ß-FRAGMENTATION OF ALKYL RADICALS.
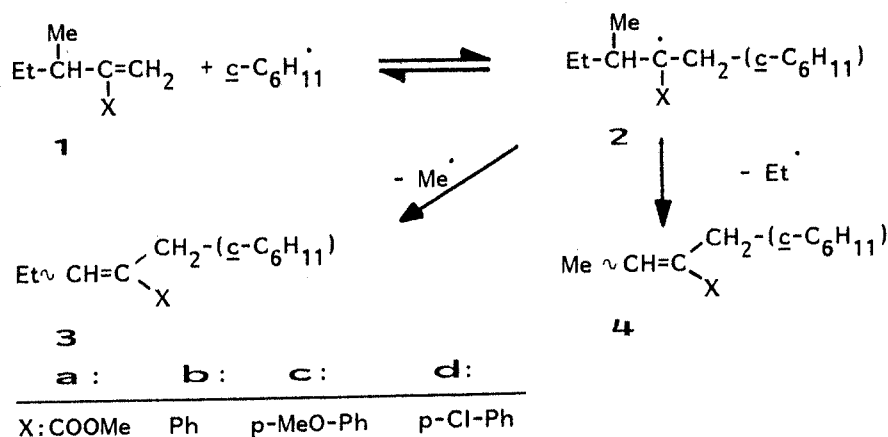## POLAR AND STERIC EFFECTS.

K. Klenke and J.O. Metzger

Department of Chemistry, University of Oldenburg
P.O.Box 25 03, D-2900 Oldenburg

Radical fragmentation is the reverse of radical addition. The importance of polar and steric effects to addition reactions is well known[1]. We report here the influence of polar and steric effects on the selectivity of ß-scission of alkyl radicals.

Polar effects: Alkyl radicals 2 have been generated by addition of cyclohexyl to alkenes 1 [2]. Methyl vs. ethyl have been eliminated from 2 to give products 3 and 4 (E- and Z-isomers). Some results are summarized in Table 1.

$$Et-\underset{X}{\underset{|}{\overset{Me}{\overset{|}{C}}}}H-C=CH_2 + c\text{-}C_6H_{11}\cdot \rightleftharpoons Et-\underset{X}{\underset{|}{\overset{Me}{\overset{|}{C}}}}H-\overset{\cdot}{C}-CH_2-(c\text{-}C_6H_{11})$$

$$1 \qquad\qquad 2$$

$$-Me\cdot$$
$$-Et\cdot$$

$$Et\sim CH=C\overset{CH_2-(c\text{-}C_6H_{11})}{\underset{X}{\diagup}}\qquad Me\sim CH=C\overset{CH_2-(c\text{-}C_6H_{11})}{\underset{X}{\diagup}}$$

$$3 \qquad\qquad\qquad 4$$

	a :	b :	c :	d :
X :	COOMe	Ph	p-MeO-Ph	p-Cl-Ph

Tab. 1: ß-Scission of alkyl radicals 2 at 350°C.

Radical 2	Yield[a] [mol%]	$4/3$	s[b]	$\Delta E_{a;4-3}$[c] [kJ/mol]	A_4/A_3[c]
a	14.7	17.8	1.25	-18.2 ± 2.0	0.6 ± 0.2
b	6.0	7.3	0.86	-4.5 ± 0.5	3.0 ± 0.3
c	7.4	8.9	0.95	-8.4 ± 0.6	1.6 ± 0.2
d	9.0	9.4	0.97	-7.2 ± 0.8	2.4 ± 0.5

a) Σ products 3 and 4. b) selectivity log [4] / [3]. c) 300 - 450°C.

The competitive rate data of Table 1 clearly indicate the influence of polar effects on fragmentation reactions. Relative rates of cleavage of the more nucleophilic ethyl are increased by electron withdrawing substituents X in radical **2**. The more reactive radical **2a** is fragmented with higher selectivity than the less reactive radical **2b**.

Steric effects: Radical **6** decomposes by two routes to give methyl and alkenes **7** and **8**. Relative rates for the decomposition have been obtained from analysis of the olefinic products. (Table 2). On a per methyl basis methyl has been eliminated faster ($k_2/k_1 > 1$) from the less substituted carbon atom in radical **6** to give the less stable alkene.

We explain this surprising result as follows: ß-scission is influenced by steric effects in the same way as the reverse radical addition. Radicals add faster to the less substituted end of an alkene due to steric effects. The same must be true for ß-scission.

$$Me_{(3-m)}H_mC\text{-}C\text{-}CMe_{(3-n)}H_n + \underline{c}\text{-}C_6\dot{H}_{11} \longrightarrow Me_{(3-m)}H_mC\text{-}\dot{C}\text{-}CMe_{(3-n)}H_n$$

with CH_2 (structure **5**) on left, and on right $CH_2\text{-}(\underline{c}\text{-}C_6H_{11})$ (structure **6**)

$-\dot{Me}$, k_1 and k_2, $-\dot{Me}$

$$Me_{(2-m)}H_mC\text{=}C\text{-}CMe_{(3-n)}H_n \qquad Me_{(3-m)}H_mC\text{-}C\text{=}CMe_{(2-n)}H_n$$
$$CH_2\text{-}(\underline{c}\text{-}C_6H_{11}) \qquad\qquad CH_2\text{-}(\underline{c}\text{-}C_6H_{11})$$

7   **8**
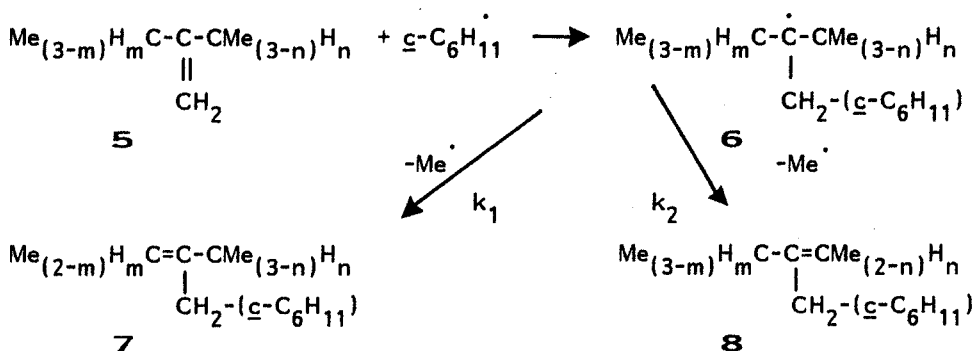
a: m=0;n=2;   **b:** m=0;n=1,   **c:** m=1;n=2.

Tab. 2: Selectivity of the ß-scission of alkyl radicals **6** at 400°C.

Radical 6	[7] mol%	[8] mol%	k_2/k_1 [a]	S [b]
a	57	43	2.3	0.36
b	52	48[c]	1.4	0.15
c	62[c]	38	1.2	0.08

[a] Relative rate on a per methyl basis; [b] $S = \log k_2/k_1$; [c] E- and Z-products.

1 J.M. Tedder (1982) Angew. Chem. **94**, 433; Angew. Chem. Int. Ed. Engl. **21**, 401; B. Giese (1983) Angew. Chem. **95**, 771; Angew. Chem. Int. Ed. Engl. **22**, 753
2 J. Hartmanns, K. Klenke und J.O. Metzger (1986) Chem. Ber. **119**, 488