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# β-Substituted cyclopropyl radicals grafted to silica surface. Methods of preparation, structure, and properties

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Cyclopropyl type radicals  (X = $\geqslant$C, $\geqslant$Si, $\geqslant$Si—O) were identified on a surface of activated silica by ESR. The possibility of their preparation by two methods, *i.e.*, by photocyclization of substituted allyl radicals and by interaction of cyclopropane molecules with particular surface defects, was demonstrated. The effects of β-substituents on radiospectroscopic characteristics and thermal stabilities of the radicals were studied. Rate constants and activation energies of decomposition of substituted cyclopropyl radicals were estimated. The experimental data obtained were compared with the results of quantum-chemical calculations of model systems. The mechanism of photocyclization of allyl radicals was discussed. The transition states of decomposition of cyclopropyl and β-fluorine-substituted cyclopropyl radicals were calculated. Electronegative substitution was found to result in a considerable decrease in the activation energy of the cyclopropane ring opening.

**Key words:** β-substituted cyclopropyl radicals; ESR; reactivity; quantum-chemical calculations.

Cyclopropyl type radicals were identified by ESR back in the early 1960s;[1,2] however, data on these radicals are still scarce owing to their low thermal stability and high reactivity toward the abstraction of H atoms from molecules of the medium.[3] The transformation of cyclopropyl radical into allyl radical is an exothermic process (the difference between the heats of formation of allyl and cyclopropyl radicals[4] is $-27\pm3$ kcal mol$^{-1}$) with an activation energy[5—7] of ~22 kcal mol$^{-1}$. This precluded the preparation of radicals of this type by low-temperature matrix isolation using high-temperature pyrolysis.[8]

Cyclopropyl radicals are usually formed in substitution reactions with halogen atoms (F,[9] Cl [10]), H,[11] or $CD_3$ [12] and OH [13] radicals.

Another method for the preparation of these radicals also exists. It has been found[14] that under the action of light with a wavelength of 410 nm, allyl radicals are converted into cyclopropyl radicals.*

The present paper continues the series of publications dealing with the development of methods for generation of intermediates of various structures stabilized on a silica surface[15—18] and is devoted to the generation of cyclopropyl radicals "grafted" to the surface of a solid and investigation of their radiospectroscopic characteristics and thermal stabilities by experimental and quantum-chemical methods.

The method being developed is based on the specified chemical modification of surface defects formed during mechanochemical[15] or thermochemical[19,20] activation of highly dispersed silica (Aerosil).

The thermal stability of grafted intermediates is governed by their chemical structure. This makes it possible to study their intramolecular isomerization or

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decomposition and to obtain information on rate constants and activation energies of the corresponding reactions. In the present study, we have investigated kinetic regularities of the thermal transformation of cyclopropyl radicals containing various β-substituents.

## Experimental

A weighed portion of type A-300 Aerosil powder (50 mg) was placed in a quartz tube with a diameter of 4 mm connected to a vacuum system. The procedure for activation of the Aerosil surface leading to the formation of so-called reactive silica (RSi) has been reported previously.[19]

Two main types of structural defects are stabilized on the surface of an activated sample, namely, $(\equiv\text{Si}-\text{O}-)_3\text{Si}^{\cdot}$ radicals and silylene groups (SG) $(\equiv\text{Si}-\text{O}-)_2\text{Si}:$ (see Refs. 20 and 21). Their concentrations are $(0.5-1)\cdot 10^{12}$ and $(1-2)\cdot 10^{13}$ cm$^{-2}$, respectively.

Commercial samples of cyclopropane and 1,3-butadiene were used. Chromatographic analysis showed that these gases contained no more than 2 % impurities. Since we worked with small quantities of gases, in which the number of molecules was approximately equal to the number of radical centers participating in the process, the possibility of an essential influence of small amounts of impurities was ruled out.

The ESR spectra were recorded in the 77—550 K temperature interval on an EPR-20 IKhF spectrometer operating in the X-range (the frequency of the HF-modulation was 100 kHz).

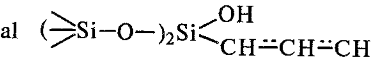
The constants of isotropic hyperfine coupling (HFC) were determined from anisotropic ESR spectra of radicals on the assumption of axial symmetry of the corresponding tensors $a_{\text{iso}} = 1/3(2a_{\perp} + a_{\parallel})$.

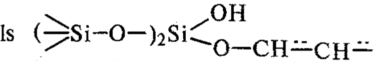
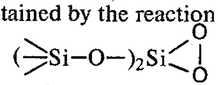
The kinetics of thermal transformations of free radicals was monitored by ESR based on the variations in the intensities of characteristic lines in their spectra.

Photoirradiation of samples was carried out by the light of a DRSh-500 mercury lamp with $\lambda > 400$ nm. The long-wavelength region was isolated using a BS-8 light filter. To prevent warming up of samples during photolysis the tube was filled with an inert gas (He).

The pressure in the system was recorded using a Pirani gauge operating in the pressure range between 0.001 and 10 Pa.

The allyl type radicals, *viz.*, $(\equiv\text{Si}-\text{O}-)_3\text{Si}-\text{O}-\text{CH}_2-\text{CH}\overset{\cdot\cdot}{-}\text{CH}\overset{\cdot\cdot}{-}\text{CH}_2$ (**1**) and $(\equiv\text{Si}-\text{O}-)_3\text{Si}-\text{CH}_2-\text{CH}\overset{\cdot\cdot}{-}\text{CH}\overset{\cdot\cdot}{-}\text{CH}_2$ (**2**), were obtained by adding 1,3-butadiene molecules to $(\equiv\text{Si}-\text{O}-)_3\text{Si}-\text{O}^{\cdot}$* or $(\equiv\text{Si}-\text{O}-)_3\text{Si}^{\cdot}$ radicals stabilized on the SiO$_2$ surface.[13]

The radical  $(\equiv\text{Si}-\text{O}-)_2\text{Si}\begin{smallmatrix}\text{OH}\\ \text{CH}\overset{\cdot\cdot}{-}\text{CH}\overset{\cdot\cdot}{-}\text{CH}_2\end{smallmatrix}$ (**3**) was generated by two methods, one of which was reported previously,[18] and the other of which is described in Section 4 of this paper.

The radicals  $(\equiv\text{Si}-\text{O}-)_2\text{Si}\begin{smallmatrix}\text{OH}\\ \text{O}-\text{CH}\overset{\cdot\cdot}{-}\text{CH}\overset{\cdot\cdot}{-}\text{CH}_2\end{smallmatrix}$ (**4**) were obtained by the reaction between the surface dioxasilirane groups  $(\equiv\text{Si}-\text{O}-)_2\text{Si}\begin{smallmatrix}\text{O}\\ |\\ \text{O}\end{smallmatrix}$ (DOSG) and cyclopropane (for details, see Section 5 of this paper).

Radicals **1**—**4** possess high thermal stabilities, which allows their ESR spectra to be recorded even at 500 K. Under these conditions, ESR signals are better resolved, which substantially facilitates the problem of determining the constants of HFC of the unpaired electron with individual protons (Table 1).

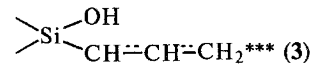
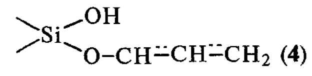
Quantum-chemical calculations were carried out by the SCF MO LCAO *ab initio* method using the "Gaussian" program[22] in a version of the Hartree—Fock calculation scheme (UHF, UMP2). The geometries of molecules and radicals were optimized by the gradient procedure and the 6-31G* basis set supplemented by 6d-polarization functions at heavy atoms. Partial allowance for electron correlation effects was based on the Meller—Plesset perturbation theory in the second order of magnitude.

Radiospectroscopic characteristics of radicals, *viz.*, the constants of HFC of the unpaired electron with magnetic nuclei, were determined from the $(|\psi_n(0)|^2)$ Fermi contact terms:

$$a_{\text{iso}} = 8\pi/3g_e\beta_e g_n\beta_n|\psi_n(0)|^2 = a_0(n)|\psi_n(0)|^2,$$

where $g_e$, $\beta_e$, $g_n$, and $\beta_n$ are gyromagnetic ratios and magnetic moments of the electron and the nucleus, and $|\psi_n(0)|^2$ is the

**Table 1.** Radiospectroscopic characteristics of substituted allyl radicals stabilized on the SiO$_2$ surface*

| Structure of the radical | $T$/K | $a_{\text{H}}$/mT | | | |
|---|---|---|---|---|---|
| | | C(1,3) | C(2) | C(4) | OH |
| $\equiv\text{Si}-\text{O}-\text{CH}_2-\text{CH}\overset{\cdot\cdot}{-}\text{CH}\overset{\cdot\cdot}{-}\text{CH}_2$** (**1**) | 300 | 1.45 | 0.42 | 1.04 | — |
| $\equiv\text{Si}-\text{CH}_2-\text{CH}\overset{\cdot\cdot}{-}\text{CH}\overset{\cdot\cdot}{-}\text{CH}_2$ ** (**2**) | 300 | 1.41 | 0.42 | 1.07 | — |
|  $\geq\text{Si}\begin{smallmatrix}\text{OH}\\ \text{CH}\overset{\cdot\cdot}{-}\text{CH}\overset{\cdot\cdot}{-}\text{CH}_2\end{smallmatrix}$*** (**3**) | 77 | 1.4 | 0.5 | — | 0.2 |
|  $\geq\text{Si}\begin{smallmatrix}\text{OH}\\ \text{O}-\text{CH}\overset{\cdot\cdot}{-}\text{CH}\overset{\cdot\cdot}{-}\text{CH}_2\end{smallmatrix}$ (**4**) | 300 | 1.46 | 0.34 | — | — |
| | 540 | 1.47 | 0.44 | — | |

* The numbering begins with the terminal carbon atom. ** See Ref. 15. *** See Ref. 18.

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* The radicals $(\equiv\text{Si}-\text{O}-)_3\text{Si}-\text{O}^{\cdot}$ were obtained from silyl radicals by treating them with nitrous oxide at 450 K.[15,20]

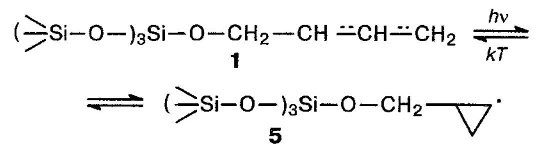
spin density on nucleus *n*. For a proton, $a_0(^1H)$ = 159.5 mT and $a_0(^{29}Si)$ = −31.7 mT when the $|\psi_n(0)|^2$ values are expressed in the atomic units.

## Results and Discussion

### 1. Phototransformation of the $(\geq Si{-}O{-})_3Si{-}O{-}CH_2{-}CH{\cdots}CH{\cdots}CH_2$ radical (1).

Photoirradiation of a sample containing type **1** radicals for 30 min at 77 K is accompanied by a decrease in the intensity of the ESR signal of the allyl radical and appearance of a new paramagnetic center (Fig. 1*). In the 77—260 K temperature range, variations of the ESR spectral pattern are reversible. As the temperature of recording the ESR signal increased, it became appreciably better resolved.

A set of HFC constants corresponding to the ESR spectrum recorded at 260 K is presented in Table 2 (radical **5**); these constants are close to the radiospectroscopic characteristics of the cyclopropyl radical *cyclo*-$C_3H_5$, which has been detected for the first time in γ-irradiated liquid cyclopropane.[1] This allows this ESR spectrum to be assigned to cyclopropyl type radicals, which are formed by phototransformation of allyl radicals (reaction (1)).



(1)

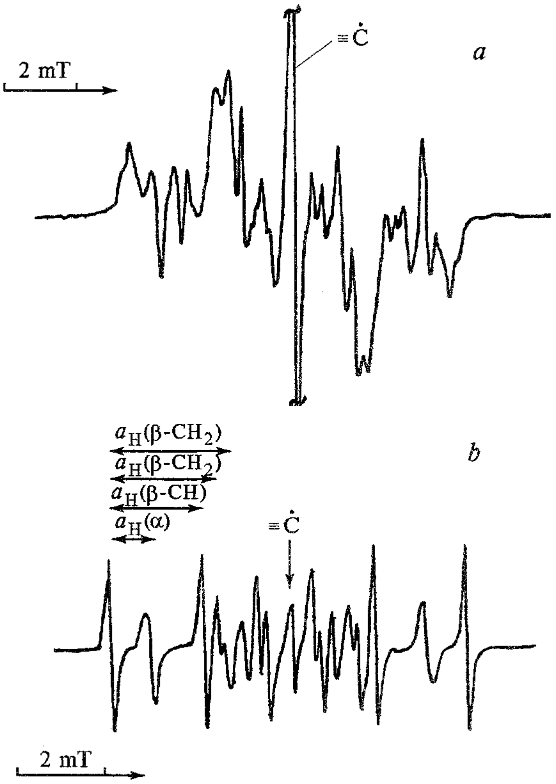
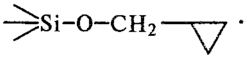
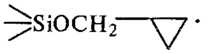
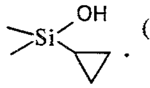
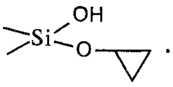
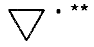


**Fig. 1.** ESR spectra of the radical  (**5**) at 77 (*a*) and 260 K (*b*).

Unlike the *cyclo*-·$C_3H_5$ radical ($C_s$ symmetry), structure **5** possesses no elements of symmetry, which results in the HFC constants of the unpaired electrons with the β-protons slightly differing from each other. A more detailed analysis of the structure and radiospectroscopic characteristics of this radical is given in Section 6 of this paper in relation to the discussion of

**Table 2**. Isotropic HFC constants in substituted cyclopropyl radicals stabilized on the $SiO_2$ surface

| Structure of the radical | T/K | $a_H$/mT | | | |
|---|---|---|---|---|---|
| | | α | β-CH$_2$ | β-CH | $^{29}$Si |
|  (5) | 260 | 0.86±0.03 | 2.45±0.2<br>2.59±0.2 | 2.11±0.02 | |
|  (7) | 243 | 0.69±0.05 | 2.19±0.05<br>2.19±0.05 | 2.86±0.05 | 2.50±0.10<br>3.05±0.15* |
|  (8) | 203 | 0.84±0.05 | 2.46±0.03<br>3.69±0.04 | 1.87±0.02 | |
|  ** | 143 | 0.65 | 2.34 | | |

* Measured at 77 K. ** See Ref. 1.

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* The central part of the ESR spectra presented in Fig. 1 contains an additional single line with a *g*-factor of 2.0026, caused by the admixture of $\geq C^{\cdot}$ paramagnetic centers.[18]

the results of quantum-chemical calculations of substituted cyclopropyl radicals.

The main reason for the broadening of individual components of the ESR spectrum of radical **5** and the complication of the spectral pattern at 77 K is the anisotropy of the hyperfine coupling of the unpaired electron with the α-proton. As the temperature increases, the contribution of the anisotropic term to the HFC tensor is partially averaged, due to freezing out of intramolecular motions in the radical. This is why the resolution of the ESR spectrum is improved.

When the sample is heated to 270—300 K, the ESR lines of the phototransformation product irreversibly disappear, and the initial intensity of the ESR signal of allyl radical **1** is restored, which is typical of cyclopropyl type radicals.[3,23]

Analogous results were obtained in the study of the phototransformation of the $(\gtrdot Si{-}O{-})_3Si{-}CH_2{-}CH{\doteq}CH{\doteq}CH_2$ radical (**2**). The shape of the signal and, hence, the radiospectroscopic characteristics of the paramagnetic product of phototransformation $(\gtrdot Si{-}O{-})_3Si{-}CH_2{-}\triangledown^{\bullet}$ (**6**) at 77 K are close to those recorded for radical **5**. Heating of the sample to 300 K is accompanied by decay of radicals **6** and quantitative recovery of the intensity of the ESR spectrum of the starting allyl radicals **2**.

Figure 2 presents the kinetic curves of the thermal transformation of cyclopropyl radicals **5** into allyl radicals at 275±1 and 293±1 K. They obey a first-order equation. The rate constants of the isomerization at these two temperatures are $(3.5\pm0.2)\cdot10^{-4}$ and $(3.8\pm0.2)\cdot10^{-3}$ $s^{-1}$, respectively. The temperature range in which the rate constants of the isomerization ($k = k_0\exp(-E_a/RT)$) were measured is rather narrow, and with allowance for errors that may arise in determining the rate constants and the temperature of the sample, the possible $k_0$ values lie in the interval of $10^{11}$—$10^{16}$ $s^{-1}$. At $k_0 = 10^{13}$ $s^{-1}$ (see Refs. 5 and 7), the $E_a$ value amounts to 20.5±0.5 kcal $mol^{-1}$. The activation energy of the decomposition of cyclopropyl radical is 20,[5] 19.1,[6] or 24 kcal $mol^{-1}$ (see Refs. 7 and 24).

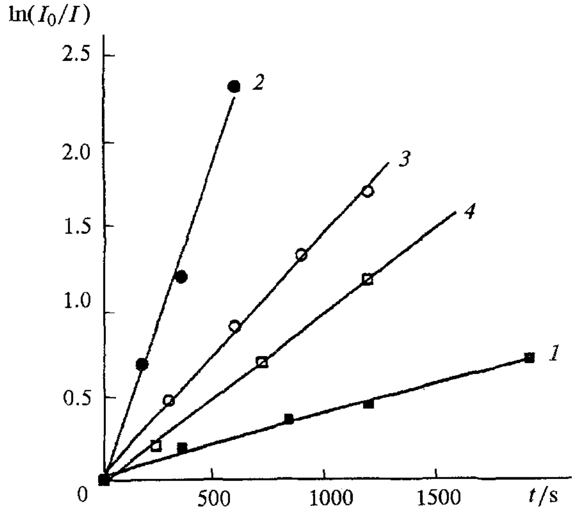


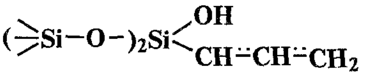
**Fig. 2**. Kinetic curves of decomposition of cyclopropyl radicals:

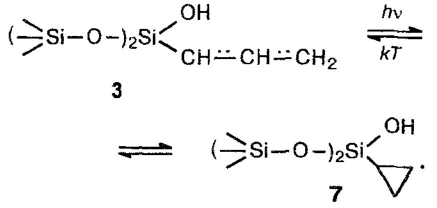
$X{-}\triangledown^{\bullet} \longrightarrow XHC{\doteq}CH{\doteq}CH_2$

with $X = (\gtrdot Si{-}O{-})_3Si{-}O{-}CH_2$ at 275 (*1*) and 293 K (*2*);

$(\gtrdot Si{-}O{-})_2Si{-}OH$ at 260 K (*3*);

$(\gtrdot Si{-}O{-})_2Si\overset{OH}{\underset{O}{<}}$ at 215 K (*4*).

**2. Phototransformation of the allyl radical**  $(\gtrdot Si{-}O{-})_2Si\overset{OH}{\underset{CH{\doteq}CH{\doteq}CH_2}{<}}$ **(3)**. The ESR spectra of radical **3** at 77 and 300 K have been studied previously;[18] its radiospectroscopic characteristics are listed in Table 1. Figure 3 presents the ESR spectrum of the product of phototransformation of radical **3** (photolysis of the sample for 30 min at 77 K).



(2)

The transformation of allyl radicals by reaction (2) is quantitative, which is indicated by the fact that the overall concentration of paramagnetic centers in the system is retained.

As in the case of radical **5**, the ESR spectrum of the phototransformation product becomes better resolved and the spectral pattern becomes simpler with the increase in the temperature of recording (see Fig. 3, *b*). The constants of HFC of the unpaired electron with some protons of this radical at 243 K are listed in Table 2.

Two additional low-intensity lines are recorded on the wings of the ESR signal of radical **7** (see Fig. 3, *b*), which are not exhibited in the ESR spectra of radicals **5** and **6**. This lines are due to the coupling of the unpaired electron of the radical with the $^{29}Si$ isotope nucleus (natural abundance 4.7 %). The magnitude of the corresponding HFC constant decreases with an increase in the temperature (see Table 2). We attribute this constant to the silicon atom present in the β-position with respect to the unpaired electron in radical **7**.

Another characteristic feature of the ESR spectrum of the phototransformation product is that the terminal components of the signal have a doublet structure with an HFC constant of ~0.1 mT (see Fig. 3, *b*). No similar splitting was observed in the ESR spectra of radicals **5** and **6**. We assign it to coupling of the unpaired electron in radical **7** with the proton of the hydroxyl group.

When the sample is heated to 255—270 K, the ESR spectrum of radical **7** disappears and the intensity of the

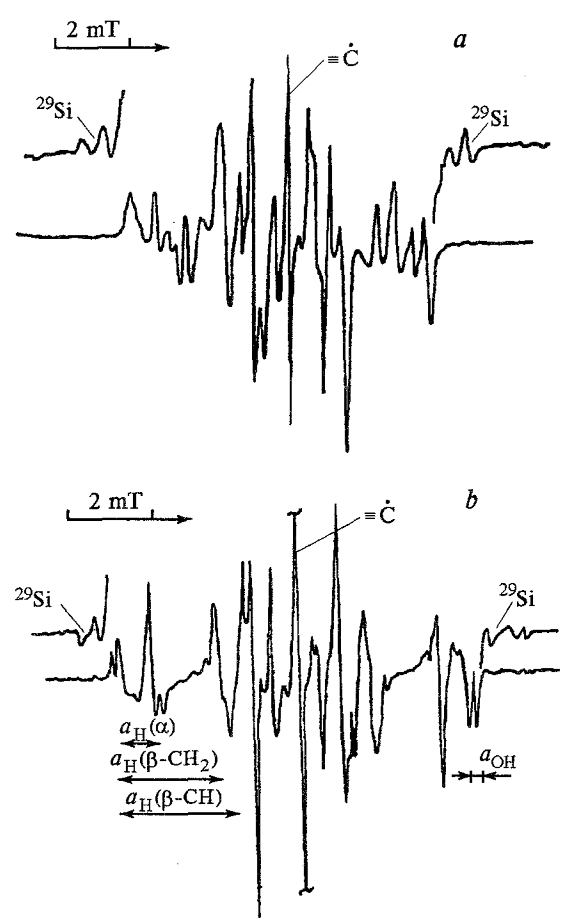
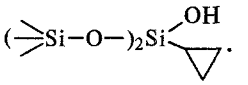


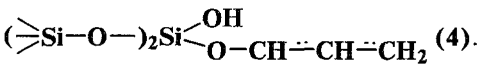
**Fig. 3**. ESR spectra of the radical



(7) at 77 (*a*) and 243 K (*b*).

signal corresponding to radical **3** is completely restored. Figure 2, curve *3* shows the kinetic curve of the isomerization at 260.5±0.5 K. The rate constant at this temperature is $(1.4\pm0.1)\cdot10^{-3}$ s$^{-1}$. With the preexponential factor being $k_0 = 10^{13}$ s$^{-1}$, this corresponds to an activation energy of the decomposition of the corresponding cyclopropyl radical of ~19 kcal mol$^{-1}$. Note a slight decrease in the thermal stability of the β-silyl-substituted radical compared to the carbon-substituted radical **5** ($E_a \approx 20.5$ kcal mol$^{-1}$).

**3. Photochemical transformation of the allyl radical**



$(\geqslant Si{-}O{-})_2Si\overset{OH}{\underset{O-CH\overset{..}{-}CH\overset{..}{-}CH_2}{<}}$

(**4**). Similar results were obtained in the study of the products of phototransformation of type **4** allyl radicals. The ESR spectrum of the resulting radical is presented in Fig. 4, and its radiospectroscopic characteristics are listed in Table 2 (radical **8**). In this radical, the difference bet1ween the constants of HFC of the unpaired electron with the β-protons are especially pronounced. Possible reasons for the regularities observed are discussed in Section 6.

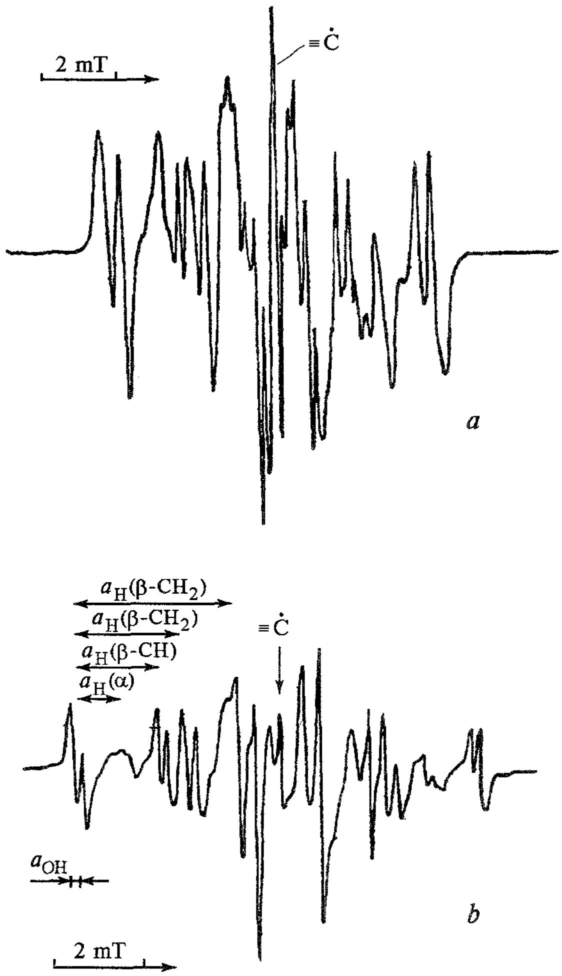
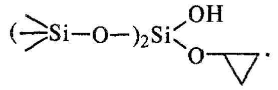


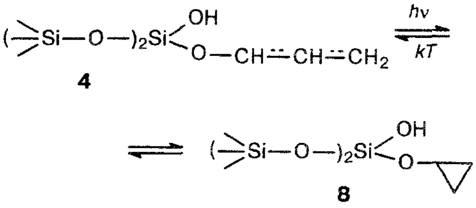
**Fig. 4** ESR spectra of the radical



(**8**) at 77 (*a*) and 203 K (*b*).

The ESR spectrum of radical **8** exhibits an additional splitting of the components of the HFS, which, in our opinion, is due to the interaction of the unpaired electron with the proton of the adjacent hydroxyl group, as in the case of radical 7 (see the previous Section).

Thus, phototransformation of the type **4** allyl radical occurs in the following way (reaction (3)).

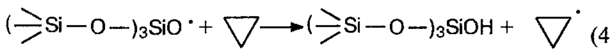


(3)

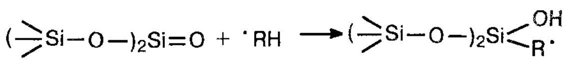
The thermal isomerization of the resulting radicals begins already at 210—225 K and leads to the recovery of the initial intensity of the ESR spectrum of the type **4** allyl radicals.

The rate constant of reaction (3) measured at 214.5±0.5 K is $(9.8\pm0.5)\cdot10^{-4}$ $s^{-1}$ (see kinetic curve *4* in Fig. 2). On the assumption that the preexponential factor for the rate constant of decomposition of radicals **8** is $10^{13}$ $s^{-1}$ we obtain an activation energy of 16 kcal $mol^{-1}$. Thus, the introduction of the electronegative substituent results in a substantial decrease in the stability of the cyclopropyl radical.

**4. Formation of cyclopropyl type radicals in the reaction $(\geq Si-O-)_2Si=O$ + ▽•.** The reaction of the oxyl radicals $(\geq Si-O-)_3SiO^{\bullet}$ with cyclopropane molecules at temperatures between 150 and 300 K was shown[18] to follow only one pathway giving cyclopropyl radicals (Eq. (4)).


(4)

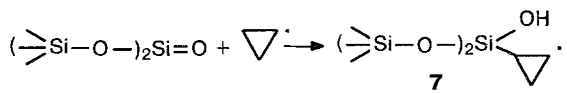
The silanone groups stabilized on the silica surface are efficient acceptors of low-molecular-weight radicals.[16,20] Their interaction with the alkyl radicals $^{\bullet}RH$ ($^{\bullet}CH_3$ or $^{\bullet}C_2H_5$) occurs by the following scheme.


$$(\geq Si-O-)_2Si=O + {}^{\bullet}RH \longrightarrow (\geq Si-O-)_2Si\begin{smallmatrix}OH\\ R^{\bullet}\end{smallmatrix}$$

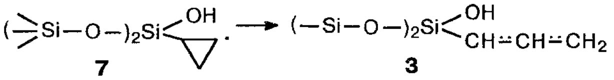
The question of the mechanism of this reaction remains open.

We analyzed the free-radical products of the interaction of the silanone groups with the cyclopropyl radicals. For this purpose, we prepared a sample, whose surface contained stabilized oxyl radicals and silanone groups (the procedure for preparing these samples is given in Refs. 16 and 20). Chemisorption of cyclopropane was carried out at 200 K. The ESR spectrum of the reaction products was identical to the signal shown in Fig. 3 and corresponds to the cyclopropyl type radical **7**.

Thus, the cyclopropyl radical like other alkyl radicals[16,20] is accepted by the silanone group according to reaction (5).

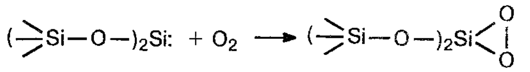

(5)

When the sample was heated to 300 K, the centers of the cyclopropyl type radical were quantitatively converted into allylic centers.

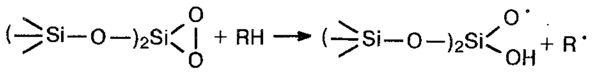


Thus, the sequence of reactions (4) and (5) leads to the formation of cyclopropyl type radicals grafted on the silica surface and may serve as a method for their preparation.

**5. Interaction of cyclopropane molecules with the $(\geq Si-O-)_2Si\begin{smallmatrix}O\\ |\\ O\end{smallmatrix}$ groups.** The samples containing DOSG were prepared by oxidation of the SG stabilized on the surface of an RSi sample with molecular oxygen (reaction (6)).

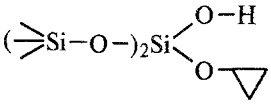

(6)

These groups, being efficient acceptors of low-molecular-weight radicals, like silylene (>Si:) and silanone (>Si=O) centers,[16,20] are also capable of abstracting H atoms from $H_2$ or saturated hydrocarbons RH (R = Me or Et) even at 300 K.[25]



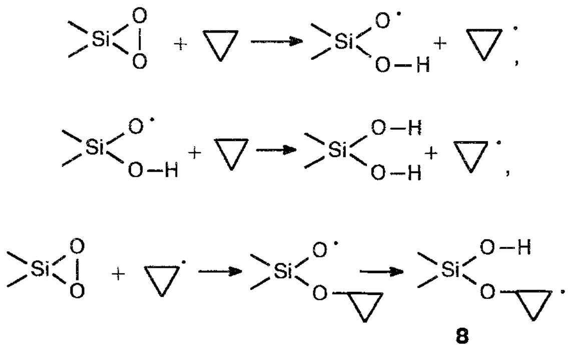
Molecules of unsaturated hydrocarbons ($C_2H_4$) add to DOSG without forming free-radical products.[25] Therefore, it has been of interest to elucidate the mechanism by which these groups react with cyclopropane, which can be involved in both free-radical substitution and addition reactions, *i.e.*, exhibits chemical properties characteristic of both saturated and unsaturated hydrocarbons.

When a DOSG-containing sample is brought into contact with cyclopropane molecules (at 200 K), free radicals are formed, whose ESR spectrum is identical to that of



(**8**) (Fig. 4).

One may assume that cyclopropane reacts with DOSG like other saturated hydrocarbons[25] by the following scheme:


(7)

(8)

(9)

A similar sequence of free-radical reactions proceeds in the oxyl radical—silanone—cyclopropane system;

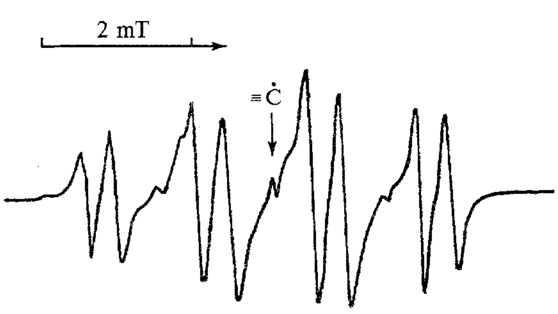
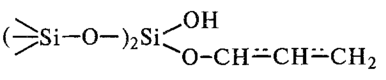


**Fig. 5**. ESR spectrum of the radical


$(\geqslant Si-O-)_2Si\begin{smallmatrix}OH\\O-CH\overset{..}{=}CH\overset{..}{=}CH_2\end{smallmatrix}$ (**4**) at 540 K.

however, in this case, the function of the oxyl radical initiating the generation of the cyclopropyl radical is fulfilled by the diamagnetic dioxasilirane group.

Heating of the sample to 300 K results in the quantitative conversion of the cyclopropyl type radicals into new paramagnetic centers, whose ESR spectrum is shown in Fig. 5 and radiospectroscopic characteristics are listed in Table 1 (radical **4**). We assign this signal to allyl radicals **4** relying on the procedure of its preparation and the following radiospectroscopic and chemical evidence.

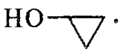
The values of the HFC constants observed (see Table 1) are typical of allyl type radicals.[15,26] Based on this, we assign the HFC constant equal to 1.46 mT to the α-protons at C(1) and C(3), and the constant, equal to 0.34 mT ($a_2$), is assigned to the proton at the C(2) atom.*

The absence of satellite lines associated with the $^{29}$Si isotope in the ESR spectrum of this radical implies that the corresponding HFC constant is no more than 0.5 mT. This is due to the fact that in radical **4**, the silicon atom is separated from the allyl fragment by the oxygen atom. The constant of HFC of the unpaired electron with $^{29}$Si in the radical $\geqslant Si-O-\dot{C}H_2$ is ~0.4 mT, and in radical **4**, it should be even smaller, because in the allyl radical, the spin density on the C(3) carbon atom is lower.

When this sample is oxidized with $O_2$, the formation of a peroxyl radical was detected. At ambient temperature, its ESR spectrum is a singlet with a *g*-factor of ~2.015. Evacuation of the sample at 300 K leads to restoration of a substantial part (more than 30 % of the intensity of the initial ESR signal) of the starting hydrocarbon radical. This behavior is typical of allyl radicals and is due to the relatively low strength of the C—O bond in the corresponding peroxyl radical.[27]

Reactions (7)—(9) can be used for preparing cyclopropyl type radicals **8**. On heating they afford allyl radicals. It is by this method that radicals **4**, whose photochemical transformations were studied in Section 4, were generated.

**6. Quantum-chemical calculations of β-substituted cyclopropyl radicals.** In order to match the HFC constants observed experimentally (see Table 2) to individual β-protons in substituted cyclopropyl radicals we carried out quantum-chemical calculations of the radiospectroscopic characteristics of simple molecular models of the  type, where X = H, Me, $SiH_3$, OH, F.

The equilibrium geometric characteristics of these radicals, except for  , were calculated previously at various theoretical levels for X = H,[14,28] Me, $SiH_3$,[29] and F [30,31] and are listed in Table 3. The numbering of individual atoms for the *cis*- and *trans*-configurations of the substituted cyclopropyl radicals used in this paper is presented in Fig. 6.

The $\langle s^2 \rangle$ values for the optimized radical structures differ slightly from 0.75, which corresponds to the doublet state of the system. This indicates that the calculations by the unrestricted version of the Hartree—Fock scheme provide a satisfactory description of the free-radical state in the systems under consideration.

Cyclopropyl type radicals are known to be σ-radicals in which the unpaired electron is localized on a hybrid orbital of the three-coordinated carbon atom, and the α-H atom bound to it deviates from the plane of the ring.[1,23] Therefore, the existence of two conformers interconverting through the inversion of the α-proton is possible.

In conformity with the results obtained previously,[29—31] the difference between the electron energies of the conformers (see Table 3) does not exceed 1 kcal $mol^{-1}$. The $\Delta H_0(0)$ values (at 0 K) determining

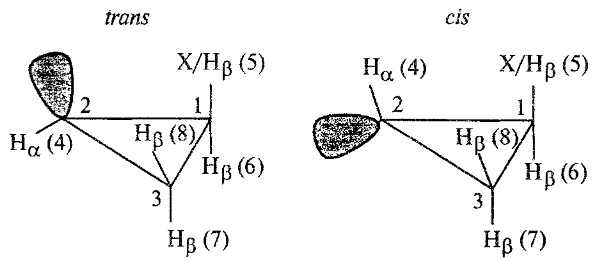


**Fig. 6**. Numbering of the atoms in β-substituted cyclopropyl radicals.

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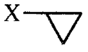
* For radical **4**, one should expect that the magnitudes of the HFC constants with the inherent three α-protons would be slightly different. In allyl type radicals, even the HFC constants corresponding to the α-protons of one methylene group differ by 0.1 mT (the constant for the proton having the *trans*-arrangement with respect to the carbon skeleton is somewhat larger). The width of an individual component of the HFS in the ESR spectrum of radical **4** is ~0.3 mT ($T$ = 500 K); therefore, based on the experimental results obtained, one may only state that the difference between the constants of the HFC with α-protons does not exceed 0.1—0.2 mT.

**Table 3**. Energies and geometric characteristics of the optimized structures of the substituted cyclopropyl radicals  (UHF/6-31G*)

| X | $-E$ (au) | $\Delta E$ /kcal mol$^{-1}$ | Bond length | | | Angle | | |
|---|---|---|---|---|---|---|---|---|
| | | | C(2)—C(1) | C(2)—C(3) | (C(1)—C(3) | C(1)C(2)C(3) | C(2)C(1)C(3) | C(2)C(3)C(1) |
| | | | | /Å | | | /deg | |
| H | 116.41554 | | 1.470 | 1.470 | 1.518 | 62.1 | 58.9 | 58.9 |
| $CH_3$(*trans*) | 155.45254 | | 1.471 | 1.473 | 1.517 | 62.0 | 59.0 | 58.9 |
| $CH_3$(*cis*) | 155.45276 | −0.15 | 1.470 | 1.473 | 1.518 | 62.1 | 59.0 | 58.9 |
| $SiH_3$(*trans*) | 406.49539 | | 1.477 | 1.463 | 1.532 | 62.8 | 58.2 | 59.0 |
| $SiH_3$(*cis*) | 406.49500 | 0.25 | 1.478 | 1.463 | 1.532 | 62.8 | 58.1 | 59.1 |
| F(*trans*) | 215.26033 | | 1.458 | 1.480 | 1.498 | 61.3 | 60.0 | 58.6 |
| F(*cis*) | 215.26171 | −0.9 | 1.456 | 1.480 | 1.501 | 61.5 | 60.1 | 58.5 |
| OH(*trans*) | 191.26197 | | 1.461 | 1.476 | 1.513 | 62.0 | 59.5 | 58.5 |
| OH(*cis*) | 191.26352 | −1.0 | 1.459 | 1.477 | 1.515 | 62.1 | 59.5 | 58.3 |

*Note*. The $<s^2>$ values are 0.76 in all cases.

their thermodynamic stabilities depend as well on the zero-point vibration energy of the system (ZPVE). Vibrational spectra of fluorine-containing conformers were calculated, and based on them ZPVE were determined (the 6-31G* basis set in the harmonic approximation). All the values of frequencies for both conformers proved to be positive, *i.e.*, the optimized structures actually correspond to local minima on the potential energy surface of the system. The ZPVE values for *cis*- and *trans*-conformers are close to each other (40.5 and 40.45 kcal mol$^{-1}$, respectively) and do not introduce substantial differences into the $\Delta H_0(0)$ values of the conformers.

The difference between the energies of the conformers increases in the order Me < $SiH_3$< F < OH (see Table 3). In the case of the silyl-substituted radical, the *trans*-configuration is more stable,[29] and for the F [30,31] and OH-substituted radicals, the *cis*-configuration is more stable.

On going from one configuration of the radical to the other, the energy of the electrostatic interaction between the α-proton and the β-substituent changes.

According to the results of the calculations, the α-hydrogen atom is positively charged ($q$ = −(0.15 to 0.17)$e$, where $e$ is the charge of the electron), and the charges on the Me, $SiH_3$, F, and OH groups are −0.01, −0.24, 0.40, and 0.29 $e$, respectively. The differences between the energies of electrostatic interaction of these groups in the *cis*- and *trans*-conformers estimated in the approximation of point charges are −0.1, 0.6, −2.0, and −1.7 kcal mol$^{-1}$ for Me, $SiH_3$, F, and OH groups, respectively (the charges on the atoms and the distances between them were taken from quantum-chemical calculations), and the differences between the electronic energies of the corresponding conformers are equal to −0.15, 0.25, −0.9, and −1.0 kcal mol$^{-1}$ (see Table 3). Thus, the electrostatic interactions make a significant, possibly, the crucial contribution to the stabilization of one of the isomeric forms.

**7. Radiospectroscopic characteristics of the radicals.** It is known[32] that satisfactory results in a calculation of HFC constants can be obtained by using extended basis sets and by taking into account the electron correlation effects. These calculations have been performed for the cyclopropyl radicals.[28] We used a semiempirical approach based on introducing scale-factors selected in the following way. The constants of isotropic HFC of the unpaired electron with the α- and β-protons in cyclopropyl type radicals, calculated at the UHF/6-31G* level from the Fermi-contact terms, are presented in Table 4. In these radicals, the β-protons incorporated in the methylene groups possess appreciably different HFC constants, *i.e.*, are magnetically nonequivalent.

The HFC constants calculated for the cyclopropyl radical are as follows: $a_H(\alpha)$ = −1.96 (−0.57) mT, $a_H(\beta_1)$ = 2.47 (2.33) mT, $a_H(\beta_2)$ = 1.63 (1.38) mT (the published data[28] are given in parentheses). According to the ESR data,[1,2] the β-protons in the radical  have identical HFC constants due to the high frequency of inversion of the α-proton ($\nu \gg 10^8$ s$^{-1}$).* In this case, $\bar{a}_H(\beta_1) = \bar{a}_H(\beta_2) = 1/2(a_H(\beta_1) + a_H(\beta_2))$ = 2.05 mT. As a result, the ratios between the calculated and experimentally observed HFC constants for the α- and β-protons amount to 0.33 and 1.14, respectively. Using these scale-factors, we corrected the results of the calculations of the constants of HFC with α- and β-protons in other radicals. They are presented in Table 4 in parentheses.

The small differences between the energies of the inversion isomers of substituted cyclopropyl radicals ($\Delta E$) can have substantial effects on the constants of HFC

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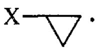
* The height of the inversion barrier for this radical is 3.9 kcal mol$^{-1}$ (determined by a quantum-chemical calculation[14,28]). At low temperatures, this process occurs by a tunneling mechanism. Therefore, the low-temperature limit of the inversion frequency is more than $10^{10}$ s$^{-1}$.[28]

**Table 4.** Radiospectroscopic characteristics ($a_H$/mT) of the substituted cyclopropyl radicals  found by quantum-chemical calculations*

| X | $H_\alpha$ | H(7) | H(8) | H(6) |
|---|---|---|---|---|
| H(5) | −1.96(−0.65) | 2.47(2.82) | 1.63(1.85) | — |
| $CH_3$(*trans*) | −1.96(−0.65) | 1.64(1.87) | 2.52(2.87) | 1.53(1.75) |
| $CH_3$(*cis*) | −1.98(−0.65) | 2.49(2.84) | 1.56(1.78) | 2.63(3.00) |
| $SiH_3$**(*trans*) | −1.77(−0.58) | 1.45(1.65) | 2.18(2.49) | 2.10(2.40) |
| $SiH_3$***(*cis*) | −1.80(−0.60) | 2.28(2.60) | 1.47(1.67) | 2.85(3.25) |
| F(*trans*) | −2.50(−0.83) | 2.23(2.55) | 3.35(3.82) | 0.83(0.95) |
| F(*cis*) | −2.44(−0.81) | 2.93(3.35) | 2.07(2.36) | 1.63(1.85) |
| OH(*trans*) | −2.31(−0.76) | 2.01(2.29) | 3.05(3.47) | 0.92(1.05) |
| OH(*cis*) | −2.18(−0.72) | 2.74(3.13) | 1.83(2.09) | 1.90(2.16) |

* The numbering of the atoms is shown in Fig. 6. ** $Si_\beta$ 1.75. *** $Si_\beta$ 1.00.

with individual β-protons ($a(T)$) and result in the dependence of these constants on temperature. At high inversion frequencies ($\nu \gg 10^8$ $s^{-1}$)

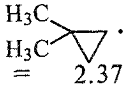
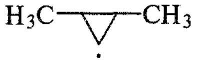
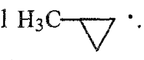
$$a(T) \approx (a_1 + \exp(-\Delta E/RT)a_2)/(1 + \exp(-\Delta E/RT)).$$

Here $a_1$ and $a_2$ are the constants of HFC of the unpaired electron with the corresponding β-proton in the two forms ($a_1$ refers to the more stable form). At $\Delta E$ = 1 kcal $mol^{-1}$ (see Table 3) and a temperature of 250 K, the contribution of the configuration with lower energy predominates (75 %), *i.e.*, the HFC constants would be close to those values, which characterize the most stable isomer. The β-protons of the $CH_2$ group would possess different HFC constants (for the second proton, $a(T) \approx (a_2 + \exp(-\Delta E/RT)a_1)/(1 + \exp(-\Delta E/RT))$.

The HFC constants of the oxygen-substituted radical **8** differ substantially from those of other cyclopropyl type radicals (see Table 2). A comparison of the observed radiospectroscopic characteristics of the OH- and F-substituted radicals with the calculated values (see Table 4) indicates that they are close to those corresponding to the more stable (*cis*) isomer. Relying on this fact, we assign a constant of 1.85 mT to the β-proton of the group CH, and the two other constants refer to the protons of the $CH_2$ group.

In the case of the silyl-substituted cyclopropyl radical **7**, a constant of 2.9 mT may be assigned to the β-proton at the substituted carbon atom, and the other two constants, having similar values, may refer to the $CH_2$-group protons. The similarity of the constants of HFC with the two protons of the methylene group indicates that the energies of the two conformations of the radical differ by no more than 0.2 kcal $mol^{-1}$, and inversion of the α-proton at 240 K occurs with a frequency of $\nu \gg 10^8$ $s^{-1}$.

For radical **7**, the HFC constant of the unpaired electron with the silicon atom, $a_{iso}(^{29}Si)$, was measured. It has a negative temperature coefficient. This fact is in agreement with the results of quantum-chemical calculations, which imply that the *trans*-form, whose constant has a larger magnitude, is more stable (see Table 4). When the temperature increases, the populations of the two conformers equalize, which should lead to a decrease in the $a_{iso}(^{29}Si)$ value.

The constants of HFC with protons in the following radicals were measured:[33]  (**A**), $a_H(\alpha)$ = 0.65, $a_H(\beta_1)$ = $a_H(\beta_2)$ = 2.37 mT, and  (**B**, **C**), $a_H(\alpha)$ = 0.71, $a_H(\beta_1)$ = $a_H(\beta_2)$ = 2.13 mT and $a_H(\alpha)$ = 0.71, $a_H(\beta_1)$ = $a_H(\beta_2)$ = 2.60 mT. The latter two sets of HFC constants refer to the radicals , in which the methyl groups are *trans*- (**B**) or *cis*- (**C**) with respect to the ring plane. From these data it follows that the constant of HFC with the β-proton decreases on introducing a methyl substituent (transition from radical **A** to radical **B**). Conversely, in radical **C**, this constant increases. This result can be explained by taking into account the following consideration. In the case of radicals **A** and **B**, both configurations resulting from the inversion of the α-proton have identical energies, while for radical **C**, this is not the case. According to the results of calculations (see Table 3), the introduction of a methyl group stabilizes the *cis*- configuration of the radical . It may be assumed that the introduction of the second methyl group located on the same side of the ring plane (radical **C**) would lead to additional stabilization of the *cis*-isomer. The latter has a larger constant of HFC with the β-proton (see Table 4).

From the above formula, using the $a_1$ and $a_2$ values taken from Table 4 (3.0 and 1.75 mT, respectively), and $a$(274 K) = 2.60 mT, we obtain $\Delta E$ equal to 0.65 kcal $mol^{-1}$.

In radical **5**, the expected difference between the energies of the two isomers is also small (see Table 3), and based on the above discussion, the HFC constant equal to 2.1 mT should be assigned to the hydrogen atom bound to the substituted carbon atom, and the other two constants refer to the protons of the methylene group.

**8. Mechanism of interconversions of cyclopropyl and allyl radicals.** On the action of light with a wavelength of 410 nm, the allyl radical transforms into an electron-excited state.[34] This transition is associated with the excitation of one of the electrons of the π-system of the radical from the bonding MO (symmetry $b_1$) to the antibonding MO (symmetry $a_2$) (variation of the electron configuration of X is $(^2A_2(...(b_1)^2(a_2)^1)) \rightarrow {}^2B_1(...(b_1)^1(a_2)^2)$.[35]

For a new σ-bond between the carbon atoms to be formed during the transition of the excited allyl radical to the cyclopropyl radical, the methylene groups should rotate with respect to the plane of the carbon skeleton and approach each other. The relaxation of the structure of the allyl radical in the $^2B_1$ ($C_{2v}$) electron-excited state after the "vertical" transition from the ($X(^2A_2)$, $C_{2v}$) ground state was analyzed by the quantum-chemistry methods* for two cases in which the system has retained either the $C_2$ or $C_s$ symmetry during relaxation. The former case (the $^2B$, $C_2$ state) corresponds to the possibility of a conrotatory displacement of the methylene groups, and the latter case (the $^2A'$, $C_s$ state) corresponds to their disrotatory displacement. As the initial structures, we chose structures, whose geometries differ slightly from the equilibrium geometry of the allyl radical in the ground state.

The relaxation of the $C_2$ structure ends in the formation of the cyclopropyl radical,** and this transition does not require overcoming any activation barrier. Thus, the cyclopropyl radical is an "equilibrium structure" of the allyl radical in the first electron-excited state $^2B_1$. This accounts for the efficiency of the phototransformation of allyl type radicals. The decrease in the energy of the system during relaxation may be estimated as 30—40 kcal mol$^{-1}$, and the energy of the electron excitation is ~3.0 eV (69 kcal mol$^{-1}$) (with the wavelength of the exciting light being 410 nm), but the allyl radical is more stable than the cyclopropyl radical by almost 30 kcal mol$^{-1}$.[4]

Conversely, the relaxation of the $^2A'$ state ($C_s$ symmetry) is accompanied by an increase in the distance between the terminal carbon atoms from 2.12 to 2.63 Å. In this case, the energy of the system diminishes, according to the calculation, by only 7.9 kcal mol$^{-1}$ (the calculation at the UMP2/6-31G*//UHF/6-31G* level).

The results obtained can be also interpreted based on qualitative considerations. The formation of a new σ-bond must involve two electrons that occupy the $(a_2)^2$ MO in the first excited state of the allyl radical. The structure of the corresponding orbitals is such that this requires a conrotatory movement of the methylene groups. During this rotation, the $b_1$ type MO is transformed into an orbital, which is occupied by the unpaired electron and which is localized at the α-carbon atom (C(2)) in the cyclopropyl radical formed.

According to the experimental data presented in Sections 1—3, cyclopropyl radicals differ in thermal stability depending on the structure of the substituent. The especially pronounced decrease in the activation energy of the transformation into the allyl radical occurs on introducing an electronegative substituent (radical **8**).

Some data indicating that the stability of the cyclopropane ring decreases on the introduction of electronegative substituents (F atoms) have been published.[31,36] We compared the transition states and activation energies of ring cleavage in the unsubstituted and β-fluorine-substituted cyclopropyl radicals.

According to the results of semiempirical (MINDO/3)[37] and *ab initio*[24] (at the CASSCF/3-21G level) quantum-chemical calculations, the transition state in the conversion of cyclopropyl radical into allyl radical is nonsymmetrical. The rotation of one of the methylene groups is accompanied by a decrease in the length of the corresponding $C_\alpha$—$C_\beta$ bond (formation of a π-bond), whereas the length of the second $C_\alpha$—$C_\beta$ bond varies slightly with respect to that in the starting cyclopropyl structure. Correspondingly, the change in the orientation of this $CH_2$-group in relation to the carbon skeleton plane is also small.

Our calculations confirm this conclusion. The results (optimization of the structures at the UMP2/6-31G* level) are presented in Tables 5 and 6 (the data obtained previously[24] are also included for comparison).

For the fluorine-substituted radical, four transition states were localized. They differ in the mutual arrangement of the α-H and β-F atoms (the *cis*- or *trans*-arrangement with respect to the plane of the carbon skeleton) as well as in the possible participation of the $CH_2$ or CHF group in the formation of the double bond. The matrices of the force constant of these structures have one negative eigenvalue each, *i.e.*, they are in fact the transition structures. The main components of the eigenvector, characterizing the movement of the system along the reaction coordinate, are associated with the variation of the C(1)C(2)C(3) bond angle and the rotation of either the CHF or CHH group.

One of the transition states considered has a substantially lower energy (it is more than 5 kcal mol$^{-1}$ lower than the energies of the other transition states differing by no more than 2.5 kcal mol$^{-1}$). The *cis*-mutual arrangement of the α-H and the F atoms and a shorter C—C bond between the central C atom and the C atom of the CHF group correspond to this state.

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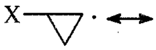
* In the SCF MO LCAO calculations, the geometry of a molecule or a radical can be optimized in several electronic states that relate to various irreducible representations of the corresponding point group, if the symmetry of the system is retained during optimization.

** In view of the symmetry restrictions accepted, the α-proton in the cyclopropyl radical formed is arranged in the carbon skeleton plane; however, the energy of this π-radical is only 3.9 kcal mol$^{-1}$ higher than the energy of its ground state.[14,28]

**Table 5.** Geometric characteristics of the transition state of the reaction



X–cyclo· ⟷ XHC$\cdots$CH$\cdots$CH$_2$ (X = H, F)*

| Characteristics | Radical | | | | |
|---|---|---|---|---|---|
| | $C_3H_5$**, CASSCF/3-21G | $C_3H_5$, UHF/6-31G* | $C_3H_5$, UMP2/6-31G* | $C_3H_4F$, UHF/6-31G* | $C_3H_4F$, UMP2/6-31G* |
| | Bond length/Å | | | | |
| C(1)—C(2) | 1.424 | 1.416 | 1.365 | 1.389 | 1.347 |
| C(2)—C(3) | 1.485 | 1.471 | 1.470 | 1.477 | 1.473 |
| C(1)—C(3) | 2.066 | 1.983 | 1.989 | 1.927 | 1.947 |
| H(4)—C(2) | | 1.075 | 1.083 | 1.074 | 1.082 |
| H(5)(F)—C(1) | | 1.079 | 1.094 | 1.332 | 1.353 |
| H(6)—C(1) | | 1.075 | 1.085 | 1.070 | 1.084 |
| H(7)—C(3) | | 1.074 | 1.084 | 1.074 | 1.084 |
| H(8)—C(3) | | 1.074 | 1.083 | 1.074 | 1.083 |
| | Angle/deg | | | | |
| C(1)C(2)C(3) | 90.5 | 86.7 | 89.1 | 84.5 | 87.2 |
| H(4)C(2)C(1) | | 122.6 | 122.9 | 120.7 | 121.5 |
| H(5)(F)C(1)C(2) | | 123.4 | 124.4 | 122.7 | 124.8 |
| H(6)C(1)C(2) | | 120.1 | 121.1 | 124.4 | 125.5 |
| H(7)C(3)C(2) | | 121.6 | 122.1 | 122.0 | 122.7 |
| H(8)C(3)C(2) | | 120.0 | 120.0 | 119.2 | 119.3 |
| H(4)C(2)C(1)C(3) | | −127.6 | −130.5 | −124.2 | −127.7 |
| H(5)(F)C(1)C(2)C(3) | | 114.8 | 127.6 | 121.5 | 127.8 |
| H(6)C(1)C(2)C(3) | | −71.5 | −57.0 | −71.4 | −58.3 |
| H(7)C(3)C(2)C(1) | | 87.3 | 83.0 | 86.0 | 81.5 |
| H(8)C(3)C(2)C(1) | | −95.7 | −96.8 | −103.7 | −105.7 |

* The numbering of the atoms is shown in Fig. 6. ** From published data.[24]

**Table 6.** Energy characteristics of the transformation of cyclopropyl radicals into allyl radicals

| Radical | $-E$(UMP2) (au) | $<s^2*>$ | $\Delta E$ /kcal mol$^{-1}$ | $-E$(PUMP2) (au) | $\Delta E$ /kcal mol$^{-1}$ | ZPVE /kcal mol$^{-1}$ | $\Delta H_0(0)$ /kcal mol$^{-1}$ | $\Delta H_0(0)$** /kcal mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| $C_3H_5$ (allyl) | 116.81022 | 0.96(0.76) | −20.3 | 116.82485 | −28.5 | 43.7 | −29.7 | −35.5 |
| TS*** | 116.71723 | 1.13(0.76) | 38.1 | 116.73513 | 27.9 | 41.9 | 24.9 | 21.9 |
| *cyclo*-$C_3H_5$ | 116.77791 | 0.76(0.75) | 0.0 | 116.77951 | 0.0 | 44.9 | 0.0 | 0.0 |
| $C_3H_4F$ (allyl) | 215.82746 | 0.95(0.76) | −23.0 | 215.84201 | −31.1 | 39.1 | −32.5 | |
| TS*** | 215.74502 | 1.02(0.76) | 28.7 | 215.75978 | 20.5 | 38.3 | 18.3 | |
| *cyclo*-$C_3H_4F$ | 215.79083 | 0.76(0.75) | 0.0 | 215.79245 | 0.0 | 40.5 | 0.0 | |

* The $<s^2>$ values after spin-projection of the wave function are given in parentheses. ** Published data[24] (calculation at the CASSCF/6-31G*//CASSCF/3-21G level). *** Transition state.

The geometry of this transition state is presented in Table 5.

The calculations at the CASSCF/3-21G [24] and UHF/6-31G* levels lead to a similar transition state geometry. However, with allowance for the electron correlation (UMP2/6-31G*), the difference between the C—C bond lengths in the transition state substantially increases. In addition, the angles of rotation of the $CH_2$ ($^{\cdot}C_3H_5$ radical) or CHF ($^{\cdot}C_3H_4F$ radical) groups with respect to the carbon skeleton plane increase, and the length of the corresponding C—C bond approaches the length of the C=C double bond in alkenes. Thus, in these calculations, the tendency to the formation of one π-bond in the transition state is more clearly manifested.

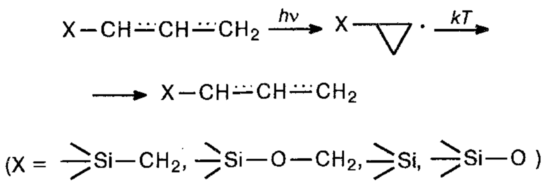
The $<s^2>$ values for the allylic and transition structures proved to be much higher than 0.75, *i.e.*, than the value corresponding to the doublet state of the system (see Table 6). This indicates that the states with higher multiplicities contribute to the wave function and results in the overestimation of the energies of the structures. The use of the spin-projected wave function (the $<s^2>$ values after spin-projection of the wave function are presented in Table 6 in parentheses) appreciably improve the situation. Calculations at this level

(PUMP2/6-31G*//UMP2/6-31G*, the PUMP2 column in Table 6) provide considerably better agreement between the experimental and theoretically calculated values of the thermal effects and activation energies of the interconversion of allyl and cyclopropyl radicals.

The introduction of the fluorine atom into the β-position of the cyclopropyl radical results in the decrease in the activation energy of ring cleavage by 6.5 kcal $mol^{-1}$ (see Table 6). This conclusion is in agreement with the experimental results obtained. Note also that according to the results of calculations, on going from the cyclopropyl radical to the corresponding fluorine-containing radical, the thermal effect of the *cyclo*-$\dot{C}_3H_4H(F) \longrightarrow CH_2{\cdots}CH{\cdots}CHH(F)$ reaction increases by approximately 3 kcal $mol^{-1}$. Thus, the introduction of an electronegative substituent has a greater effect on the kinetic (decrease in the activation energy of the ring cleavage) rather than on the thermodynamic (thermal effect of the reaction) stability of the cyclopropyl radical.

* * *

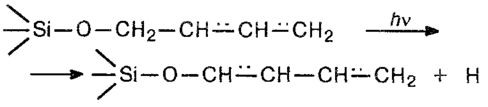
The presented experimental results concerning phototransformations of the substituted allyl radicals (λ ≥ 400 nm) indicate that as a result of the sequence of transformations



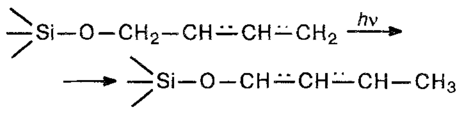
the concentration of paramagnetic centers remains constant.* This means that the reaction channel involving photocyclization of the allyl type radicals studied predominates.

Extensive literature is devoted to phototransformations of allyl type radicals.[26] These processes have been studied mostly in the solid state in hydrocarbon matrices. Several hypotheses concerning the possible mechanisms of phototransformations of these radicals have been put forward; in particular, participation of photoexcited allyl type radicals in intra- and intermolecular transfer of a hydrogen atom was discussed.[26]

In the studies of phototransformations of grafted allyl radicals, intermolecular reactions of the excited radical are excluded, and only the channels involving its intramolecular rearrangements are retained. The presence of substituents (with respect to the $CH_2{\cdots}CH{\cdots}CH_2$) in the allyl radicals studied by us could lead to the appearance of phototransformation pathways involving, for example, elimination

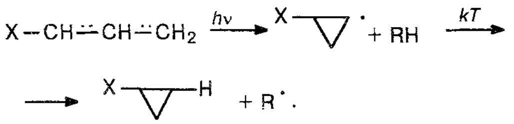


or intramolecular migration



of the H atom. However, even though these reactions occur on photoirradiation (λ ≥ 400 nm) of the systems studied, their efficiency is at least an order of magnitude lower than that of photocyclization.

Cyclopropyl type radicals possess high reactivity toward the abstraction of an H atom.[3] Therefore, it cannot be ruled out that the products of the H atom transfer in hydrocarbon matrices are formed *via* the formation of a cyclopropyl center, rather than in the direct inter- or intramolecular abstraction of the H atom by the photoexcited allyl radical. For example, in the case of the intermolecular process:



The use of the methods developed for preparing cyclopropyl type radicals stabilized on the silica surface makes it possible to pass to the investigation of their reactions with various compounds: CO, $O_2$, $CH_2{=}CH_2$, HC≡CH, *etc.* These studies are already in progress.

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* The high (for ESR) accuracy of these measurements (above 90 %) is caused by the fact that in the initial and final steps of the cycle, we obtain ESR spectra of the same radicals and can merely compare their intensities.

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