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THE INFLUENCE OF ALKOXY GROUPS ON THE NUCLEOPHILICITY OF ALKYL RADICALS

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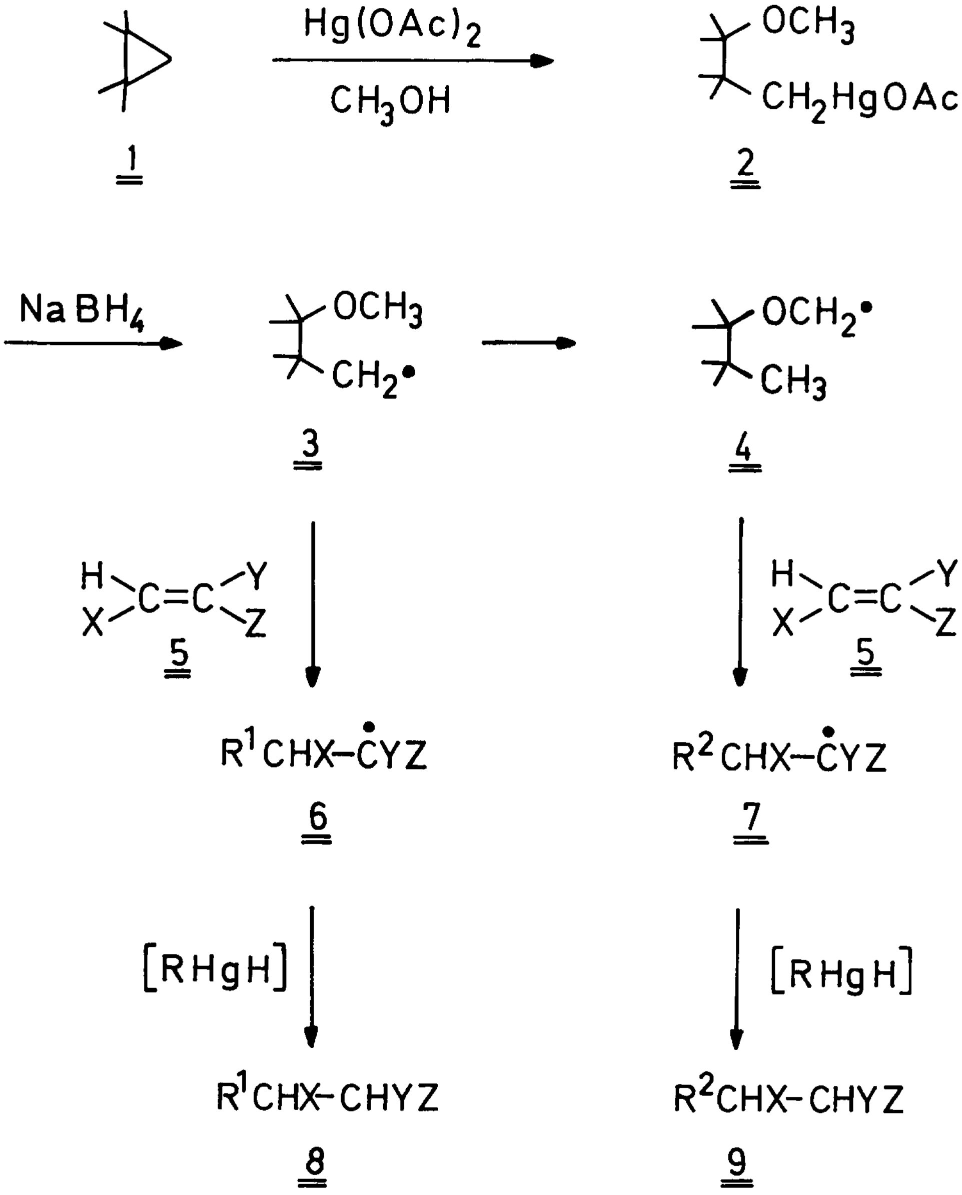
Summary: One alkoxy substituent increases the nucleophilicity of alkyl radicals in addition reactions at alkenes more than three methyl groups.

Rates and selectivities of radical additions to alkenes can be explained by the frontier molecular orbital theory$^{1)}$, as long as steric effects are negligible$^{2)}$. For reactions between nucleophilic radicals and alkenes, bearing electron-withdrawing substituents, the SOMO-LUMO interaction is of main importance$^{1)}$ The smaller the SOMO-LUMO energy difference the higher the reactivity and the selectivity of radicals and alkenes$^{1,3)}$. Electron-donating substituents at the radical carbon atom increase the SOMO energy. Therefore, in going from methyl via prim. and sek. radicals to the t-butyl radical, reactivities$^{4)}$ and selectivities$^{5)}$ increase. Reactions with heterocyclic π-systems show that this effect should even be larger if the hydrogen atom of the radical is substituted by an alkoxy group$^{6)}$. A recently observed reaction$^{7)}$ has made it now feasible to measure the selectivity of alkoxymethyl radicals in their addition reactions at alkenes.

Solvomercuration of tetramethyl cyclopropane **1** yields the organomercuric compound **2**. In reduction with $NaBH_4$ alkyl radical **3** is formed which gives the alkoxymethyl radical **4** by intramolecular hydrogen abstraction$^{7)}$. In the presence of alkenes **5** both radicals react to adduct radicals **6** and **7** which are trapped quantitatively to yield products **8** and **9**. With substituted fumaric esters **5** ($X=Y=CO_2CH_3$) the rearranged compounds **9** are the main products of the reaction$^{7)}$. We have, therefore, carried out competition experiments with fumaric esters **5** using the "mercury-method"$^{5)}$. To compare the influences of alkoxy and alkyl groups with each other, selectivities of n-heptyl, cyclohexyl and t-butyl radicals have also been measured in the same competition system (Table I).



R^1: $CH_3OC(CH_3)_2\text{–}C(CH_3)_2CH_2$ R^2: $(CH_3)_3C\text{–}C(CH_3)_2OCH_2$

Table I

Rel. Rates of radical additions at fumaric esters **5** ($X=Y=CO_2CH_3$) in CH_2Cl_2 at $20^{\circ}C$.

Alkene **5**	Radical			
Z	$n-C_7H_{15}\cdot$	$c-C_6H_{11}\cdot$	$t-C_4H_9\cdot$	**4**
a:OCH_3	≡1.0	≡1.0	≡1.0	≡1.0
b:CH_3	2.2	2.9	2.0	3.0
c:H	9.1	10	15	20
d:Cl	20	35	49	50
e:CO_2CH_3	30	56	95	130
ρ-value	2.2	2.5	2.9	3.0

In going from the prim. via the sek. to the tert. radical, the selectivity k_{5e}/k_{5a} increases from 30 via 56 to 95 (Table I). The ρ-values of the Hammett-plots increase in the same order from 2.2 via 2.5 to 2.9. But the prim. alkoxymethyl radical **4** is even more selective ($k_{5e}/k_{5a}=130$, $\rho=3.0$) than the t-butyl radical. This shows that one alkoxy group has at least the effect of three methyl groups. The π-donor effect of an alkoxy group, therefore, overcomes the inductive electron-withdrawing effect of oxygen. This can be best explained by a planar structure of the alkoxymethyl radical in which the interaction of the singly occupied orbital of the radical carbon atom with the orbitals of the alkoxy group is most effective. In contrast to hydroxyalkyl radicals[8] and silyloxyalkyl radicals[9], which are bent σ-radicals, the alkoxymethyl radical behaves more like a planar π-radical.

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