CAPTODATIVE SUBSTITUENT EFFECTS IN SYNTHESIS

H.G. Viehe, Z. Janousek and R. Merényi
Université Catholique de Louvain
Laboratoire de Chimie Organique
Place L. Pasteur 1
1348 Louvain-la-Neuve
Belgium

ABSTRACT. In contrast to the effect of two substituents with like polarity, captodative (cd) substitution leads to a synergy of the individual substituent effects. In synthetic organic chemistry this results in preferential recombination of cd radicals, increased reactivity in thermal (2+2) and (4+2) cycloadditions. A number of rearrangements are facilitated by such substitution such as vinyl-cyclopropane - to cyclopentene and especially oxazines to epoxy-epimines. Thus cyclodienes are stereospecifically transformed via chiral oxazines to epoxy-epimines with four chiral centers at all the original four dienic sp2 carbon atoms.

10 years ago we found a rearrangement reaction of captor substituted iminium salts which, together with other results, led us to the formulation of the captodative effect: "The combined action of a captor (electron withdrawing) and a dative (electron releasing) substituent on a radical center leads to enhanced stabilisation". Similar ideas have been formulated earlier, but today it appears that especially this postulate of the cd-effect together with experimental support which we have provided has stimulated many other theoretical and experimental studies. More generally the role of polar effects on the ground state of molecules and on the transition state of their homolysis became of interest.

Let us first remind the experimental facts which were one starting point of recognition of the cd-effect in our group:

The 1.3-Cl-H- rearrangement is a monomolecular reaction which, with negligibly low solvent effects, is not ionic and appears to be triggered by the presence of the captodative substitution on CCl2-group (Fig. 1). The captor group may be electron-withdrawing σ-substituents, e.g. trifluoromethyl and trichloromethyl groups. The rates are lowered (ΔAE = 7.6 Kcal) as compared to an ester group, but the reaction is very clean (Fig. 2).

The rearrangement of oxalyl amide chloride leads to follow-up reactions thereby giving a trichloroimidazolium salt (Fig. 3).
1,3-Cl-H rearrangement starting from captodative center

Captors: -C≡N, -C=O, -C=N⁻, -CCl₃, -CF₃.

![Fig. 1](image)

\[ \text{E}_a = 21.3 \text{ Kcal/mol} \]

\[ \text{E}_a = 28.9 \text{ Kcal/mol} \]

σ and π acceptors produce the rearrangement

![Fig. 2](image)

96% from Dithio-oxamide

![Fig. 3](image)