XCHRO— group, forming the $\overset{1}{X}CH_2CH_2O\overset{1}{C}R$ radicals [1-3]. Our investigation into the radical telomerization of ethylene with 1,3-diheterocyclopentanes (X = O, R = H, CH_3; X = NC_4H_9, R = H and X = S, R = CH_3) [3-5] showed that telomerization takes place with the formation of telomers having cyclic (T_n^c) and linear (T_n^l) structures:



Here, as seen from the data in Table 1, the ratio of the yields of the telomers T_n^c and T_n^l depends significantly on the structure of the telogen. It seemed of interest to compare the effect of the nature of the heteroatoms and the presence or absence of the substitutent R in the OCHRX group on the reaction path and also to determine the relationships governing the variation in the character of the ^{13}C NMR spectra (given for the first time in the present work) in relation to the structure of the telomers T_n^c and T_n^l (Tables 2-4).

In the case of unsubstituted 1,3-dioxolane X = O, R = H the ratio of telomers ΣT_n^c: $\Sigma T_n^l \approx 1:1$, whereas the ratio for 2-methyl-1,3-dioxolane (X = O, R = CH_3) changes significantly in favor of the telomers with cyclic structures (Table 1). Such a difference in the

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TABLE 1. Telomerization of Ethylene (M) with 1,3-Diheterocyclopentanes (S), T = 140-150°C, 3 mole % TBP

Serial No.	$CH_2OCHRXCH_2$ X	R	K_M^*, %	M/S average	Product yield, mole % T_1^C/T_1^l	T_2^C/T_2^l	T_3^C/T_3^l	$\Sigma T_{n\geq 3}^C/\Sigma T_{n\geq 3}^l$	$\Sigma T_n^C/\Sigma T_n^l$
1	O	H	28,2	0,30	19/18	10,5/10,5	8/9,5	11,5/13	49/51
2	O	CH_3	28	0,36	40,5/3	20,5/2	11/1	20/2	92/8
3	NC_4H_9	H	31,3	0,31	–/64	–/21	–/11	–/4	–/100
4	S	CH_3	70	0,32	65/16	12/2,5	2/1	1/0,5	80/20

*K_M is the degree of conversion of the monomer.

TABLE 2. Data from the ^{13}C NMR Spectra of 1, 3-Dioxolanes (δ, ppm)

Serial No.	Compound	OCO	OCH_2	$\underline{CH_3}CO$	CH_2
1		95,0	64,5		
2		101,6	64,9	20,3	
3		108,4	64,7	25,7	
4			65,7		27,5

ratio of the rates of opening of the ring may be due to a difference in the stability of the unsubstituted (secondary, R = H) and substituted (tertiary, R = CH_3) cyclic radicals (D). The appearance of the substituent stabilizes the radical (D), increasing its average lifetime, and this changes the ratio of the monomolecular (isomerization) and bimolecular (addition) reactions in favor of the latter.

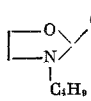
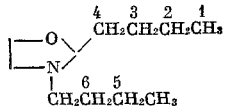
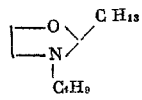
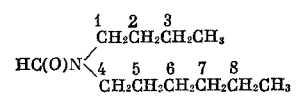
In the case of N-butyl-1,3-oxazolidine (X = NBu, R = H) under analogous conditions only one series of linear telomers T_n^l is formed, i.e., the radical (D) derived from this compound largely isomerizes to the linear radical (D'). Comparison of the data for N-butyl-1, 3-oxazolidine and the corresponding 1,3-dioxolane shows that the introduction of a nitrogen atom into the ring in place of the oxygen accelerates the isomerization of the cyclic radical (D) to the corresponding linear radical.

At the same time, the cyclic telomers predominate in the case of the telomerization of 2-methyl-1,3-oxothiolane (X = S, R = CH_3), as in the case of the corresponding 2-methyl-1, 3-dioxolane (Table 1, No. 2). Thus, substitution of the oxygen in the ring by a sulfur atom does not introduce any fundamental changes in the reaction path, and in this case the presence of the substituent at the second position of the ring evidently plays a significant role.

On the whole it can be seen that the direction of the radical transformations in the 1, 3-diheterocyclopentanes is determined to a significant degree both by the presence of a substituent at the second position and by the nature of the heteroatom. The latter shows up to the greatest degree for the nitrogen atom and to a significantly lesser degree for the oxygen and sulfur atoms, which are more similar in nature.

Extremely complex mixtures of telomers are formed in all the investigated reactions and as a rule contain two series of compounds with various structures. For identification the individual telomers were isolated from the reaction mixture by preparative GLC or were obtained by alternative syntheses [4, 5]. The most informative for structural interpretation were the data from the ^{13}C NMR spectra, which were studied for compounds both with cyclic

TABLE 3. Data from the ^{13}C NMR Spectra of N-Butyl-1,3-oxazolidines and Formamides (δ, ppm)

Serial No.	Compound	OCN, HC(O)	OCH_2, NCH_2 in ring	NCH_2	CH_2	CH_3
1		87,0	63,8 54,1	52,7	32,2(2) 20,9(3)	14,2
2		97,6	64,7 53,2	52,7	27,4(4) 31,8(2) 20,9(3)	14,2 8,8
3		96,8	64,4 53,2	52,4	34,4(4) 31,8(2) 27,4(5) 23,2(6) 20,8(3)	14,2
4		96,9	64,8 53,1	52,3	34,5(4) 32,4(6) 31,7(2) 29,3(7) 25,0(5) 22,9(8) 20,6(3)	14,1
5	$HC(O)N(C_4H_9)C_2H_5$	161,9		46,8 (1) 41,8 47,0 (4) 41,3	20,3 19,6 30,0 31,3(2)	14,1 12,8
6	$HC(O)N(C_4H_9)C_4H_9$	161,8		47,1 41,4	20,1 (3) 19,5 30,7 (2) 29,5	13,5
7		162,7		47,1 (4) 42,5 46,9 (1) 42,5	22,8* (3) 20,5 19,9 (8) 19,4 26,5 27,1 (5)	14,1 13,7

*Remainder in the region of 27.8-31.7.

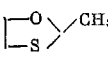
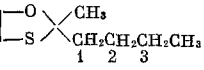
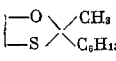
and with linear structures (Tables 2-4). By comparison of the obtained data it was possible to detect the signals most characteristic of the various types of compounds and also to trace the relationships governing the variation of the chemical shifts of the signals of the ^{13}C atoms with the nature of the heteroatom.

The signals of the $O^{13}CO$ and $^{13}CH_2O$ groups proved most informative for the 1,3-dioxolanes (Table 2). The combination of signals indicates a cyclic structure. With the appearance of an alkyl substituent the signal for the $O^{13}CO$ carbon is shifted downfield (by ∿7 ppm), and the signal for the methyl group $OC(^{13}CH_3)O$ is also shifted downfield with the appearance of a second methyl substituent in this unit (by 5.4 ppm). These results correspond to the α and β effects of the carbon atom but are somewhat smaller in value than for the effect on the carbon atom in a normal alkane, and this may be due to the presence of branching at the $O^{13}CO$ point. The spectra of the corresponding linear compounds (formic esters) are well known from published data. The most characteristic here is the $H^{13}COO$ signal (160 ppm) in conjunction with the normal signals of the CH_2O group for esters (61-62 ppm).

For the series of telomer homologs containing an oxazolidine ring the ^{13}C NMR signals of the $O^{13}CN$ groups are 4-8 ppm upfield (Table 3, Nos. 1-4) from the signals for the similarly substituted groups in 1,3-dioxolanes, and this is due to the smaller α effect of the nitrogen compared with the oxygen. It is surprising that increase in the chain length of the substituent R (C_2H_5 to C_6H_{13}) does not affect the chemical shifts of the remaining signals of the ring (Table 3, Nos. 2-4). This means that the γ effect of the carbon atom in these compounds is practically equal to zero.

In the spectra of these compounds the difference in the chemical shifts of the signals of the $^{13}CH_2O$ (64-65 ppm) and $^{13}CH_2N$ (52-54 ppm) groups situated in the ring is very pronounced (Table 3, Nos. 1-4). These signals are extremely characteristic of this type of compound, whereas the chemical shift of the $^{13}CH_2O$ signal both in the dioxolanes and in the oxazolidines is practically identical (see Table 2, Nos. 1-3, and Table 3, Nos. 1-4).

TABLE 4. Data from the ^{13}C NMR Spectra of 1,3-Oxothiolanes and Thioethers (δ, ppm)

Serial No.	Compound	OCS C(O)S	OCH_2 SCH_2	$\underline{C}H_3C(O)S$	CH_2	CH_3
1		72,2	71,5 32,0			
2		82,6	71,3 33,5	22,3		
3		96,0	70,4 34,1	28,8	36,5	9,9
4		95,5	70,4 34,1	29,3	43,6(1) 28,0(2) 23,8(3)	14,3
5		95,5	70,3 34,1	29,3	43,9(1) 25,8(2) 32,2(3) 29,3(4) 23,0(5)	14,4
6	$CH_3C(O)SC_2H_5$	194,6	23,5	30,1		14,8
7	$CH_3C(O)SC_6H_9$	194,4	32,1 *	30,3	29,0 22,2	13,7
8	$CH_3C(O)SC_6H_{13}$	193,7	31,7 *	30,2	30,2 30,0 28,8 29,2 22,8	14,1
9	$CH_3C(O)SC_8H_{17}$	193,6	32,2	30,3	30,1 29,5 † 29,3 † 23,0	14,3

*The assignment of the signals is conditional.
†Signals with double intensity.

In addition to the characteristic signal of $^{13}C(O)N$ (162 ppm), the spectra of the corresponding linear N,N-dialkylformamides contain extremely different signals for $^{13}CH_2N$. A peculiarity of this type of compound is the fact that two signals in the ^{13}C NMR spectrum with an extremely significant difference in chemical shifts (42 and 47 ppm) correspond to each CH_2N group in the linear telomers. This can be explained by the existence of such compounds as two different conformers on account of restricted rotation due to the formation of a semiamide bond O⋯C⋯N. On removal from the functional group the difference in the chemical shifts of the signals for the $^{13}CH_2$ groups is considerably reduced (to 0.5-1.5 ppm).

The introduction of a sulfur atom into the five-membered heterocycle leads to an even greater upfield shift of the signals for the $S^{13}CRO$ groups than for the nitrogen atom (Table 4, No. 1), which agrees fully with the subsequent decrease in the α effect of the second heteroatom (sulfur). A distinguishing feature in the spectra of the 1,3-oxothiolanes is the appreciable downfield shift of the $^{13}CH_2O$ signal in relation to the $^{13}CH_2S$ signal (32-34 ppm) on account of the difference in the α effects of the oxygen and sulfur, and this makes it possible to detect the presence of the oxothiolane ring in the compound.

It is interesting that in the five-membered heterocycles $\overline{CH_2OC(R)XCH_2}$ with X = O, NR, and CH_2 the $^{13}CH_2O$ signal remains in the range of 64-65 ppm, and only for X = S is it shifted into the region of 70-71 ppm. It can be supposed that in the case of dioxolane and oxazolidine rings the chemical shift of the OCH_2 groups is due to the opposite effect of the two strongly electronegative substituents, and in the case of oxothiolanes the electronegativity of the oxygen is appreciably greater than the electronegativity of the sulfur, so that the $^{13}CH_2O$ shift is only affected by the oxygen atom.

In comparison with acetic esters, thioacetic esters (Table 4, Nos. 6-9) are characterized by a downfield shift of the $^{13}C(O)S$ signals from 165-170 to 194-195 ppm and of the $^{13}CH_3CO$ signal by approximately 10 ppm compared with the oxygen-containing analogs.

On the whole it should be noted that the combination of characteristic signals in the ^{13}C NMR spectra of the investigated compounds makes it possible to assign the compounds reliably to the linear or cyclic series.

EXPERIMENTAL

The ^{13}C NMR spectra were recorded on a Bruker HX-90 spectrometer in benzene solution (20% benzene) with C—H decoupling. The spectral data are given in Tables 2-4.

The experiments on the telomerization of ethylene with 1,3-diheterocyclopentanes were carried out in stainless-steel autoclaves with a capacity of 10 ml by the method in [4] with identical M/S ratios. The results are given in Table 1.

The reaction mixtures were analyzed on an LKhM-8MD-9 chromatograph with a thermal-conductivity detector on the following columns: a) 2000 × 3 mm, 20% SKTFT-50Kh on Chromaton N-AW-HMDS, 0.165-0.200, temperature programming, helium; b) 3000 × 3 mm, 15% Carbowax 20 M on Chromaton N-AW-HMDS, 0.165-0.200, stationary regime, helium.

CONCLUSIONS

1. The behavior of 1,3-diheterocyclopentanes $\overline{CH_2OCHRXCH_2}$(X = O, NC_4H_9, S; R = H, CH_3) in radical telomerization with ethylene was compared. The nature of the heteroatom and the presence of a substituent in the OCHRX group have a significant effect on the ratio of the competing addition and ring-opening reactions in the radical $\overline{XCH_2CH_2OC}\cdot R$.

2. The relationships governing the variation of the chemical shifts of the signals in the ^{13}C NMR spectra of the telomers of 1,3-diheterocyclopentanes in relation to the nature of the heteroatoms were investigated. The combination of the characteristic signals in the ^{13}C NMR spectra makes it possible to assign the investigated compounds reliably to the linear and cyclic series.

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