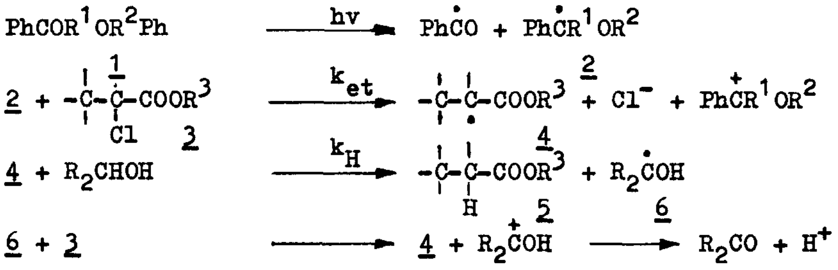
P-95 bis

MECHANISM OF THE PHOTOCHEMICAL REDUCTION OF C–Cl BOND IN FLUORINE COMPOUNDS

Oldrich Paleta, Hans-Joachim Timpe, Vojtech Dědek and Roland Wagner

Institute of Chemical Technology Prague (Czechoslovakia) and Technical University 'Carl Schorlemmer' Leuna-Merseburg (G.D.R.)

The substitution of Cl in chlorofluoropropionic esters is a necessary reaction step for synthesis of fluoroacrylic esters. This reaction can carried out selectively by an electron transfer reaction (k_{et}) of α-ether or ketyl radicals (2 or 6) with propionic esters 3. Such radicals are produced



$$\begin{aligned}
&PhCOR^1OR^2Ph \xrightarrow{h\nu} Ph\dot{C}O + Ph\dot{C}R^1OR^2 \quad \underline{2}\\
&\underline{2} + -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{Cl}{C}}-COOR^3 \;\; \underline{3} \xrightarrow{k_{et}} -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{\bullet}{C}}-COOR^3 \;\; \underline{4} + Cl^- + Ph\overset{+}{C}R^1OR^2\\
&\underline{4} + R_2CHOH \xrightarrow{k_H} -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{H}{C}}-COOR^3 \;\; \underline{5} + R_2\dot{C}OH \;\; \underline{6}\\
&\underline{6} + \underline{3} \longrightarrow \underline{4} + R_2\overset{+}{C}OH \longrightarrow R_2CO + H^+
\end{aligned}$$

by light induced C-C bond scission (λ = 300–350 nm) of benzoine derivatives or benzile ketales. In solvents like i-propanole or tetrahydrofurane a chain reaction is possible.

The discussed reaction mechanism (see Schme) is detected by the determination of k_{et} by means of flash photolysis experiments, by quantitative measurements of 5-formation and protonic acid formation in dependence of 3-concentration.

It was found, that also the C-Cl bond in β-position to the ester group can reduced selectively by this way. But, this reaction possesses smaller k_{et}. Vicinal dichloro group is substitutable with a higher quantum yield as the monochloro substituent.