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THERMOLYSIS OF (SILYL)METHYL-BENZYL-ETHERS:
EVIDENCE FOR ANCHIMERICALLY ACCELLERATED BOND HOMOLYSIS

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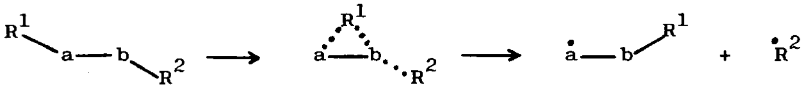
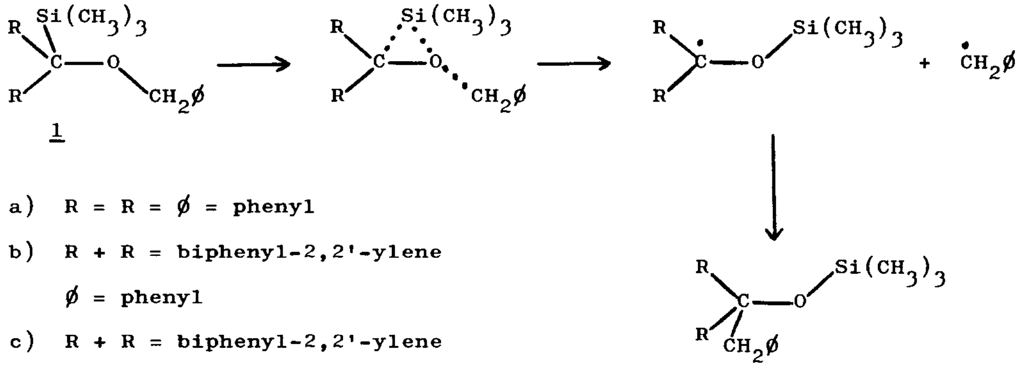
Anchimerically assisted unimolecular bond homolysis represents a very rare organic reaction type[1)]. Unambiguous examples in which the assisting group <u>migrates</u> to the site at which bond cleavage occurs have not been described to date:



Reactions of this type may occur generally if the radicals a and R^2 are stabilized, and if the new bond b-R^1 is very strong. We wish to report some observations which may be explained on the basis of this proposal. Heating compounds <u>1</u> to 150-195° results in smooth positional exchange of the silyl and benzyl groups (96-99 % yield of <u>2</u>).



<u>1</u>

<u>2</u>

a) R = R = ø = phenyl

b) R + R = biphenyl-2,2'-ylene
ø = phenyl

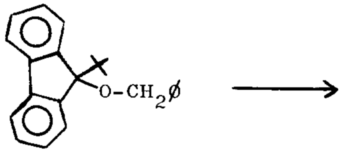
c) R + R = biphenyl-2,2'-ylene
ø = p-methylphenyl

d) R + R = biphenyl-2,2'-ylene
ø = p-methoxyphenyl

e) R + R = biphenyl-2,2'-ylene
ø = p-nitrophenyl

Although this rearrangement formally represents a dyotropic process$^{2)}$, the following studies point to a homolytic cleavage with neighboring group participation of the Si-group: 1) Benzyl radicals can be intercepted (up to 84 %) by carrying out the reaction in the presence of a radical trapping agent (p-benzoquinone). 2) The Si-groups migrate 100 % intramolecularly, as shown by crossover experiments. 3) The rate dependence on solvent polarity is small: for <u>1b</u> → <u>2b</u>, k_{rel} = 1,0 (benzene), 1,5 (o-dichlorobenzene), 4,9 (propylene carbonate). 4) The activation parameters for <u>1b</u> → <u>2b</u> were found to be $\Delta G^{\ddagger}$ = 32,6 ± 0,6 kcal/mol, $\Delta H^{\ddagger}$ = 31,7 ± 0,6 kcal/mol, $\Delta S^{\ddagger}$ = -8,6 ± 0,8 e.u. 5)Addition of radical initiators or inhibitors has no influence on the reaction rate.

Homolyses of C-O bonds liberating alkoxy and benzyl (or allyl) radicals require activation energies of more than 45 kcal/mol$^{3)}$. The present value of 32,6 kcal/mol as well as the negative $\Delta S^{\ddagger}$ is consistent with the involvement of the Si-group. Rate determining migration of the Si-group toward the O-atom weakens the O-C (benzyl) bond. Collapse of the activated complex leads to resonance stabilized benzhydryl (or fluorenyl) and benzyl radicals and brings about the complete formation of the strong Si-O bond. Steric factors appear to be unimportant, since the t-<u>butyl</u> analog of <u>1b</u> was found to be stable under the reaction conditions:



no reaction after 4 days at 195°

The relative rates of the p-substituted benzyl ethers (<u>1b-e</u>) reveal a small polar effect: k_{rel} = 1,0(H), 1,5(CH_3), 2,2(OCH_3), 0,2(NO_2). The O-C bond does not appear to be stretched to a large extent in the transition state. Further studies including groups other than Si are under way.

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<u>References</u>:

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