

# Rearrangement and Ion–Molecular Reactions of $C_5H_8^{+\cdot}$ -Related Radical Cations as Studied by EPR Spectroscopy in the Solid and Liquid Phase<sup>†</sup>

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Radical cations (RC) of vinylcyclopropane (VCP) generated at 77 K in X-ray irradiated freonic matrices (*gauche* and *anti*-VCP) rearranged at 105–110 K in  $CF_2ClCFCl_2$ –(Freon-113) with ring-opening to different distonic RC. Two types of allyl radical were formed after heating to 120–130 K. In liquid VCP, X-irradiated at 293 K using 2,4,6-tri-*tert*-butylnitrosobenzene (BNB) as a spin trap, five different BNB adducts with primary alkyl, cycloalkyl, *tert*-alkyl and allylic radicals were recorded as the products of rearrangement and ion–molecular reactions. We have examined the thermal reactions of RC of 1,3- and 1,4-dienes and cyclopentene in X-irradiated frozen matrices and also in the liquid phase. 1,3-Pentadiene radical cations in  $CFCl_3$  matrix at 77 K rearrange into the cyclopentene RC, and in Freon-113 matrix 1,3-pentadiene RC are transformed mostly into the allylic radicals.  $\sigma$ -Dimerization of 1,3- and 1,4-pentadiene RC and H-transfer from neutral molecules to RC proceed in Freon-113 matrix concurrently at 110 K upon phase transition. 1,4-Pentadiene RC in Freon-113 matrix are transformed into pentadienyl radicals. In liquid solutions containing BNB in 1,3- and 1,4-dienes, X-irradiated at 293 K, two radical adducts were recorded selectively from trapped radicals of *sec*-alkyl type and from primary allylic radicals as the result of two concurrent processes:  $\sigma$ -dimerization of diene RC dominated in the case of 1,3-diene and an ion–molecular reaction of H-atom transfer dominated in the case of 1,4-pentadiene. Radical cations of cyclopentene in Freon-113 matrix at 110 K upon phase transition are transformed into cyclic allylic radicals as a result of deprotonation from positions of highest spin population.

The technique of radiolytic generation and trapping of radical cations in frozen Freon matrices is widely used for studies of the structure and reactions of radical cations of a wide variety of organic compounds.<sup>1–7</sup> Investigation of the radical cations of unsaturated hydrocarbons is of particular interest since these compounds undergo efficient radiation-induced polymerization.<sup>2–5</sup> Prior to the development of the Freon matrix technique, the mechanisms of radiation-induced polymerization were mainly speculative. According to mass-spectrometric data<sup>8</sup> (collisional ionization and charge exchange between  $CS_2$  and a hydrocarbon molecule), eleven kinds of radical cation of general formula  $C_5H_8^{+\cdot}$  rearrange selectively to the radical cations of pentadiene, isoprene, or cyclopentene. The structures of the last three radical cations proved to be stable, that is, no interconversion occurred under the given gas-phase conditions.

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We have shown previously<sup>9,10</sup> that X-irradiation of solutions of vinylcyclopropane (VCP) in Freon-11 and Freon-113 at 77 K results in the selective formation of the primary VCP radical cations (in *gauche*- or *anti*-conformations). These conformers rearrange into distonic forms of the VCP radical cations of different structures designated as  $dist(0,90)-C_5H_8^{+\cdot}$  and  $dist(90,0)-C_5H_8^{+\cdot}$  upon warming of the samples to the phase transition point of Freon-113 (110 K). In this work we studied further thermal transformations of the distonic radical cations occurring in X-irradiated solutions of VCP in Freon-113 matrix after warming of the samples to temperatures above 115 K. We also consider the transformations of the radical cations of 1,3-pentadiene, 1,4-pentadiene, and cyclopentene, as studied by EPR techniques, in X-irradiated frozen Freon matrices at 77 K. Freon-11 ( $CFCl_3$ ) and Freon-113 ( $CF_2ClCFCl_2$ ) were used. The formation of radicals resulting from the transformations of primary radical cations was studied using 2,4,6-tri-*tert*-butylnitrosobenzene (BNB) as a spin

trap. The techniques of experiments with spin traps<sup>11</sup> have been described previously. All the samples were degassed to a residual pressure of  $10^{-4}$  Torr in SK-4B glass ampoules and irradiated with X-rays (30 keV) up to the doses of 5 kGy at 77 K (Freon solutions of hydrocarbons) or 100–200 Gy at 295 K (hydrocarbon solutions of spin traps). The hydrocarbon concentration in Freons varied from 0.01 to 16 mol%. The EPR spectra were measured at 77 and 293 K, and in the range 100–160 K.

## Results

**1. Vinylcyclopropane.** Many spin traps have provided little information in studies of the radical products of the radiolysis of cyclopropane and its derivatives. BNB was found to be the only acceptable spin trap. This spin trap reacts selectively with 1-alkyl type radicals via radical addition to a nitrogen atom yielding nitroxide radicals. Radicals with a tertiary carbon atom show addition only to an oxygen atom, resulting in *N*-alkoxyaminyl radicals, owing to steric reasons. Secondary alkyl radicals add to both sites (nitrogen and oxygen atoms). Figure 1 shows the EPR spectra of the VCP solutions containing BNB irradiated at 77 (a) and 295 (b)–(d) K and measured at 295 K. The spectra exhibit superimposed well-resolved lines from five different BNB adducts (three nitroxide radicals 1–3 and two oxyaminyl radicals, 4 and 5). The contribution from each adduct to the spectrum is affected strongly by the BNB concentration and the irradiation temperature. The EPR spectrum of adduct 1 is a  $3 \times 3 \times 3$  multiplet with splitting constants  $a^N = 13.5$  G ( $1 \text{ G} = 0.1 \text{ mT}$ ) due to nitroxide nitrogen atom,  $a_\beta(2 \text{ H}) = 18.6$  G due to the terminal protons of the added  $\cdot\text{CH}_2\text{CH}_2\text{R}$  radical, and  $a_m(2 \text{ H}) = 0.9$  G due to the *meta*-protons of the aryl group of BNB. These constants are characteristic of the BNB adducts with 1-alkyl radicals. Adduct 2 shows a  $3 \times 3 \times 3$  multiplet [ $a^N = 13.5$ ,  $a_\beta(2 \text{ H}) = 16.7$ , and  $a_m = 0.9$  G]. Considering the splitting constant due to the  $\beta$ -protons of the added radical, we can ascribe this multiplet only to the BNB adducts with allyl-type radicals. Nitroxide radical 3 gives a  $3 \times 2 \times 3$  multiplet [ $a^N = 13.5$ ,  $a_\beta(1 \text{ H}) = 21.2$ , and  $a_m = 1.0$  G], and oxyaminyl radical 4 a  $3 \times 4$  multiplet [ $a^N = 10.9$  and  $a_\beta(1 \text{ H}) = a_m(2 \text{ H}) = 2.0$  G] with  $g = 2.0040$ . These two adducts result from the addition of secondary alkyl radicals to a nitrogen atom (adduct 3) and to an oxygen atom (adduct 4) of the BNB molecule. Adduct 5 is an oxyaminyl radical, which exhibits a  $3 \times 3$  multiplet [ $a^N = 10.9$  and  $a_m(2 \text{ H}) = 1.9$  G]. This adduct results from the addition of *tert*-alkyl radicals to BNB. The hyperfine splitting constants of all the adducts observed are in accordance with the data reported for similar nitroxides and oxyaminyl radicals.<sup>12</sup>

Decrease of the BNB concentration from 0.5 to 0.01 M results in a considerable decrease in the relative yields of adducts 1 with *n*-alkyl radicals and an increase in the

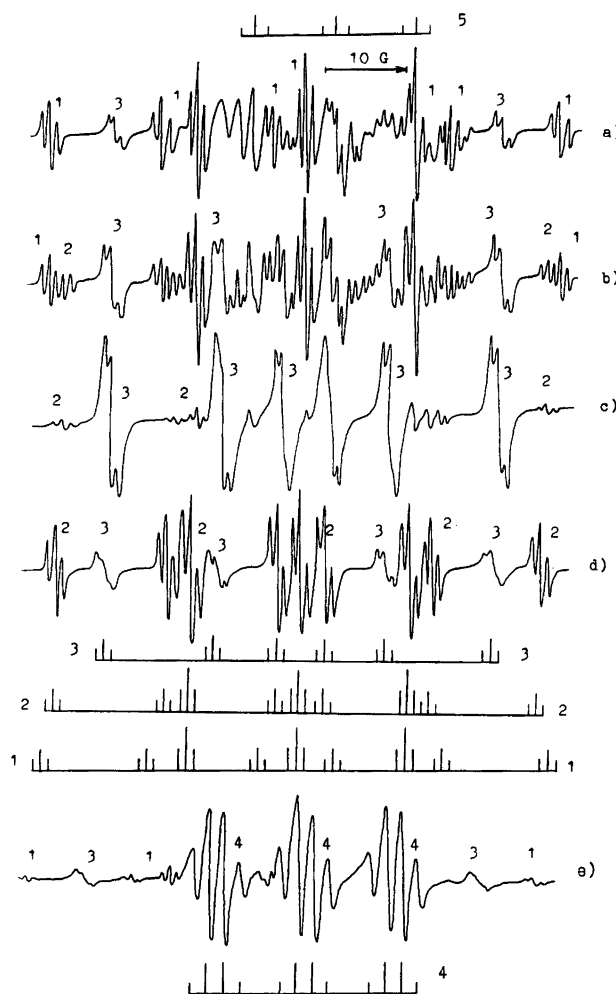
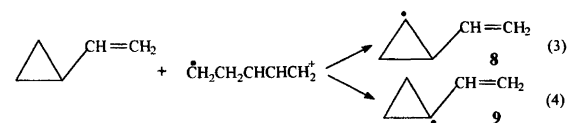
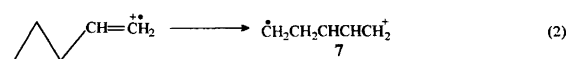
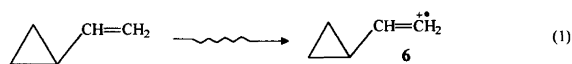
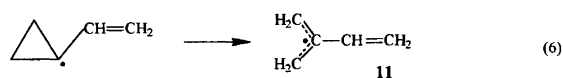
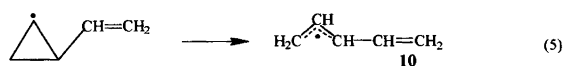


Fig. 1. EPR spectra of solutions of BNB, X-irradiated and measured at 293 K: (a), (b) 0.2 M BNB in VCP, irradiated at 77 K (a), and at 293 K (b). (c) 0.3 M BNB in 1,3-pentadiene; (d) 0.15 M BNB in 1,4-pentadiene; (e) 0.1 M BNB in cyclopentene. Numbers correspond to the BNB adducts with (3) *sec*-allyl radicals; (2) 1-allyl radicals; (1) 1-alkyl radicals; (4) cyclic allyl-type radicals in cyclopentene; (5) *tert*-alkyl radicals in 2,3-dimethylbutadiene. Adducts 1–3 are nitroxide radicals; adducts 4 and 5 are oxyaminyl radicals.

yield of adducts 3 (Fig. 2). This observation shows that approximately one-half of the secondary alkyl (cyclopropyl) radicals 8 result from reaction (3) of the  $\cdot\text{CH}_2\text{CH}_2\text{R}$  type radicals 7 with VCP matrix.

On the other hand, the concentration of the spin trap





does not affect the yield of adducts **2** with allyl radicals within the limits of experimental error (irradiation at 293 K). Irradiation at 77 K does not result in formation of allyl radicals after melting of the sample [Fig. 1(a)]. The effect of the BNB concentration on the yield of the trapped radicals can be explained by the occurrence of reactions (1)–(6) in the liquid phase. Taking into account high rate constants of trapping of alkyl-type radicals ( $2 \times 10^4$ – $10^5 \text{ M}^{-1} \text{ s}^{-1}$ ), one can see that 95% of the radicals formed in the primary processes are trapped by BNB at large BNB concentration (0.5 M). The yield of secondary alkyl radicals (determined in the form of adducts **3**) is suppressed only to one-half in the presence of 0.5 M of BNB. This result implies that the unaffected fraction of these radicals is formed by an independent path different from reaction (3). Computer simulation of the EPR spectra of the BNB spin adducts for solutions containing 0.5 M of BNB at 293 K shows the best fit with the experimental spectrum assuming the following fractions of the radical adducts in the spectrum: 0.15 for **1**, 0.1 for **2**, 0.3 for **3**, 0.4 for **4**, and 0.05 for **5**. Thus, cycloalkyl radicals **8** trapped by BNB as adducts **3** and **4** yield approximately 70% of the total amount of radicals.

VCP molecules exist in the condensed state mainly in the form of *anti*-conformers.<sup>13</sup> Therefore, X-irradiation results in the predominant formation of the radical cations *anti*-VCP (6), which rearrange into a distonic form **7** via reaction (2). Radicals **7** abstract H atoms

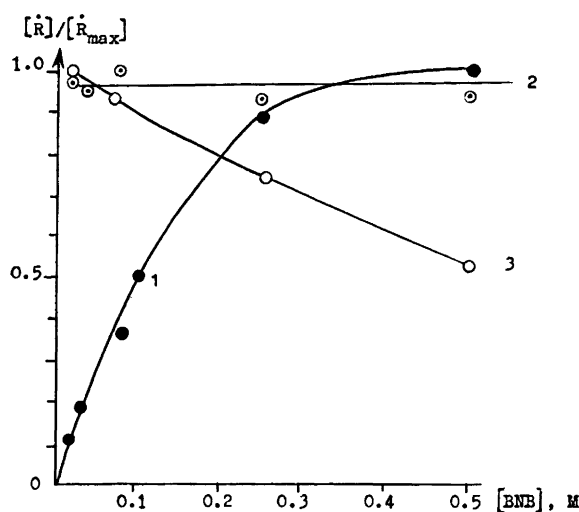


Fig. 2. The effect of concentration of spin trap on the relative yields  $[R]/[R]_{\max}$  of the BNB adducts **1**, **2** and **3** observed in the VCP solutions containing BNB after irradiation with X-rays at 293 K.

from two possible sites in the cyclopropane ring resulting in the formation of radicals **8** and **9**. Radical **9** has been observed previously in EPR spectra only in a  $\text{CFCl}_3$  matrix.<sup>10</sup> Ring opening in the cyclopropyl radicals **8** and **9** results in the formation of allyl radicals [reactions (5) and (6)]. Figure 2 shows that the cyclopropyl radical **8** and allyl radicals are formed not only in reaction (3) involving a distonic radical cation, but also by an alternative route. This latter way is an ion-molecule reaction (7) occurring via H-atom transfer from a neutral VCP molecule to the primary radical cation. Deprotonation from the ring sites of *anti*-VCP radical cation is unlikely because the spin density in this radical cation is localized mainly at the vinyl group.<sup>9,10</sup> In contrast, it is logical to assume that radicals **9** result from deprotonation of the *gauche*-VCP radical cations (**13**) occurring from the ring site with maximum spin population [position 1,  $a(1 \text{ H}) = 26 \text{ G}$ ] via reaction (8). The latter reaction competes with ring opening (9) resulting in a distonic radical cation  $\text{dist}(0,90)\text{-C}_5\text{H}_8^{+\cdot}$  (**14**).

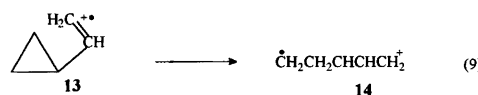
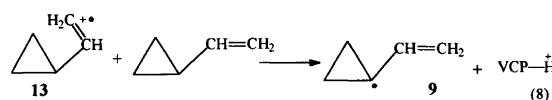
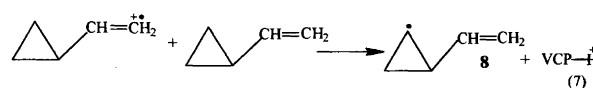


Figure 3 shows the EPR spectra of a Freon-113 solution containing 1.0% VCP and irradiated with X-rays at 77 K. Warming of the irradiated sample to 113 K results in almost complete conversion of *anti*-VCP radical cations into their distonic form  $\text{dist}(90,0)\text{-C}_5\text{H}_8^{+\cdot}$  **7** with splitting constants  $a_x(2 \text{ H}) = 22.7$  and  $a_\beta(2 \text{ H}) = 30.4 \text{ G}$ . The assignment of these EPR spectra and chemical behavior of the forms of VCP have been discussed in detail in Refs. 9 and 10. Warming of the samples to the temperatures above 113 K results in irreversible transformation of the triplet of triplets of radicals **7** into a quintet spectrum of an allyl radical with a splitting constant  $a(4 \text{ H}) = 15.8 \text{ G}$  (**11**). The formation of allyl radical **11** connected with the decay of a distonic radical cation **7** can be easily explained by reactions (5) and (6). The conversion of **7** into **9** is complete at 130 K [Fig. 3(c)]. Further warming of the sample from 130 to 135 K leads to a sharp decrease in the integrated intensity of the EPR signal and transformation of the quintet signal from the allyl radical **11** to a poorly resolved sextet-like signal. This latter spectrum can be interpreted as a quartet of doublets with splitting constants  $a_x(3 \text{ H}) = 13.8 \text{ G}$  and  $a_\beta(1 \text{ H}) = 27.7 \text{ G}$ . Such a set of splitting constants may result from three  $\alpha$ -protons of an

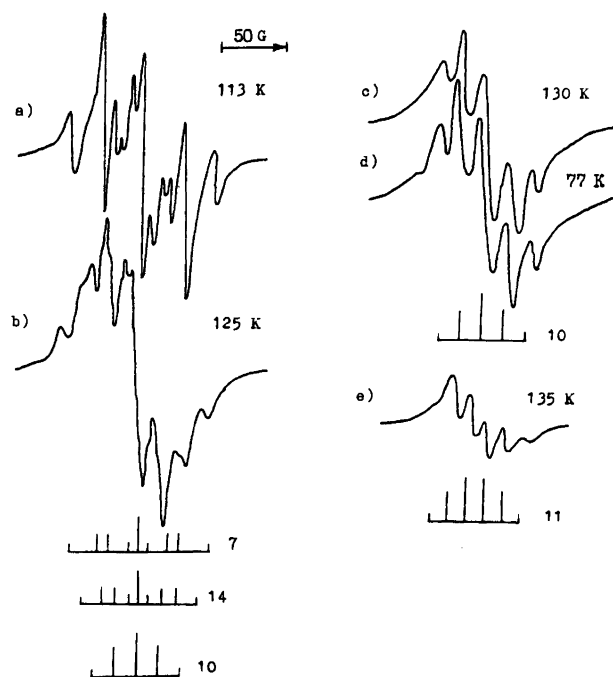


Fig. 3. EPR spectra of a  $\text{CFCl}_2\text{CF}_2\text{Cl}$  solution containing 1.0 mol% of VCP irradiated with X-rays at 77 K. The spectra were measured at (a) 113, (b) 125, (c) 130, and (e) 135 K. Spectrum (d) was recorded at 77 K after warming of the sample to 130 K.

allylic system and one  $\beta$ -proton, which is oriented parallel to the axes of the atomic p-orbitals of the allylic system. A structure of this kind is realized in the allyl radical **10** resulting from ring opening of the cyclopropyl radical **8**.

The chemical behavior of the VCP radical cations in solid and gaseous states of VCP is determined by the type of conformation of the parent molecule (*gauche*- or *anti*). A selective path for the conversion of the primary VCP radical cations into their distonic forms is realized in a given aggregative state. This selectivity is determined by the electronic structure of the primary radical cations.<sup>9,10</sup> In contrast with this behavior, in liquid VCP, fast rearrangement, eqn. (2), is followed by a relatively slow non-selective H-atom transfer from *anti*-VCP to a distonic radical cation **7** or to the primary radical cation. The transfer occurs simultaneously from two sites of cyclopropane ring. In this case, the energies of H-atom abstraction from the different cyclopropane ring sites appear to be nearly the same, whereas molecular motion in the liquid phase allows the mutual spatial arrangement of a VCP molecule and radical cation **7** to occur, which is required for occurrence of the reactions (3) and (4).

We should note that, unlike in liquid VCP, in a frozen Freon-113 matrix cyclopropyl radicals are not stabilized, but undergo immediate ring opening and rearrangement to the allylic structures **10** and **11**. A similar behaviour is observed for the cyclopropane radical cations under the same conditions.<sup>14,15</sup> This is presumably due to the fact that the radical (allylic) and vinylic  $\pi$ -systems are positioned in perpendicular planes in 1-vinylallyl radical.

According to calculations carried out with an extended 6–31 G\* basis,<sup>16</sup> such a conformation of  $\text{C}_5\text{H}_7$  radical **10** corresponds to a transition state in the isomerizations of the planar forms of pentadienyl radicals.<sup>16</sup> Allyl radical **10** was not observed in EPR studies in the liquid phase, when pentadienyl radicals were generated, in particular, from linear pentadienes.<sup>16</sup> Thus, the conformation of allyl radical **10** is unstable and can be stabilized only by external factors.

On the other hand, 2-vinylallyl radical **11** seems to be more stable because the orientation of vinyl group relative to C–C bonds of the allylic system (or to the cyclopropane ring) in **11** is the same as in the parent *anti*-VCP molecule and cyclopropyl radical). Therefore, it is not surprising that radical **11** occurs as the main product of an ion–molecule reaction (4) in Freon-113 matrix, whereas radical **10** is formed in considerably smaller amount. This selectivity is not observed in liquid VCP. Assuming the energies of the C–H bond cleavage in positions 1, 2 and 3 to be equal, one can see that the probability of H-atom abstraction from positions 2 and 3 [reactions (3) and (7)] is much higher than that from position 1, owing to statistic factors. For this reason, radical **8** is formed mainly in the liquid phase. This radical is trapped by the BNB molecules yielding two kinds of adducts, which account for approximately 70% of the total amount of the trapped radicals

2. *1,3-Pentadiene*. Irradiation of  $\text{CFCl}_3$  solutions of 1,3-pentadiene (0.1–2%) at 77 K results in the appearance of  $5 \times 5$  multiplets with splitting constants  $a_1(4\text{H}) = 50.17$  and  $a_2(4\text{H}) = 8.6$  G in the EPR spectra measured at 100–150 K (Fig. 4). These splitting constants are characteristic of cyclopentene radical cations.<sup>2</sup> A similar spectrum was observed at 100–130 K after irradiation of a  $\text{CFCl}_3$  solution of cyclopentene (0.5–2%) at 77 K [Fig. 4(b)]. Irradiation of a  $\text{CF}_3\text{CCl}_3$  solution of 1,3-pentadiene (1%) also results mainly in the formation of the cyclopentene radical cations with an identical hyperfine structure. This result is in accordance with the data reported in Ref. 2. Thus, our results provide evidence for the quantitative conversion (rearrangement) of 1,3-pentadiene radical cations into cyclopentene radical cations occurring in polycrystalline Freon matrices of  $\text{CFCl}_3$  and  $\text{CF}_3\text{CCl}_3$ .

We have shown previously<sup>7</sup> that these matrices are characterized by the presence of ‘cavities’, which are large enough to allow the occurrence of intramolecular transformations (such as rearrangements). On the other hand, the rigid walls of the ‘cavities’ in a polycrystalline matrix prevent radical cations from undergoing intermolecular interactions (ion–molecule reactions). The latter reactions occur with high efficiency in a glassy Freon-113 matrix as a result of reorganization of the matrix structure upon phase transition of the kind ‘glass–polycrystal’ near 110 K.<sup>7</sup>

Irradiation of Freon-113 solutions containing 1,3-pentadiene (0.01–10%) with X-rays results in a different

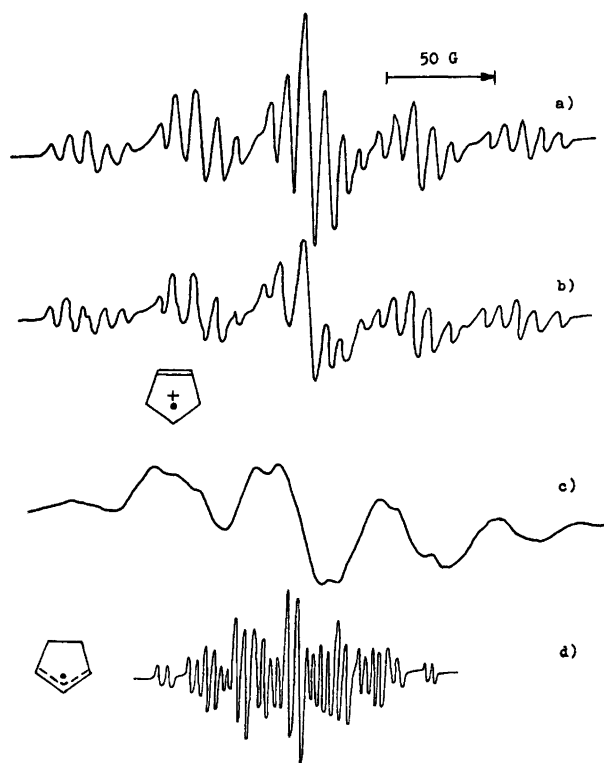


Fig. 4. EPR spectra of Freon solutions X-irradiated at 77 K: (a) 2% 1,3-pentadiene in  $CFCl_3$ ; (b) 0.5% cyclopentene in  $CFCl_3$ ; (c), (d) 0.1% cyclopentene in  $CFCl_2CF_2Cl$ . The spectra were measured at (a), (b) 133 K, (c) 77 K and (d) 110 K.

EPR spectrum (Fig. 5). The characteristic hyperfine structure of cyclopentene radical cations is not observed. In the case of small solute concentration (0.01–0.2%) in Freon-113, we observed a broadened septet with a splitting constant  $a(6H) = 15.8$  G (measurement at 100–105 K). This septet can be ascribed to a 1,3-pentadiene radical cation. Upon increasing the temperature to 110–120 K, we observed multiplets of broadened lines that resulted from at least three kinds of radical present in the EPR spectra over the entire concentration range studied (0.1–10% of 1,3-pentadiene). The following species were identified in the concentrated Freon-113 solution (10% 1,3-pentadiene): -cyclic allyl-type radical with splitting constants  $a_1(4H) = 23.2$ ,  $a_2(2H) = 14.2$ , and  $a_3(1H) = 3.1$  G (see section 4 below); a  $\sigma$ -dimeric distonic radical cation of 1,3-pentadiene (product of addition of the primary 1,3-pentadiene radical cation to a neutral diene molecule) with splitting constants  $a(3H) = 16.0$  G due to methyl group protons,  $a(1H_4) = 11.0$  G due to a  $\beta$ -proton of the  $CH_2$  group,  $a(2H_{1,3}) = 11.0$  G due to the CH terminal protons of the allylic system, and  $a(2H_{1,4}) = 4$  G due to protons in positions 2 and 4 (in the case where the  $CH_3$  group is in a *trans*-position).

In addition, the lines of the pentadienyl radical [ $a(5H) = 9$  G] are present in the spectrum under consideration. It is the  $\sigma$ -dimeric radical that makes the major contribution to the spectrum. The computer-simulated

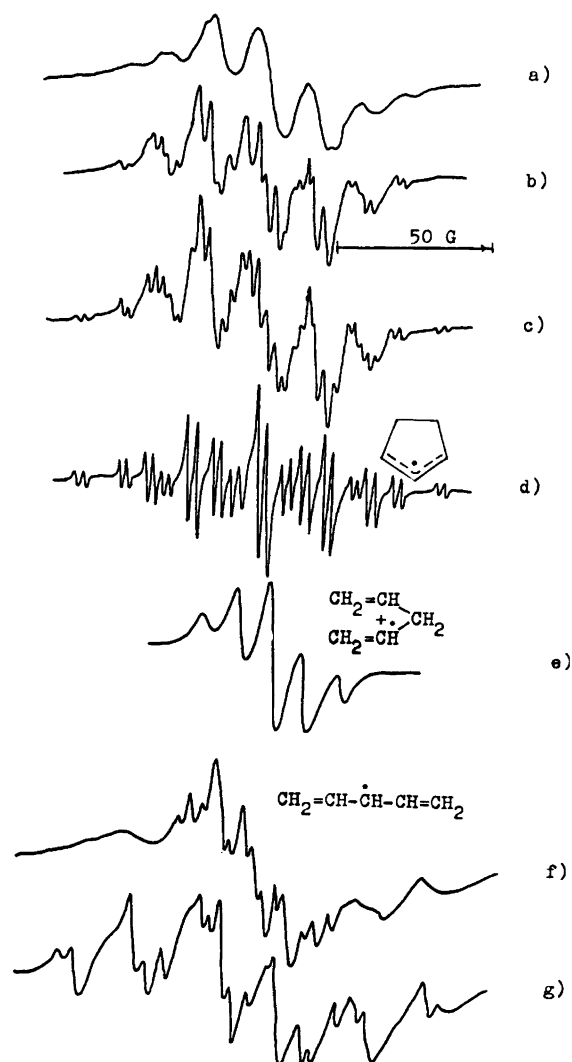
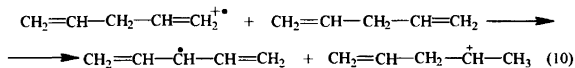


Fig. 5. EPR spectra of  $CFCl_2CF_2Cl$  solutions X-irradiated at 77 K: (a), (b) 0.1% 1,3-pentadiene measured at (a) 105 and (b) 130 K; (c) 10% 1,3-pentadiene measured at 130 K; (d) 0.1% cyclopentene measured at 110 K; (e) EPR spectrum of a Freon solution of 0.1% 1,4-pentadiene in  $CFCl_3$  (spectrum measured at 140 K); (f), (g) 1.2% 1,4-pentadiene in Freon-113 measured at (f) 118 and (g) 125 K.

spectrum shows the best agreement with the experimental spectrum assuming the fraction of this radical to be ca. 80%. The fractions of each of two other radicals cannot exceed 10%. It should be noted that the cyclic allyl-type radical is not observed in dilute solutions of the diene in Freon-113. One can observe the presence of this cyclic radical from the comparison of the spectra shown in Fig. 5(c) (note the outermost lines of the spectrum) and Fig. 5(d). In the latter case, the radical under consideration is observed as the main product of transformation of the primary cyclopentene radical cations, which occurs upon warming of the irradiated solutions of cyclopentene (0.1–10%) to 110 K. In the case of concentrated solutions of 1,3-pentadiene in Freon-113, this radical results from the rearrangement of a 1,3-pentadiene radical cation to

a cyclopentene radical cation followed by subsequent deprotonation (see below). The addition reaction of a 1,3-pentadiene radical cation to a neutral diene molecule competes with this rearrangement.

3. *1,4-Pentadiene*. Irradiation of  $\text{CFCl}_3$  solutions containing 1,4-pentadiene (0.1–10%) with X-rays at 77 K results in the appearance of similar EPR spectra, independent of the diene concentration and of measurement temperature variations in the range of 100–160 K. In all cases, we observed a quintet with a splitting constant  $a(4\text{ H})=11\text{ G}$  [Fig. 5(e)] due to similar splittings from the hydrogen atoms in positions 1 and 5. Such a spectrum should correspond to a planar structure of the primary 1,4-pentadiene radical cation and not to a twisted structure. A similar spectrum with  $a(4\text{ H})=10.4\text{ G}$  was observed previously for the butadiene radical cation in a  $\text{CFCl}_3$  matrix at 77 K.<sup>2</sup> 1,5-Hexadiene radical cations also appear to exhibit a planar structure with splitting constant  $a(4\text{ H})=11.4\text{ G}$  in Freon-113 matrix at 77 K. All three radicals are likely to have *gauche*-configuration. We should note that a sextet with a splitting constant  $a(5\text{ H})=9.0\text{ G}$  resulting from pentadienyl radicals is also observed in the EPR spectrum of concentrated solution of 1,4-pentadiene (16%) in  $\text{CFCl}_3$  (in addition to the quintet from the radical cation). The formation of these radicals directly after irradiation at 77 K provides evidence for the occurrence of H-atom transfer from a neutral diene molecule to its radical cation [eqn. (10)].



The sextet with  $a(5\text{ H})=9.0\text{ G}$  due to pentadienyl radical (the splitting constants from the protons in positions 1, 3 and 5 are approximately equal, and the splittings from the protons in positions 2 and 4 are not resolved) is also observed in the EPR spectra of the irradiated solutions of 1,4-pentadiene (0.2–1%) in Freon-113 matrix at 77 K and after warming to 110 K [Fig. 5(f)]. An additional splitting of  $a(2\text{ H})=4\text{ G}$  is observed at 118 K. Pentadienyl radical is formed in Freon-113 matrix, even in relatively dilute solutions, as a result of an ion-molecule reaction (10) occurring due to reorganization of the matrix structure upon phase transition. This is the case for many systems studied in this glassy matrix.<sup>7</sup> Increase in the measurement temperature to 125 K results in the appearance of poorly resolved multiplets with splitting constants  $a_{\beta 1}(2\text{ H})=30$ ,  $a_{\alpha}(1\text{ H})=20$ ,  $a_{\beta 2}(2\text{ H})=18$ , and  $a_{\gamma}(2\text{ H})=6.0\text{ G}$  [Fig. 5(g)]. This spectrum can be ascribed to a 1,4-distonic radical cation. However, this identification is not unequivocal since the simulated spectrum fails to reproduce all the lines of the experimental spectrum.

4. *Cyclopentene*. Only a quintet of quintets with splitting constants  $a_1(4\text{ H})=50.2$  and  $a_2(4\text{ H})=8.6\text{ G}$  resulting from cyclopentene radical cations is observed in the EPR

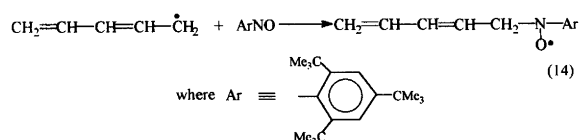
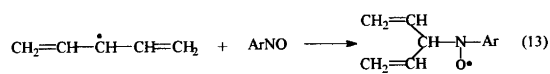
spectra of irradiated  $\text{CFCl}_3$  solutions containing cyclopentene (0.1–2%), as shown in Fig. 4(b). These radicals are stable at 77–150 K (almost up to the matrix melting point). In the case of more concentrated solutions (2–5%) in Freon-111, formation of cyclic allyl-type radicals was observed after warming of the sample to 160 K. These radicals result from a bimolecular reaction (3) occurring upon softening of the matrix near its melting point (163 K). Irradiation of 0.01–1% solutions of cyclopentene in Freon-113 also results in the formation of the cyclopentene radical cations (the broadened spectra shown in Fig. 4(c)). Warming of irradiated Freon-113 solutions to 100–110 K leads to a quantitative transformation of the cyclopentene radical cations into cyclic allyl-type radicals [Figs. 4(d) and 5(d)]. This latter species is the only radical observed in the EPR spectra at higher solute concentrations (1–20%) in Freon-113: a  $5 \times 3 \times 2$  multiplet with  $a(4\text{ H}_{4,5})=23.2$ ,  $a(2\text{ H}_{1,3})=14.2$ , and  $a(1\text{ H}_2)=3.1\text{ G}$ . Formation of this radical occurs via deprotonation from the sites with maximum spin population (positions 3 and 5) by an ion-molecule reaction (11).



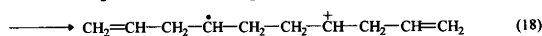
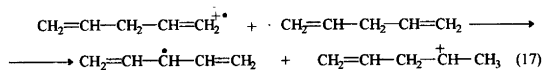
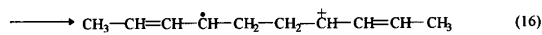
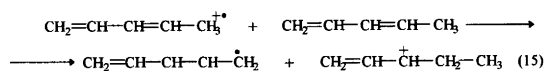
Study of extremely dilute solutions of cyclopentene in Freon-113 (0.02%), which were warmed to 110 K after irradiation, provided evidence for the formation of a distonic form of the radical cation  $\text{dist}(0,90)\text{-C}_5\text{H}_8$  (*gauche*-form as in a distonic vinylcyclopropane radical)<sup>12</sup> the corresponding splitting constants being  $a(2\text{ H}_\alpha)=14.2$  and  $a(2\text{ H}_\beta)=21.7\text{ G}$ . The distonic form results from ring opening of the cyclopentene radical cation. Formation of such a distonic radical cation is supported by the results of studies of cyclopentene solutions of 0.01–0.1 M BNB irradiated with X-rays at 295 K [Fig. 1(c)]. Major BNB adducts are nitroxide radicals **1** [ $a^{\text{N}}=13.2$ ,  $a_{\beta}(1\text{ H})=21.2$ , and  $a_m(2\text{ H})=0.8\text{ G}$ ] and oxyaminyl radicals **4** [ $a^{\text{N}}=10.9$  and  $a_m(2\text{ H})=a_{\beta}(1\text{ H})=2.0\text{ G}$ ], which result from addition of cyclic allyl-type radicals to nitrogen or oxygen atoms of BNB molecules, respectively. In addition to these adducts, we observed BNB adducts of type **3** with *n*-alkyl-type radicals [the corresponding splitting constants are typical for this type of nitroxide radical [10]:  $a^{\text{N}}=13.7$ ,  $a_{\beta}(2\text{ H})=18.0$ , and  $a_m(2\text{ H})=0.7\text{ G}$ ]. This observation provides evidence for ring opening [reaction (12)].

5. *1,3-Pentadiene and 1,4-pentadiene: irradiation in the liquid phase*. Irradiation of 0.02–0.2 M solutions of BNB (spin trap) in 1,3-pentadiene at 295 K results in the formation of BNB adducts **3** in the form of nitroxide

radicals [ $3 \times 3 \times 3$  multiplet with  $a^N = 13.6$ ,  $a_\beta(1\text{H}) = 21.2$ , and  $a_m(2\text{H}) = 0.9\text{ G}$ ]. The fraction of these adducts is larger than 90% of the total amount of the radicals observed in the EPR spectrum. Adducts **2** resulting from addition of allyl radicals with a primary carbon [ $3 \times 3 \times 3$  multiplet with  $a^N = 13.7$ ,  $a_\beta(2\text{H}) = 17.0$ , and  $a_m(2\text{H}) = 0.9\text{ G}$ ] also make a minor contribution to the spectrum. The parameters of the EPR spectra of the BNB radical adducts are in accordance with those reported for these nitroxides in the literature.<sup>12</sup> Adduct **3** may result from addition of a radical with a secondary carbon (*sec*-allyl or *sec*-allyl radical) to BNB. In turn, these latter radicals may arise from addition of the primary 1,3-pentadiene radical cation to a neutral diene molecule in the liquid phase or during the course of defreezing of diffusion mobilities upon phase transition in Freon-113 (110 K).



A pentadienyl radical has two equivalent reaction sites (terminal CH<sub>2</sub> group and internal CH group) with roughly equal spin densities:  $a(2\text{H}_1) = 10.3$ ,  $a(2\text{H}_5) = 9.7$ ,  $a(1\text{H}_3) = 11.6$ , and  $a(2\text{H}_{2,4}) = 3.2\text{ G}$ .<sup>17</sup> Therefore, addition of the pentadienyl radicals to both kinds of reaction site occurs with almost equal probability (provided that the addition is controlled by electronic effects). It is pentadienyl radical that is mainly formed in the case of 1,4-pentadiene. The diene structure strongly affects the ratio of these adducts at large BNB concentration (when all the radicals that have escaped into the bulk solution are trapped). In the case of 1,3-pentadiene, the fraction of *sec*-allyl radicals exceeds 90% of the total number of trapped radicals, whereas for 1,4-pentadiene the amounts of adducts **3** and **2** are almost equal. This difference can be easily explained by competition of two processes:  $\sigma$ -dimerization of a radical cation and a diene molecule [eqns. (16) and (18)], and H-atom transfer from a diene molecule to a radical cation [eqns. (15) and (17)]:



$\sigma$ -Dimerization of the radical cation and 1,4-pentadiene molecule is unlikely since this process should result in formation of a 1,4-distonic radical cation with destabilized cationic and radical sites [reaction (18)]. For this reason, H-atom transfer from the 1,4-pentadiene molecule to its radical cation is more favorable than  $\sigma$ -dimerization. H-atom transfer results in the formation of a pentadienyl radical. On the other hand, in the case of 1,3-pentadiene, both cationic and radical sites can be contained within the allylic systems. Such a stabilization results in favorable  $\sigma$ -dimerization and formation of more than 90% of adducts **3** with *sec*-allyl radicals. Formation of a small amount of adducts **2** with radicals is due to hydrogen abstraction [eqn. (15)]. However, the contribution of this process is minor.

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