

# Abiotic Hydrolysis Reaction Library

The Abiotic Hydrolysis Reaction Library has been developed as a component of the Chemical Transformation Simulator (CTS), a web-based software tool under development in EPA's Office of Research and Development. The library will be implemented in CTS to predict the likely hydrolytic transformation products in the environment for an organic chemical of interest.

Version 1.7 of the Abiotic Hydrolysis Reaction Library contains 25 reaction schemes:

- [Halogenated Aliphatics: Nucleophilic Substitution](#)
  - Scheme A: C-X with no other adjacent halogens
  - Scheme B: C-X with vicinal halogen atoms
  - Scheme C: C-X with geminal halogen atoms
- [Halogenated Aliphatics: Elimination](#)
- [Epoxide Hydrolysis](#)
- [Organophosphorus Ester Hydrolysis 1 \(Base-Catalyzed\)](#)
- [Organophosphorus Ester Hydrolysis 2 \(Neutral or Acid-Catalyzed\)](#)
- [Carboxylic Acid Ester Hydrolysis](#)
- [Lactone Hydrolysis](#)
- [Carbonate Hydrolysis](#)
- [Cyclic Carbonate Hydrolysis](#)
- [Anhydride Hydrolysis](#)
- [Cyclic Anhydride Hydrolysis](#)
- [Amide Hydrolysis](#)
- [Lactam Hydrolysis](#)
- [Carbamate Hydrolysis](#)
- [Thiocarbamate Hydrolysis](#)
- [Urea Hydrolysis](#)
- [Cyclic Urea Hydrolysis](#)
- [Sulfonylurea Hydrolysis](#)
- [Nitrile Hydrolysis](#)
- [N-S Cleavage](#)
- [Imide Hydrolysis](#)
- [Acid Halide Hydrolysis](#)
- [Dehydration of Geminal Diols](#)

The reaction schemes are written as generic reaction equations defining how a particular structural fragment will be modified by the transformation reaction. These schemes are not balanced reactions showing all reactants and products (e.g., H<sub>2</sub>O, OH<sup>-</sup> and/or H<sup>+</sup> are not shown as reactants in the hydrolysis schemes). Additionally, the structural fragments in the reaction schemes are written with a minimal amount of specificity. For example, the inclusion of hydrogen atoms in the scheme implies that there is

a requirement for a hydrogen atom to present be in the specified position for the reactions to proceed; otherwise, it is assumed that, for simplicity, hydrogen atoms are not explicitly included.

The schemes are encoded using the notation and structural query features (L, ~L, L1-X, etc) from ChemAxon's Marvin tools. Definitions of some common symbols used in the reaction schemes are provided below:

- L[a<sub>1</sub>;a<sub>2</sub>;...] is a list of possible atoms (a<sub>1</sub>, a<sub>2</sub>, ...) that can occupy the position within the fragment
- ~L![a<sub>1</sub>;a<sub>2</sub>;...] is a list of atoms (a<sub>1</sub>, a<sub>2</sub>, ...) that cannot occupy the position within the fragment
- A is any atom except hydrogen
- AH is any atom including hydrogen
- X is any halogen
- (A) is used to indicate an aliphatic carbon atom
- (a) is used to indicate an aromatic carbon atom
- (L1-N) is used to indicate a string of atoms (acyclic or cyclic) of length N
- (X#) is used to indicate the # of connections (= substituents including hydrogen) attached to the atom
- (s#) indicates the substituent count on the atom
- (s\*) indicates substituent count is as drawn for the atom

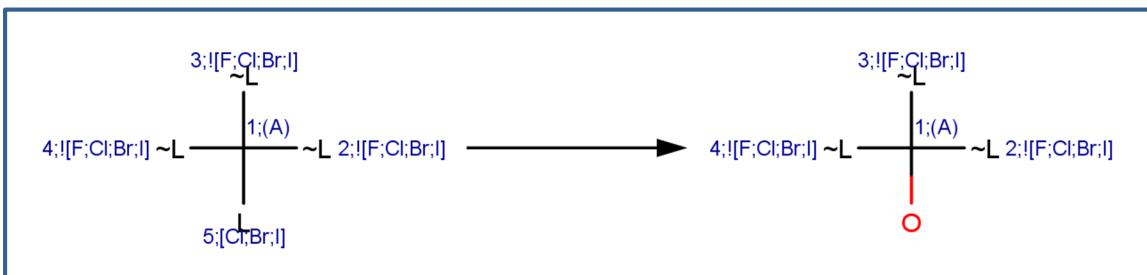
Examples are provided for each reaction scheme in the library. As is the case for the reaction schemes themselves, the example reactions do not show all of the reactants and products involved in the hydrolysis reaction. The example chemical is shown as the only reactant, and the products are the major hydrolysis products reported in the study. These example transformations from the peer-reviewed literature and government regulatory reports were used to test the reaction schemes in the library.

The schemes within the hydrolysis library are ranked on a scale of one to six according to their relative rate of transformation, with a higher rank indicating a faster hydrolysis rate. A database of measured rate constants or half-lives was compiled from a survey of peer-reviewed scientific literature and reports by government regulatory agencies to assign these ranks to each hydrolysis reaction scheme. Separate [rank assignments are established for pH 5, 7 and 9](#) to represent standard conditions in hydrolysis studies required for registration of pesticides in OECD member countries.

## Halogenated Aliphatics: Nucleophilic Substitution

The replacement of a halogen atom with an OH group through the nucleophilic substitution mechanism is represented by three schemes within the Abiotic Hydrolysis Reaction Library to capture the effects of molecular structure on reactivity in the immediate vicinity of the carbon-halogen bond. The removal of a halogen from a carbon atom with no other halogens in vicinal and geminal positions, represented by Scheme A, occurs at a faster rate than removal of halogen with other halogens in the vicinity of the reaction site. The removal of halogen atoms with other halogens in vicinal and geminal positions are represented by Schemes B and Scheme C, respectively. Observed half-lives for the hydrolytic removal of fluoride atoms under environmentally relevant conditions generally exceed 20 years and are often in the range of hundreds of years; therefore, no scheme is included for the removal of fluoride atoms.

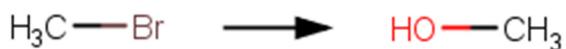
### SCHEME A:



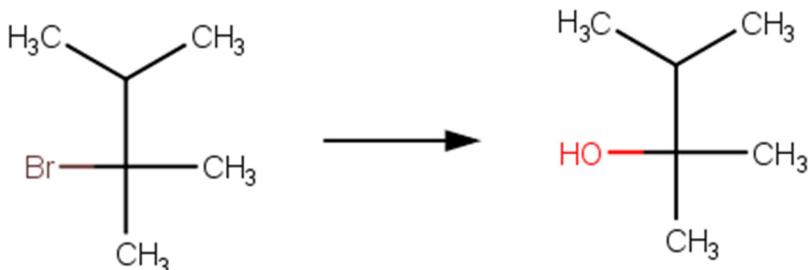
To differentiate Scheme A from Scheme B (for vicinal dehalogenation), this scheme includes an exclude rule specifying that reactant atom #1 is not part of the pattern X-C-C-X, where X represents a halogen.

### EXAMPLES FOR SCHEME A:

- methyl bromide (EFSA, 2006; U.S. EPA, 1992)



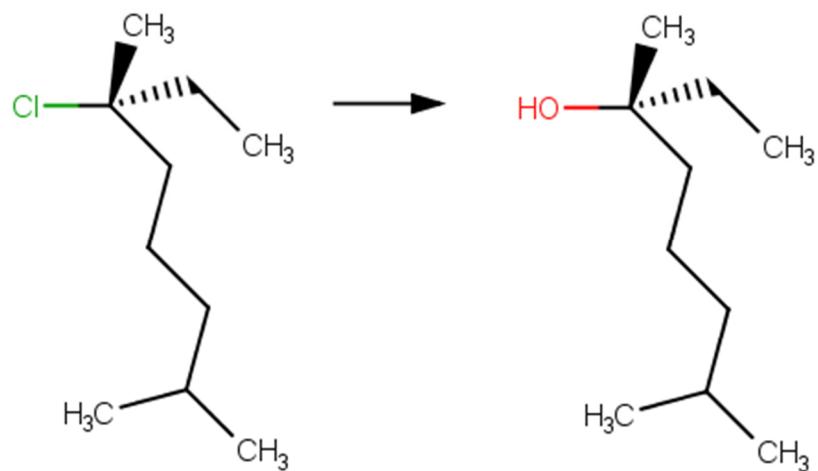
- 2-bromo-2,3-dimethylbutane (McMurry, 2011, p. 372)



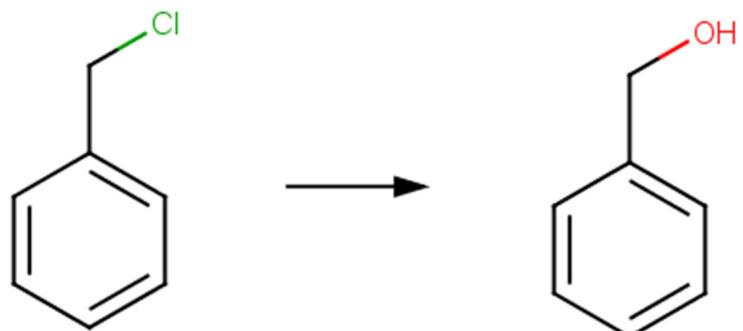
- 1,3-dichloropropene (EFSA, 2004; Guo *et al*, 2004)

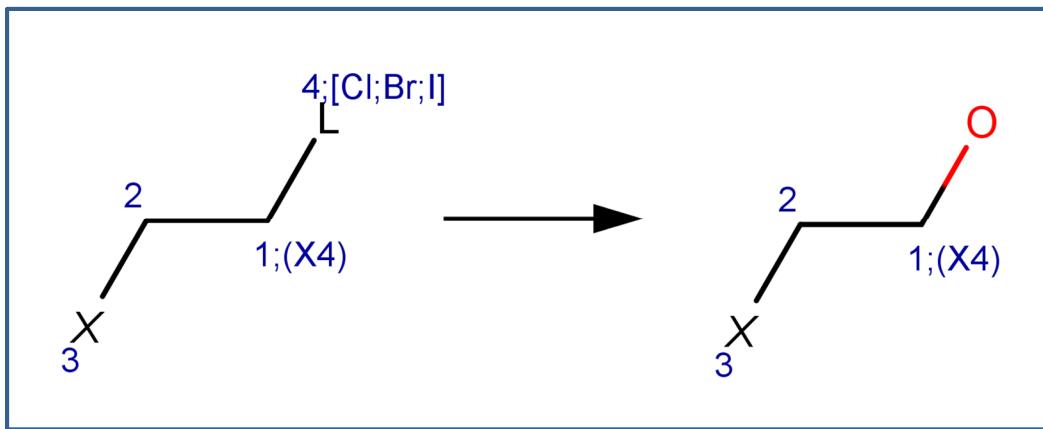


- (6R)-6-chloro-2,6-dimethyloctane (McMurry, 2011, p. 388)



- benzyl chloride (U.S. EPA, 1992)



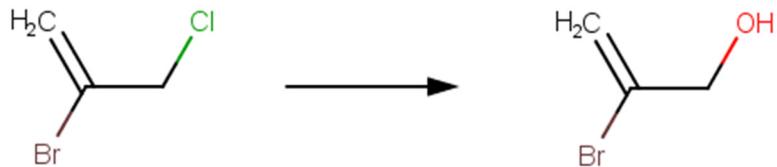
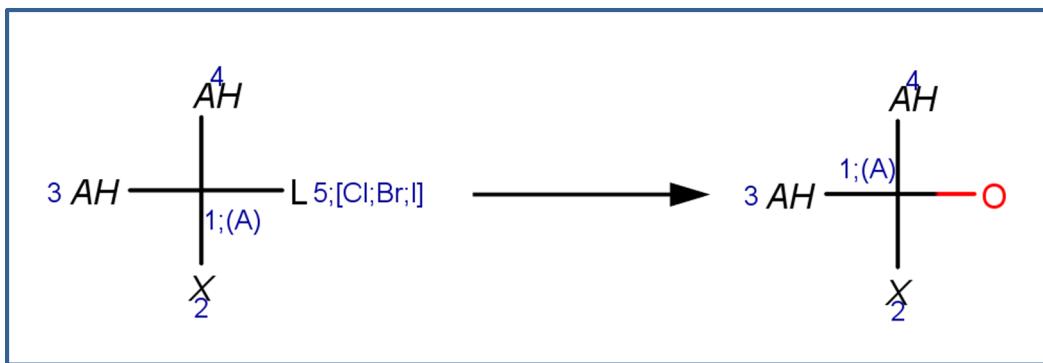
**SCHEME B:**

This scheme includes an exclude rule to distinguish the scheme from Scheme C for dehalogenation at a reaction site with more than one halogen attached to the same carbon. The exclude rule specifies that atom #1 can only be attached to one halogen.

This scheme also includes a selectivity rule to indicate the order of removal of halogens for molecules with different halogen substituents. The order of removal of the leaving halogen (labeled reactant atom 4 in the scheme) is inverse to its atomic number, i.e., I>Br>Cl. This is due to the fact that the carbon-halogen bond strength is greatest for the most electrophilic halogen. (Larson and Weber, 1994)

**EXAMPLES FOR SCHEME B:**

- 2-bromo-3-chloropropene (Burlinson *et al*, 1982)

**SCHEME C:**

This scheme includes a selectivity rule to indicate the order of removal of halogens for molecules with different halogen substituents. The order of removal of the leaving halogen (labeled reactant atom 5 in the scheme) is inverse to its atomic number, i.e., I>Br>Cl. This is due to the fact that the carbon-halogen bond strength is greatest for the most electrophilic halogen. (Larson and Weber, 1994)

#### EXAMPLES FOR SCHEME C:

- 2,2-Dichloropropane (Ellington *et al*, 1988) Reported products are 2-chloropropene (due to elimination) and acetone. The example shown below, with formation of 2-chloro-2-propanol, is the first step in the formation of acetone. 2-Chloro-2-propanol is hydrolyzed according Nucleophilic Substitution Scheme A to 2,2-propanediol, which is a geminal diol that rapidly undergoes dehydration to form acetone.



- 1,1,1-trichloroethane (Cline *et al*, 1986; Cline and Delfino, 1989; Dilling *et al*, 1975) Reported products are acetic acid and a minor amount of vinylidene (due to elimination). The example shown below, with formation of 1,1-dichloroethanol, is the first step in the formation of acetic acid. 1,1-dichloroethanol is hydrolyzed according Nucleophilic Substitution Scheme A to 1-chloroethane-1,1-diol, which is a geminal diol that rapidly undergoes dehydration to form acetyl chloride. Acetyl chloride is rapidly hydrolyzed to acetic acid according to the Acid Halide Scheme.



#### REFERENCES:

Burlinson, N.E., L.A. Lee and D.H. Rosenblatt. 1982. Kinetics and products of hydrolysis of 1,2-dibromo-3-chloropropane. *Environmental Science and Technology*. 16(9): 627-632.

Cline, P.V., J.J. Delfino and W.J. Cooper. 1989. Transformation kinetics of 1,1,1-trichloroethane to the stable product 1,1-dichloroethene. In R.A. Larsen, ed. *Biohazards of Drinking Water Treatment*. Chelsea, MI: Lewis Publishers, Inc. pp. 47-56.

Cline, P.V., J.J. Delfino and W.J. Cooper. 1986. Hydrolysis of 1,1,1-trichloroethane; formation of 1,1-dichloroethene. *Proceedings of NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration* (Dublin, OH), 239-247.

Dilling, W.L., N.B. Tefertiller and G.J. Kallos. 1975. Evaporation rates and reactivities of methylene chloride, chloroform, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, and other chlorinated compounds in dilute aqueous solutions. *Environmental Science and Technology*. 9(9): 833-838.

Ellington, J.J., F.E. Stancil, W.D. Payne and C.D. Trusty. 1988. Measurement of hydrolysis rate constants for evaluation of hazardous waste land disposal: Volume 3. Data on 70 chemicals. U.S. Environmental Protection Agency. EPA/600/3-88/028.

EFSA (European Food Safety Authority), 2004. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State Spain for the existing active substance 1,3-Dichloropropene of the second stage of the review programme referred to in Article 8(2) of Council Directive 91/414/EEC, Volume 3, Annex B, part 5, B.8. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

EFSA (European Food Safety Authority), 2006. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State The United Kingdom for the existing active substance Methyl Bromide of the third stage (part A) of the review programme referred to in Article 8(2) of Council Directive 91/414/EEC, Volume 3, Annex B, B.8. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

Guo, M., S.K. Papiernik, W. Zhang and S.R. Yates. 2004. Effects of environmental factors of 1,3-dichloropropene hydrolysis in water and soil. *Journal of Environmental Quality*. 33(2): 612-618.

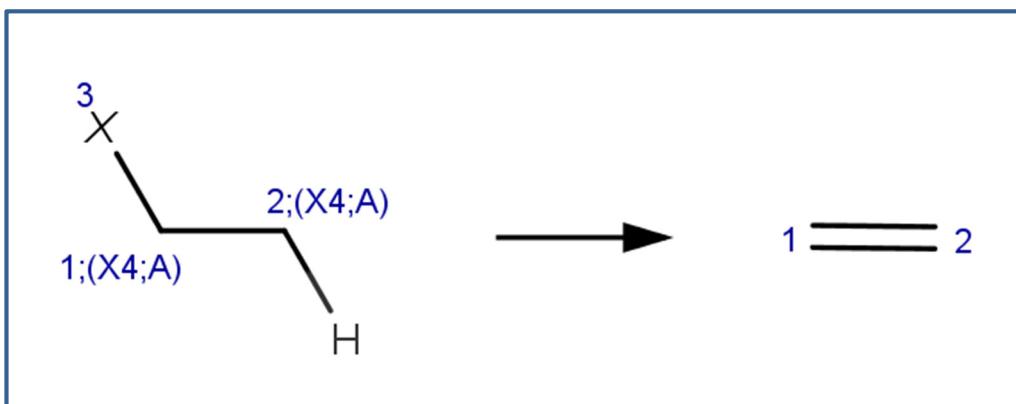
Larson, R.A. and E.J. Weber. *Reaction Mechanisms in Environmental Organic Chemistry*. Boca Raton: CRC Press, Inc., 1994.

McMurry, J.E. 2011. *Organic Chemistry*, 8<sup>th</sup> ed. Boston, MA: Cengage Learning.

U.S. EPA (United States Environmental Protection Agency). 1992. Environmental fate constants for organic chemicals under consideration for EPA's Hazardous Waste Identification Rule. EPA/601/R-92/006.

## Halogenated Aliphatics: Elimination

### SCHEME:

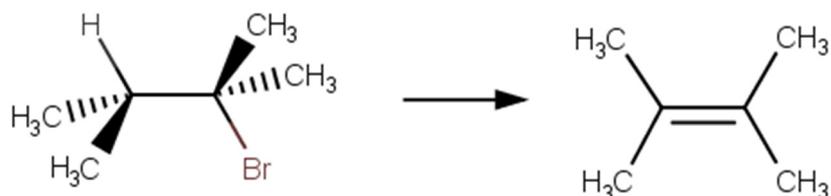


This scheme includes two selectivity rules:

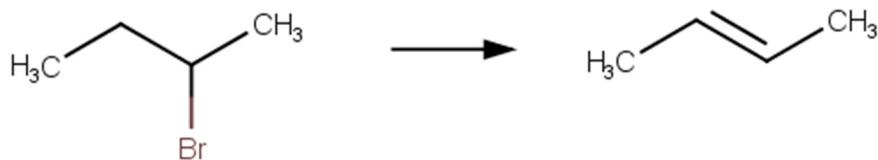
1. The carbon atom with the hydrogen leaving group (labeled reactant atom 2 in the scheme) is the one that has the most steric hindrance. In effect, this is Zaitsev's Rule, which states that "The alkene formed in greatest amount is the one that corresponds to removal of the hydrogen from the  $\beta$ -carbon having the fewest hydrogen substituents." (Reusch, 2010)
2. The order of removal of halogens (labeled reactant atom 3 in the scheme) is inverse to their atomic number, i.e., I>Br>Cl>F. This is due to the fact that the carbon-halogen bond strength is greatest for the most electrophilic halogen. (Larson and Weber, 1994)

### EXAMPLES:

- 2-bromo-2,3-dimethylbutane (McMurry, 2011, p. 372; Reusch, 2010)



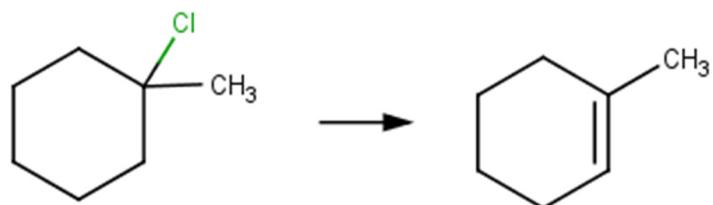
- 2-bromobutane (McMurry, 2011, p. 397; Reusch, 2010)



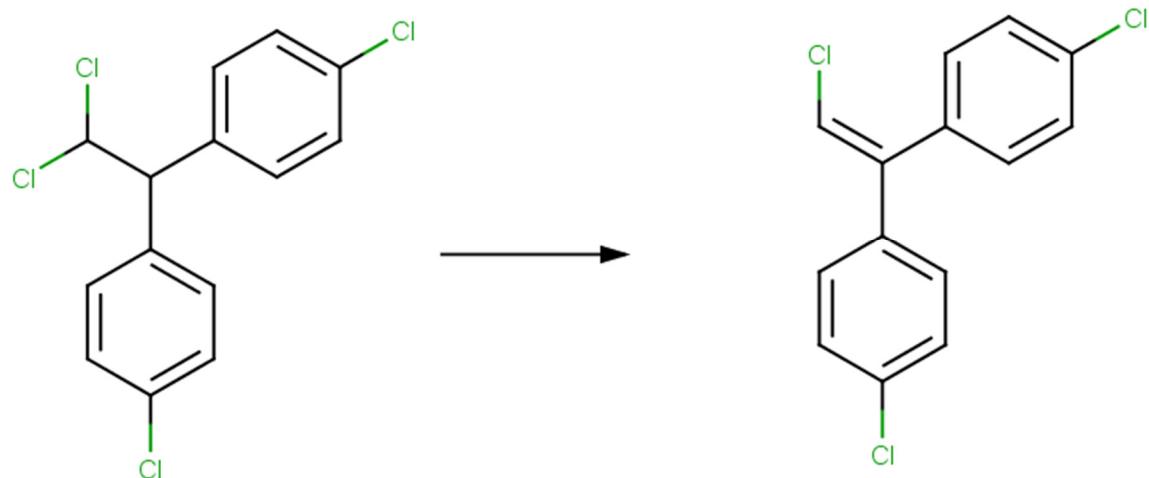
- 2-bromo-2-methylbutane (McMurry, 2011, p. 397)



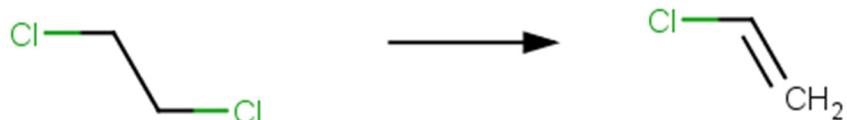
- 1-chloro-1-methylcyclohexane (McMurry, 2011, p. 399)



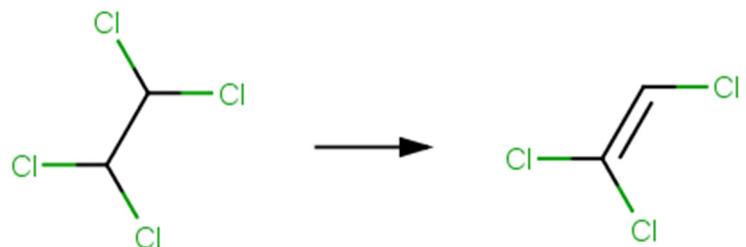
- DDD (dichlorodiphenyldichloroethane) (U.S. EPA, 1992)



- 1,2-dichloroethane (U.S. EPA, 1992; Miyamoto and Urano, 1996)



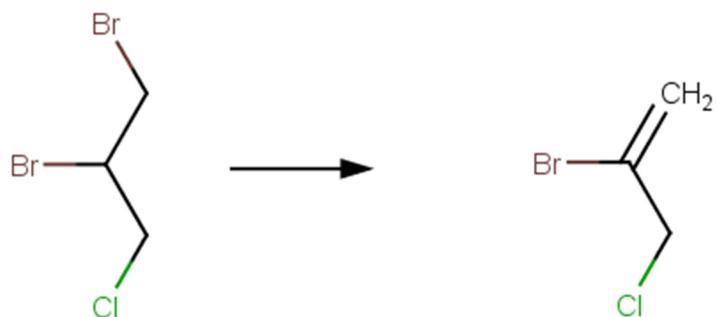
- 1,1,2,2-tetrachloroethane (Cooper *et al*, 1987)



- 1,1,1-trichloroethane (Cline and Delfino, 1989; Gerkens and Franklin, 1989; Miyamoto and Urano, 1996)



- 1,2-dibromo-3-chloropropane (Burlinson *et al*, 1982)



#### REFERENCES:

- Burlinson, N.E., L.A. Lee and D.H. Rosenblatt. 1982. Kinetics and products of hydrolysis of 1,2-dibromo-3-chloropropane. *Environmental Science and Technology*. 16(9): 627-632.
- Cline, P.V. and J.J. Delfino. 1989. Transformation kinetics of 1,1,1-trichloroethane to the stable product 1,1-dichloroethene. In Larsen, R.A., editor, *Biohazards of Drinking Water Treatment*. Lewis Publishers, Inc., Chelsea, Michigan, pp. 47-56.
- Cooper, W.J., M. Mehran, D.J. Riusech and J.A. Joens. 1987. Abiotic transformation of halogenated organics: 1. Elimination reaction of 1,1,2,2-tetrachloroethane and formation of 1,1,2-trichloroethene. *Environmental Science and Technology*. 21(11): 1112-1114.

Gerkens, R.R. and J.A. Franklin. 1989. The rate of degradation of 1,1,1-trichloroethane in water by hydrolysis and dehydrochlorination. *Chemosphere*. 19(12): 1929-1937.

Larson, R.A. and E.J. Weber. *Reaction Mechanisms in Environmental Organic Chemistry*. Boca Raton: CRC Press, Inc., 1994.

McMurry, J.E. 2011. *Organic Chemistry*, 8<sup>th</sup> ed. Boston, MA: Cengage Learning.

Miyamoto, K. and K. Urano. 1996. Reaction rates and intermediates and chlorinated organic compounds in water and soil. *Chemosphere*. 32(12): 2399-2408.

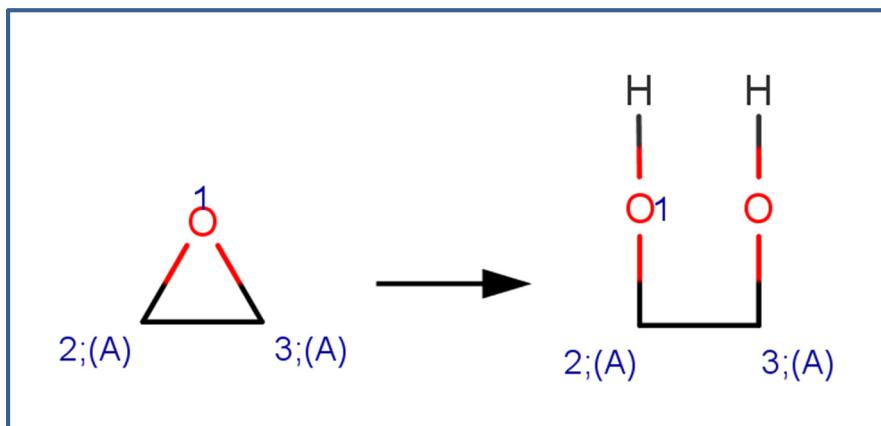
Reusch, W.H. 2010. *Virtual Textbook of Organic Chemistry*.

<http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/intro1.htm>.

U.S. EPA (United States Environmental Protection Agency). 1992. Environmental fate constants for organic chemicals under consideration for EPA's Hazardous Waste Identification Rule. EPA/601/R-92/006.

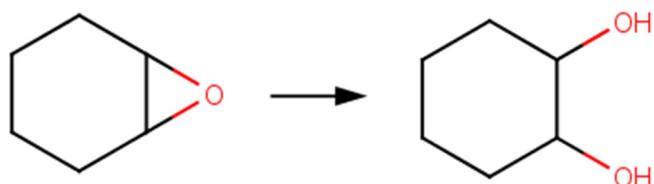
## Epoxide Hydrolysis

### SCHEME:

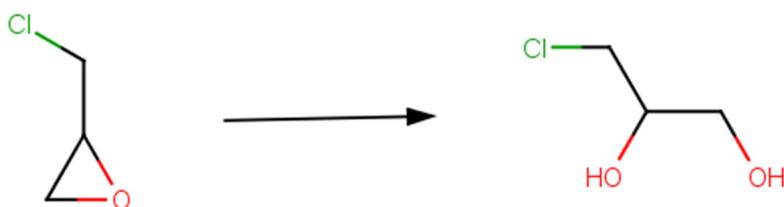


### EXAMPLES:

- 1,2-Epoxycyclohexane (McMurry, 2011)



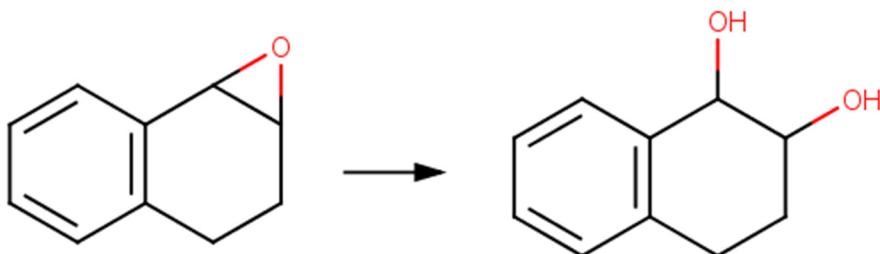
- Epichlorohydrin (Gaca *et al*, 2011)



- Endrin (Larson and Weber, 1994; U.S. EPA, 1992)



- 1,2-Epoxy-1,2,3,4-tetrahydronaphthalene (Becker *et al*, 1979)



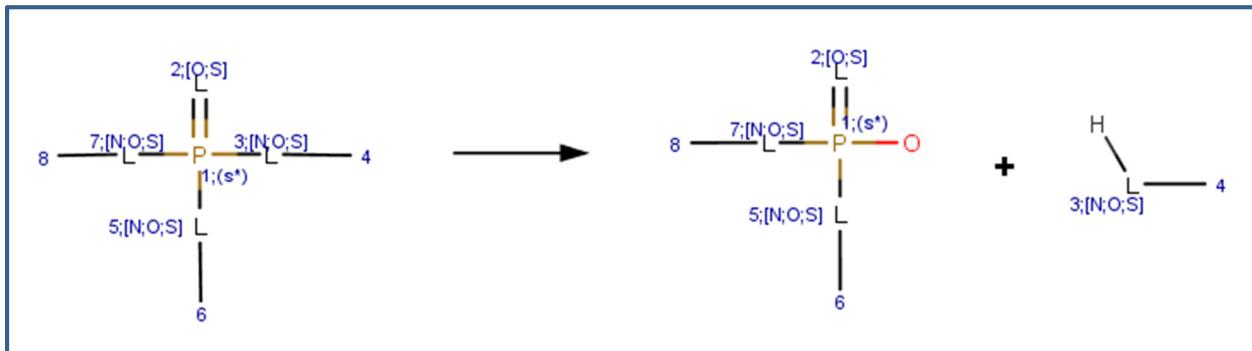
#### REFERENCES:

- Becker, A.R., J.M. Janusz and T.C. Bruice. 1979. Solution chemistry of the *syn*- and *anti*-tetrahydrodiol epoxides, the *syn*- and *anti*-tetrahydrodimethoxy epoxides, and the 1,2- and 1,4-tetrahydro epoxides of naphthalene. *Journal of the American Chemical Society*. 101(19): 5679-5687.
- Gaca, J., G. Wejnerowska and P. Cysewski. 2011. Mechanism of the acidic hydrolysis of epichlorohydrin. *Journal of Physical Organic Chemistry*. 24: 1045-1050.
- Larson, R.A. and E.J. Weber. *Reaction Mechanisms in Environmental Organic Chemistry*. Boca Raton: CRC Press, Inc., 1994.
- McMurry, J.E. 2011. *Organic Chemistry*, 8<sup>th</sup> ed. Boston, MA: Cengage Learning.

U.S. EPA (United States Environmental Protection Agency). 1992. Environmental fate constants for organic chemicals under consideration for EPA's Hazardous Waste Identification Rule. EPA/601/R-92/006.

## Organophosphorus Ester Hydrolysis 1 (Base-Catalyzed)

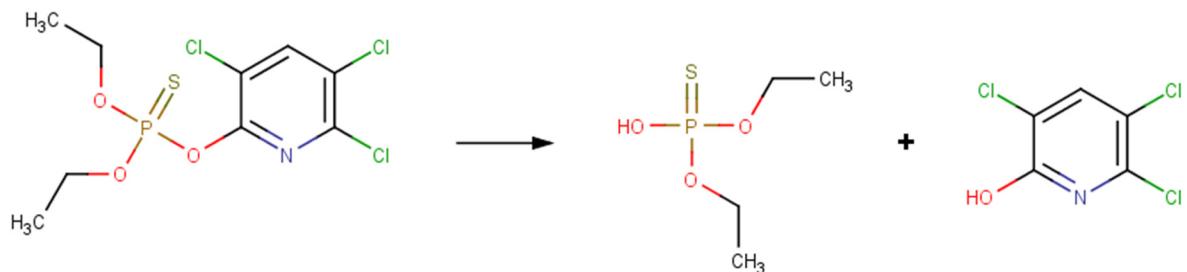
### SCHEME:



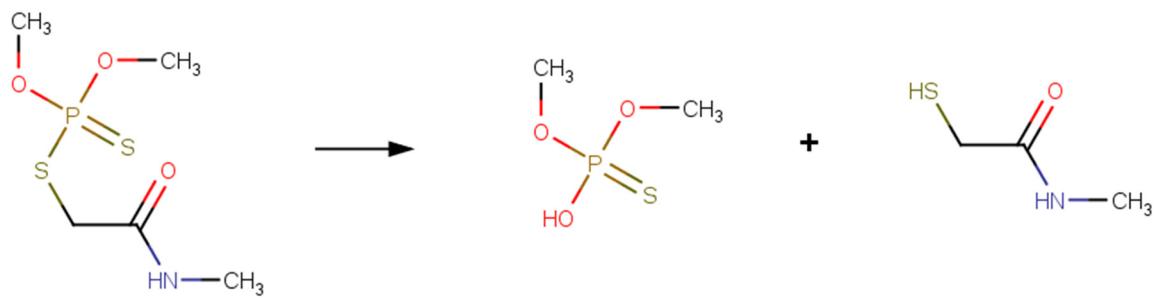
This scheme covers the base-catalyzed hydrolysis of all organophosphorus triesters, including phosphates, phosphorothiolates, phosphorothioates, phosphorodithioates and N derivatives, such as phosphorodiamidates. This scheme includes a selectivity rule to identify the most likely leaving group. Base-catalyzed cleavage favors P-L cleavage (where L is O, S, or N) at the L group that is attached to the most electron-withdrawing group (Larson and Weber, 1994). The selectivity rule specifies that the leaving group (labeled atom 3) is attached to the carbon atom (labeled atom 4) with the highest electrophilicity.

### EXAMPLES:

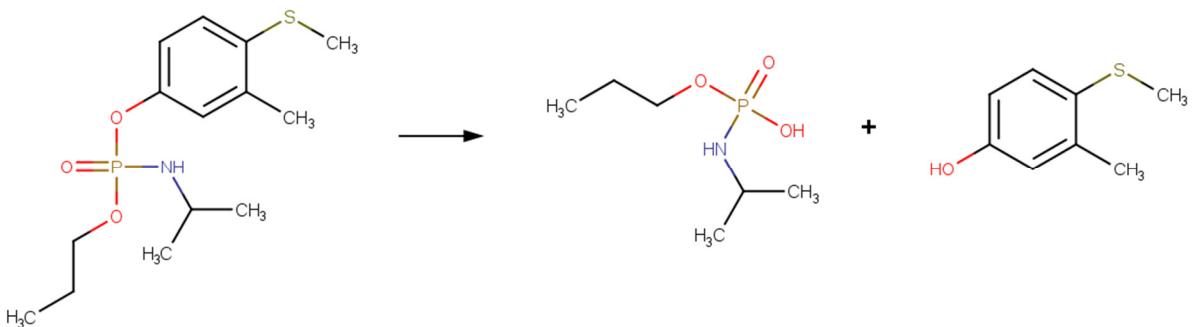
- Chlorpyrifos (Macalady and Wolfe, 1983)



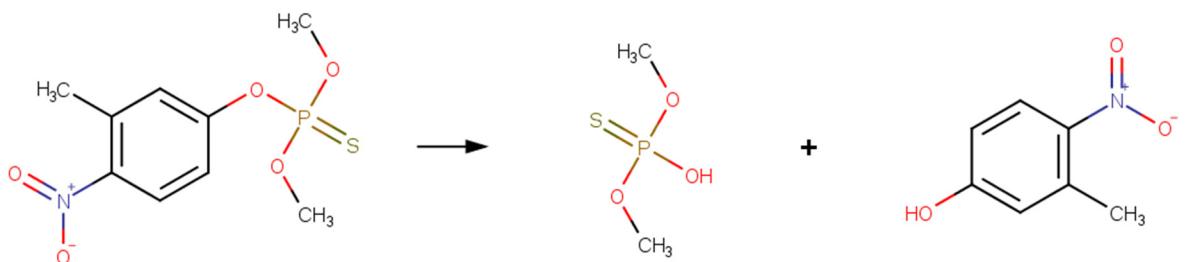
- Dimethoate (EFSA, 2005a)



- Fenamiphos (EFSA, 2005b)

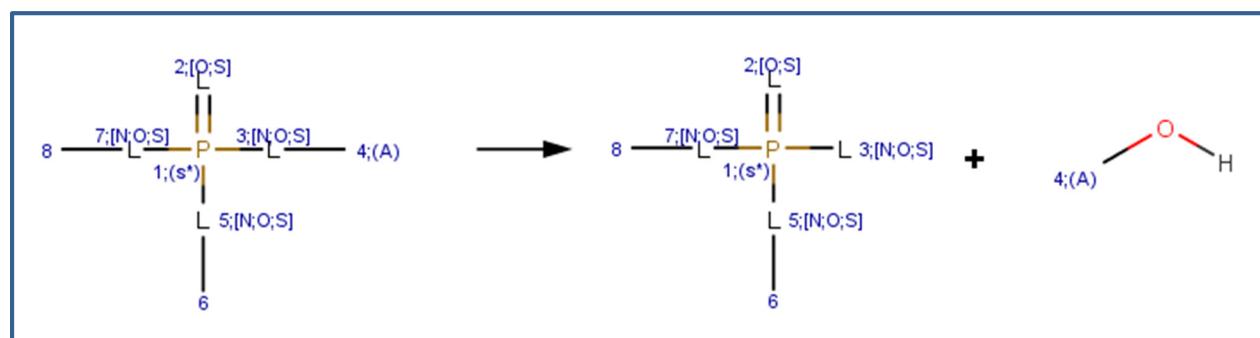


- Fenitrothion (EFSA, 2005c; Greenhalgh *et al*, 1980)



## Organophosphorus Ester Hydrolysis 2 (Neutral and Acid-Catalyzed)

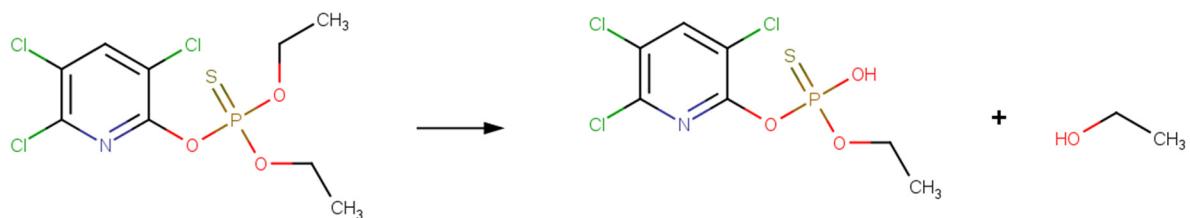
**SCHEME:**



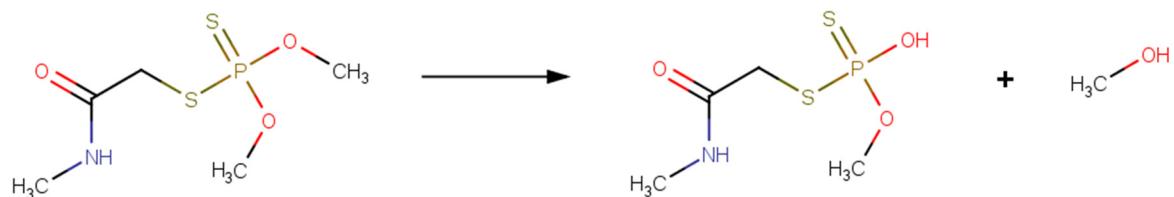
This scheme covers the neutral and acid-catalyzed hydrolysis of all organophosphorus triesters, including phosphates, phosphorothiolates, phosphorothioates, phosphorodithioates and N derivatives, such as phosphorodiamides. This scheme includes a selectivity rule to identify the most likely leaving group. Neutral and acid-catalyzed cleavage favors L-C cleavage (where L is O, S, or N), but not at the L group that is attached to the most electron-withdrawing group (Larson and Weber, 1994). The selectivity rule specifies that the leaving group (labeled atom 4) is the carbon atom with the lowest electrophilicity.

### EXAMPLES:

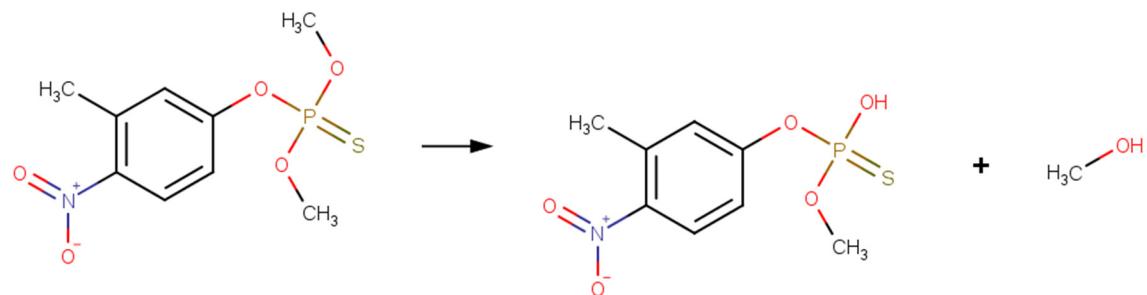
- Chlorpyrifos (Macalady and Wolfe, 1983)



- Dimethoate (EFSA, 2005a)



- Fenitrothion (EFSA, 2005c; Greenhalgh *et al*, 1980)



### REFERENCES:

EFSA (European Food Safety Authority), 2005a. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State the United Kingdom for the existing active substance Dimethoate of the second stage of the review programme referred to in Article 8(2) of Council Directive 91/414/EEC, Volume 3, Annex B, B.8. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

EFSA (European Food Safety Authority), 2005b. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State the Netherlands for the existing active substance Fenamiphos of the second stage of the review programme referred to in Article 8(2) of Council Directive 91/414/EEC, Volume 3, Annex B, B.8. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

EFSA (European Food Safety Authority), 2005c. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State the United Kingdom for the existing active substance Fenitrothion of the second stage of the review programme referred to in Article 8(2) of Council Directive 91/414/EEC, Volume 3, Annex B, B.8. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

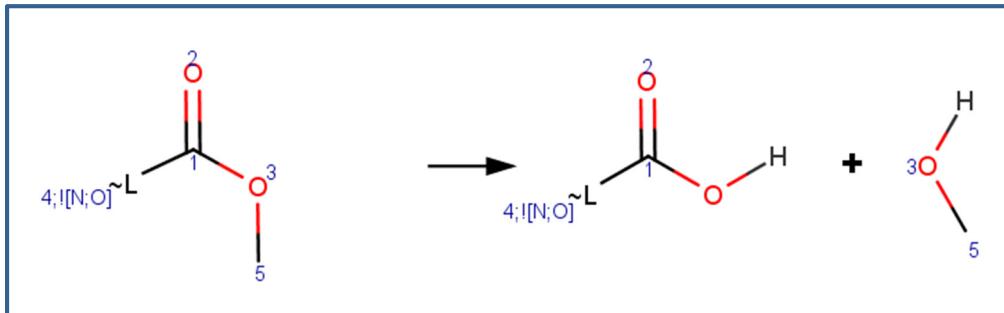
Greenhalgh, R. K.L. Dhawan and P. Weinberger. 1980. Hydrolysis of fenitrothion in model and natural aquatic systems. *Journal of Agricultural and Food Chemistry*. 28(1): 102-105.

Larson, R.A. and E.J. Weber. *Reaction Mechanisms in Environmental Organic Chemistry*. Boca Raton: CRC Press, Inc., 1994.

Macalady, D.L. and N.L. Wolfe. 1983. New perspectives on the hydrolytic degradation of the organophosphorothioate insecticide chlorpyrifos. *Journal of Agricultural and Food Chemistry*. 31(6): 1139-1147.

## Carboxylic Acid Ester Hydrolysis

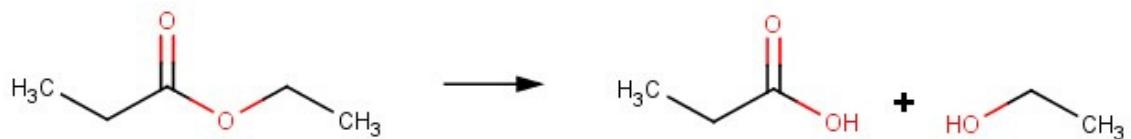
### SCHEME:



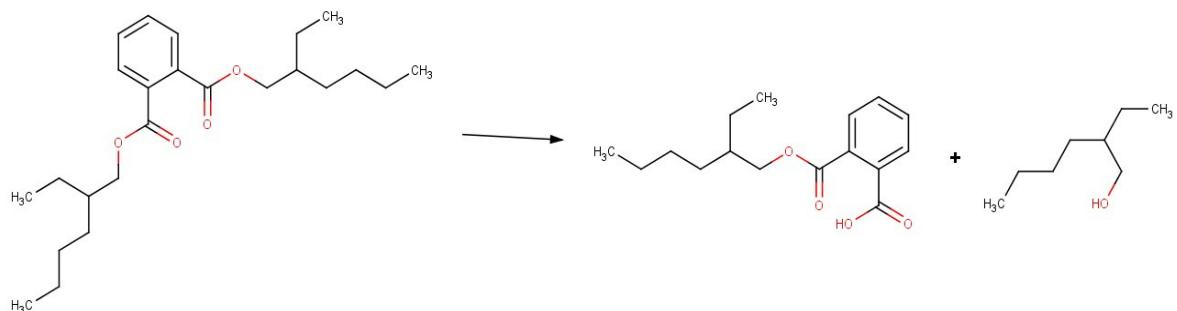
Two reactivity rules are included for this scheme. To distinguish this scheme from the Anhydride Hydrolysis scheme, the first reactivity rule specifies that atom 3 is not part of an anhydride structural fragment. To distinguish this scheme from the Lactone scheme, the second reactivity rule specifies that atom 3 is a chain atom.

### EXAMPLES:

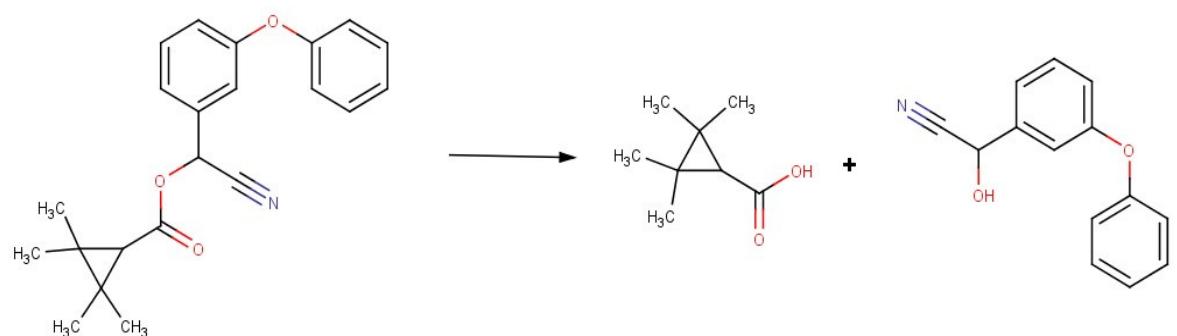
- Ethyl propanoate (McMurry, 2012)



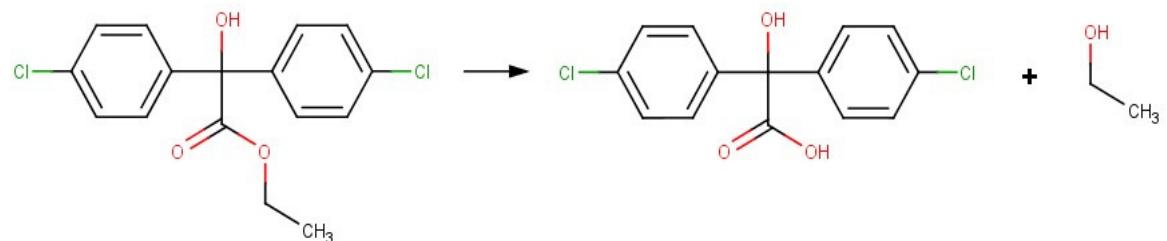
- Bis(2-ethylhexyl)phthalate (Larson and Weber, 1994)



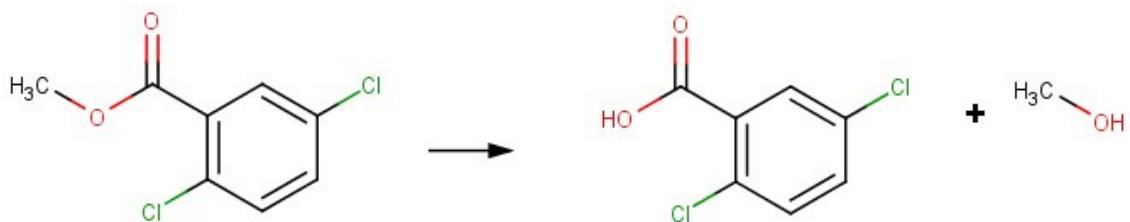
- Fenpropathrin (Larson and Weber, 1994)



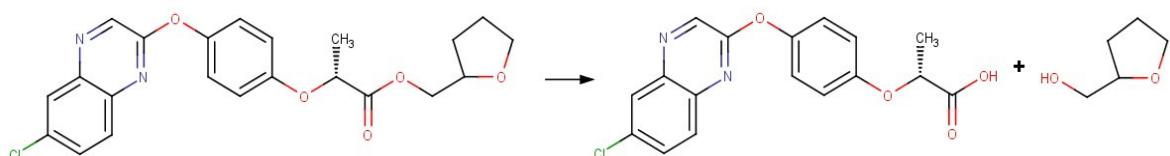
- Chlorobenzilate (Larson and Weber, 1994)



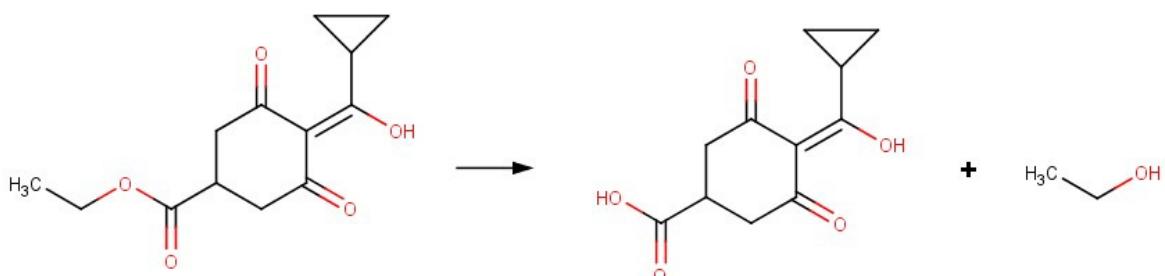
- 2,5-dichlorobenzoic acid methylester (EFSA, 2007a)



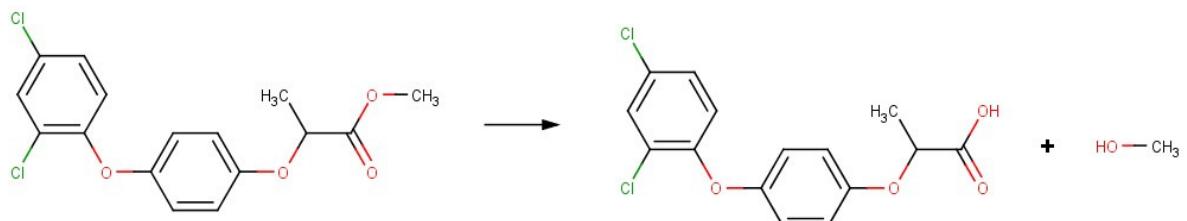
- Propaquizafop (EFSA, 2006)



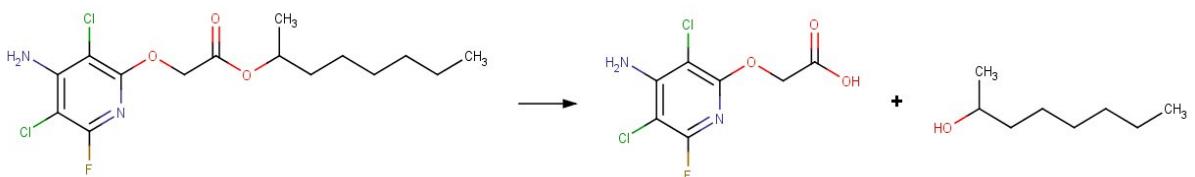
- Trinexapac (EFSA, 2005)



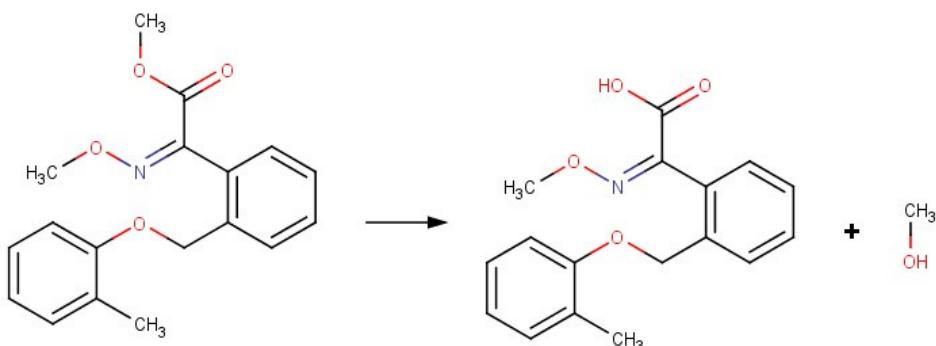
- Diclofop-methyl (EFSA, 2007b)



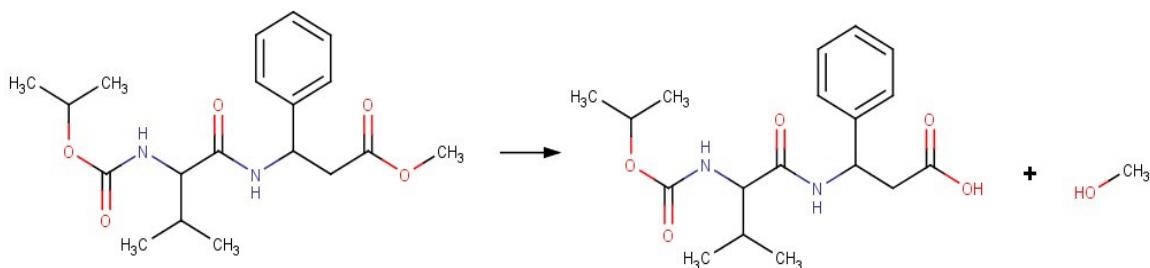
- Fluroxypyr (EFSA, 2009)



- Kresoxim-methyl (EFSA, 2010)



- Valifenalate (EFSA, 2012)



## REFERENCES:

Larson, R.A. and E.J. Weber. *Reaction Mechanisms in Environmental Organic Chemistry*. Boca Raton: CRC Press, Inc., 1994.

McMurry, J.E. 2011. *Organic Chemistry*, 8<sup>th</sup> ed. Boston, MA: Cengage Learning.

EFSA (European Food Safety Authority), 2005. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State the Netherlands for the existing active substance Trinexapac of the second stage of the review programme referred to in Article 8(2) of Council Directive 91/414/EEC, Volume 3, Annex B, B.7, part 1. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

EFSA (European Food Safety Authority), 2006. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State Italy for the existing active substance Propaquizafop of the third stage (part A) of the review programme referred to in Article 8(2) of Council Directive 91/414/EEC, Volume 3, Annex B, B.8. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

EFSA (European Food Safety Authority), 2007a. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State Germany for the existing active substance Dichlorobenzoic Acid Methylester of the third stage (part B) of the review programme referred to in Article 8(2) of Council Directive 91/414/EEC, Volume 3, Annex B, part 2, B.6. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

EFSA (European Food Safety Authority), 2007b. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State France for the existing active substance Diclofop-Methyl of the third stage (part A) of the review programme referred to in Article 8(2) of Council Directive 91/414/EEC, Volume 3, Annex B, part 4, B.8. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

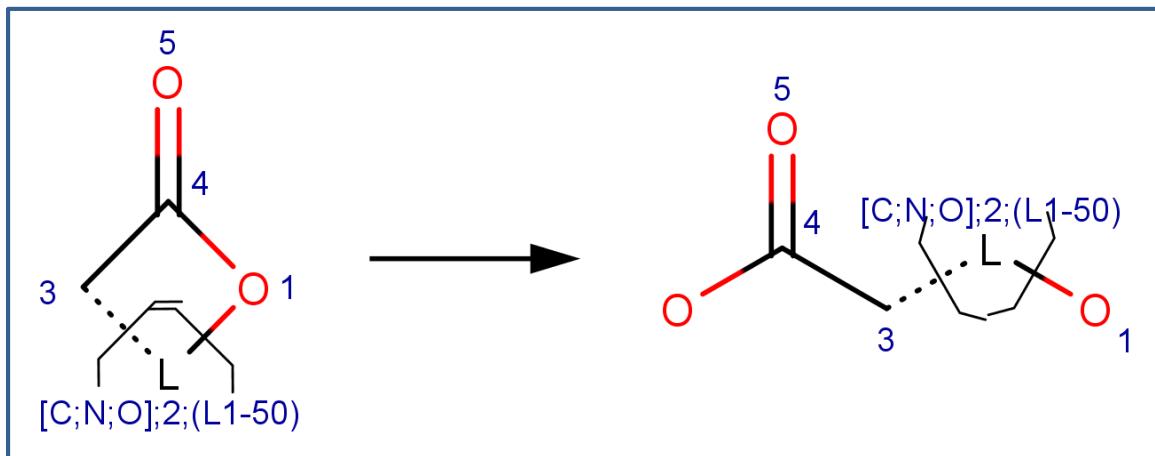
EFSA (European Food Safety Authority), 2009. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State Ireland for the existing active substance Fluroxypyrr upon submission in the framework of the renewal of the inclusion of a first group of active substances in Annex I to Council Directive 91/414/EEC in accordance with Commission Regulation (EC) No 737/2007, Volume 3, B7. <http://dar.efsa.europa.eu/dar-web/provision>.

EFSA (European Food Safety Authority), 2010. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State Belgium for the existing active substance Kresoxim-Methyl of the third stage (part A) of the review programme referred to in Article 8(2) of Council Directive 91/414/EEC, Volume 3, Annex B, B.8. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

EFSA (European Food Safety Authority), 2012. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State Hungary for the existing active substance Valifenalate of the third stage (part A) of the review programme referred to in Article 8(2) of Council Directive 91/414/EEC, Volume 3, Annex B, B.8. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

## Lactone Hydrolysis

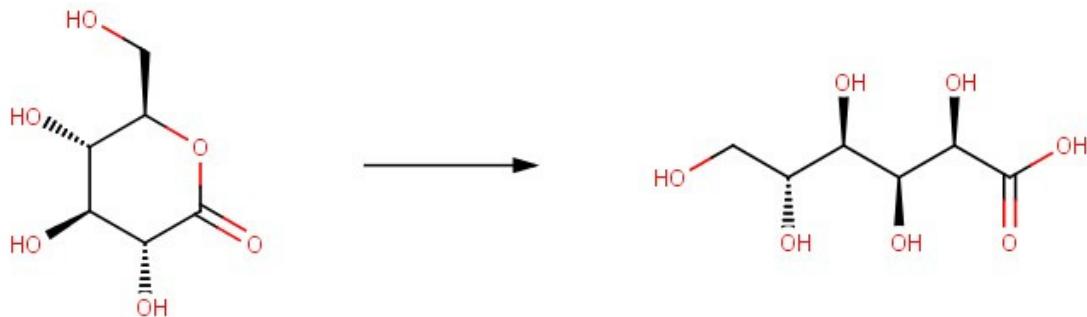
SCHEME:



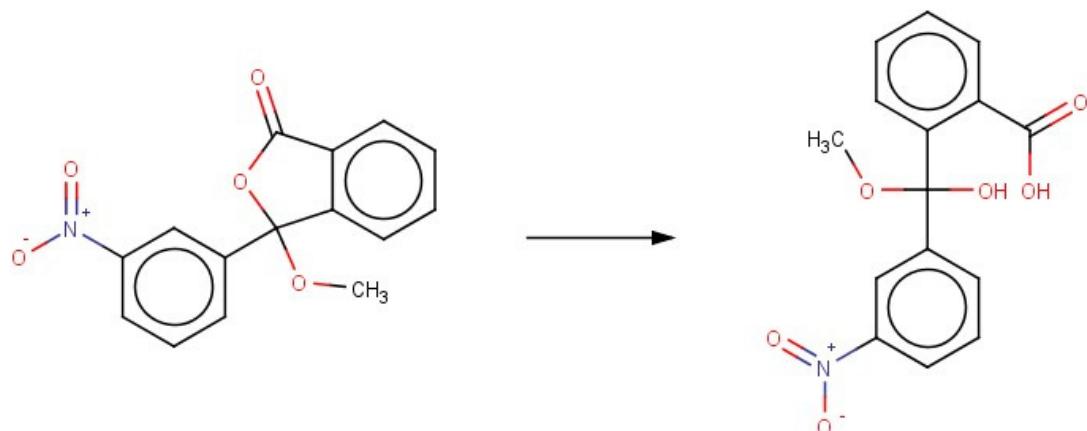
To distinguish this scheme from the Carboxylic Acid Ester scheme, the scheme includes a reactivity rule which specifies that atom 1 is a ring atom. Additionally, to distinguish this scheme from hydrolysis of cyclic anhydrides, the scheme includes a reactivity rule which specifies that atom 1 is not part of an anhydride structural fragment.

**EXAMPLES:**

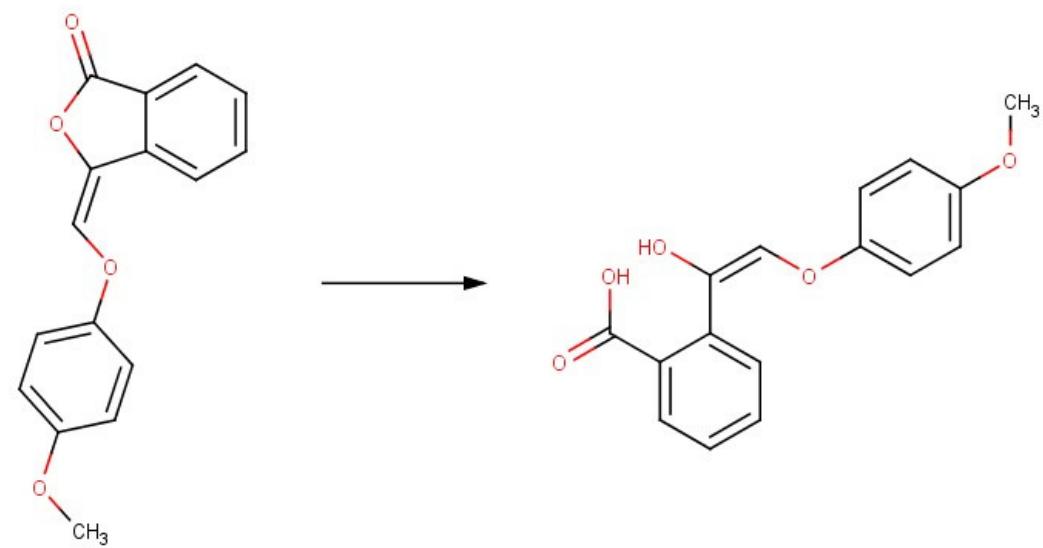
- Gluconolactone (Pocker and Green, 1973)



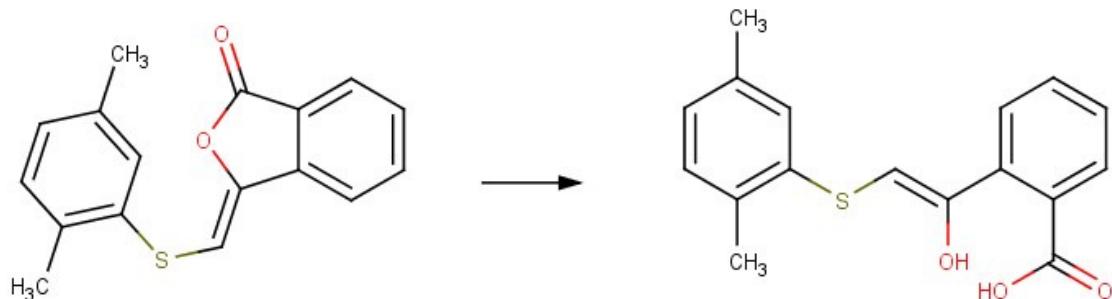
- 3-methoxy-3-(3-nitrophenyl)-2-benzofuran-1-one (Weeks and Whitney, 1981)



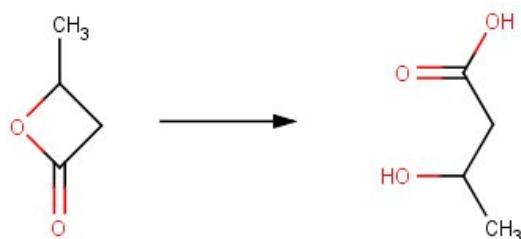
- (3E)-3-(4-methoxyphenoxy)methylidene)-2-benzofuran-1-one (Bowden *et al*, 1998)



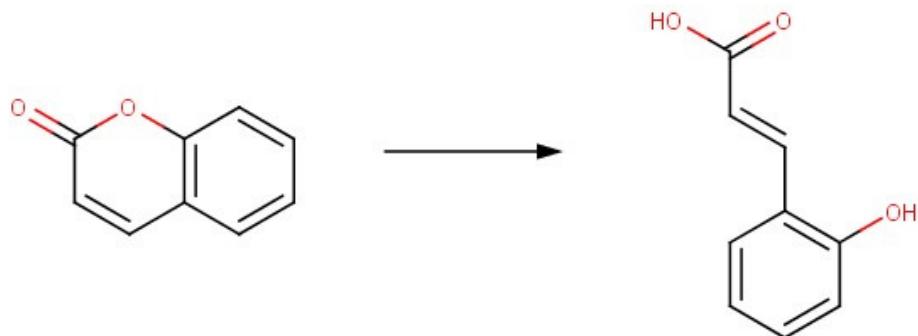
- (3Z)-3-{[(2,5-dimethylphenyl)sulfanyl]methylidene}-2-benzofuran-1-one (Bowden *et al*, 1998)



- Beta-butyrolactone (Olson and Voule, 1951)



- Coumarin (El-Khatib and Nassr, 2007)



#### REFERENCES:

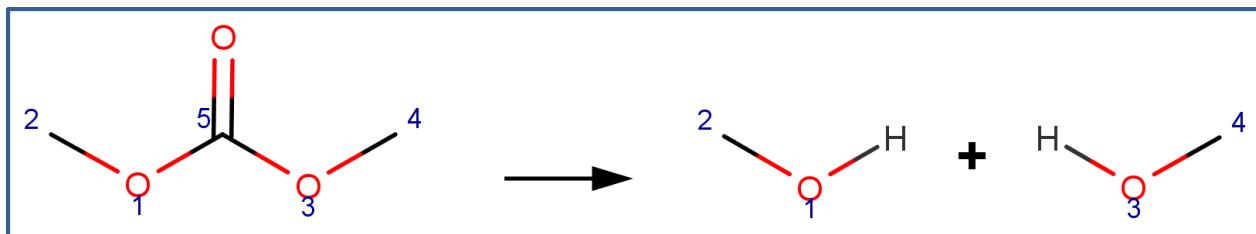
- Bowden, K.; R.J. Ranson, A. Perjessy, M. Lacova, O. Hritzova, and W.W.F. Fabian. 1998. Base-catalyzed hydrolysis of gamma-lactones: reactivity-structure correlations for 3-(substituted phenoxy and thiophenoxy)methylene)-(Z)-1(3H)-isobenzofuranones. *J. Phys. Org. Chem.* 11: 467-474.
- El-Khatib, R.M. and L.A.M.E. Nassr. 2007. Reactivity trends of the base hydrolysis of coumarin and thiocoumarin in binary aqueous-methanol mixtures at different temperatures. *Spectrochimica Acta Part A*. 67: 643-648.
- Olson, A.R. and P.V. Voule. 1951. The Hydrolysis of Beta-Butyrolactone. *J. Am. Chem. Soc.* 73: 2468-2471.

Pocker, Y. and E. Green. 1973. Hydrolysis of D-glucono-delta-lactone. I. General Acid-Base Catalysis, Solvent Deuterium Isotope Effects, and Transition State Characterization. *J. Am. Chem. Soc.* 95: 113-119.

Weeks, D.P. and D.B. Whitney. 1981. Hydrolysis of 3-(m-nitrophenyl)-3-methoxyphthalide. *J. Am. Chem. Soc.* 103: 3555-3558.

## Carbonate Hydrolysis

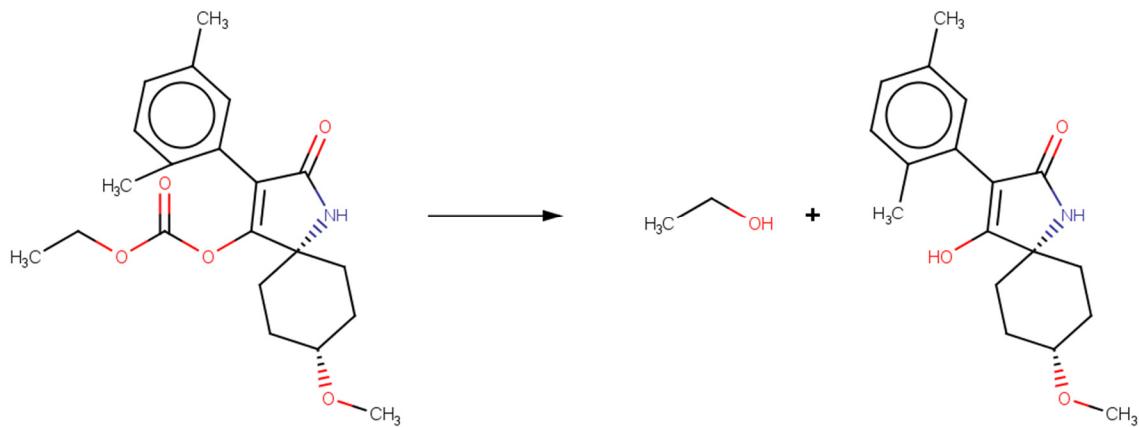
### SCHEME:



Note that a selectivity rule is included for this scheme to eliminate duplication of products. Specifically, to distinguish between the carbon atoms labelled 1 and 3, atom 1 is identified as the less sterically hindered atom. Additionally, to distinguish this scheme from the Cyclic Carbonate scheme, the scheme includes a reactivity rule which specifies that atom 5 is a chain atom.

### EXAMPLES:

- Spirotetramat (EFSA, 2008)



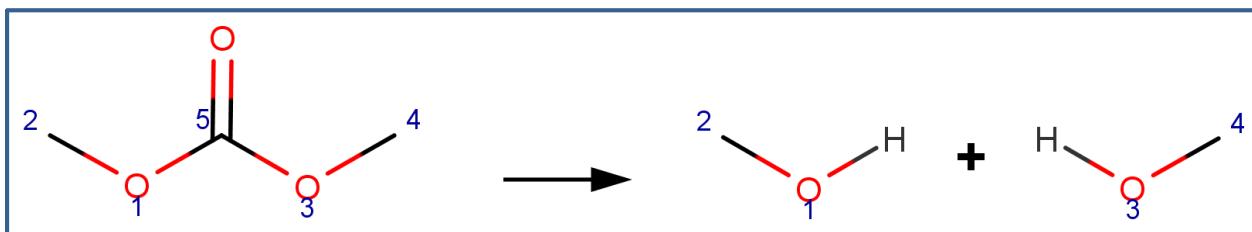
### REFERENCES:

EFSA (European Food Safety Authority). 2008. Draft Assessment Report (DAR): Joint Review Project/OECD Monograph on Spirotetramat provided by the regulatory authorities of Austria, Canada and the

United States of America, Volume 3, Annex B, B.8. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

## Cyclic Carbonate Hydrolysis

### SCHEME:



This scheme is similar to the [Carbonate scheme](#), except that the scheme includes a reactivity rule which specifies that atom 5 is a ring atom.

### EXAMPLES:

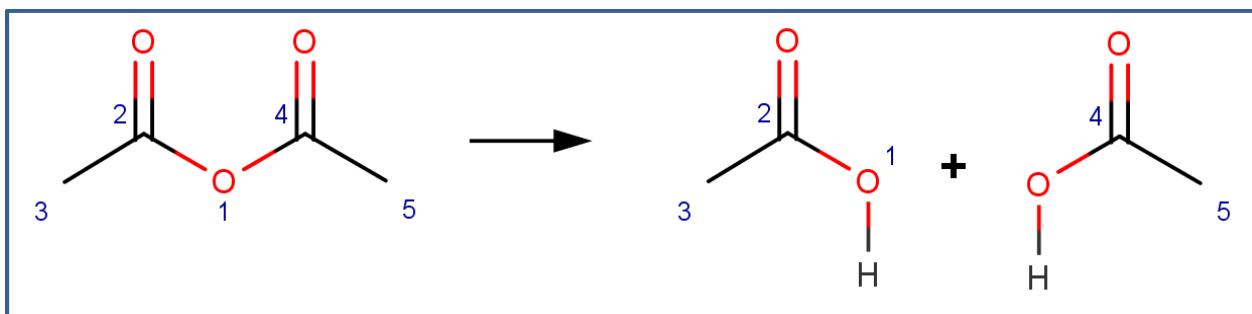
No examples were found for the Cyclic Carbonate Hydrolysis pathway.

### REFERENCES:

N/A

## Anhydride Hydrolysis

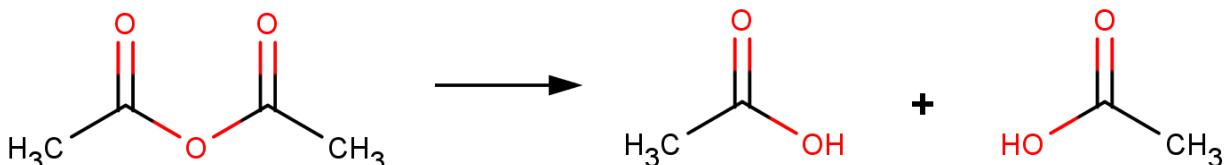
### SCHEME:



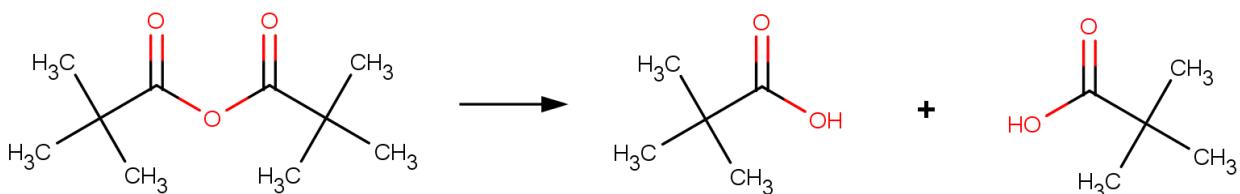
Note that a selectivity rule is included for this scheme to eliminate duplication of products. Specifically, to distinguish between the carbon atoms labelled 2 and 4, atom 2 is identified as the less sterically hindered atom.

**EXAMPLES:**

- Acetic anhydride (Bunton and Fendler, 1965)

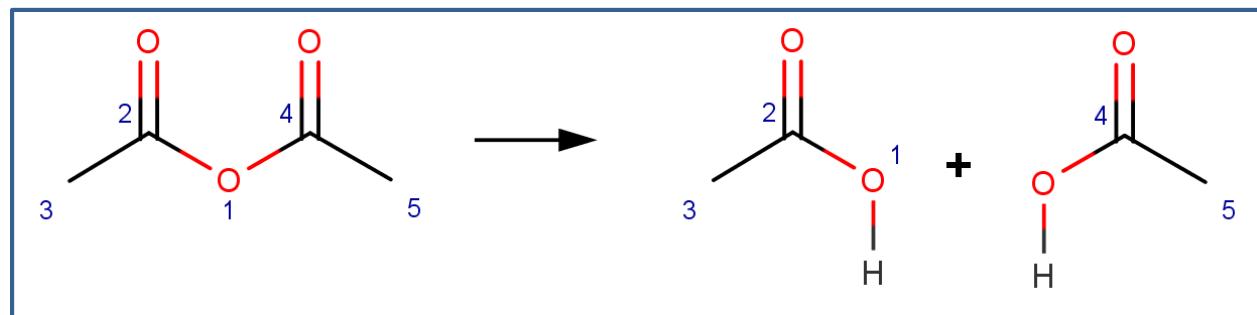


- Trimethylacetic anhydride (Bunton and Fendler, 1965)

**REFERENCES:**

Bunton, C.A. and J.H. Fendler. 1965. The hydrolysis of carboxylic anhydrides. V. The acid hydrolysis of acetic and trimethylacetic anhydride. *Journal of Organic Chemistry*. 30(5): 1365-1371.

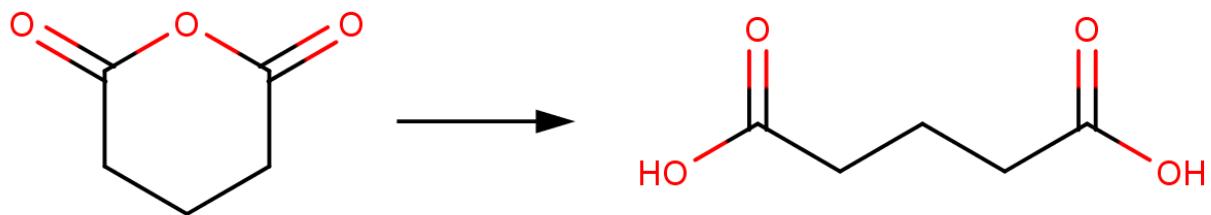
## Cyclic Anhydride Hydrolysis

**SCHEME:**

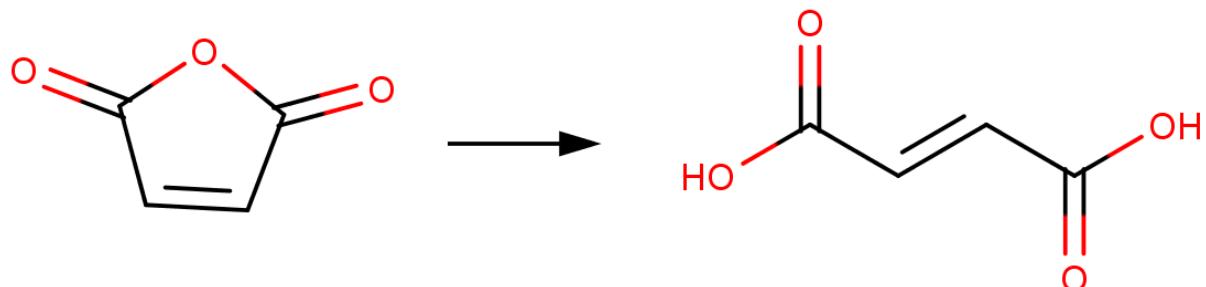
This scheme is similar to the [Anhydride scheme](#), except that the scheme includes a reactivity rule which specifies that atom 1 is a ring atom.

**EXAMPLES:**

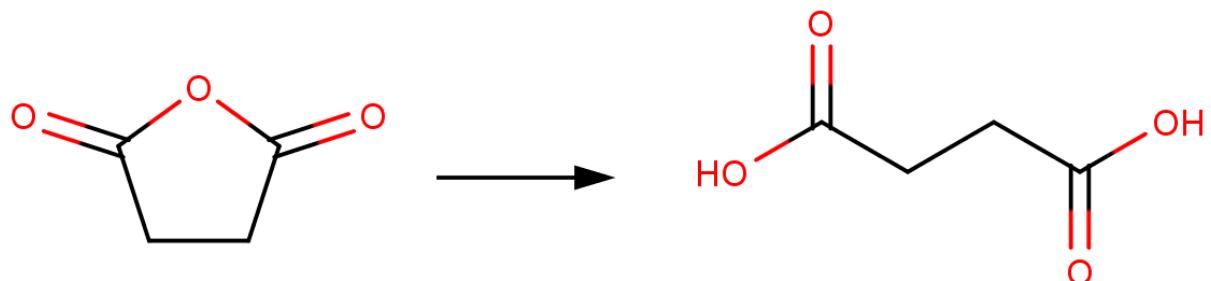
- Glutaric anhydride (Bunton *et al*, 1963)



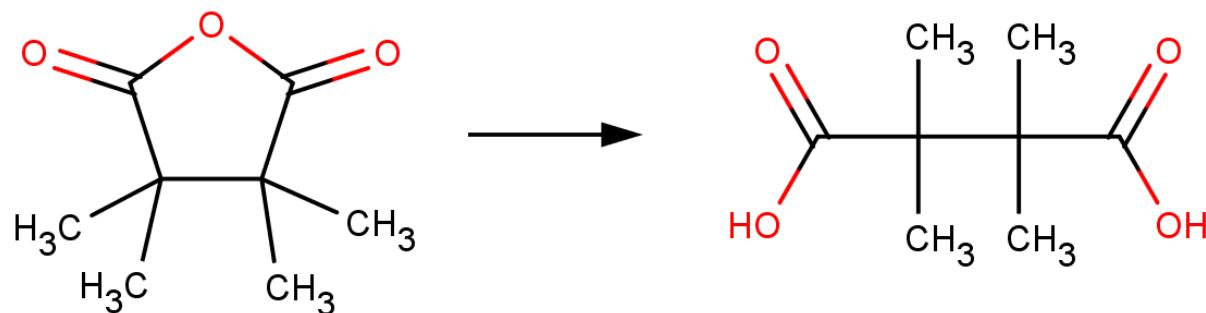
- Maleic anhydride (Bunton *et al*, 1963)



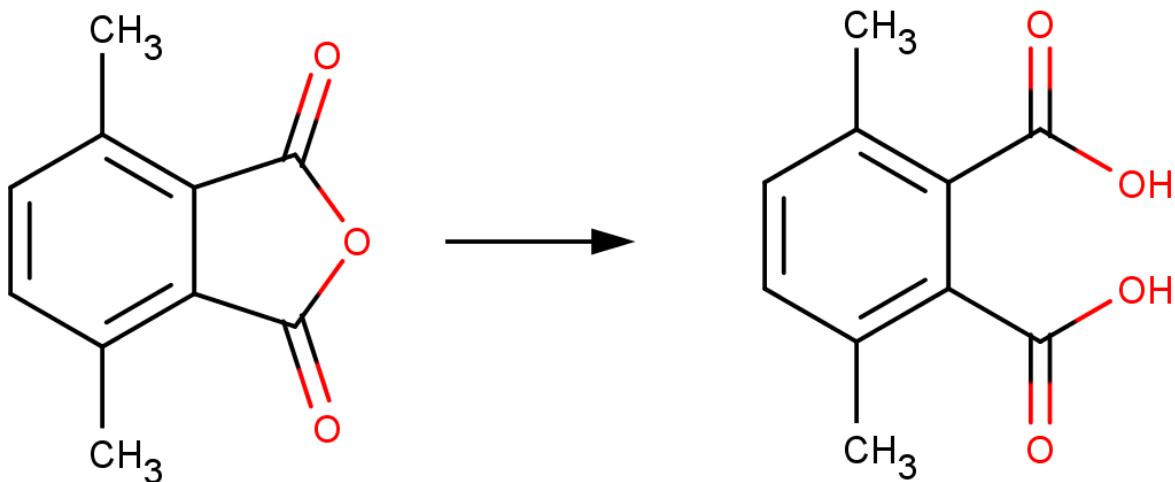
- Succinic anhydride (Bunton *et al*, 1963)



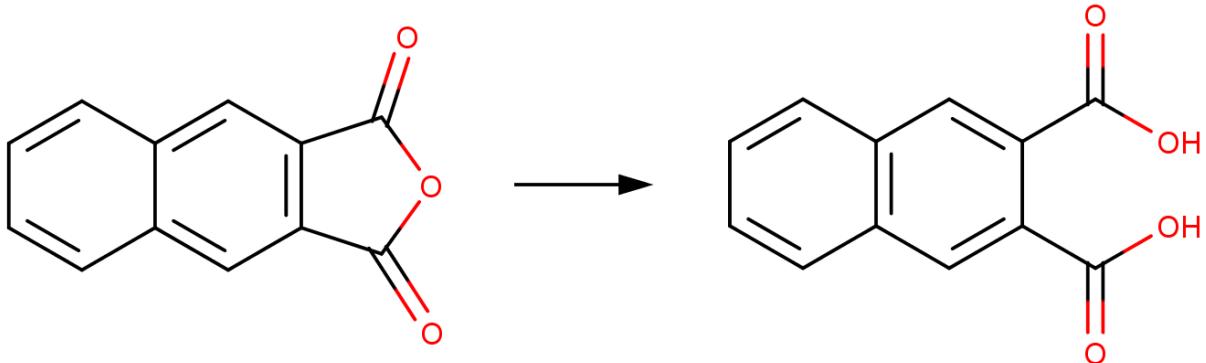
- Tetramethylsuccinic anhydride (Bunton *et al*, 1963)



- 3,6-Dimethylphthalic anhydride (Hawkins, 1975a,b)



- Naphtho(2,3-c)furan-1,3-dione (Barros *et al*, 2001)

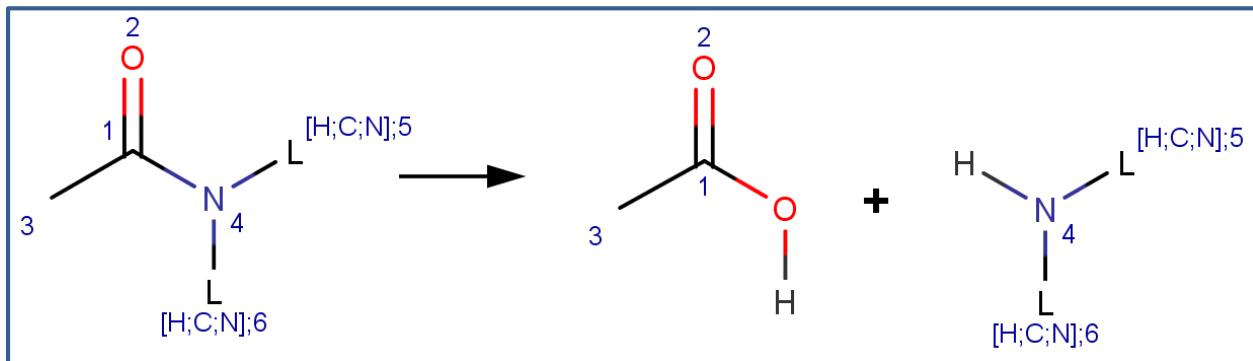


#### REFERENCES:

- Barros, T.C., S. Yunes, G. Menegon, F. Nome, H. Chaimovich, M.J. Politi, L.G. Dias and I.M. Cuccovia. 2001. Hydrolysis of 1,8- and 2,3-naphthalic anhydrides and the mechanism of cyclization of 1,8-naphthalic acid in aqueous solutions. *Journal of the Chemical Society, Perkin Transactions 2*. 2001(12): 2342-2350.
- Bunton, C.A., N.A. Fuller, S.G. Perry and V.J. Shiner. 1963. The hydrolysis of carboxylic anhydrides. Part III. Reactions in initially neutral solution. *Journal of the Chemical Society*. 1963: 2918-2926.
- Hawkins M.D. 1975a. Hydrolysis of phthalic and 3,6-dimethylphthalic anhydrides. *Journal of the Chemical Society, Perkin Transactions 2*. 1975(4): 282-284.
- Hawkins M.D. 1975b. Hydrolysis of 2,2,2-trifluoroethyl hydrogen 3,6-dimethylphthalate. *Journal of the Chemical Society, Perkin Transactions 2*. 1975(4): 285-287.

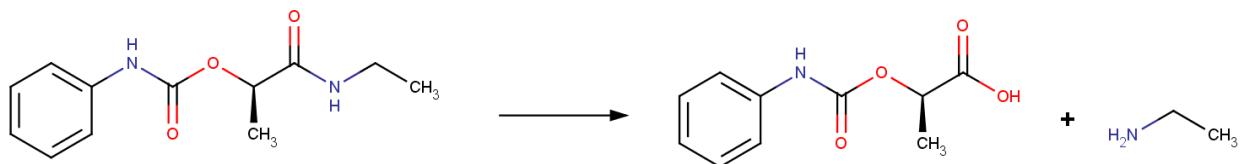
## Amide Hydrolysis

SCHEME:

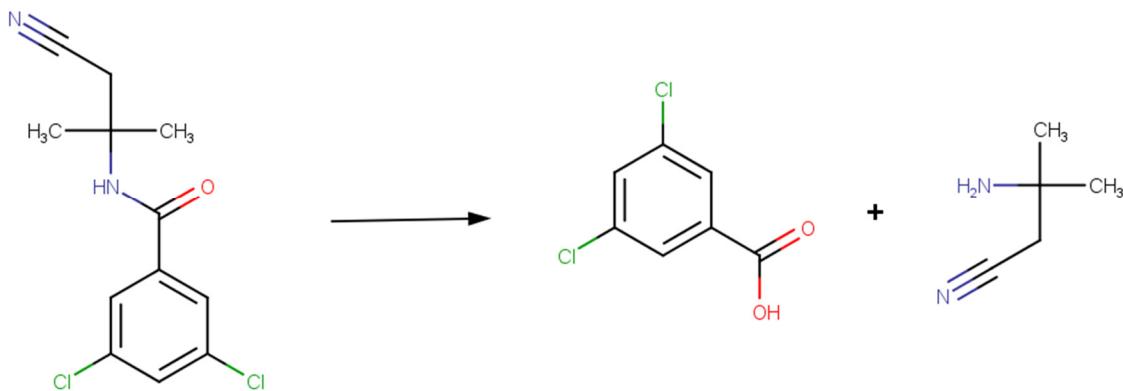


EXAMPLES:

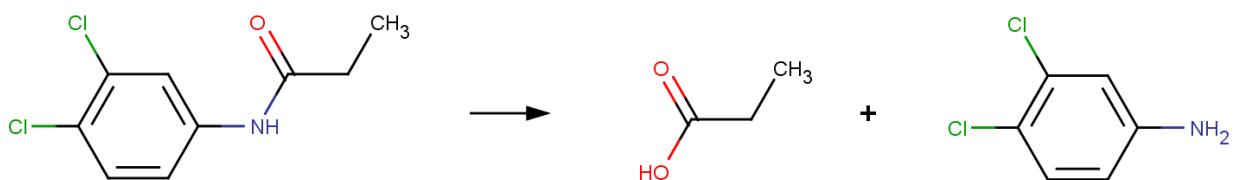
- Carbetamide (EFSA, 2006a)



- Pronamide (Larson and Weber, 1994)

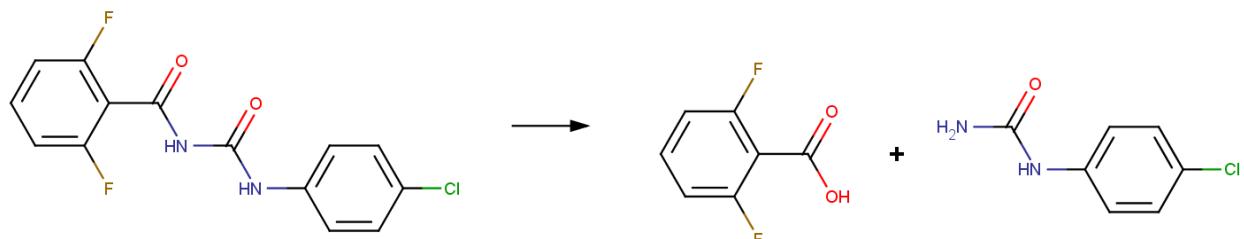


- Propanil (EFSA, 2008b)

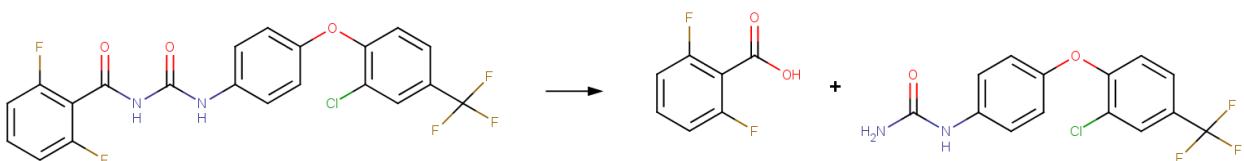


FORMYLUREA EXAMPLES: (Urea group adjacent to an amide group)

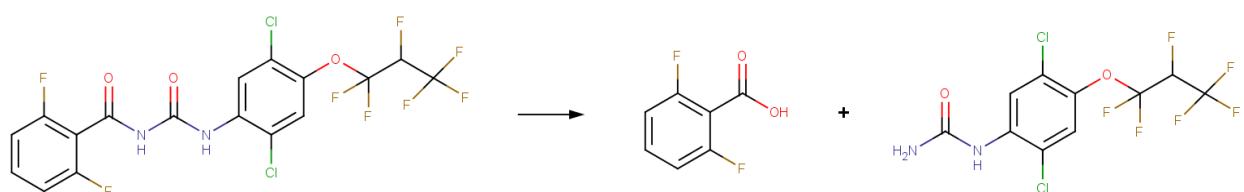
- Diflubenzuron (EFSA, 2006b)



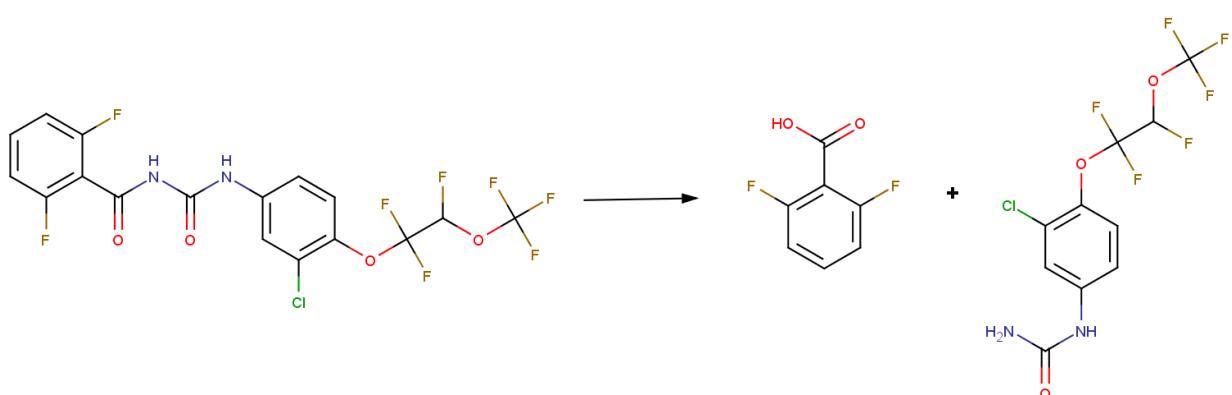
- Flufenoxuron (EFSA, 2008a)



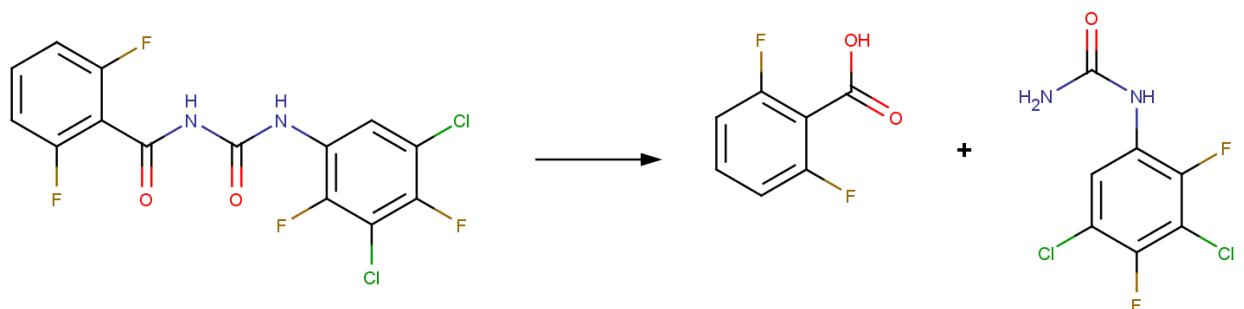
- Lufenuron (EFSA, 2007b)



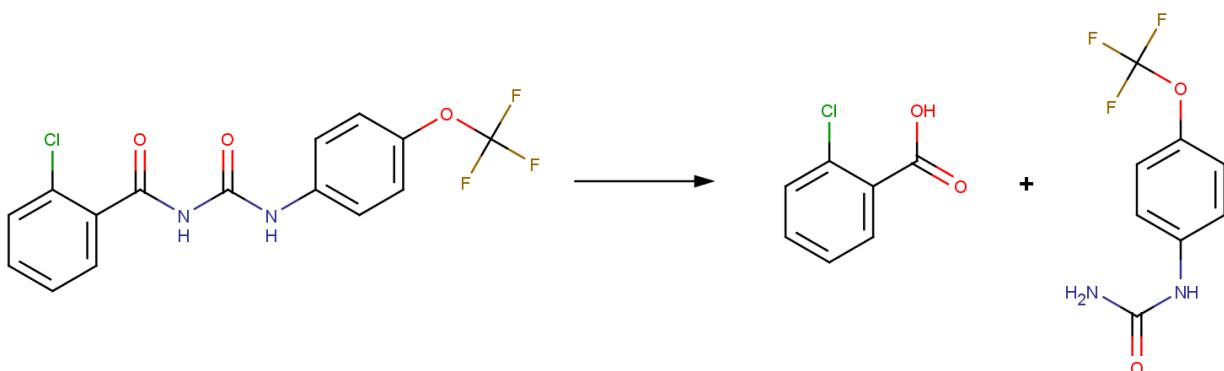
- Novaluron (EFSA, 2008c)



- Teflubenzuron (EFSA, 2007c)



- Triflumuron (EFSA, 2007a)



#### REFERENCES:

EFSA (European Food Safety Authority), 2006a. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State France for the existing active substance Carbetamide of the third stage (part A) of the review programme referred to in Article 8(2) of Council Directive 91/414/EEC, Volume 3, Annex B, part 4, B.8. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

EFSA (European Food Safety Authority), 2006b. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State Sweden for the existing active substance Diflubenzuron of the third stage (part A) of the review programme referred to in Article 8(2) of Council Directive 91/414/EEC, Volume 3, Annex B, B.2 and B.8. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

EFSA (European Food Safety Authority). 2007a. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State Italy for the existing active substance Triflumuron of the third stage (part A) of the review programme referred to in Article 8(2) of Council Directive 91/414/EEC, Volume 3, Annex B, part 4, B.8. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

EFSA (European Food Safety Authority). 2007b. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State Portugal for the existing active substance Lufenuron of the third stage (part B) of the review programme referred to in Article 8(2) of Council Directive 91/414/EEC, Volume 3, Annex B, part 4, B.8. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

EFSA (European Food Safety Authority). 2007c. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State the United Kingdom for the existing active substance Teflubenzuron of the third stage (part B) of the review programme referred to in Article 8(2) of Council Directive 91/414/EEC, Volume 3, Annex B, part 4, B.8. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

EFSA (European Food Safety Authority), 2008a. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State France for the existing active substance Flufenoxuron of the third stage (part A) of the review programme referred to in Article 8(2) of Council Directive 91/414/EEC, Volume 3, Annex B, B.2 and B.8. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

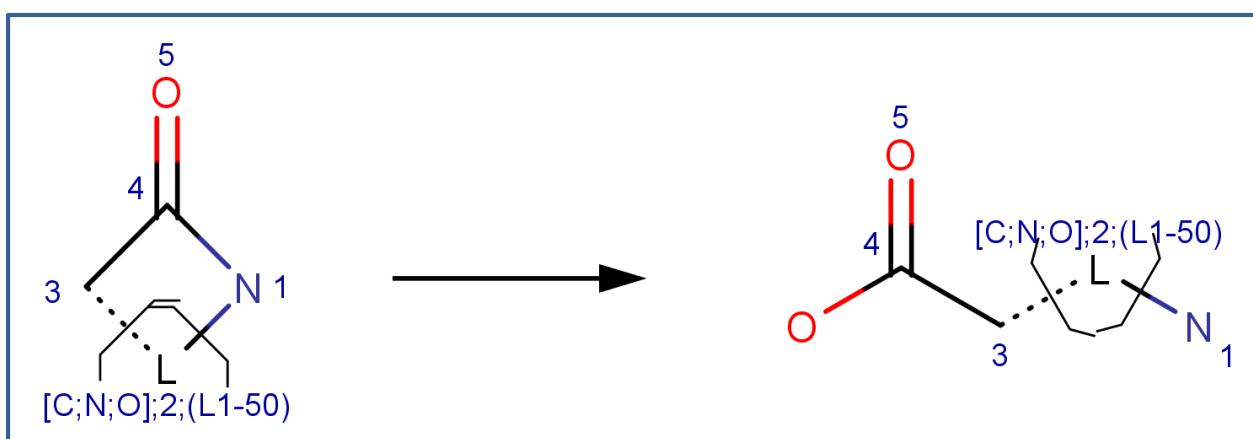
EFSA (European Food Safety Authority), 2008b. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State Italy for the existing active substance Propanil of the review programme referred to in Article 8(1) of Council Directive 91/414/EEC, Volume 3, Annex B, part 4, B.8. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

EFSA (European Food Safety Authority), 2008c. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State the United Kingdom for the existing active substance Novaluron of the review programme referred to in Article 8(1) of Council Directive 91/414/EEC, Volume 3, Annex B, part 4, B.8. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

Larson, R.A. and E.J. Weber. *Reaction Mechanisms in Environmental Organic Chemistry*. Boca Raton: CRC Press, Inc., 1994.

## Lactam Hydrolysis

### SCHEME:

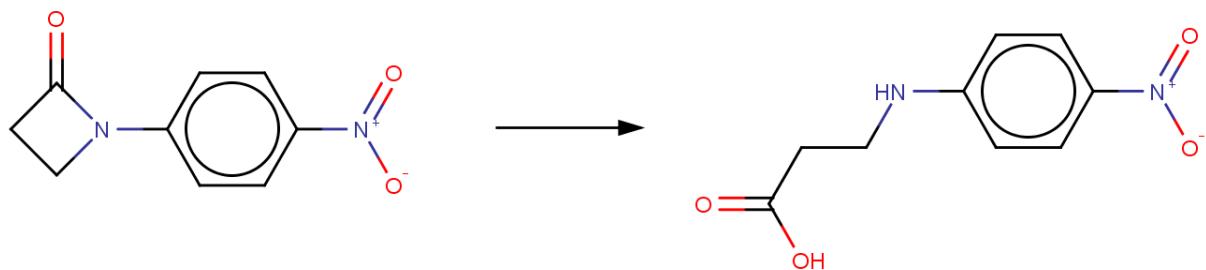


To distinguish this scheme from the Amide scheme, the scheme includes a reactivity rule which specifies that atom 1 is a ring atom. Additionally, to distinguish this scheme from hydrolysis of cyclic imides, the scheme includes a reactivity rule which specifies that atom 1 is not part of an imide structural fragment.

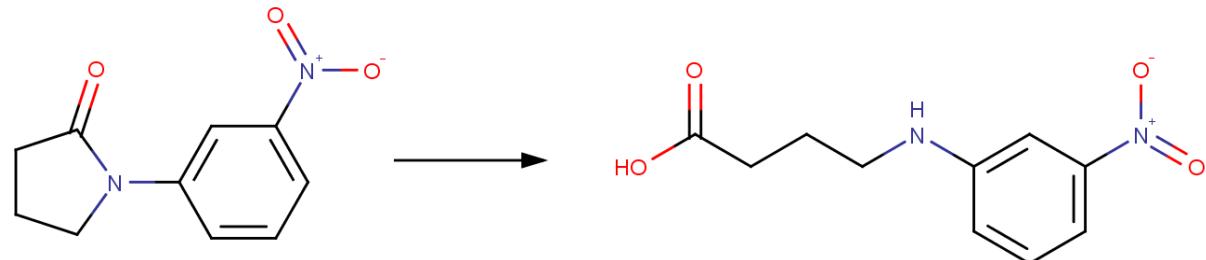
Studies comparing the rates of hydrolysis of lactam rings of various sizes indicate that the four-member β-lactam ring is more susceptible to hydrolysis than larger ring sizes (Bowden and Bromley, 1990; Imming *et al*, 2000; Wan *et al*, 1980); however, this trend is not currently captured in the hydrolysis reaction library. Lactam rings of four to 50 atoms are assigned the same rank.

### EXAMPLES:

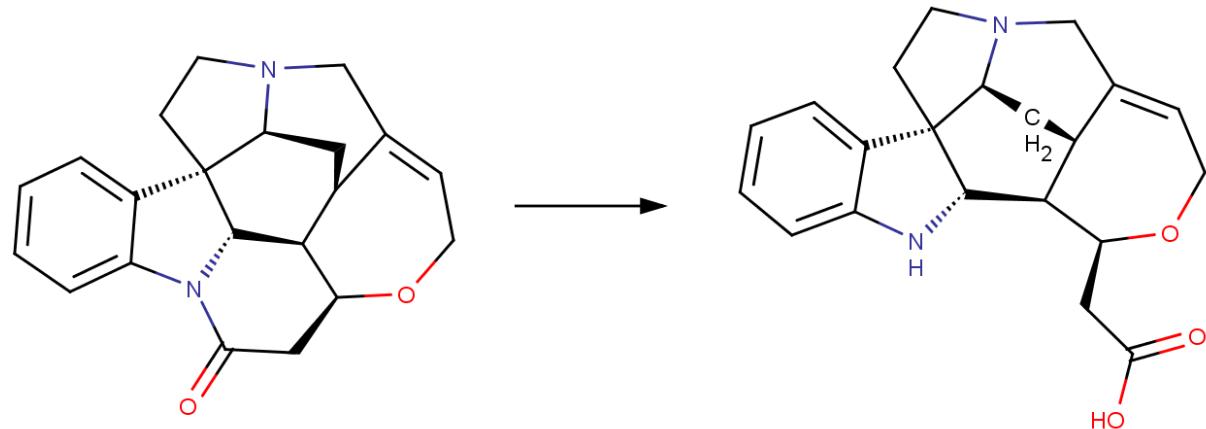
- 1-(4-Nitrophenyl)-2-azetidinone (Blackburn and Plackett, 1972)



- 1-(3-Nitrophenyl)-2-pyrrolidinone (Bowden and Bromley, 1990)



- Strychnine (Abbas *et al*, 1996)



## REFERENCES:

Abbas, K.A., P.Hurst and J.T. Edward. 1996. Reexamination of the Kirkwood-Westheimer theory of electrostatic effects. V. Effect of charged substituents on the rates of alkaline hydrolysis of substituted strychnines. *Canadian Journal of Chemistry*. 75: 441-448.

Blackburn, G.M. and J.D. Plackett. 1972. Strain effects in acyl transfer reactions. Part 1. The kinetics of hydrolysis of some N-aryl-lactams. *Journal of the Chemical Society, Perkin Transactions 2*. 1972(10): 1366-1371.

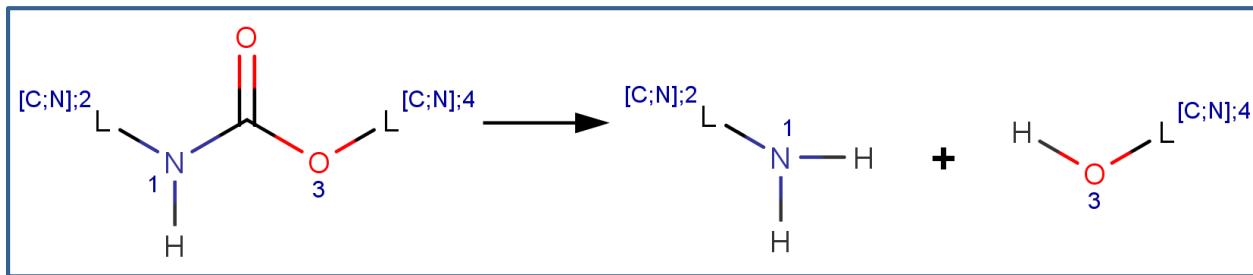
Bowden, K. and K. Bromley. 1990. Reactions of carbonyl compounds in basic solutions. Part 14. The alkaline hydrolysis of substituted N-Methylformanilides, N-Methylacetanilides, 1-Phenylazetidin-2-ones, 1-Phenyl-2-pyrrolidones, and 1-Phenyl-2-piperidones. *Journal of the Chemical Society, Perkin Transactions 2*. 1990(12): 2103-2109.

Imming, P., B. Klar and D. Dix. 2000. Hydrolytic stability versus ring size in lactams: Implications for the development of lactam antibiotics and other serine protease inhibitors. *Journal of Medicinal Chemistry*. 43(22): 4328-4331.

Wan, P., T.A. Modro and K. Yates. 1980. The kinetics and mechanism of acid catalysed hydrolysis of lactams. *Canadian Journal of Chemistry*. 58: 2423-2432.

## Carbamate Hydrolysis

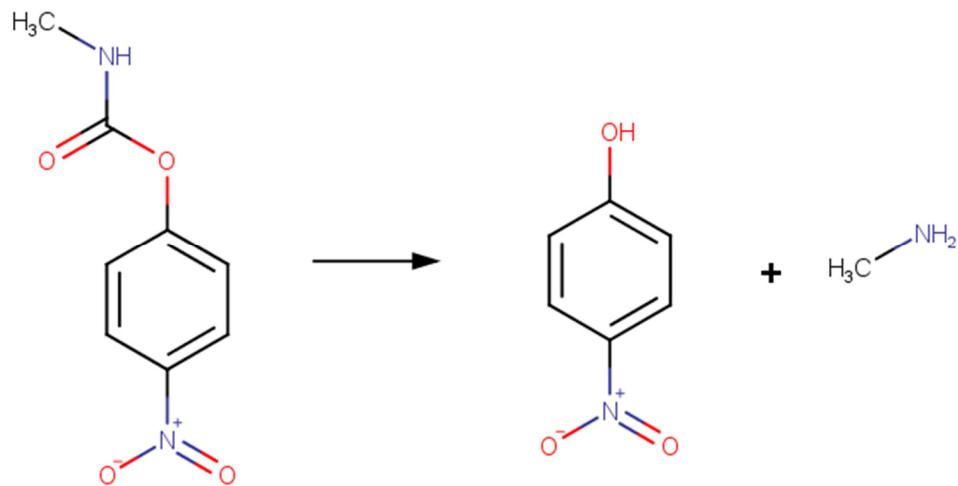
### SCHEME:



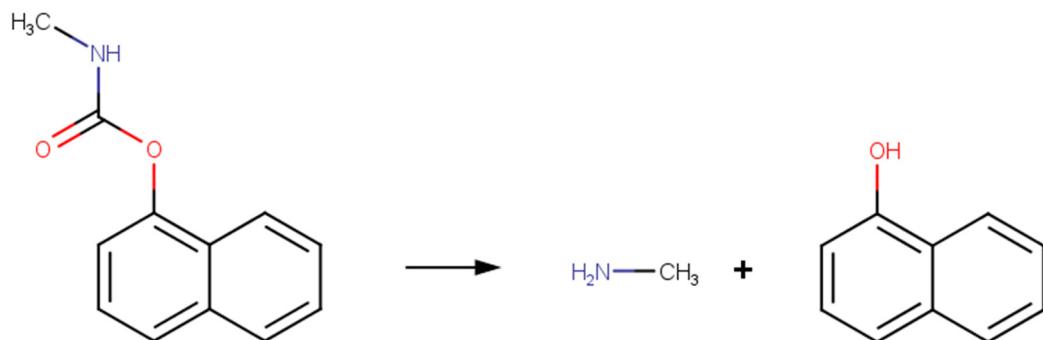
As is shown in the examples below, a number of N-alkyl and N-aryl carbamates have been observed to undergo hydrolysis according to the scheme shown above. The N,N-disubstituted carbamates (a.k.a. secondary carbamates) are resistant to hydrolysis (Aly and El-Dib, 1971; Christenson, 1964; EFSA, 2004c; Larson and Weber, 1994; Wolfe et al. 1978a).

### EXAMPLES:

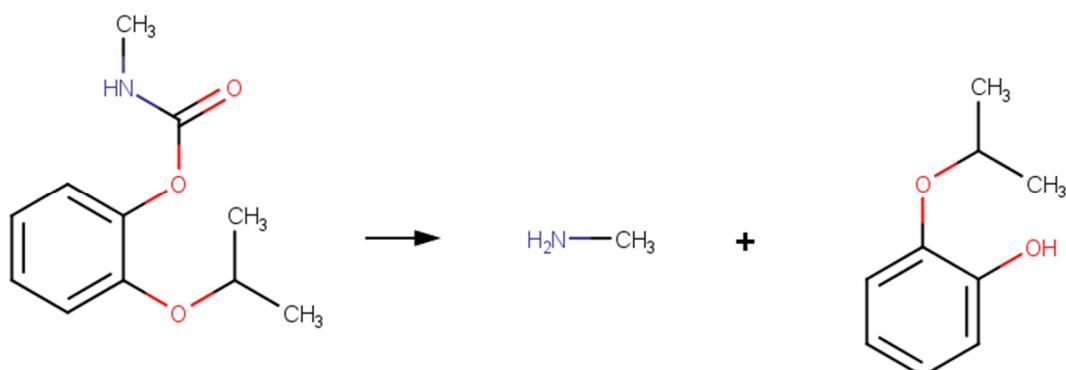
- 4-nitrophenyl N-methylcarbamate (Bender and Homer, 1965)



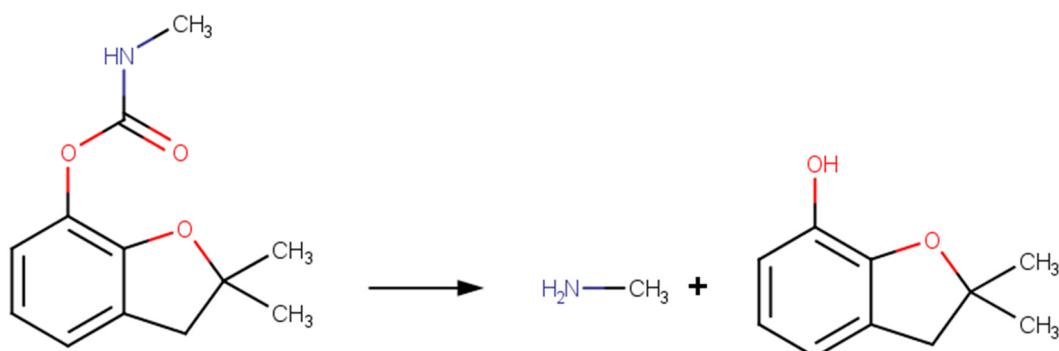
- Carbaryl (a.k.a. Sevin) (Aly and El-Dib, 1971; EFSA, 2005a; Wolfe *et al*, 1978b)



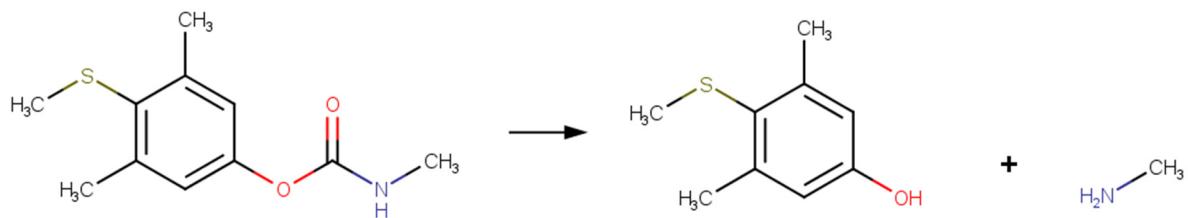
- Propoxur (a.k.a. Baygon) (Aly and El-Dib, 1971)



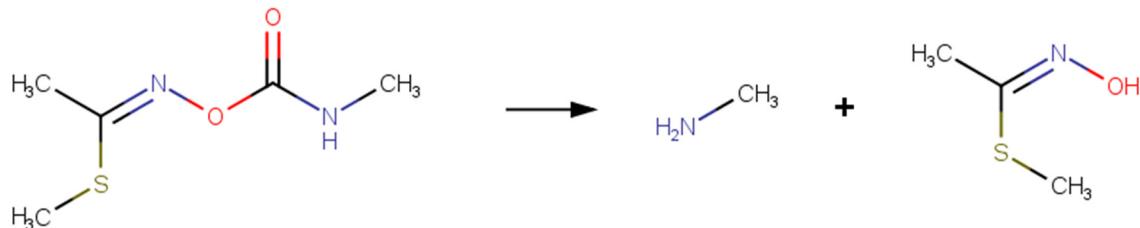
- Carbofuran (EFSA, 2004a; lesce *et al*, 2006)



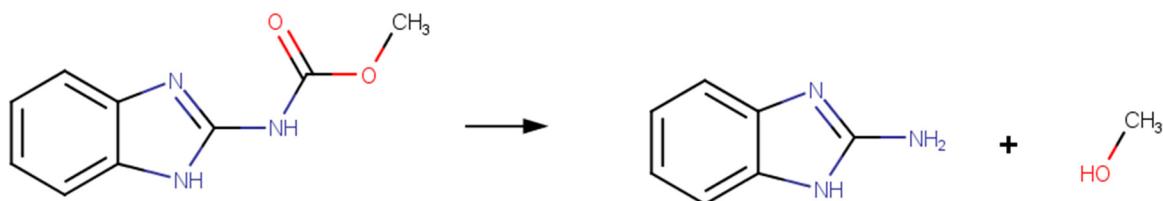
- Methiocarb (EFSA, 2005b)



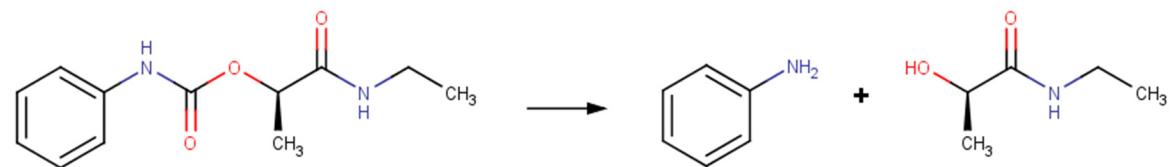
- Methomyl (EFSA, 2004b)



- Carbendazim (EFSA, 2009)



- Carbetamide (EFSA, 2006)



## REFERENCES:

Aly, O.M. and M.A. El-Dib. 1971. Studies on the Persistence of Some Carbamate Insecticides in the Aquatic Environment. *Water Research.* 5: 1191-1205.

Bender, M.L. and R.B. Homer. 1965. The mechanism of the alkaline hydrolysis of *p*-nitrophenyl N-methylcarbamate. *Journal of Organic Chemistry.* 30(11): 3975-3978.

Christenson, I. 1964. Alkaline hydrolysis of some carbamic acid esters. *Acta Chemica Scandinavica.* 18(4): 904-922.

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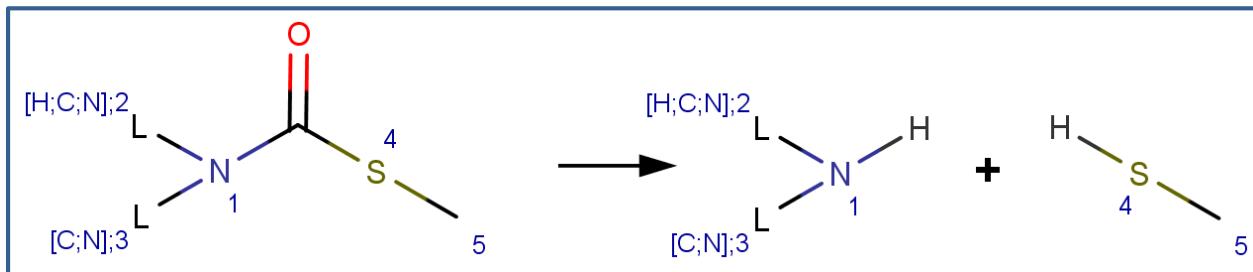
Larson, R.A. and E.J. Weber. *Reaction Mechanisms in Environmental Organic Chemistry*. Boca Raton: CRC Press, Inc., 1994.

Wolfe, N.L., R.G. Zepp, and D.F. Paris. 1978a. Use of Structure-Reactivity Relationships to Estimate Hydrolytic Persistence of Carbamate Pesticides. *Water Research*. 12: 561-563.

Wolfe, N.L., R.G. Zepp, and D.F. Paris. 1978b. Carbaryl, Propham and Chlorpropham: A Comparison of the Rates of Hydrolysis and Photolysis with the Rate of Biolysis. *Water Research*. 12: 565-571.

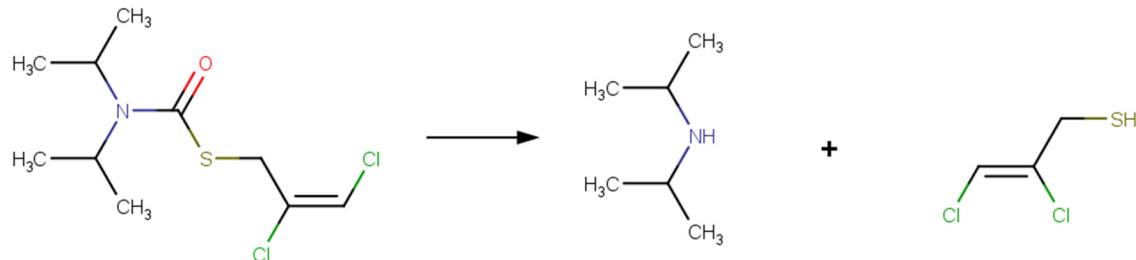
## Thiocarbamate Hydrolysis

SCHEME:



EXAMPLES:

- Diallate (U.S. EPA, 1992, p. 88)

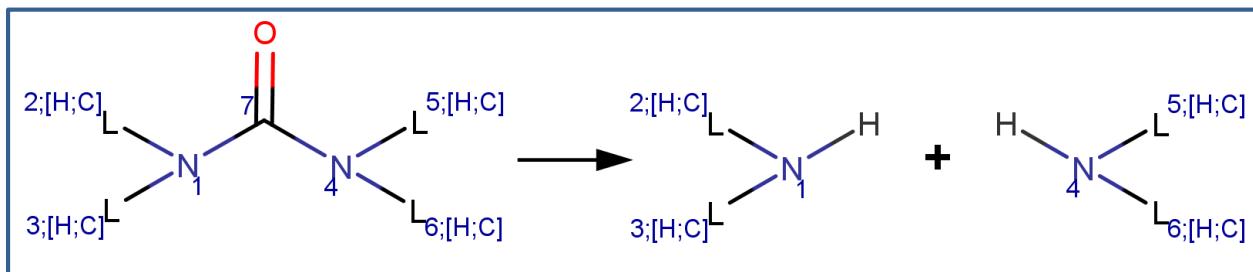


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U.S. EPA (United States Environmental Protection Agency). 1992. Environmental fate constants for organic chemicals under consideration for EPA's Hazardous Waste Identification Rule. EPA/601/R-92/006.

## Urea Hydrolysis

SCHEME:

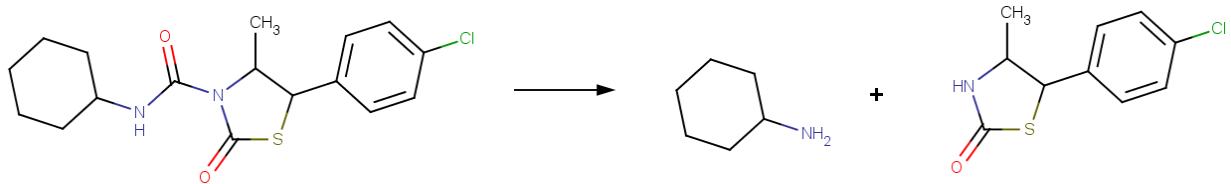


To distinguish this scheme from the Cyclic Urea Hydrolysis scheme, the scheme includes a reactivity rule which specifies that atom 7 is a chain atom. Additionally, a selectivity rule is included for this scheme to eliminate duplication of products. Specifically, to distinguish between the nitrogen atoms labelled 1 and 4, atom 1 is identified as the less sterically hindered atom.

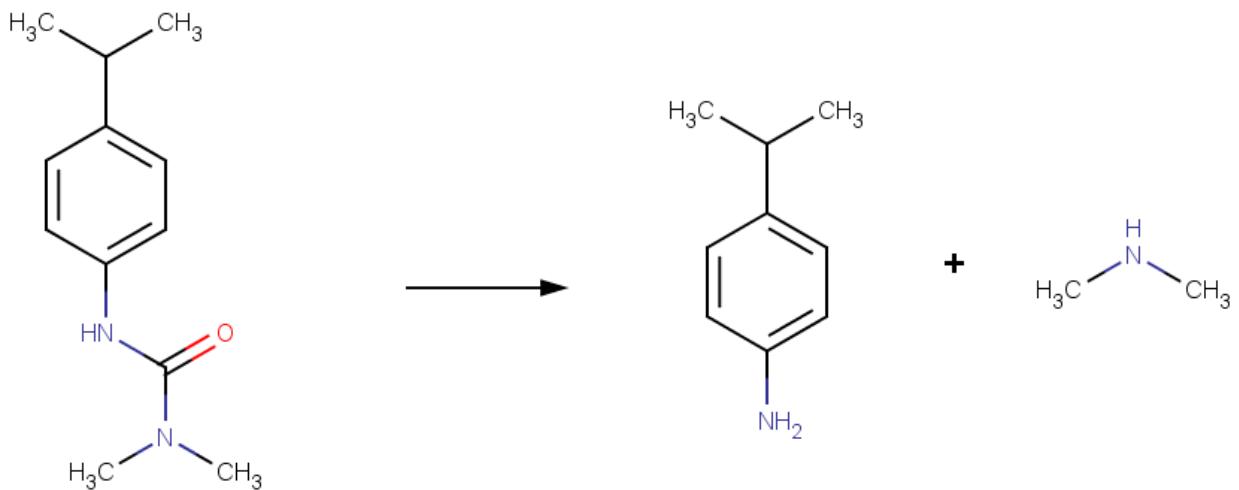
In molecules with a urea group adjacent to an amide group, hydrolysis is generally observed to follow the amide pathway ([formylurea examples](#)). However, at high temperature (> 50°C), significant formation of the products of the urea hydrolysis pathway has been observed (EFSA, 2006a; EFSA, 2006b; EFSA, 2014).

#### EXAMPLES:

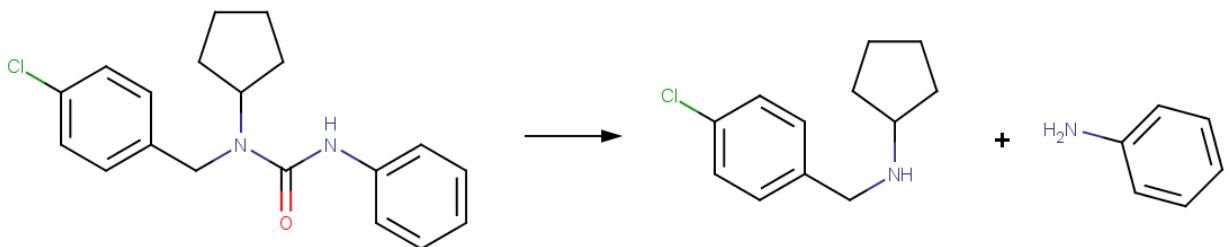
- Hexythiazox (EFSA, 2006a)



- Isoproturon (EFSA, 2014; Penning *et al*, 2008)



- Pencycuron (EFSA, 2006b)



#### REFERENCES:

EFSA (European Food Safety Authority). 2006a. Draft Assessment Report (DAR): Initial risk assessment provided by the rapporteur Member State Finland for the existing active substance Hexythiazox of the third stage (part A) of the review programme referred to in Article 8(2) of Council Directive 91/414/EEC, Volume 3, Annex B, B.8. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

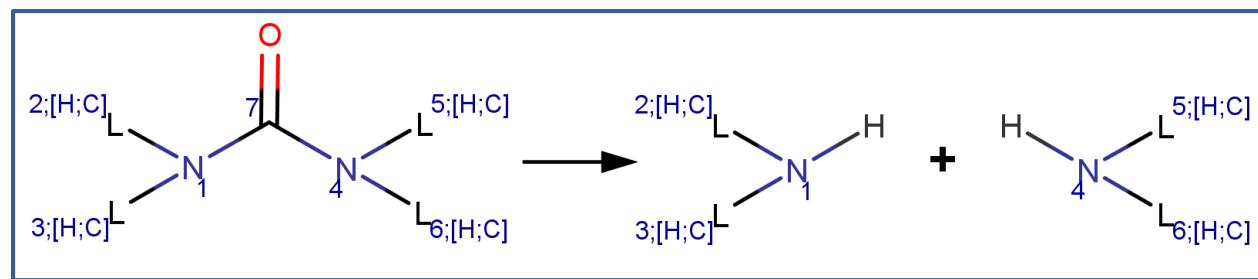
EFSA (European Food Safety Authority). 2006b. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State the Netherlands for the existing active substance Pencycuron of the third stage (part A) of the review programme referred to in Article 8(2) of Council Directive 91/414/EEC, Volume 3, Annex B, B.8. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

EFSA (European Food Safety Authority). 2014. Renewal Assessment Report: Isoproturon, Volume 3, Annex B.8, Environmental fate and behavior. RMS: Germany, Co-RMS: Czech Republic. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

Penning, H., C.J. Cramer and M. Elsner. 2008. Rate-dependent carbon and nitrogen kinetic isotope fractionation in hydrolysis of isoproturon. *Environmental Science and Technology*. 42(21): 7764-7771.

## Cyclic Urea Hydrolysis

### SCHEME:



This scheme is similar to the [Urea scheme](#), except that the scheme includes a reactivity rule which specifies that atom 7 is a ring atom.

### EXAMPLES:

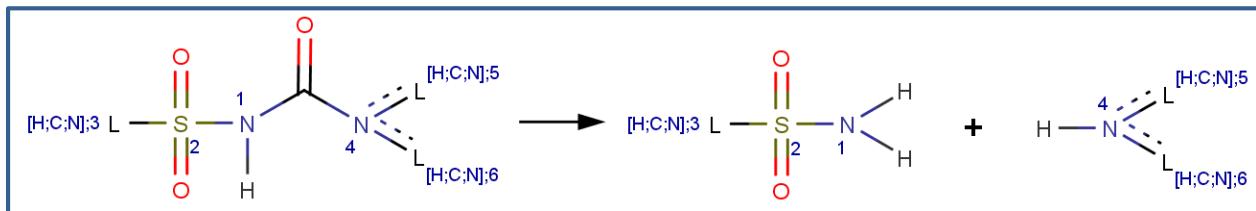
No examples were found for the Cyclic Urea Hydrolysis pathway.

### REFERENCES:

N/A

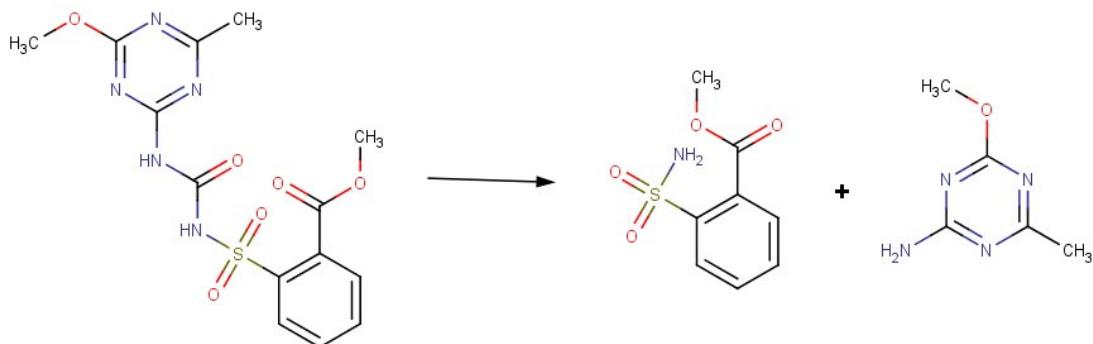
## Sulfonylurea Hydrolysis

### SCHEME:

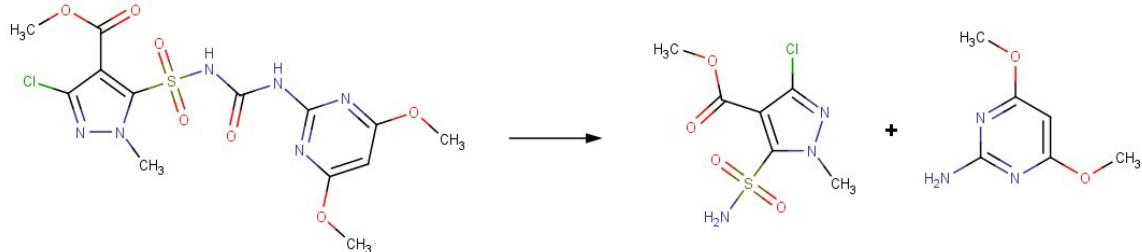


### EXAMPLES:

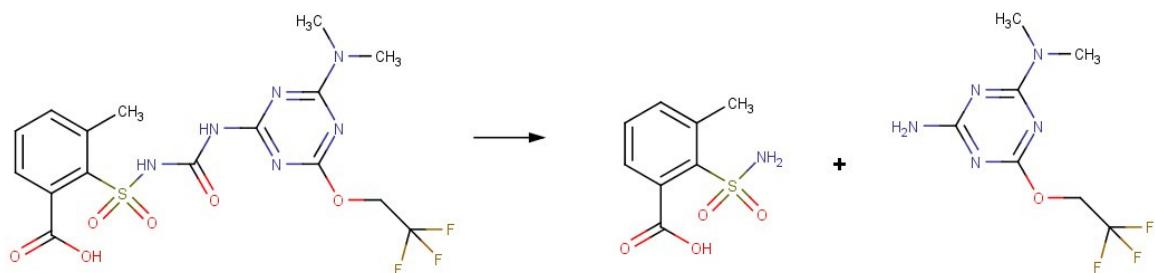
- Metsulfuron-methyl (EFSA, 2013)



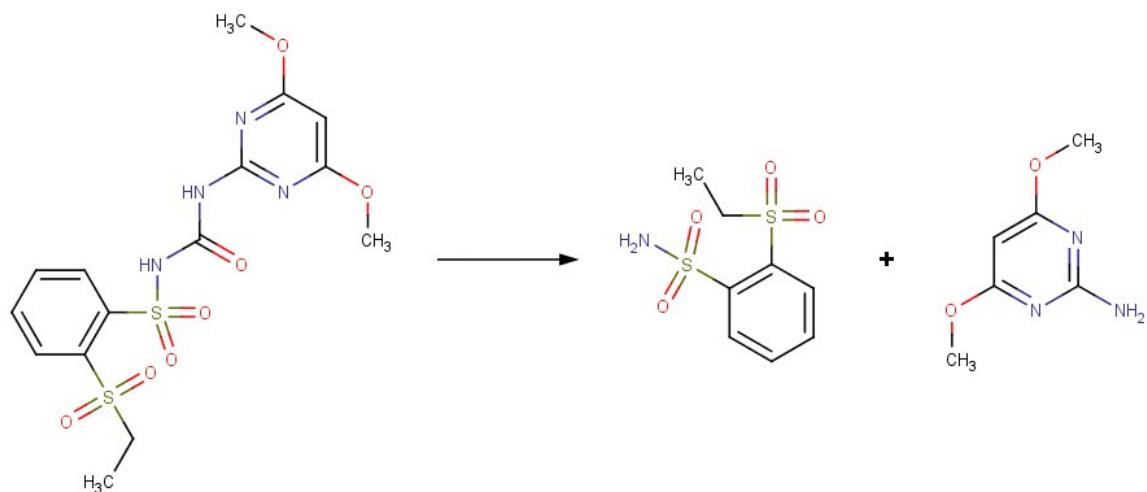
- Halosulfuron-methyl (EFSA, 2011)



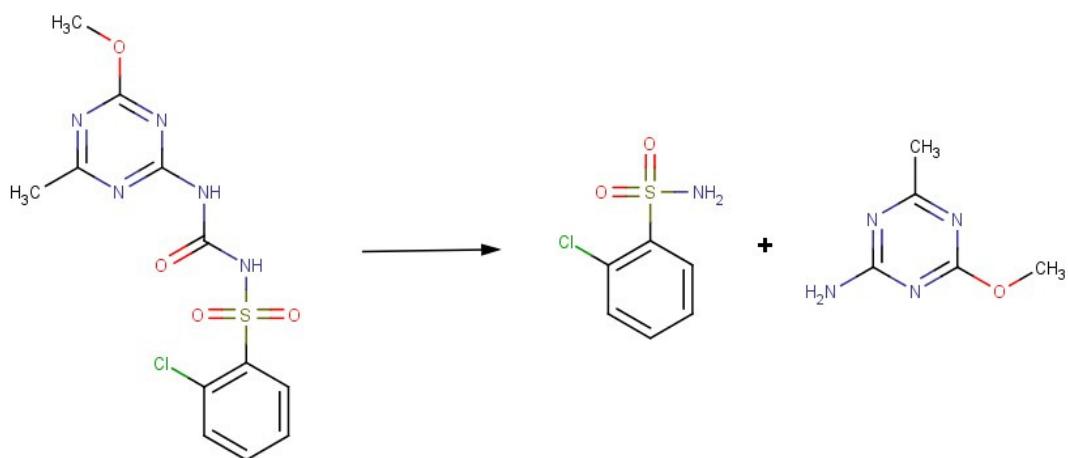
- Triflusulfuron-Methyl (EFSA, 2007a)



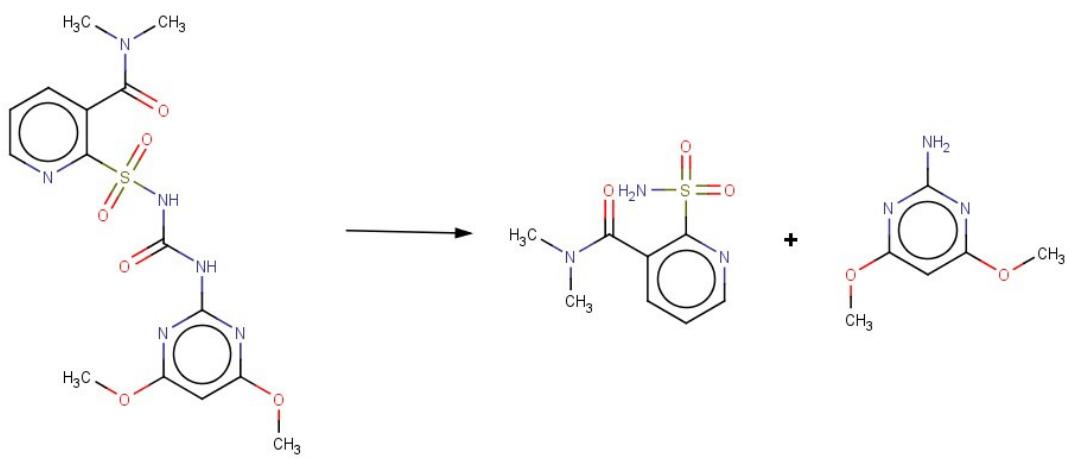
- Rimsulfuron (EFSA, 2005)



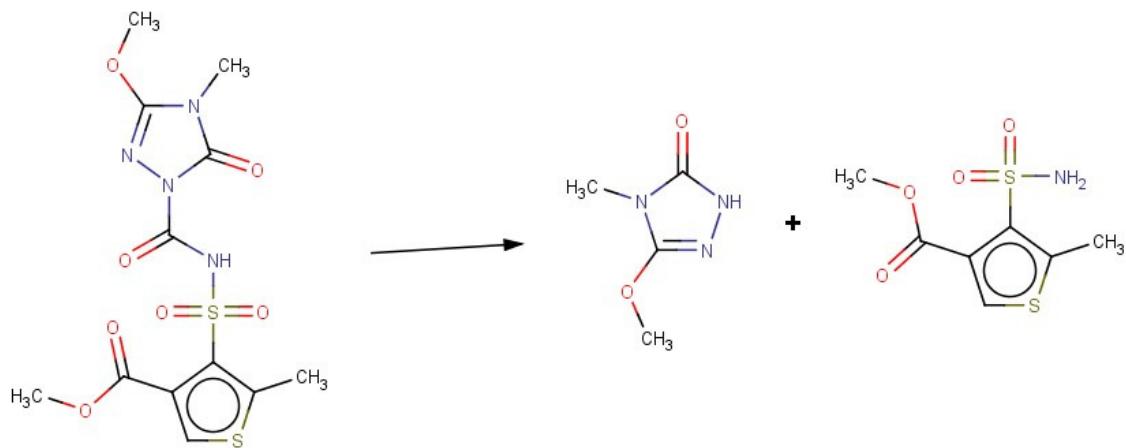
- Chlorsulfuron (EFSA, 2007b)



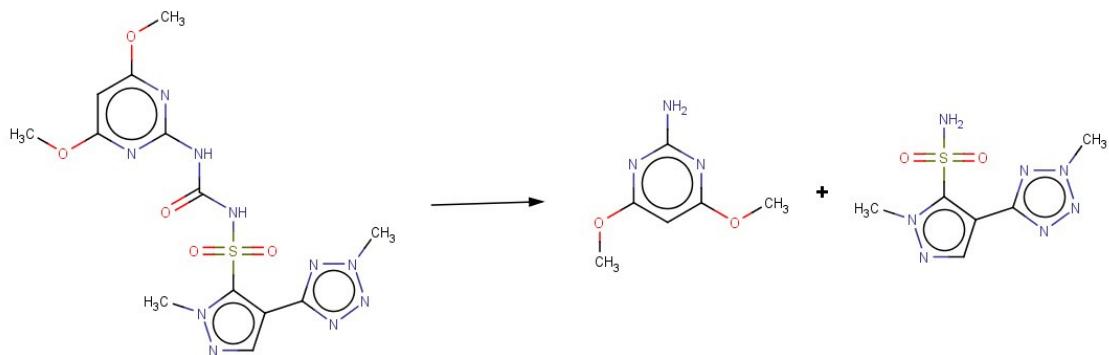
- Nicosulfuron (EFSA, 2006c)



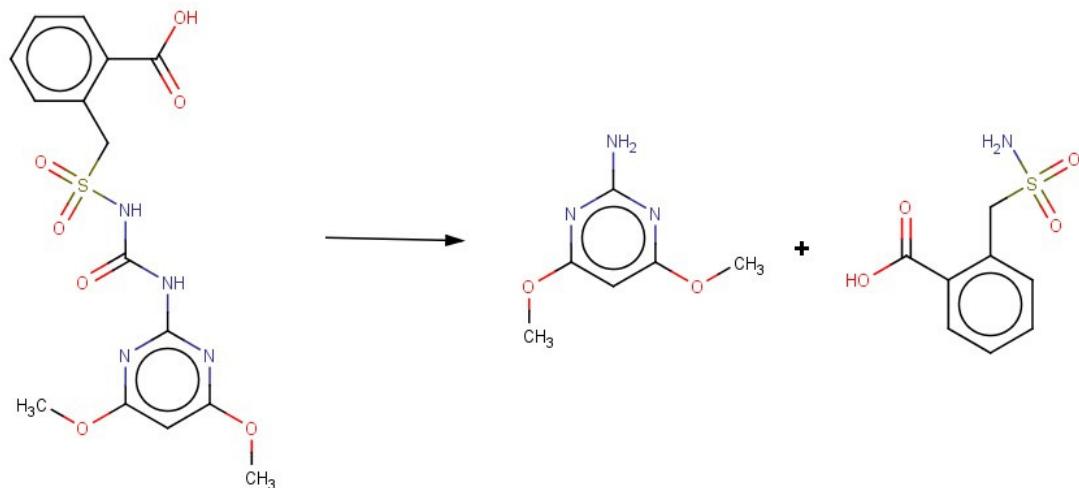
- Thienecarbazone-Methyl (EFSA, 2012).



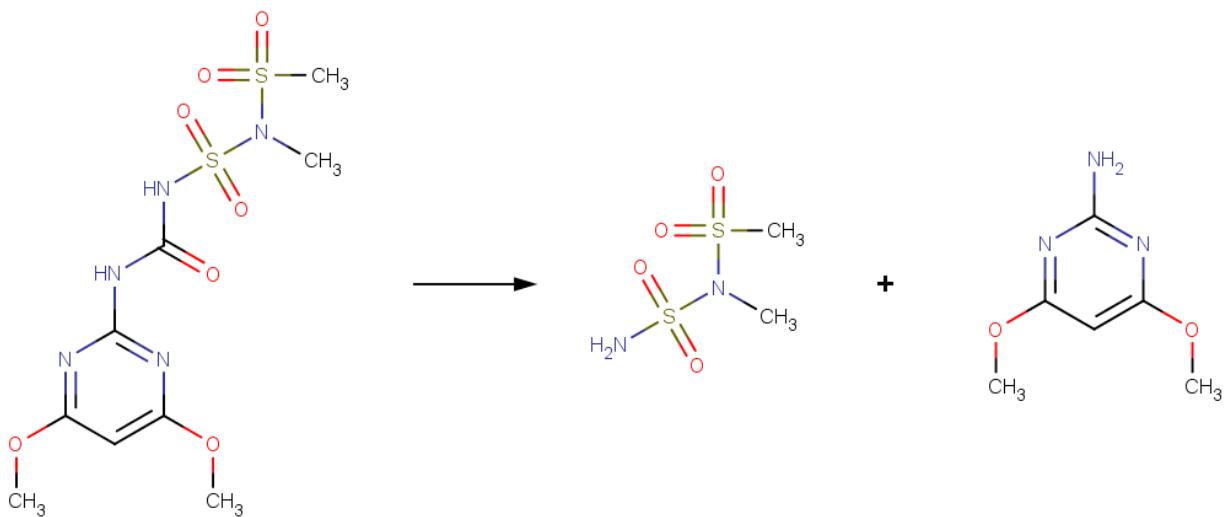
- Azimsulfuron (Boschin *et al*, 2007; EFSA, 2009)



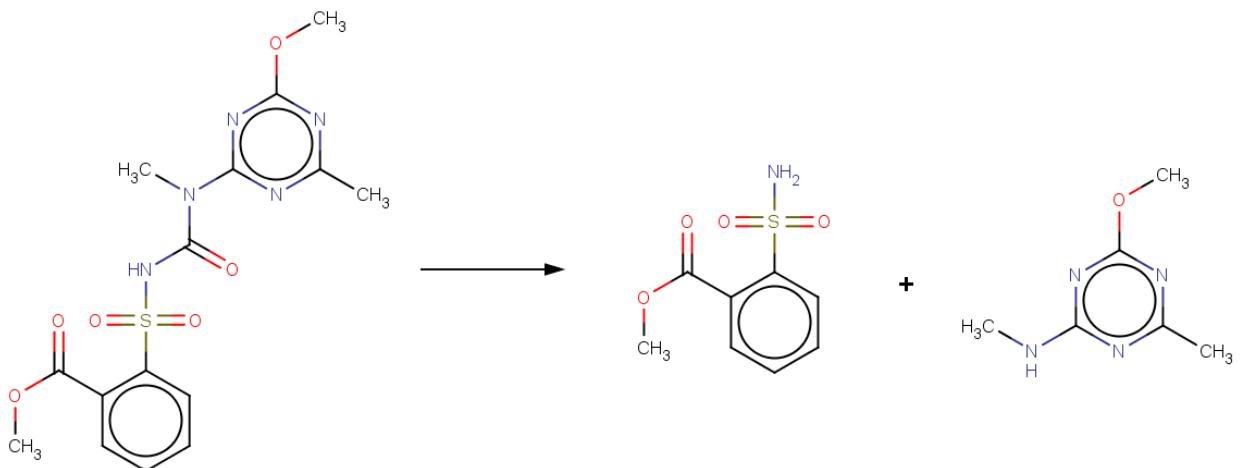
- Bensulfuron Methyl (EFSA, 2006b)



- Amidosulfuran (EFSA, 2006a)



- Tribenuron-methyl (EFSA, 2004)



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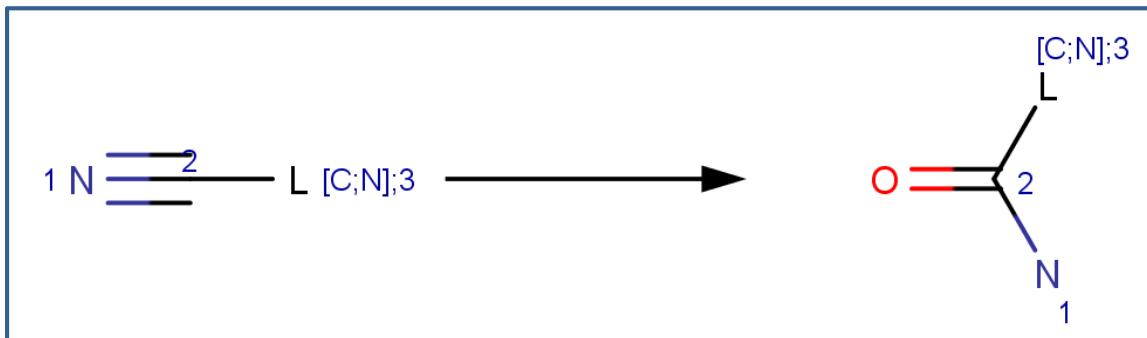
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the existing active substance Metsulfuron-methyl of Annex I inclusion under Regulation (EC) 1107/2009, Volume 3, Annex B, B.8. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

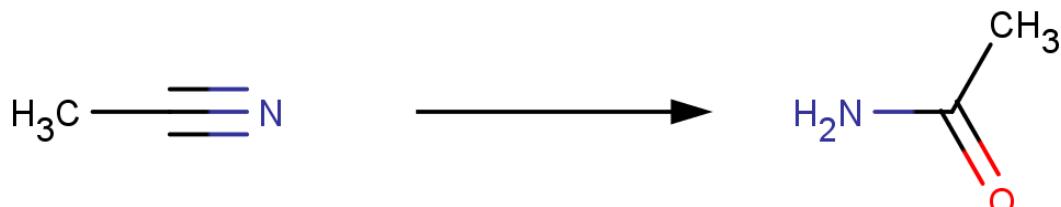
## Nitrile Hydrolysis

### SCHEME:

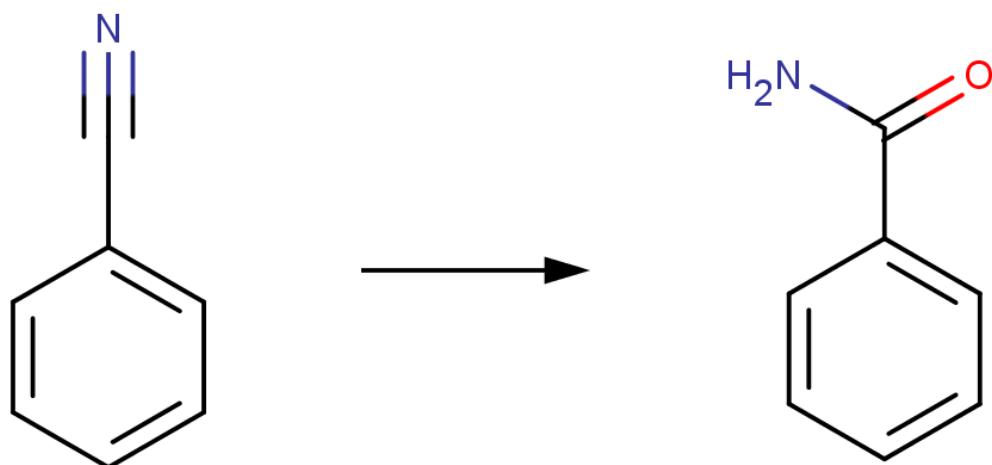


### EXAMPLES:

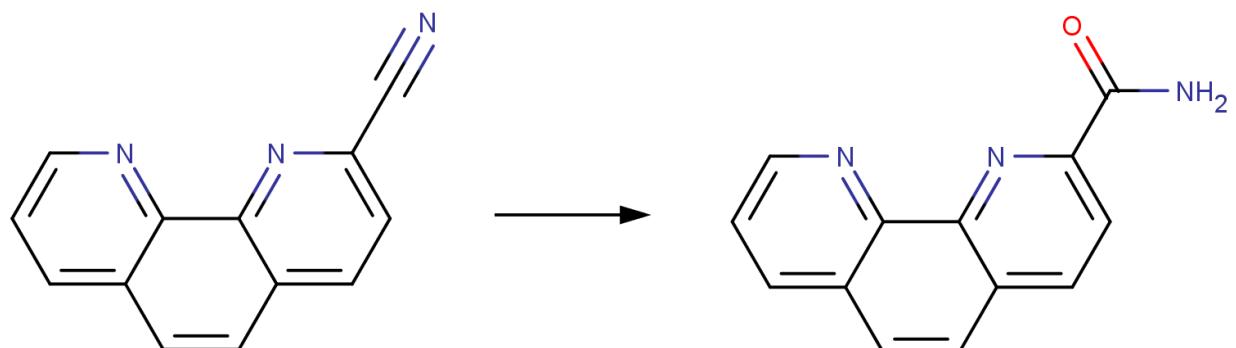
- Acetonitrile (Peskoff and Meyer, 1913; U.S. EPA, 1987)



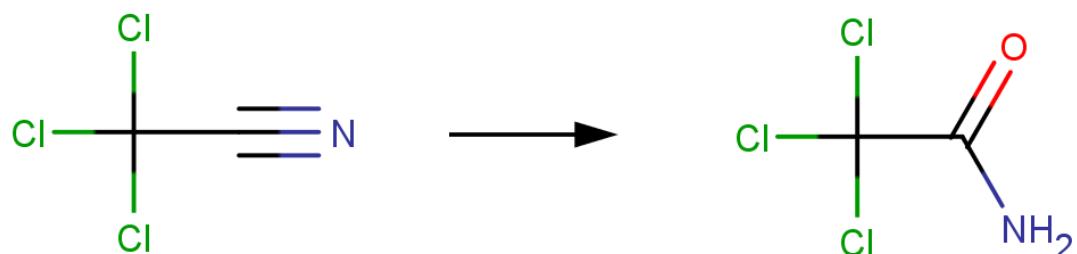
- Benzonitrile (Wiberg, 1955)



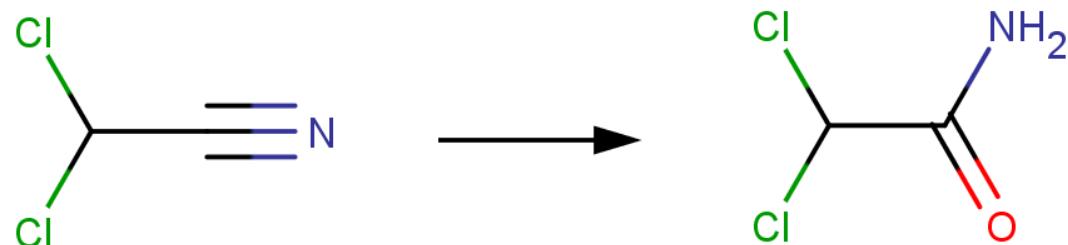
- 1,10-phenanthroline-2-carbonitrile (Breslow *et al*, 1967)



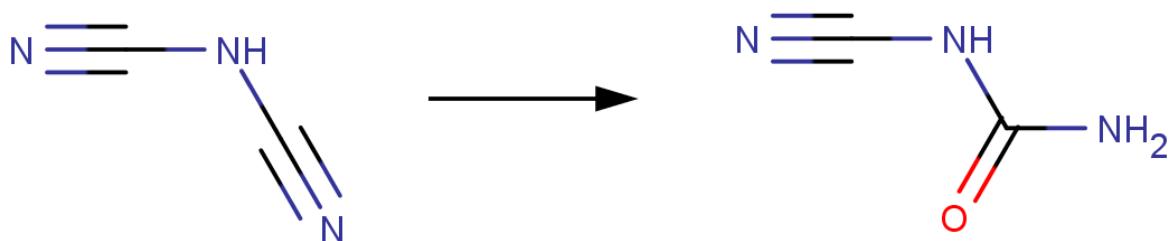
- Trichloroacetonitrile (Glezer *et al*, 1999)



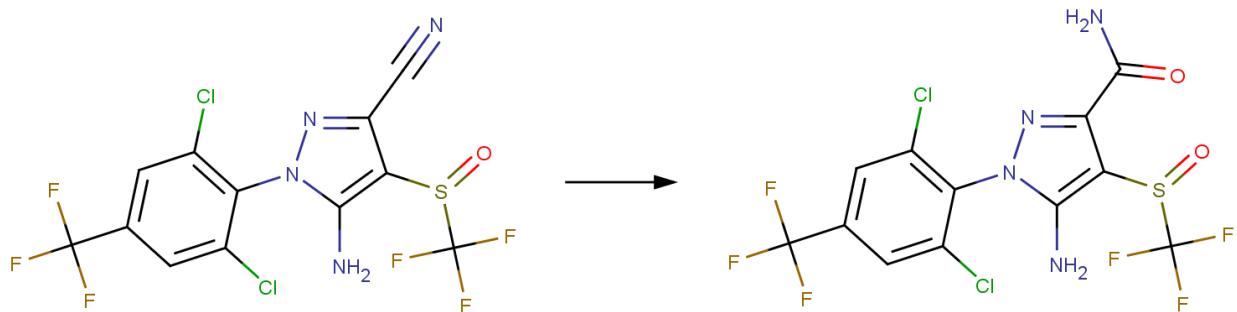
- Dichloroacetonitrile (Reckow *et al*, 2001)



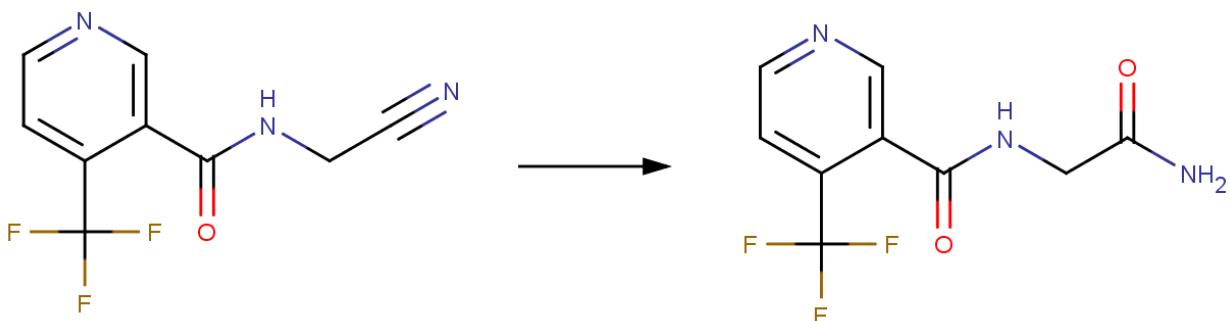
- Dicyanamide (Hill *et al*, 1984)



- Fipronil (EFSA, 2005a)



- Flonicamid (EFSA, 2005b)



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Glezer, V., B. Harris, N. Tal, B. Iosefzon and O. Lev. 1999. Hydrolysis of haloacetonitriles: Linear free energy relationship, kinetics and products. *Water Research*. 33(8): 1938-1948.

Hill, S.V., A. Williams and J.L. Longridge. 1984. Acid-catalyzed hydrolysis of cyanamides: estimates of carbodi-imide basicity and tautomeric equilibrium constant between carbodi-imide and cyanamide. *Journal of the Chemical Society, Perkin Transactions 2*. 1984(6): 1009-1013.

Peskoff, N. and J. Meyer. 1913. Zur Kenntnis der Folgereaktion. III. Die Hydrolyse von saureamiden und nitrile. *Zeitschrift für Physikalische Chemie*. 82: 129.

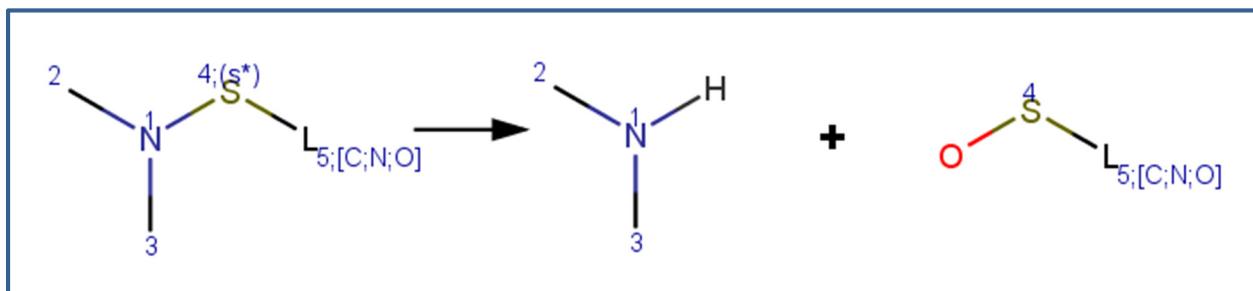
Reckow, D.A., T.L. Platt, A.L. MacNeill and J.N. McClellan. 2001. Formation and degradation of DCAN in drinking waters. AQUA. 50(1): 1-13.

U.S. EPA (United States Environmental Protection Agency). 1987. Measurement of hydrolysis rate constants for evaluation of hazardous waste land disposal: Volume 2. Data on 54 chemicals. EPA/600/3-87/019.

Wiberg, K.B. 1955. The mechanisms of hydrogen peroxide reactions. II. A comparison of the reactivity of hydroxyl ion and hydroperoxide ion toward benzonitrile. *Journal of the American Chemical Society*. 77: 2519-2522.

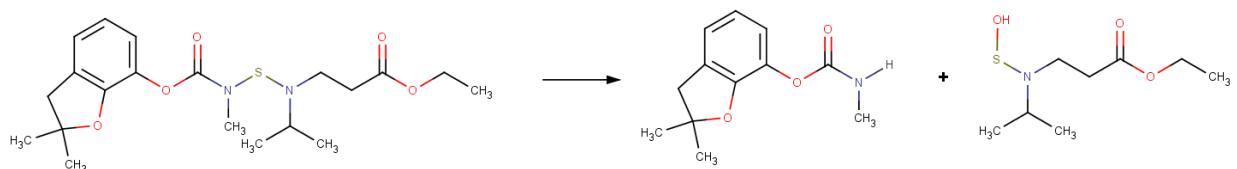
## N-S Cleavage

### SCHEME:

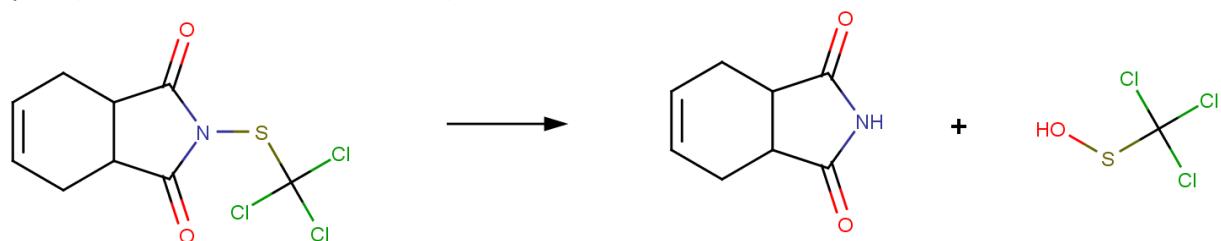


### EXAMPLES:

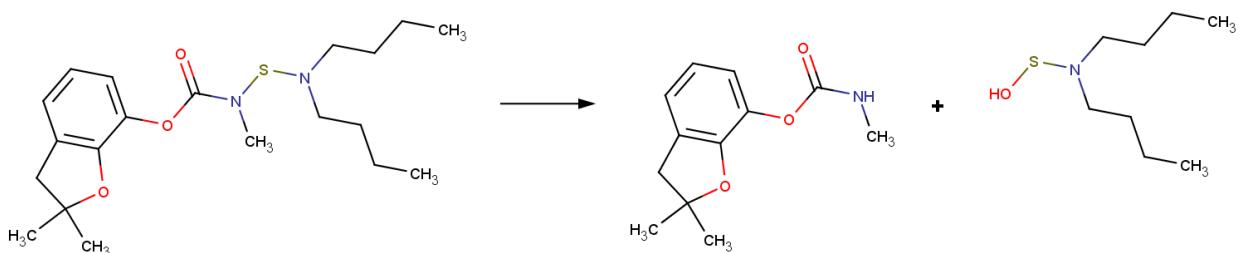
- Benfuracarb (EFSA, 2004a; lesce *et al*, 2006)



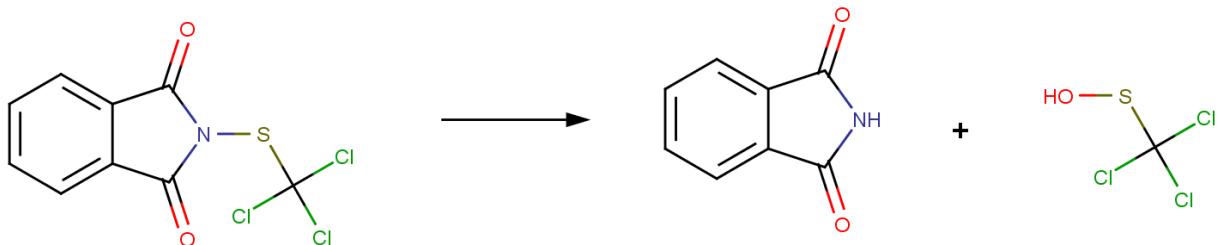
- Captan (EFSA, 2005a; Wolfe *et al*, 1976)



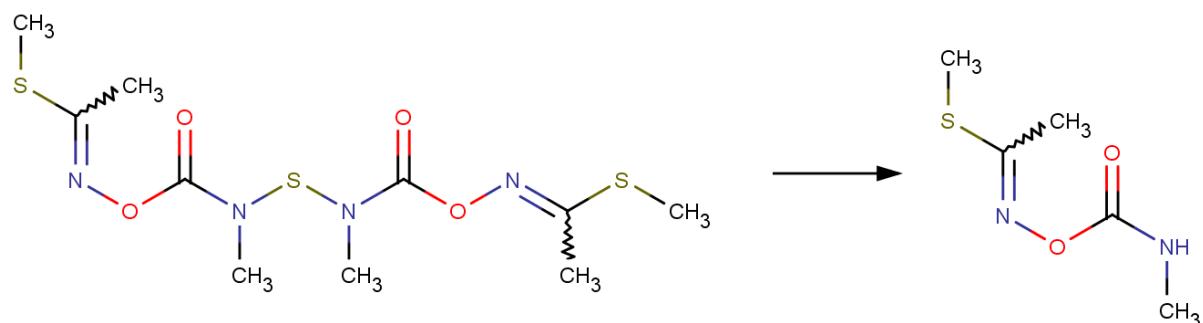
- Carbosulfan (de Melo Plesse *et al*, 2005; EFSA, 2004b; lesce *et al*, 2006; Umetsu *et al*, 1980)



- Folpet (EFSA, 2005b)



- Thiodicarb (EFSA, 2005c) The only major reported hydrolysis product of thiodicarb is methomyl (shown below). This product forms after two sequential N-S cleavage reactions. The first N-S cleavage results in a hydroxysulfanyl intermediate, which undergoes a second N-S cleavage reaction to form methomyl. The hydroxysulfanyl intermediate was not reported as an observed product in hydrolysis studies.



## REFERENCES:

De Melo Plesse, L.P., L.C. Paraiba, L.L. Foloni and L.R. Pimentel Trevizan. 2005. Kinetics of carbosulfan hydrolysis to carbofuran and the subsequent degradation of this last compound in irrigated rice fields. *Chemosphere*. 60: 149-156.

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stage of the review programme referred to in Article 8(2) of Council Directive 91/414/EEC, Volume 3, Annex B, B.8. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

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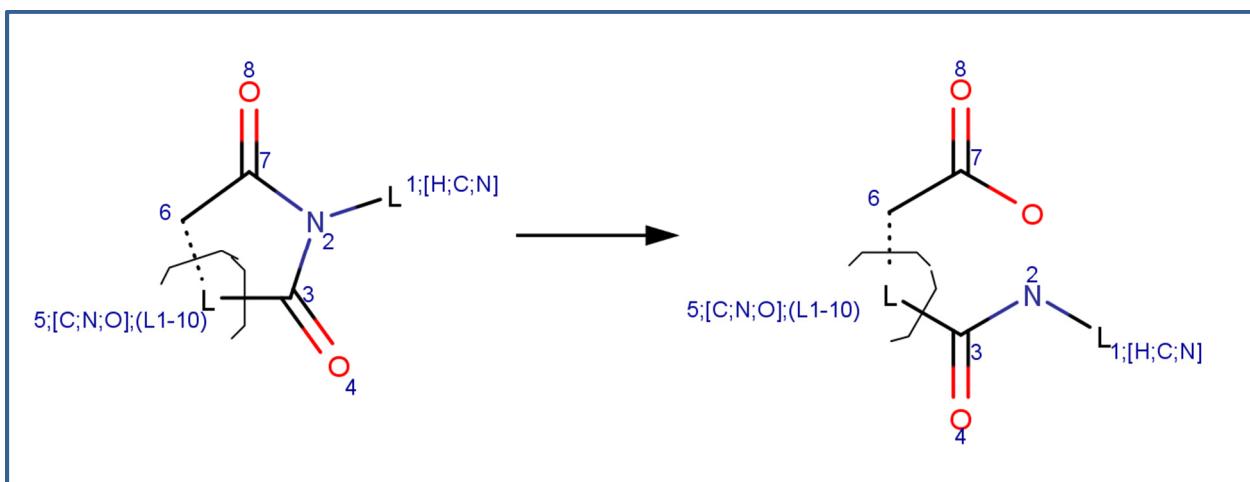
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Wolfe, N.L., R.G. Zepp, J.C. Doster and R.G. Hollis. 1976. Captan hydrolysis. *Journal of Agricultural and Food Chemistry*. 24(5): 1041-1045.

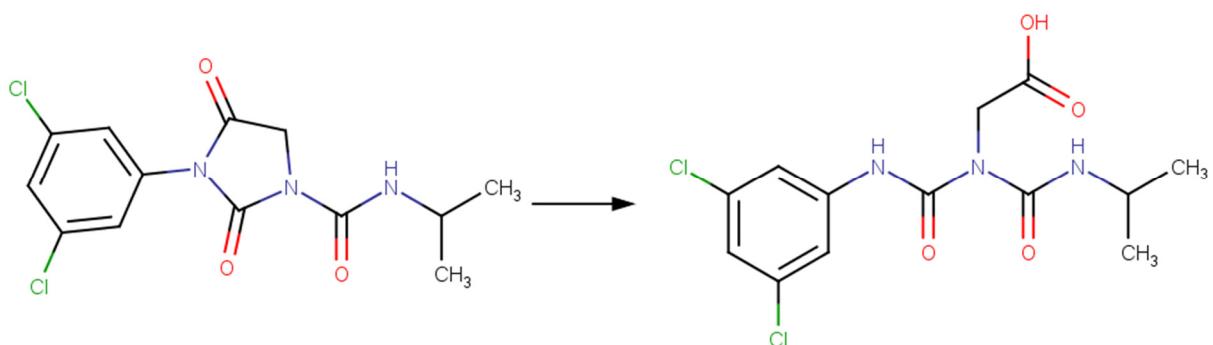
## Imide Hydrolysis

SCHEME:

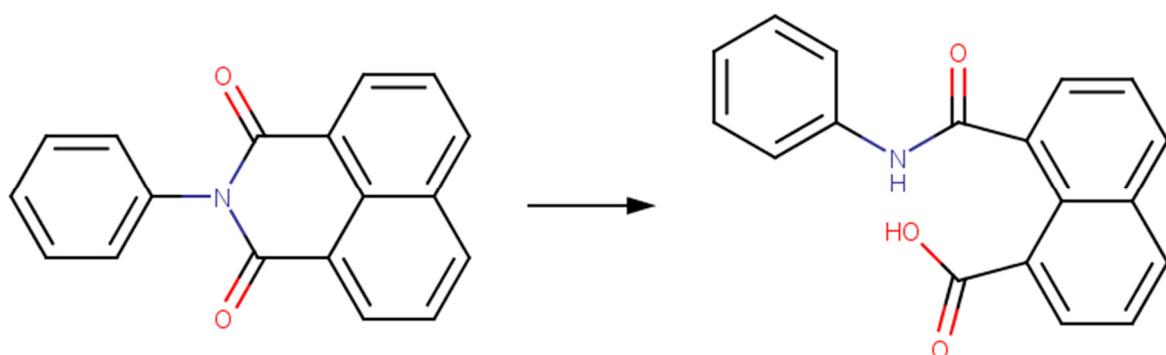


**EXAMPLES:**

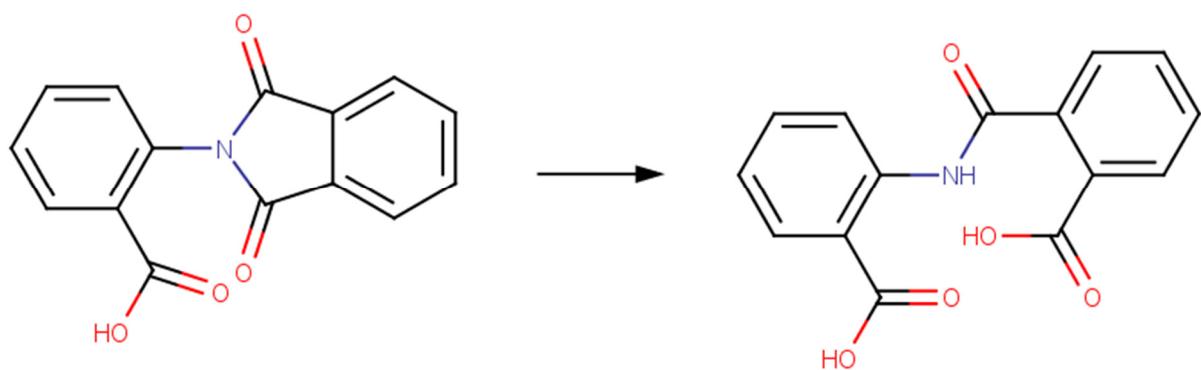
- Iprodione (Belafdal *et al*, 1986)



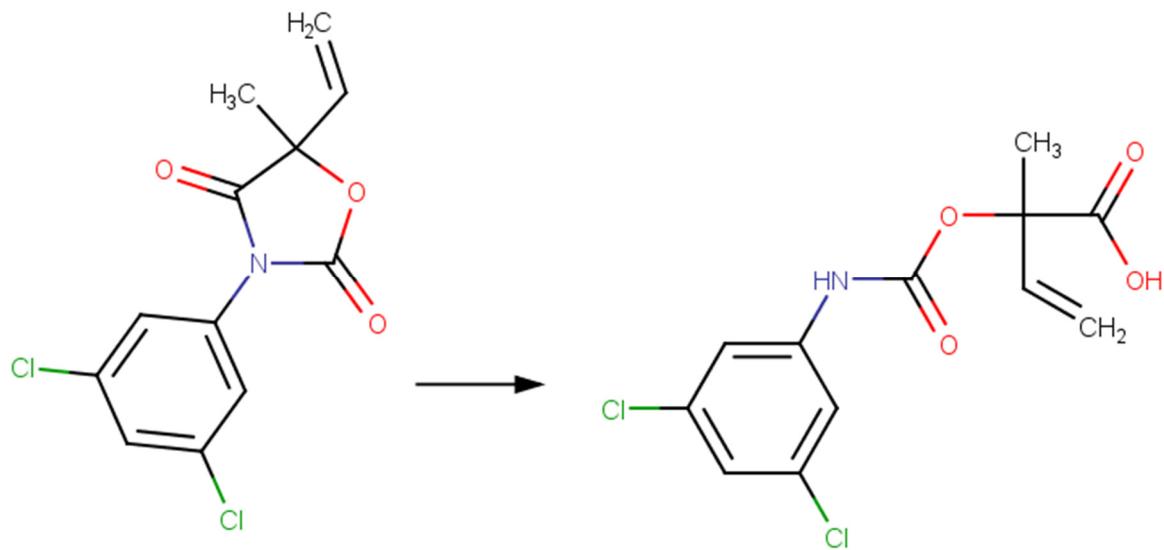
- N-phenylnaphthalimide (Donskikh *et al*, 1987)



- N-(o-carboxyphenyl)-phthalimide (Donskikh *et al*, 1987)



- Vinclozolin (Mercadier *et al*, 1998; Szeto *et al*, 1989)

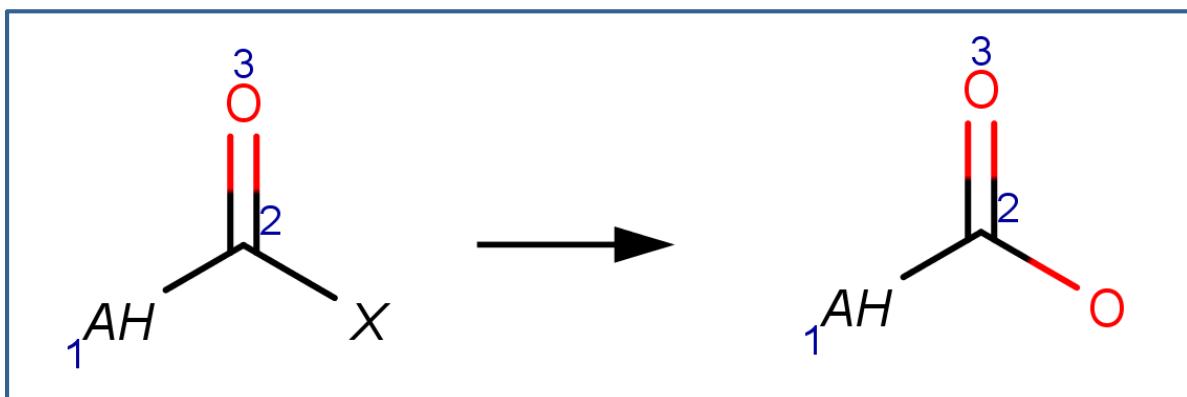


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## Acid Halide Hydrolysis

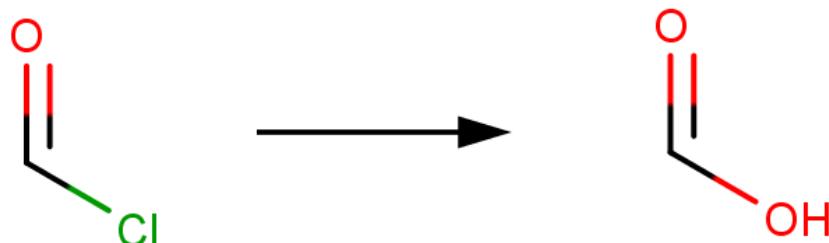
SCHEME:



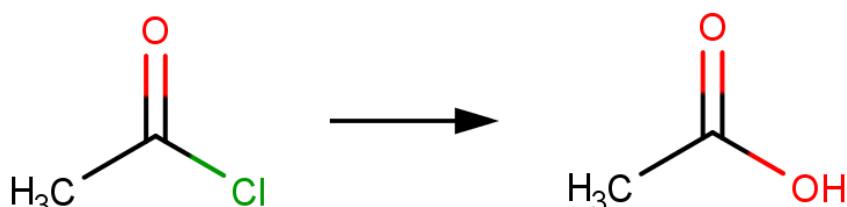
Hydrolysis of an acid halide yields a carboxylic acid through nucleophilic acyl substitution (McMurry, 2011, p. 830).

EXAMPLES:

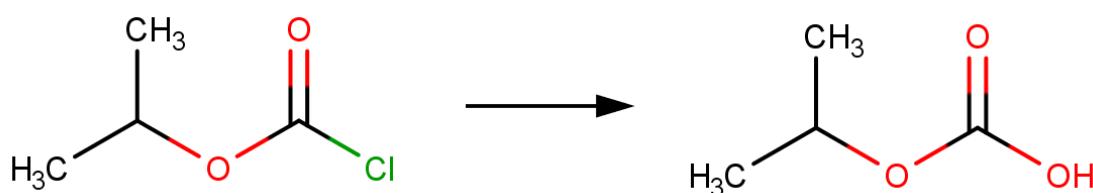
- Formyl chloride (Dowideit et al (1996), Prager et al, 2001)



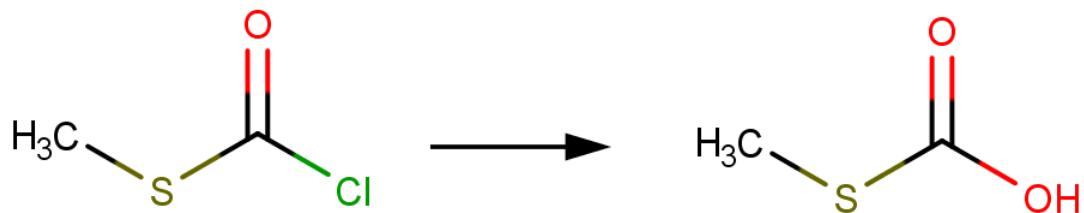
- Acetyl chloride (Prager et al, 2001)



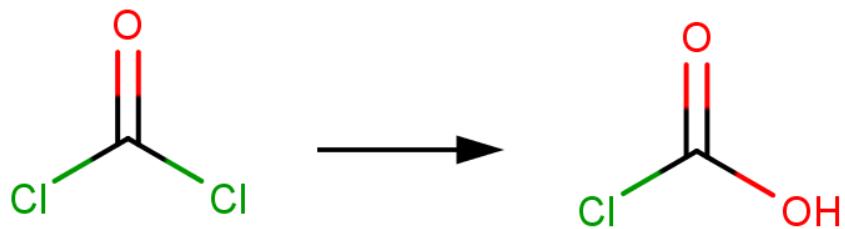
- Isopropyl chloroformate (Queen, 1967)



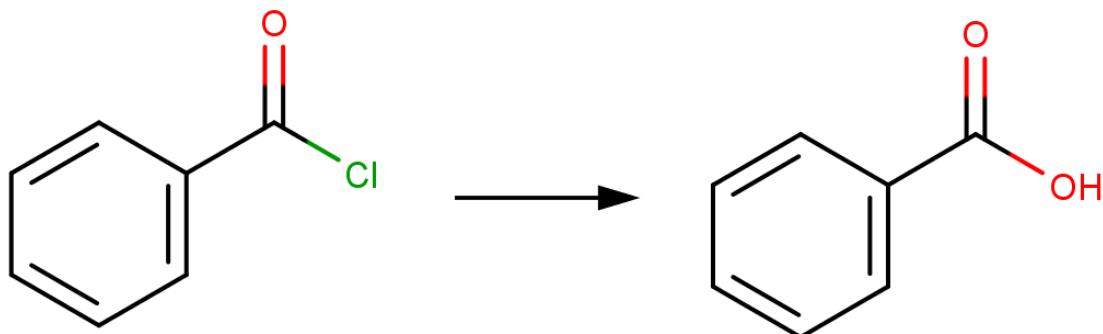
- S-Methyl chloridothiocarbonate (Queen et al, 1970)



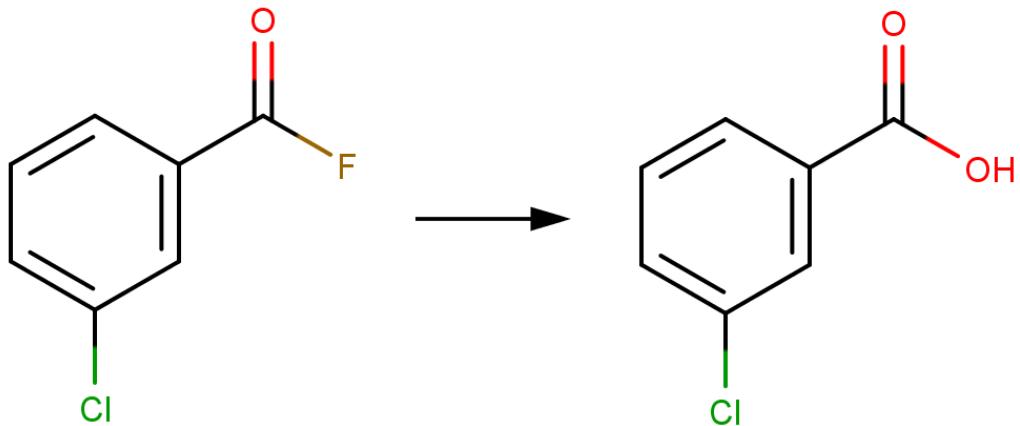
- Phosgene (Prager et al, 2001)



- Benzoyl chloride (Song and Jencks, 1989)



- 3-Chlorobenzoyl fluoride (Song and Jencks, 1989)



## REFERENCES:

Dowideit, P., R. Mertens and C. von Sonntag. 1996. Non-hydrolytic decay of formyl chloride into CO and HCl in aqueous solution. *Journal of the American Chemical Society*. 118: 11288-11292.

McMurry, J.E. 2011. *Organic Chemistry*, 8<sup>th</sup> ed. Boston, MA: Cengage Learning.

Prager, L., P. Dowideit, H. Langguth, H.-P. Schuchmann and C. von Sonntag. 2001. Hydrolytic removal of the chlorinated products from the oxidative free-radical-induced degradation of chloroethylenes: Acid chlorides and chlorinated acetic acids. *Journal of the Chemical Society, Perkin Transactions 2*. 2001: 1641-1647.

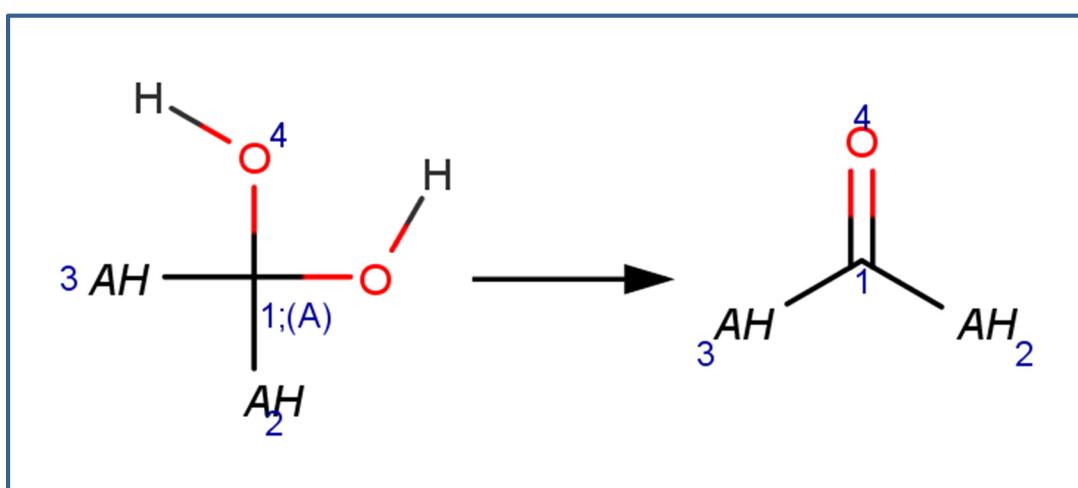
Queen, A. 1967. Kinetics of the hydrolysis of acyl chlorides in pure water. *Canadian Journal of Chemistry*. 45: 1619-1629.

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Song, B.D. and W.P. Jencks. 1989. Mechanism of solvolysis of substituted benzoyl halides. *Journal of the American Chemical Society*. 111: 8470-8479.

## Dehydration of Geminal Diols

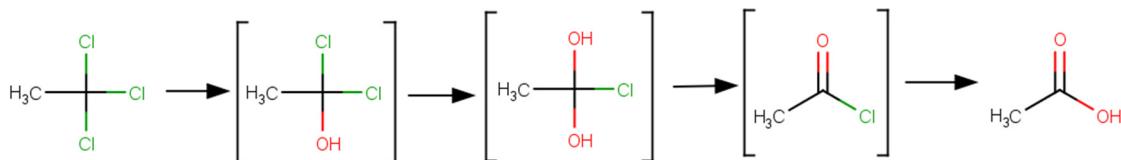
### SCHEME:



This scheme is not a hydrolysis reaction; however, it is necessary to include the scheme for dehydration of geminal diols in the Abiotic Hydrolysis Reaction Library to correctly predict the observed products in many hydrolysis studies. The reaction is actually an equilibrium between a geminal diol and a carbonyl compound; however, the carbonyl compound is dominant, except in the case of simple aldehydes (e.g., formaldehyde) (McMurry, 2011, p. 731).

### EXAMPLES:

- 1,1,1-trichloroethane (Gerkens and Franklin, 1989; Miyamoto and Urano, 1996; U.S. EPA, 1992)



#### REFERENCES:

Gerkens, R.R. and J.A. Franklin. 1989. The rate of degradation of 1,1,1-trichloroethane in water by hydrolysis and dehydrochlorination. *Chemosphere*. 19(12): 1929-1937.

McMurry, J.E. 2011. *Organic Chemistry*, 8<sup>th</sup> ed. Boston, MA: Cengage Learning.

Miyamoto, K. and K. Urano. 1996. Reaction rates and intermediates and chlorinated organic compounds in water and soil. *Chemosphere*. 32(12): 2399-2408.

U.S. EPA (United States Environmental Protection Agency). 1992. Environmental fate constants for organic chemicals under consideration for EPA's Hazardous Waste Identification Rule. EPA/601/R-92/006.

## Ranking of Hydrolysis Reaction Schemes

The schemes within the hydrolysis library are ranked on a scale of one to six according to their relative rate of transformation, with a higher rank indicating a faster hydrolysis rate. The pH-specific ranks in the table below were assigned based on the median half-life for all molecules included in a database of literature-reported rate data compiled for each scheme in the library.

Scheme	pH 5 Rank	pH 7 Rank	pH 9 Rank
Nucleophilic Substitution w/ no adjacent X	3	3	3
Nucleophilic Substitution w/ vicinal X	1	1	1
Nucleophilic Substitution w/ geminal X	1	1	1
Elimination	1	1	2
Epoxide Hydrolysis	6	5	1
OP Ester Hydrolysis 1 (Base-Catalyzed)	2	3	4
OP Ester Hydrolysis 2 (Neutral or Acid-Catalyzed)	2	3	3
Carboxylic Acid Ester Hydrolysis	2	2	5
Lactone Hydrolysis	1	5	5
Carbonate Hydrolysis	1	3	5
Cyclic Carbonate Hydrolysis	1	3	5
Anhydride Hydrolysis	6	6	6
Cyclic Anhydride Hydrolysis	6	6	6
Amide Hydrolysis	1	1	3
Lactam Hydrolysis	4	4	4
Carbamate Hydrolysis	3	3	5
Thiocarbamate Hydrolysis	1	1	1
Urea Hydrolysis	3	2	2
Cyclic Urea Hydrolysis	3	2	2
Sulfonylurea Hydrolysis	3	2	2
Nitrile Hydrolysis	4	5	5
N-S Cleavage	5	5	5
Imide Hydrolysis	2	5	5
Acid Halide Hydrolysis	6	6	6
Dehydration of Geminal Diols	6	6	6

The following table defines the six ranking levels, which span residence times of environmental relevance.

Rank	Range of Median Hydrolysis Half-Life
6	Less than 2.4 hours
5	2.4 hours to 24 hours
4	24 hours to 7 days
3	7 days to 60 days
2	60 days to 1 year
1	Greater than 1 year