Intramolecular cyclisaion under chlorinated pesticides photoirradiaion

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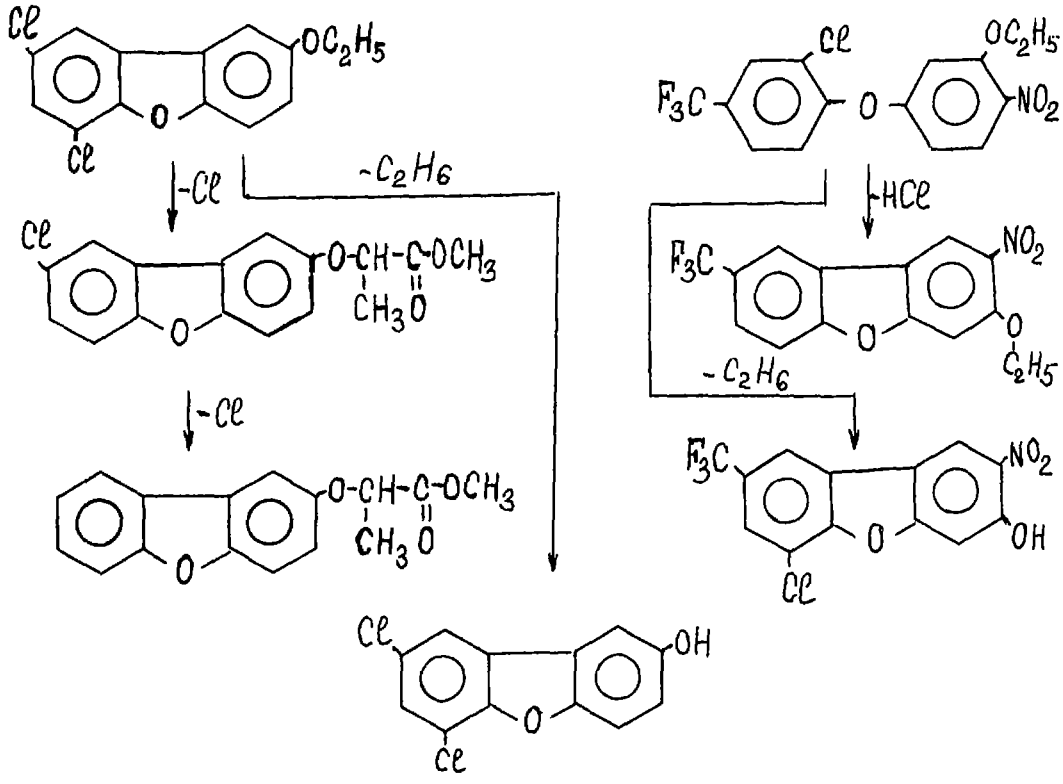
Photolysis is an important transformation pathway for many chlorinated pesticides in the environment and may lead to toxic products formation. A particulal interest is determination of photochemical transformation products of chlorinated diphenyl ethers becouse of their structural similarity to some chlorinated dibenzo-p-dioxine and dibenzofuran precursors. Such type of compounds and their heterocyclic analogs are widely used as pesticides. They are very sencitive to irradiation and their photodegradation was shawn to occure principally via reducing or oxidative dechlorination or of aryl- or hetaryl-bond cleavage accompanied by chlorphenols formation. Also intramolecular photocyclisation can occurs that leeds to dibensofurans formation. Some of these chlorinated potodegradation products are very toxic and are concidered as environmental priority pollutants.

The objective of this study was to determine a significance of photocyclisation in photoderadation reactions of some pesticides on the base of chlorinated diphenyl ethers - (2-chloro-α,α,α-trifluoro-p-tolyl 3-ethoxy-4-nitrophenyl ether, the active ingredient of the herbicide Goal, and 2-[4-(2,4-dichlorphenoxyphenylenen propionic acid methyl ether, the active ingredient of the herbicide dichlophop methyl (trade mark illoxan).

To estimate an influence of kind of light source on fotodegradation processes the initial substances were irradiate by Hg-lamp of mediate pressure (λ_{max}=254 nm; 5,13 and 18 h.) and Xe lamp of ultrahigh pressure (λ_{max} >290 nm; 13,30 and 48 h.), spectrum of the last was similar to that of sunshine of north semisphere.

Photodegradaion products were analysed using GC-MS system included gas chromatograph HP 5890A and ion trap detector Finnigan MAT ITD 700.

Reaction mixtures after irradiation conained some phoocyclisaion products. These compounds may be formed by two pahways: 1) cyclization accompaniated by HCl elimination and 2) oxydaive cyclisation accompanied by dehydrogenation:



The first cyclisation process probability raises when convercion is increased and for Hg lamp this rising is faster. The yields of cyclisation products of both processes are similar for goal containing only one chlorine. Illoxan containing two chlorine atoms yields only traces of oxydative cyclisation products:

		Xe			Hg	
Goal (conversion, 10^{-3}):	0	54	196	289	66	203	321
oxidative cyclisation	-	3,0	5,7	10,4	0,9	7,5	18,6
dechlorinated cycl.	-	2,0	8,8	11,6	1,6	8,1	11,4
Illoxan (conversion, 10^{-3}):	0	167	580	767		568	
oxidative cyclisation	-	-	-	0,03		0,5	
dechlorinated cycl.	-	3,0	5,1	17,3		8,3	

A characteristic feature of the oxidative cyclisation is that it occures only simultaneously with alyphatic substituent eliminating.