Absolute Rate Constants for the Addition of the 1-(*tert*-Butoxy)carbonylethyl Radical onto Cyclic Alkenes in Solution

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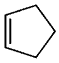
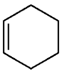
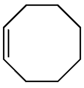
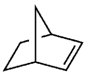
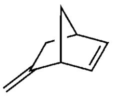
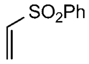
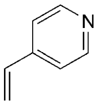
This paper is dedicated to Professor *Hanns Fischer*, deceased on February 22, 2005

Absolute rate constants are reported for the addition of the 1-[(*tert*-butoxy)carbonyl]ethyl (=2-(1,1-dimethylethoxy)-1-methyl-2-oxoethyl) radical $^{\bullet}CHMeCO_2(t\text{-}Bu)$ to several cyclic and monosubstituted alkenes in MeCN as obtained by time-resolved electron paramagnetic resonance (EPR). The activation energies for the addition of this alkyl radical are mainly governed by the addition enthalpy but are also substantially lowered by the ambiphilic effect and by relief of cyclic strain.

Introduction. – The addition of C-centered radicals onto C=C bonds has many applications in organic and polymer chemistry [1]. In the case of radical and substrate substitution, the rate constants vary by many orders of magnitude and reflect an interplay of polar, steric, and enthalpic effects. To quantify these effects, the rate constants and their temperature dependence for the addition of a large variety of C-centered radicals onto many alkenes in liquid solution have been measured by time-resolved electron paramagnetic resonance (EPR) and other techniques [2]. The addition of radicals onto mono- and 1,1-disubstituted alkenes has been studied extensively, but the addition onto cyclic alkenes has deserved scarce studies [3]. Among all the radicals studied, the 1-[(*tert*-butoxy)carbonyl]ethyl radical (=2-(1,1-dimethylethoxy)-1-methyl-2-oxoethyl; **EEst$^{\bullet}$**) arouse a keen interest as radical model for studying the polymerization of alkyl acrylate (=alkyl prop-2-enoate) monomers [4]. While studying extensively the addition of **EEst$^{\bullet}$** onto mono- and 1,1-disubstituted alkenes, we also turned our interest to the effects of the cyclic strain on the addition of 1-[(*tert*-butoxy)carbonyl]ethyl radical onto cyclic alkenes.

Results and Discussion. – All the values for the addition rate constants k at 295 K, the range of alkene concentrations c, the number n of experiments evaluated for the determination of k, and the calculated activation energy E_a^{cal} are given in the *Table*. As expected for 1,2-disubstituted alkenes, the values of k for **1**–**3** are roughly 4 times lower than the value for the 1,1-dimethylethene (=2-methylprop-1-ene; $k = 880\ \text{M}^{-1}\ \text{s}^{-1}$). One would have expected an increase in k from **3** to **1** as the cyclic-strain release is expected to increase. On the other hand, the reverse would suggest better accessibility of the C=C bond for the larger ring, as observed with the small increase in k (*Table*). The k value for **4** (8,9,10-trinorborn-2-ene) or **5** (5-methylene-8,9,10-trinorborn-2-ene)

Table. *Absolute Rate Constants* k *at* 295 ± 1 *K, calculated Activation Energies* E_a^{cal} *for the Addition of the 1-[(*tert*-Butoxy)carbonyl]ethyl Radical* **EEst**$^\bullet$ *onto Cyclic and Monosubstituted Alkenes in MeCN*

	Alkene	c [mM][a])	n[b])	k [M^{-1} s^{-1}][c])	E_a^{cal}[d]) [kJ/mol]
1		100–500	12	160 (20)	32.5
2		100–600	12	190 (20)	31.7
3		100–700	12	230 (20)	31.3
4		45–97	8	3900 (300)	24.3
5		5–80	12	5400 (300)	23.5
6		2.5–30	10	6140 (370)	23.2
7		0.25–3	12	119800 (6500)	15.9

[a]) Range of alkene concentration. [b]) Number of evaluated kinetic experiments. [c]) Standard deviation in parentheses. [d]) Estimated with log (A/M^{-1} s^{-1}) = 7.9.

are roughly 14 times larger than for **1** (five-membered ring) and **2** (six-membered ring), which are the model rings. Such a striking increase in k from **1** or **2** to **4** is probably due to the significant release of the ring strain occurring after the addition of **EEst**$^\bullet$ onto the endocyclic C=C bond. As expected, the addition of **EEst**$^\bullet$ onto **5**, which owns an exocyclic C=C bond, is faster than onto **4**. It is noteworthy that the k value for **5** is larger than the sum (*ca.* 4800 M^{-1} s^{-1}) of the values for the addition onto **4** and onto 1,1-dimethylethene. Therefore, the faster addition of **EEst**$^\bullet$ onto the exocyclic C=C bond of **5** than onto the 1,1-dimethylethene is probably due to the release of the cyclic strain from the exocyclic C=C bond occurring after the formation of the tertiary alkyl radical.

The value of k for the addition onto **6** is very close to the values observed for electron-deficient alkenes such as 1,1-dichloroethene (k = 11000 M^{-1} s^{-1}) denoting the weak nucleophilic character of **EEst**$^\bullet$. The k value for **7** is larger than the value of the styrene (= ethenylbenzene) homologue (k = 93000 M^{-1} s^{-1}) and, as expected, smaller than for the α-methylstyrene (= (1-methylethenyl)benzene) homologue (k = 129000 M^{-1} s^{-1}).

In conclusion, the addition of alkyl radicals onto cyclic alkenes can reveal the significant influence of the cyclic strain. Thus, the addition of alkyl radicals onto cyclic and more exotic alkenes deserves detailed studies.

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Experimental Part

The experimental arrangement and the procedures for steady-state and time-resolved EPR spectroscopy have been described earlier in detail [5]. Typical EPR parameters of **EEst**$^{\bullet}$ and adducts, and typical kinetic profiles and analyses have been well exemplified in a previous work [4]. MeCN was chosen as solvent because it is relatively inert to radical attack, and solvent effects on the rate constants should be of minor importance [6]. Alkenes and MeCN were purchased from *Acros* and used as received.

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