^{13}C NMR SPECTRA OF SUBSTITUTED CYCLOPROPANES.

COMMUNICATION 1. CHEMICAL SHIFTS OF ^{13}C AND ABSENCE OF $\sigma_\pi-p_\pi$ INTERACTION IN CYCLOPROPYLALKYL ETHERS

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It is known that the cyclopropyl group promotes stabilization of carbocations, like vinyl or other unsaturated fragments [1-3]. There is no unanimity on the question of its effectiveness as a bridge group in the transmission of π-electronic effects. In a number of publications [3], the ability of the cyclopropyl and vinyl groups to participate in the interaction according to the mechanism of π conjugation is almost identical. Most of the results for substituted cyclopropanes, cited in [4], also agree with this concept. At the same time, more and more results of independent experimental [5-7] and theoretical [2, 8] investigations continue to appear, which cast doubts on the possibility of participation of the cyclopropyl group in the transmission of electronic effects according to a mechanism of σ—π conjugation.

In a study of cyclopropane and its derivatives by the methods of NMR spectroscopy, the above-mentioned contradiction is also manifested. Thus, the results of a measurement of the diamagnetic susceptibility and the shielding of ^1H and ^{13}C nuclei of unsubstituted cyclopropane are in good agreement, if we assume the existence in this molecule, analogously to aromatic rings, of an effect of a "ring current," due to 3.5 electrons, moving around a circle with radius 1.1 Å [9]. There is no theoretical explanation for such aromaticity. In a study of the ^{19}F NMR spectra of 1,2-disubstituted fluorine-containing cyclopropanes [10], it was found that in ability to transmit π-electronic effects, they are only one fourth as effective as the ethylene analogs. Finally, a comparison of the changes in the chemical shifts (CS) of ^{13}C in the series of substituted cyclopropanes and analogous derivatives of methane, ethylene, and benzene [11], the presence of a reliable linear relationship between the CS of the α-carbon atoms in cyclopropanes and the corresponding methane derivatives has been demonstrated. There is no relationship with the CS of vinyl and phenyl derivatives, which unquestionably casts doubts on the applicability of the model of σ—π conjugation in the series of cyclopropane derivatives.

In a study of the Raman spectra of cyclopropyl ethers [12], results were obtained, agreeing with the assumption of the presence of an effect of conjugation between the three-membered ring and the unsaturated groups, transmitted through the ether oxygen atom. A certain analogy in the chemical behavior of cyclopropyl ethers and their unsaturated vinyl analogs was noted earlier [13].

Below are discussed the results of an analysis of the ^{13}C NMR spectra of a number of cyclopropyl ethers, which proved convenient for studying the question of σ—π interaction in substituted cyclopropanes. We studied the ^{13}C NMR spectra of their vinyl analogs in detail and established the nature of the relationship of the parameters of the spectra and structural characteristics of the substituting groups [14].

Table 1 cites experimental values of the CS of ^{13}C of a number of cyclopropyl ethers, as well as the CS of the α- and β-carbon atoms of the cyclopropane fragment, calculated

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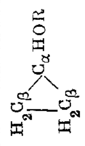
TABLE 1. Physicochemical Characteristics and Chemical Shifts in the ^{13}C NMR Spectra of Cyclopropyl and Vinyl Ethers* (25°, δ, ppm from TMS)

Compound	Substituent	Yield, % of theoretical	bp, °C	n_D^{20}									$H_2C_\beta{=}C_\alpha HOR$	
					C_α	C_β	C_α†	C_β†	C_γ†	C_δ†	C_α††	C_β'††	C_α	C_β
(I)	H	49	101	—	45,71	6,81					46,40	7,50	153,33**	85,13**
(II)	C_2H_5	71	69	—	52,71	5,45	65,76	15,45			53,30	5,30	152,09	85,70
(III)	C_3H_7-*n*	50	93	1,3978	52,95	5,51	72,21	23,47	10,94		53,60	5,30	152,25	85,63
(IV)	C_4H_9-*n*	81	123	1,4070	52,99	5,51	70,25	32,44	19,93	14,11	53,60	5,30	152,23	85,62
(V)	C_3H_7-*i*	66	83	1,4050	50,37	5,61	71,22	22,49			50,80	5,60	150,50	87,50
(VI)	C_3H_5 cyclo	71	97	1.4245	52,68	5,11	52,68	5,11			50,80	5,60	151,59	87,93
(VII)	C_4H_9-*t*	65	105	1,4109	45,52	5,92	73,87	28,42			48,30	5,90	146,23	90,55
(VIII)	C_2H_4Cl-β	72	142	1,4420	53,43	5,69	70,87	42,95			52,80	5,30	151,50	87,29
(IX)	$CH_2{=}CH$	62	68	1,4078	50,63	5,60	151,59	87,93			51,20	5,80	148,51	92,72

*The spectra of pure liquid were measured.

†The α–δ positions of the C atoms of the substituents R relative to the cyclopropyloxy group.

††Values calculated according to an additive scheme [15].

**Values cited for R = CH_3.

according to an active scheme of calculation of sp^3-hybridized ^{13}C nuclei in aliphatic compounds [15]. For comparison, the values of the CS of $^{13}C_\alpha$ and $^{13}C_\beta$ of the double bond of the corresponding vinyl ethers are cited.

As can be seen from Table 1, the CS of $^{13}C_\alpha$ and $^{13}C_\beta$ of the double bond undergo substantial changes, opposite in sign, in the transition from primary to tertiary alkyl substituents at the oxygen. The nature of the change in the CS of C_β in a first approximation, without considering the direct steric and anisotropic contributions, permits us to judge the degree of change of the electron density on it and is in good agreement with the model of steric inhibition of p–π conjugation by the substituent in vinyloxy derivatives [14].

The experimental and calculated values of the CS of ^{13}C of the cyclopropyl fragment are in good agreement quantitatively. An estimation of the degree of this interrelationship according to the method of least squares gives coefficients of correlation both for C_α and for C_β ~ 0.97, with a moderate dispersion (0.79 and 0.01, respectively). Considering the region of applicability of the additive scheme used for the calculation, we can conclude that the absolute values and the nature of the change in the CS of the carbon atoms in cyclopropyl esters are rather completely determined by the effects characteristic of derivatives of saturated hydrocarbons, i.e., do not require a consideration of such effects as the electron delocalization according to the mechanism of σ_π–p_π conjugation.

A comparison of the nature of the changes in the CS of $^{13}C_\alpha$ and $^{13}C_\beta$ in cyclopropyl and vinyl ethers reveals the far lower sensitivity of the CS of $^{13}C_\beta$ in the first case to the effects of the substituents. This is especially clearly manifested in a comparison of the changes in the CS of ^{13}C of cyclopropyl and vinyl derivatives, occurring when an ethoxy group changes to a vinyloxy group (see Table 1). In the first case the signal is shifted by 0.15 ppm in the weak-field direction, and in the second case by 7.02 ppm. The nature of such a substantial change in the series of vinyl derivatives is due to the mutual competition of the two vinyl groups for the unshared electron pairs of the ether oxygen according to the mechanism of p–π conjugation, which leads to a decrease in the electron density on C_β of each of them. In cyclopropyl ethers this change is almost 50 times smaller, which permits us to assume virtual absence of π-electronic interaction of the ring with the substituent.

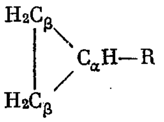
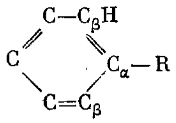
Formally, the absence of an interrelationship between the nature of the changes in the CS of $^{13}C_\beta$ in cyclopropyl and vinyl ethers follows from the parameters of the correlation equations (Tables 2, 1 and 2).

TABLE 2. Parameters of Regression Equations of the CS of $^{13}C_{\alpha,\beta} = a + bx$

Equation	^{13}C	x	a	b	r	s_0
1	C_α	$C_{\alpha'}$*	−122,64	−1,15	0,934	1,09
2	C_β	$C_{\beta'}$*	2,63	0,03	0,581	0,14
3	C_α	σ^*	57,39	38,72	0,986	0,62
4	C_α	Δn	38,86	5,91	0,987	0,59
5	C_α	E_s^0(R)	54,71	4,28	0,974	0,83
6	C_α	E_s^0(OR)	56,11	5,38	0,996	0,29
7	C_β	σ^*	5,22	−2,27	0,989	0,03
8	C_β	Δn	6,29	−0,34	0,966	0,05
9	C_β	E_s^0(R)	5,37	−0,26	0,998	0,01
10	C_β	E_s^0(OR)	5,30	−0,31	0,986	0,03

*$C_{\alpha'}$ and $C_{\beta'}$ are the CS of the corresponding carbon atoms of the vinyl ethers $H_2C{=}CHR$.

TABLE 3. Chemical Shifts (ppm) in the ^{13}C NMR Spectra of Certain Hydrocarbons, the Corresponding Ethyl Ethers,* and Their Changes ($\Delta C_{\alpha,\beta}$)

Compound	R	C_α	C_β	ΔC_α†	ΔC_β‡
$H_3C_\beta{-}C_\alpha H_2{-}R$	H	5,70	5,70	+60	+10
	OC_2H_5	66,12	15,56		
$(H_3C_\beta)_2C_\alpha H{-}R$	H	15,90 ††	15,40 ††	+55	+7
	OC_2H_5	71,10	22,41		
	H	−2,60	−2,60	+55	+8
	OC_2H_5	52,77	5,45		
$H_2C_\beta{=}C_\alpha H{-}R$	H	123,00 ††	123,00 ††	+28	−37
	OC_2H_5	151,33	85,70		
	H	128,50	127,50	+31	−15
	OC_2H_5	159,06	113,22		
$HC_\beta{\equiv}C_\alpha{-}R$	H	75,00 **	75,00 **	+14	−52
	OC_2H_5	89,40	23,20		

*The CS of ^{13}C are cited for the pure liquids relative to TMS.

†$\Delta C_{\alpha,\beta} = C_{\alpha,\beta}(R = OC_2H_5) - C_{\alpha,\beta}(R = H)$. The values of ΔC are rounded off to whole numbers in view of the nonidentity of the conditions of recording of the spectra.

††Taken from [9].

**±5 ppm, taken from the values of the CS in aklynes [9].

An alternative explanation of the low sensitivity of the CS of $^{13}C_\beta$ to changes in the substituent might be the absence of a dependence of the $\sigma_\pi{-}p_\pi$ conjugation of the ring with the oxygen atom from the nature of the substituent, since cyclopropyl ethers differ in conformation from vinyl ethers, and the model of steric inhibition of conjugation is unjustified for them. The inadequacy of such an alternative becomes evident in a consideration of the values of the CS of ^{13}C of a number of model compounds.

Table 3 cites the CS of $^{13}C_\alpha$ and $^{13}C_\beta$ relative to the substituent R and some of the simplest hydrocarbons and their changes (ΔCS) due to replacement of R = H by R = OC_2H_5. ΔCS of cyclopropyl, isopropyl, and ethyl derivatives quantiatively coincide and agree with one another. For compounds possessing sp^2- (ethylene, benzene) or sp-hybridized (acetylene) carbon atoms, the CS of C_α is halves or more, while the CS of C_β has the opposite sign (when H is replaced by the OC_2H_5 group, the signal is shifted in the strong-field direction). As was noted above, this effect is due to delocalization of the unshared electron pairs of the ether oxygen to the β-position of the unsaturated fragment (o-position in the case of the aromatic ring) according to a mechanism of p–π conjugation.

The data of Table 3 confirm the fact that ΔCS in the ^{13}C NMR-spectra of cyclopropyl ethers is due to the same combination of effects as in other alkyl ethers, which give no basis for citing analogies with unsaturated ethers on account of the absence of delocalization of electron density from the oxygen to the three-membered ring according to any mechanism.

To clarify the question of the determining effect of the substituent on the shielding of the carbon atoms of the three-membered ring, we considered the equations of paired regressions, relating the CS of $^{13}C_{\alpha,\beta}$ to the inductive (σ^*), hyperconjugation (Δn), and steric $[E_s{}^0(R)]$ constants of the substituents R, as well as the steric constants of the substituents OR as a whole $[E_s{}^0(OR)]$. The latter were assumed equal to the steric constants of the substituents CH_2R, in accord with the principle of isosterism.

The parameters of these equations are cited in Table 2 (Eqs. 3-10). On the basis of the correlation coefficients and dispersions, it is difficult to give preference to one dominant type of interaction. On the other hand, this is not unexpected, since for a number of alkyl substituents the arguments used are strongly "correlated," and cannot be considered as independent [14]. However, for the CS of C_α and the CS of C_β, we can note a somewhat closer relationship (higher values of the coefficients of correlation r and lower standards of regressions s_0) with steric parameters (see Table 2, Eqs. 6 and 9).

As we showed earlier [14], the relationship of the CS of $^{13}C_\beta$ of vinylalkyl ethers to the steric parameter of the substituent OR is described by the equation

$$\mathrm{CS}\ {}^{13}C_\beta = 83.75 - 3.34\ E_s{}^0(\mathrm{OR}) \qquad r = 0.995;\ s_0 = 0.22$$

A comparison of the coefficients in the case of the arguments in this and the analogous equation for C_β of the cyclopropyl fragment (see Table 2, Eq. 10) shows that in the latter case the sensitivity of the CS of ^{13}C to the influence of the substituent is 10 times lower. Consequently, if we assume the existence of a $\sigma_\pi - p_\pi$ interaction in cyclopropylalkyl ethers, its intensity is an order of magnitude lower than the conjugation in alkoxyethylenes. The same relationship was obtained in a comparison of the constants of long-range spin–spin interaction in the PMR spectra [16] and from quantum chemical calculations [2].

The detected absence of interaction may be characteristic of cyclopropanes containing not only an α-heteroatom with unshared electron pairs. One of the basis for this was the possibility of a rather precise calculation of the CS of ^{13}C in 1,2-disubstituted cyclopropanes according to an additive scheme [17], which by nature does not presuppose an interaction between substituents, in particular, according to the mechanism of conjugation. A study of the transmission of the effects of substituents through various bridge systems by the ^{19}F NMR method also leads to such a conclusion [18].

EXPERIMENTAL METHOD

Compounds (I)-(IX) were pure liquid with an addition of 10 mole % of an internal standard (TMS).

The ^{13}C NMR spectra were recorded at 25° and the natural content of the isotope on a XL-100/12 spectrometer (25.2 MHz). To improve the signal/noise ratio and assign the individual signals, we used various methods of double heteronuclear resonance $^{13}C-\{^1H\}$. The accuracy of the measurement of the CS was ±0.02 ppm. The regression equations were treated on a BESM-4 electronic computer.

Cyclopropanol (I) was produced according to [19].

Cyclopropyl Ethyl Ether (II). To a Zn–Cu couple, prepared from 35 g (0.5 g-atom) Zn-dust and 4.95 g (0.05 mole) CuCl in 500 ml of ether, we added 78 g (0.05 mole) C_2H_5I over a period of 1 h. The mixture was mixed with boiling in an atmosphere of nitrogen for 3 h. The liquid above the precipitate was transferred to another flask without access to air, and 17.7 ml (0.22 mole) CH_2I_2 was added to it with mixing (1 h). The mixture was mixed with boiling for 1 h, 19.1 ml (0.2 mole) of vinyl ethyl ether was added to it, and it was boiled for 2 h. Then 200 ml of the ether was distilled off, the residue decomposed with water, with a 5% solution of HCl, the organic layer removed and washed with water, with sodium thiosulfate, and with water, and dried with $MgSO_4$. Redistillation yielded 11.4 g (71%) (II) with bp 69° (compare [20]).

Compounds (III)-(VIII) were produced analogously. The physicochemical characteristics are cited in Table 1.

Cyclopropyl Vinyl Ether (IX). To a mixture of 120 g KOH, 12 ml dimethyl sulfoxide, 4 ml H_2O, and 1 g triethylbenzylammonium chloride, 36 g (0.3 mole) cyclopropyl-β-chloroethyl ether was added at 140-150° with mixing. The product was distilled off through a fractionating column into a cooled trap and redistilled over sodium.

CONCLUSIONS

1. The ^{13}C NMR spectra of a number of cyclopropyl ethers were studied for the first time.

2. An analysis of the values of the chemical shifts of ^{13}C in cyclopropyl alkyl ethers indicates the absence of $\sigma_{\pi}-p_{\pi}$ conjugation between the ring and the oxygen atom in the ground state.

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