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FREE RADICAL ADDITIONS. PART VIII [1]. PMO-TREATMENT OF DICYANOMETHYL AND TRIFLUOROMETHYL RADICAL ADDITIONS TO VARIOUS ALKENES

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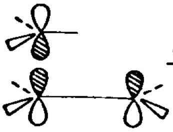
Since the elucidation of the anti-Markownikoff addition of hydrogen bromide to alkenes as radical reaction [2,3] there has been a controversial discussion about factors governing regioselectivity and reactivity in free radical additions [4]. Although the PMO-treatment of chemical reactivity [5,6] rationalises very well a lot of different reactions [7,8] as hydrogen abstraction reactions by free radicals [9,10] it has to our knowledge never been applied to free radical additions. To rationalise the relative rate constants for the addition of dicyanomethyl radicals to various alkenes [1,11] we calculated Fukui's superdelocalizability $S_r^{(R)}$ [12,13] for each addition. We calculated the data using MINDO/3 [14,15]

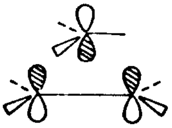
$$S_r^{(R)} = \sum_i^{\text{occ.}} \frac{c_{ri}^2 \cdot (-\beta)}{\alpha - \varepsilon_i} + \sum_i^{\text{unocc.}} \frac{c_{ri}^2 \cdot (-\beta)}{\varepsilon_i - \alpha}$$

We made the following assumptions:

1) The transition state is a "σ-complex" type, i. e. it resembles a and not b. This is in agreement with the work of J. M. Tedder and J. C. Walton [16]. Moreover b should be spin symmetry forbidden [17].



a

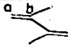
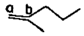
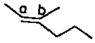
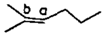
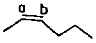
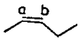
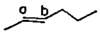


b

2) The resonance integral β is nearly constant. This may be justified in this case, because the reagent (radical) is always the same and the substrates (alkenes) are very similar [8].

The additions of trifluoromethyl radicals to various alkenes [18-21] were treated in the same manner. The results are listed in the following tables and illustrated in fig. 1 and 2.

Table 1: Relative rate constants, superdelocalizabilities and selectivities [1,11] for the addition of dicyanomethyl radicals to various alkenes

alkene	$S_r^{(R)}$ for the addition to C_a	addition to C_b	% addition to C_a	to C_b	k_{rel}
	- 0.1799 ß	- 0.1592 ß	⩾ 95	⩽ 5	2 x 136.6
	- 0.1765 ß	- 0.1611 ß	⩾ 95	⩽ 5	18.4
	- 0.1757 ß	- 0.1697 ß	⩾ 95	⩽ 5	15.0
	- 0.1754 ß	- 0.1697 ß	⩾ 95	⩽ 5	13.9
	- 0.1684 ß	- 0.1600 ß	⩾ 95	⩽ 5	1.16
	- 0.1680 ß	- 0.1679 ß	ca. 50	ca. 50	2 x 0.63
	- 0.1681 ß	- 0.1680 ß	ca. 50	ca. 50	2 x 0.62
	- 0.1671 ß	- 0.1683 ß	ca. 50	ca. 50	2 x 0.50

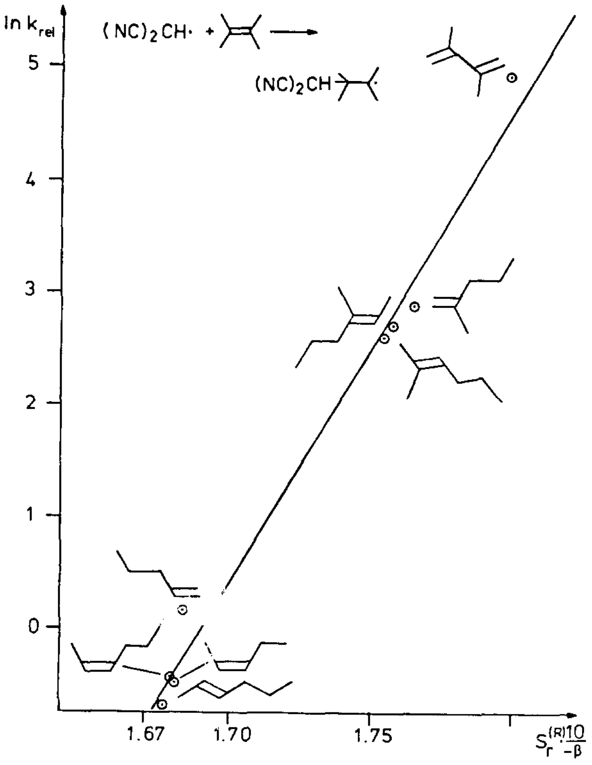
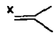
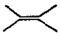
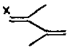
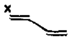


Figure 1: Plot of ln k_{rel} versus superdelocalizabilities [22] for the addition of dicyanomethyl radicals to various alkenes.

Table 2: Activation energies 18-21) and superdelocalizabilities for the addition of trifluoromethyl radicals to various alkenes

alkene	$S_r^{(R)}$ for the addition to the asterisked carbon atom 23)	E_A kJ/mol
	- 0.1800 ß	10.1
	- 0.1940 ß	8.38
	- 0.2042 ß	5.20
	- 0.1937 ß	5.50
	- 0.1943 ß	5.50
	- 0.2085 ß	3.41
	- 0.2125 ß	1.44
	- 0.2064 ß	4.11

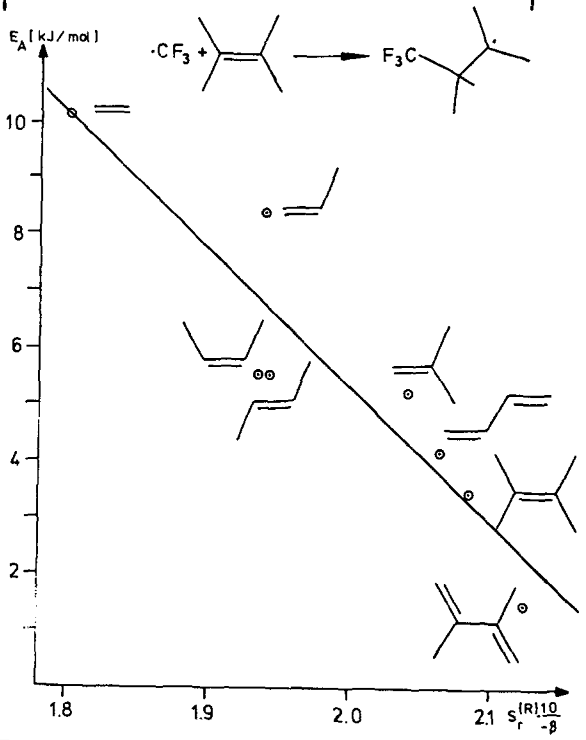


Figure 2: Plot of E_A versus superdelocalizablities for the addition of trifluoromethyl radicals to various alkenes.

As can be seen in fig. 1 and 2, the kinetic data of dicyanomethyl and trifluoromethyl radical additions correlate very well ($r = 0.99$ resp. 0.93) with the calculated superdelocalizabilities. The PMO-treatment of these typical free radical additions is successful in rationalising reactivity and regioselectivity (see table 1, the attack of the radical takes place at the site of maximum overlap). The influence of steric effects can be neglected. This seems to be valid at least for n-alkyl and vinyl substituents. For alkenes with more bulky groups as i-propyl or t-butyl a steric influence on regioselectivity was observed [24].

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