120. The Radical Cation of Cyclobutene and its Photoproduct

Preliminary Communication

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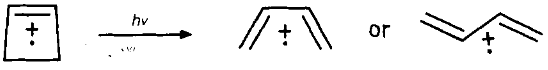
The hitherto unknown radical cation of cyclobutene (**2**) has been generated in a $CFCl_3$ matrix by γ rays at 77 K. The coupling constants, as determined from the ESR spectrum of $\mathbf{2}^{+}$, are 2.80 and 1.11 mT for the four CH_2 and the two CH= protons, respectively. Photo-induced ring opening of $\mathbf{2}^{+}$ yields a radical cation which exhibits the same ESR and ENDOR spectra as those observed upon direct ionization of s-*trans*-buta-1,3-diene (s-*trans*-**1**). The radical cation s-*trans*-$\mathbf{1}^{+}$, and not s-*cis*-$\mathbf{1}^{+}$, should, therefore, be the final product of this conversion.

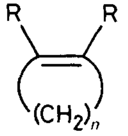
Introduction. – The radical cation of cyclobutene (**2**) has not yet been characterized by its hyperfine data, although those of cyclopentene (**3**) and cyclohexene (**4**) were investigated eight years ago [1]. The photo-induced ring opening of $\mathbf{2}^{+}$ *(Scheme)* has been the subject of one MS investigation [2] and several theoretical studies [3] [4]. The radical cation of buta-1,3-diene (**1**), the product of the ring opening, was either left unspecified with respect to its configuration [2] or it was alternately formulated as the s-*cis*- [3a] [4b] or the s-*trans*-isomer [3b] [4a]. In [5], an analogous conversion has been described for complexed 3,4-diarylcyclobutenes; the (*Z*)-configuration of the double bonds was assumed for the resulting 1,4-diarylbuta-1,3-dienes.

Scheme



$\mathbf{2}^{+}$ s-*cis*-$\mathbf{1}^{+}$ s-*trans*-$\mathbf{1}^{+}$

Here, we report on the ESR spectra of $\mathbf{2}^{+}$ and its photoproduct. The hyperfine data for $\mathbf{2}^{+}$ are compared with those of $\mathbf{3}^{+}$ and $\mathbf{4}^{+}$, as well as with some of the analogous values for the radical anions of the corresponding 1,2-diphenylcycloalkenes (Ph_2)**2**, (Ph_2)**3**, and (Ph_2)**4** which have previously been studied in fluid solution by ESR spectroscopy [6–8].



2 $n = 2$, R = H (Ph_2)**2** $n = 2$, R = Ph
3 $n = 3$, R = H (Ph_2)**3** $n = 3$, R = Ph
4 $n = 4$, R = H (Ph_2)**4** $n = 4$, R = Ph

Results and Discussion. – The radical cation $\mathbf{2}^{+}$ was generated from **2**1)) in a $CFCl_3$ matrix by γ rays (^{60}Co source) at 77 K. The ESR spectra of $\mathbf{2}^{+}$ in this matrix, taken at 100 and 130 K, are shown in the *Figure* (g = 2.0030 ± 0.0002). Their hyperfine patterns are readily analyzed in terms of two coupling constants of 2.80 ± 0.01 and 1.11 ± 0.01 mT, due to the four CH_2 (β) and the two CH= protons (α), respectively. There is a conspicuous broadening of the central lines of the 1.11-mT 'triplets' (1:2:1) which becomes less pronounced on going from 100 to 130 K. This effect indicates that the two α-protons are not completely equivalent at low temperatures. A proton ENDOR spectrum of $\mathbf{2}^{+}$ could not be observed.

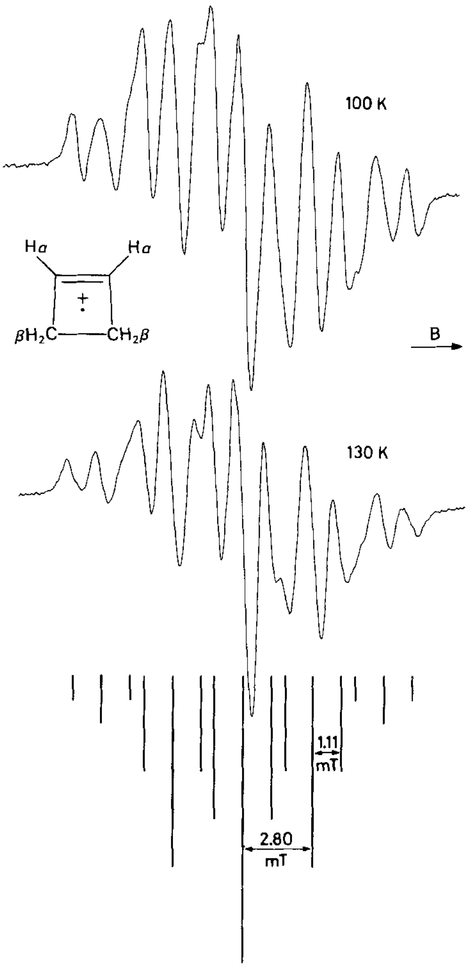


Figure. *ESR spectra of* $\mathbf{2}^{+}$ *and their reproduction by a stick diagram*

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1) Prepared according to a procedure described in [9].

Table. *α- and β-Proton Coupling Constants* [mT] *for the Radical Cations of Cyclobutene* (**2**), *Cyclopentene* (**3**), *and Cyclohexene* (**4**), *Together with the β-Proton Values for the Radical Anions of the Corresponding 1,2-Diphenyl Derivatives* $(\mathrm{Ph}_2)\mathbf{2}$, $(\mathrm{Ph}_2)\mathbf{3}$, *and* $(\mathrm{Ph}_2)\mathbf{4}$

	$\mathbf{2}^{+}$ a)	$\mathbf{3}^{+}$ b)	$\mathbf{4}^{+}$ b)	$(\mathrm{Ph}_2)\mathbf{2}^{\overline{\cdot}}$ c)	$(\mathrm{Ph}_2)\mathbf{3}^{\overline{\cdot}}$ c)	$(\mathrm{Ph}_2)\mathbf{4}^{\overline{\cdot}}$ d)
α	1.11 (2 H)	0.86 (2 H)	0.88 (2 H)			
β	2.80 (4 H)	5.30 (2 H)	5.40 (2 $\mathrm{H_{ax}}$)	0.431 (4 H)	0.659 (2 H)	1.003 (2 $\mathrm{H_{ax}}$)
		4.85 (2 H)	2.25 (2 $\mathrm{H_{eq}}$)		0.293 (2 H)	0.429 (2 $\mathrm{H_{eq}}$)

a) This work. b) [1]. c) [7]. d) [8].

The coupling constants $a_{\mathrm{H}(\alpha)}$ and $a_{\mathrm{H}(\beta)}$ of the α- and β-protons in $\mathbf{2}^{+}$ are compared in the *Table* with corresponding data for $\mathbf{3}^{+}$ and $\mathbf{4}^{+}$. The large $a_{\mathrm{H}(\beta)}$ values, which by far surpass those of $a_{\mathrm{H}(\alpha)}$, are the prominent feature of all three radical cations. They indicate a substantial delocalization of the spin population from the two olefinic C π centres into the polymethylene chain. The decrease in the $a_{\mathrm{H}(\alpha)}$ values on going from $\mathbf{2}^{+}$ to $\mathbf{3}^{+}$ and $\mathbf{4}^{+}$ can be caused by an enhancement of this delocalization with the lengthening of the chain and/or by an increase in the deviations of the π system from planarity. Such deviations are known to reduce the absolute values of $a_{\mathrm{H}(\alpha)}$, due to a 'break-down' of the π–σ separation [10]. The considerable differences in the coupling constants $a_{\mathrm{H}(\beta)}$ for $\mathbf{2}^{+}$, $\mathbf{3}^{+}$, and $\mathbf{4}^{+}$ ought to arise mainly from different conformations of the polymethylene chains. In the case of $\mathbf{2}^{+}$ and $\mathbf{4}^{+}$, this statement is supported by the finding that the ratios of the β-proton coupling constants for these radical cations, $a_{\mathrm{H}(\beta)}$ (4 H; $\mathbf{2}^{+}$): $a_{\mathrm{H}(\beta)}$ (2 $\mathrm{H_{ax}}$; $\mathbf{4}^{+}$): $a_{\mathrm{H}(\beta)}$ (2 $\mathrm{H_{eq}}$; $\mathbf{4}^{+}$) resemble those of the analogous values for the radical anions of the 1,2-diphenyl-substituted cyclobutene ($(\mathrm{Ph}_2)\mathbf{2}$) and cyclohexene ($(\mathrm{Ph}_2)\mathbf{4}$) *(Table)*. These ratios are 2.80 mT/5.40 mT/2.25 mT = 1.2:2.4:1.0 for $\mathbf{2}^{+}$ and $\mathbf{4}^{+}$, and 0.431 mT/1.002 mT/0.429 mT = 1.0:2.3:1.0 for $(\mathrm{Ph}_2)\mathbf{2}^{\overline{\cdot}}$ and $(\mathrm{Ph}_2)\mathbf{4}^{\overline{\cdot}}$. On the other hand, the coupling constants of the β-protons in $\mathbf{3}^{+}$ and in the radical anion of 1,2-diphenylcyclopentene ($(\mathrm{Ph}_2)\mathbf{3}$) *(Table)* do not follow an analogous relationship.

When $\mathbf{2}^{+}$ was photolyzed in the $\mathrm{CFCl_3}$ matrix at 110 K by VIS irradiation (*XBO-250W-Osram* lamp; *RG-610-Schott* filter), a new ESR spectrum was obtained which consisted of five broad components spaced by 1.1 mT and arising from a hyperfine interaction with four protons. The corresponding ENDOR spectrum yielded three coupling constants of 1.119, 1.050, and 0.283 mT, each due to two equivalent protons. Both ESR and ENDOR spectra of the photo-produced paramagnetic species are *identical* with those recently obtained from s-*trans*-buta-1,3-diene upon γ irradiation in a $\mathrm{CFCl_3}$ matrix and arising from s-*trans*-$\mathbf{1}^{+}$ [11]. This finding indicates that the product of the photo-induced ring opening in $\mathbf{2}^{+}$ has the s-*trans*-configuration, *i.e.* it is s-*trans*-$\mathbf{1}^{+}$ and not s-*cis*-$\mathbf{1}^{+}$. The reaction pathway for the conversion of $\mathbf{2}^{+}$ into s-*trans*-$\mathbf{1}^{+}$ will be discussed in a forthcoming paper [12] which will include the results of studies by optical spectroscopy and quantum-chemical methods.

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REFERENCES

[1] T. Shida, Y. Egawa, H. Kubodera, *J. Chem. Phys.* **1980,** *73,* 5963.
[2] M. L. Gross, D. H. Russell, *J. Am. Chem. Soc.* **1979,** *101,* 2082.
[3] a) E. Haselbach, T. Bally, Z. Lanyova, *Helv. Chim. Acta* **1979,** *62,* 577; b) E. Haselbach, T. Bally, R. Gschwind, U. Klemm, Z. Lanyova, *Chimia* **1979,** *33,* 405.
[4] a) D. J. Belville, R. Chelsky, N. L. Bauld, *J. Comput. Chem.* **1982,** *3,* 548; b) N. L. Bauld, D. J. Belville, R. Pabon, R. Chelsky, G. Green, *J. Am. Chem. Soc.* **1983,** *105,* 2378.
[5] T. Miyashi, K. Wakamatsu, T. Akiya, K. Kikuchi, T. Mukai, *J. Am. Chem. Soc.* **1987,** *109,* 5270.
[6] I. B. Goldberg, *Org. Magn. Reson.* **1973,** *5,* 29.
[7] F. Gerson, W. B. Martin, Jr., Ch. Wydler, *Helv. Chim. Acta* **1979,** *62,* 2517.
[8] F. Gerson, W. B. Martin, Jr., *Helv. Chim. Acta* **1987,** *70,* 1558.
[9] J. Salaün, A. Fadel, *Org. Synth.* **1986,** *64,* 50.
[10] F. Gerson, K. Müllen, E. Vogel, *Helv. Chim. Acta* **1971,** *54,* 2731; *J. Am. Chem. Soc.* **1972,** *94,* 2924.
[11] F. Gerson, X.-Z. Qin, *Helv. Chim. Acta* **1988,** *71,* 1065.
[12] T. Bally, F. Gerson, E. Haselbach, X.-Z. Qin, in preparation.