Phenoxy-phenoxypropionic Acid Derivatives and Related Compounds

H. J. Nestler

Hoechst AG, Pflanzenschutzforschung-Chemie D-6230 Frankfurt am Main 80

Contents

1.	Introduction
2.	The PPP System
3.	Chemical Structure Variations
	3.1.1. Variation of the Aromatic Ring A Substituents X and Y
	3.1.2. Variation of the Ring B Substituent Z
	3.1.3. Variation of the Carboxylic Acid Functional Group Q
	3.2. Variations Including Alteration of the Basic PPP System
	3.2.1. Alteration of the Aromatic Ring A
	3.2.2. Alteration of the Propionic Acid Moiety
	3.3. Systems Significantly Deviating from the Basic PPP Structure 9
	3.3.1. Variation of the Bridge Atoms V and W
	3.3.2. Variation of the Aromatic Ring B
	3.3.3. <i>meta</i> -Phenoxy-phenoxy-alkanecarboxylic Acid Derivatives 11
	3.3.3.1. Aromatic Ring Substituents
	3.3.3.2. Aliphatic Moieties
	3.3.3.3. Bridge Atoms
	3.3.4. <i>ortho</i> -Phenoxy-phenoxy-alkanecarboxylic Acid Derivatives . 12
4.	Structure-Activity Correlations
	4.1. Quantitative Structure-Activity Relationship (QSAR)
	4.2. Stereoisomers
	Herbicide Combinations
6.	Chemical Synthesis
	6.1. Pathway I
	6.1. Pathway I
	6.3. Preparation of L- and D-2-(Phenoxy-phenoxy)-propionic Acid
	Enantiomers
	6.4. Secondary Transformations and Derivatizations

7.	Produ	cts
	7.1. Co	ommercial Products
	7.	1.1. 2-[4-(2,4-Dichlorophenoxy)-phenoxy]-propionic Acid Methyl
		Ester
	7.	1.2. 2-[4-(3,5-Dichloropyridyl-2-oxy)-phenoxy]-propionic
		Acid Sodium Salt
	7.2. Ex	xperimental Products
		2.1. 2-[4-(4-Chlorophenoxy)-phenoxy]-propionic Acid Isobutyl
		Ester
	7.2	2.2. 2-[4-(4-Bromo-2-nitrophenoxy)-phenoxy]-propionic Acid Ethyl
		Ester
	7.2	2.3. 2-[4-(4-Trifluoromethylphenoxy)-phenoxy]-propionic Acid
		Methyl Ester
	7.2	2.4. 4-Methyl-4-[4-(4-trifluoromethylphenoxy)-phenoxy]-crotonic
		Acid Ethyl Ester
8	Referen	nces 22

1. Introduction

Phenoxy-phenoxypropionic acid derivatives were detected to be a new class of grass herbicides in 1971. The selective activity of these compounds against monocotyledonous species is a surprising fact, as this group of substances may be regarded as a mere phenoxy homologous series of the predominantly broad-leaf herbicidal phenoxy fatty acids like, for example, dichlorprop, mecoprop, or fenoprop [1]. Furthermore, it is very surprising that this class of compounds was not investigated until 1971, in spite of the enormous amount of labor invested into the systematic structural variation of the auxin-like acting phenoxy-alkane-carboxylic acids since their discovery in 1941/42 [2].

Following the first report about the herbicidal properties of the phenoxy-phenoxypropionic acid derivatives in a patent application by Hoechst in 1972 [3], many companies have been starting research in this field. Nearly 140 patents and applications have been filed since, the majority of contributions originating from Hoechst, Ciba-Geigy, Ishihara Sangyo Kaisha, and Rohm and Haas¹.

It is estimated that about five to six thousand individual compounds have been synthesized and biologically tested within seven years after the first publication, providing a relatively wide field of experience and information about this scientifically and economically interesting new class of probably systemicly acting herbicides.

2. The PPP System

The general structure of the phenoxy-phenoxypropionic acid system, which will be referred to as the "PPP" system throughout this report, is given in formula 1, to be compared with the corresponding general structure of the hormone-type broad-

¹ Cf. Vol. 5 of this series, pp. 190-191; patent review suppl. Vols. 5 and 8, Sect. 5.7.3c