Rearrangements of Free Radicals, XII[1])

ESR Spectroscopic Study of the Ring Opening of the Homobenzvalenyl Radical

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Abstraction of an allylic hydrogen atom in homobenzvalene (4) either in solution by photolytically generated tert-butoxyl radicals or in an adamantane matrix by X-rays produces the homobenzvalenyl radical (5), which thermally rearranges to the tropylium radical (7). In solution the activation energy for the rate determining step of the reaction sequence was determined to be 13.4 ± 0.5 kcal/mol.

Rearrangements of free radicals have been investigated thoroughly in recent years[2]. It is now well recognized that free radicals show a behavior in rearrangement reactions which is not different in principle from that of other reactive intermediates. Particularly, studies in an adamantane matrix[1] have disproved the widespread opinion that free radicals do not rearrange as easily as carbocations or carbanions. The possibility to undergo reactions with low activation barriers in solution, i.e. the recombination or disproportionation of radicals, has obscured their rearrangement capabilities. Under conditions of long lifetime (e.g. adamantane matrix) the latter reactions are suppressed and others therefore become apparent.

Recently, we have described rearrangements on the potential surface of C₇H₇ radicals[1]. The most stable species in this series is the tropylium radical (7). Radical 5 derived from homobenzvalene is isomeric to bicyclo[3.2.0]heptadienyl radical 1, 3-quadricyclanyl radical (2), and 7-norbornadienyl radical (3).
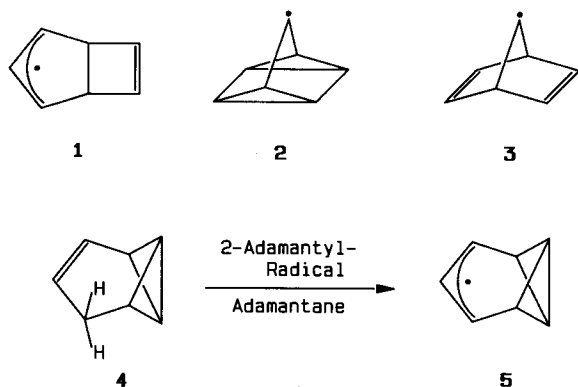
Two methods were applied to generate 5. First, homobenzvalene (4) was exposed to X-rays in an adamantane matrix at −196 °C. After transfer of the matrix into the cavity of the ESR spectrometer at low temperature we observed at temperatures below −100 °C only signals due to the 2-adamantyl radical[3]. Close to −100 °C the intensity of this signal decreased slowly and a new spectrum, identified as that of the tropylium radical (7) [a_H (−100 °C) = 0.396

± 0.004 mT], appeared. These signals became visible already 5 min after heating the matrix from −196 to −100 °C, and their intensity increased steadily for three hours at −100 °C. Spectral simulations, which included the 2-adamantyl radical, 7, and 5 (see below), gave evidence that also 5 is present at −100 °C. However, the multiplicity of its lines prohibits an unambiguous identification. The appearance of 7 indicates hydrogen abstraction from the substrate homobenzvalene by the initially generated 2-adamantyl radicals to form the homobenzvalenyl radical (5), which obviously undergoes a facile rearrangement to the tropylium system, possibly via the intermediate 6.
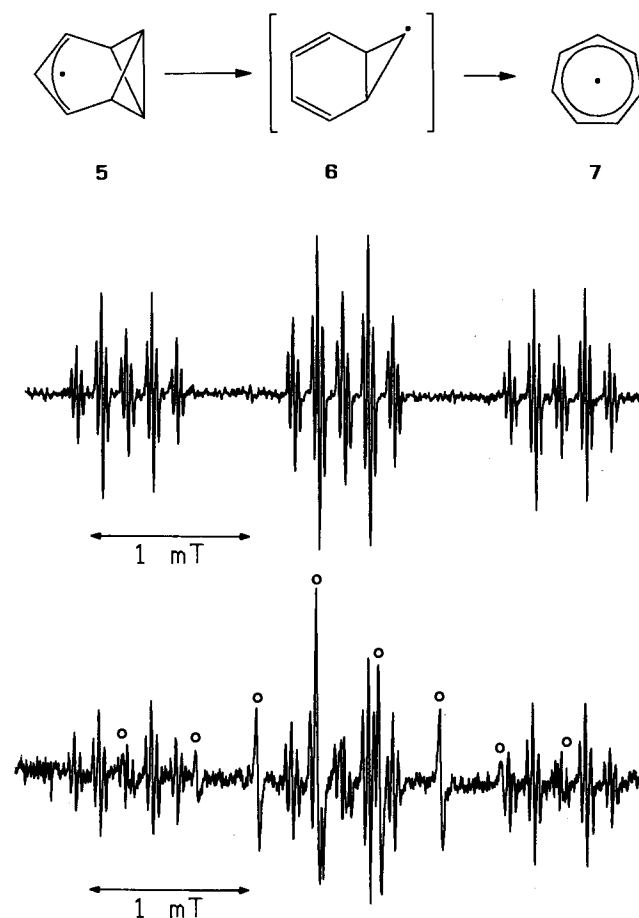

Figure 1. ESR spectrum of the homobenzvalenyl radical (5) in trichlorofluoromethane at −80 °C (top) and in liquid paraffine at +2 °C (bottom). Circles denote the hyperfine lines of the tropylium radical (7)

In further experiments we studied the hydrogen abstraction by photolytically generated *tert*-butoxyl radicals in solution. In trichlorofluoromethane solution a high-resolution ESR spectrum of **5** could be recorded from −100 to 20 °C (Figure 1). The spectrum is characterised by a large hyperfine coupling constant of 1.337 mT from two hydrogen atoms, typical for hydrogens in allylic position. The coupling of 0.320 mT is due to the central hydrogen atom in the allylic system and compares well with other allylic radicals[4].

Two more coupling constants can be recognized (a_H = 0.155 and a_H = 0.032 mT), each due to the interaction of the unpaired electron with two equivalent hydrogen atoms. The hyperfine coupling constant of 0.155 mT is assigned to the lateral bicyclobutane hydrogen atoms by comparison with the ESR spectrum of the bicyclo[3.1.1]heptenyl radical (**8**)[4]. In **8** an additional coupling constant of 0.155 mT for two hydrogen atom atoms is observed, attributed to the *anti* hydrogen atoms at the methylene bridges[4,5]. The small hyperfine coupling constant of 0.032 mT (2H) in **5** must arise from the interaction with the two hydrogen atoms at the bicyclobutane bridgeheads. The corresponding coupling constant (*syn* hydrogen atoms at the methylene bridges) could not been detected in the spectrum of **8** because of the line broadening effect of the adamantane matrix.

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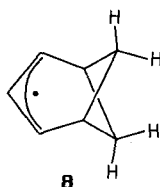
In trichlorofluoromethane solution we could not observe the rearrangement of **5** to **7**. The competing dimerisation, which can safely be assumed to be diffusion-controlled, is much faster than the isomerisation and thus reduces the lifetime of **5**. However, in the higher viscous liquid paraffine the mean lifetime of **5** is increased and now the rearrangement to **7** at temperatures above 0 °C can be observed (Figure 1). With increasing temperature, radical **7** becomes dominant in the ESR spectrum. A kinetic analysis of the reaction in paraffine solution, analogous to that for other rearrangements[5,6], led to the determination of the activation barrier of the rate determining step of the isomerisation. Experimentally, the ratio of the concentration of the radicals **5** and **7** as a function of the temperature is measured and the activation energy is obtained from a plot of the logarithm of the concentration ratio vs. $1/T$ according to equation (1).

$$\lg([7]/[5]) = \lg\{A_r/(I \cdot A_t)^{1/2}\} - (E_r - E_t/2)/2.3\,RT \qquad (1)$$

Here, E_r denotes the Arrhenius activation energy for rearrangement and E_t the activation energy for termination (dimerisation). A_r and A_t stand for the corresponding frequency factors, I describes the rate of formation of radicals **5**, assumed to be constant in the temperature range of our measurements[5]. For the analysis, the activation energy E_t for recombination of **5** in our solvent system is required. The recombination of sterically unhindered allylic radicals is diffusion-controlled[6,7]. The activation energy of this process, therefore, is governed solely by the temperature dependence of the solvent viscosity. A similar situation should hold in our case. According to the von Smoluchowski equation[8,9], the rate constant for diffusion-controlled reactions can be determined if the diffusion coefficient of the substrate is known. The latter can be approximated by the dynamic viscosity of the solvent via the Stokes-Ein-

stein equation[10]. From the determination of η as a function of temperature we obtained a value of 7.4 ± 0.2 kcal/mol for E_t. Using this value we calculated the activation energy for the rearrangement of **5**→**7** to be 13.4 ± 0.5 kcal/mol.

Although releasing considerable strain energy, the process **5**→**6** may well be slightly endothermic since an unfavourable cyclopropyl radical is produced on the account of an allylic radical. Therefore, the driving force for the rearrangement must be provided by the subsequent formation of **7**, the most stabilized member of the C_7H_7 family. Since conjugating substituents in position 2 or 3 of the cyclopropyl radical facilitate its electrocyclic ring opening[1,11], the norcaradiene radical **6** should undergo the ring enlargement readily. Hence, the rate determining step should be the transformation **5**→**6** rather than **6**→**7**.

Experimental

ESR measurements: Bruker ER-420 instrument, attached to a PDP 11/34 computer[6,7]. For the measurements in solution we used either mixtures of trichlorofluoromethane or liquid paraffine[12] with di-*tert*-butyl peroxide and homobenzvalene[13] (**4**) in a v/v ratio of 10:5:1. The solutions were thoroughly purged with argon to remove oxygen. The adamantane matrix of homobenzvalene was prepared by subliming 50 mg of adamantane (Aldrich Gold Label) in a sealed tube in the presence of 5 µl of **4** and preparing from this material suitable pellets (5 mm diam.) in an IR press. X-ray irradiation (Siemens Stabiliplan; 300 kV, Cu anode) was carried out according to ref.[1].

The temperature dependence of the solvent viscosity of the ESR solution, determined with a Micro-Ubbelohde viscosimeter from 3 to 44 °C, is described by the equation $\lg \eta/cp = -(4.64 \pm 0.13) + (7.34 \pm 0.17\,\text{kcal/mol})/2.3\,RT$. The steady-state kinetics was measured with 10:5:1 v/v mixtures of paraffine oil/di-*tert*-butyl peroxide/substrate. The evaluation was performed by comparing suitable signals in the experimental spectra with integrated computer-simulated spectra and plotting the determined concentration ratios as a function of $1/T$.

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