

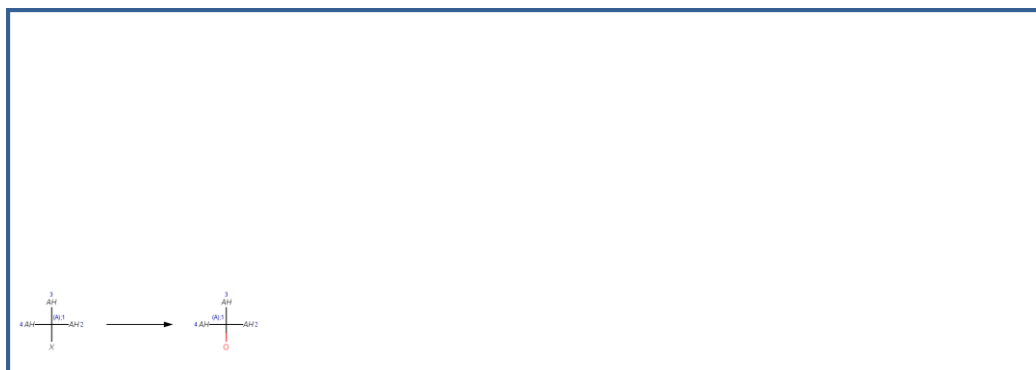
Abiotic Hydrolysis Reaction Library

Version 1.5 of the Abiotic Hydrolysis Reaction Library contains 17 reaction schemes:

- [Halogenated Aliphatics: Nucleophilic Substitution](#)
- [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](#)
- [Anhydride Hydrolysis](#)
- [Amide Hydrolysis](#)
- [Lactam Hydrolysis](#)
- [Carbamate Hydrolysis](#)
- [Urea Hydrolysis](#)
- [Sulfonylurea Hydrolysis](#)
- [Thiocarbamate Hydrolysis](#)
- [Nitrile Hydrolysis](#)
- [N-S Cleavage](#)

Halogenated Aliphatics: Nucleophilic Substitution

SCHEME:

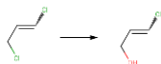


EXAMPLES:

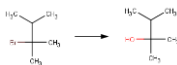
- methyl bromide (EFSA, 2006; U.S. EPA, 1992)



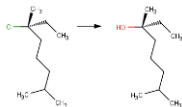
- 1,3-dichloropropene (EFSA, 2004; Guo *et al*, 2004)



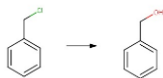
- 2-bromo-2,3-dimethylbutane (McMurry, 2011, p. 372)



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



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



REFERENCES:

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>.

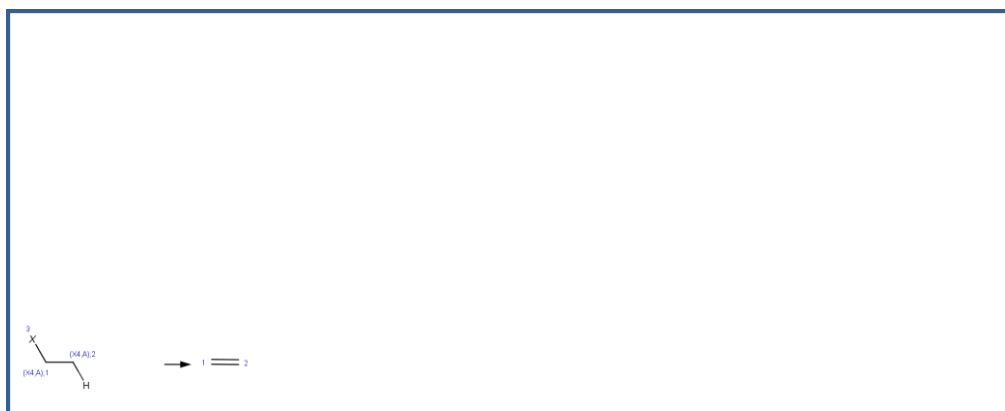
Guo, M., S.K. Papiernik, W. Zhang and S.R. Yates. 2004. Effects of environmental factors of 1,3-dichloropropene hydrolysis in water and soil. *Journal of Environmental Quality*. 33(2): 612-618.

McMurry, J.E. 2011. *Organic Chemistry*, 8th 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:

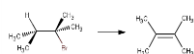


This scheme includes two selectivity rules:

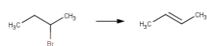
1. The carbon atom with the hydrogen leaving group (labeled reactant atom 2 in the scheme) is the one that has the most steric hindrance. In effect, this is Zaitsev's Rule, which states that "The alkene formed in greatest amount is the one that corresponds to removal of the hydrogen from the β -carbon 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. (Larsen and Weber, 1994)

EXAMPLES:

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



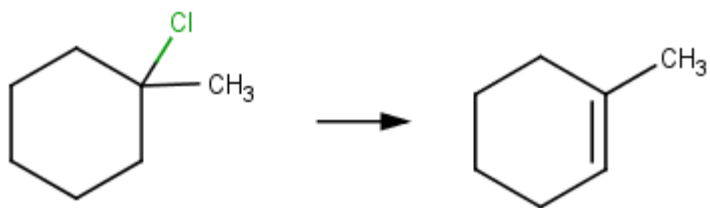
- 2-bromobutane (McMurry, 2011, p. 397; Reusch, 2010)



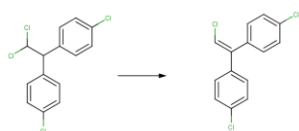
- 2-bromo-2-methylbutane (McMurry, 2011, p. 397)



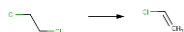
- 1-chloro-1-methylcyclohexane (McMurry, 2011, p. 399)



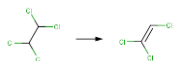
- DDD (dichlorodiphenyldichloroethane) (U.S. EPA, 1992)



- 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.

McMurry, J.E. 2011. *Organic Chemistry*, 8th 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.

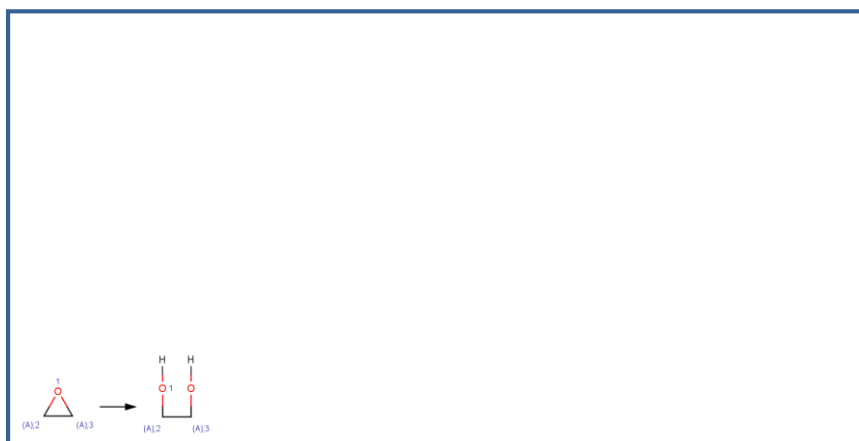
Reusch, W.H. 2010. *Virtual Textbook of Organic Chemistry*.

<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.

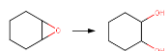
Epoxide Hydrolysis

SCHEME:

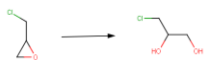


EXAMPLES:

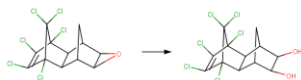
- 1,2-Epoxycyclohexane (McMurry, 2011)



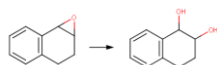
- Epichlorohydrin (Gaca *et al*, 2011)



- Endrin (Larsen 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.

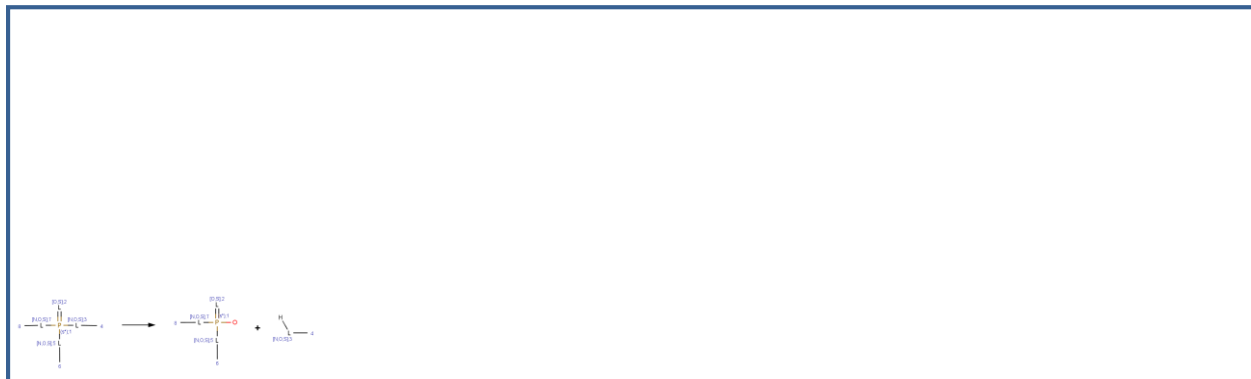
Larson, R.A. and E.J. Weber. *Reaction Mechanisms in Environmental Organic Chemistry*. Boca Raton: CRC Press, Inc., 1994.

McMurry, J.E. 2011. *Organic Chemistry*, 8th 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)

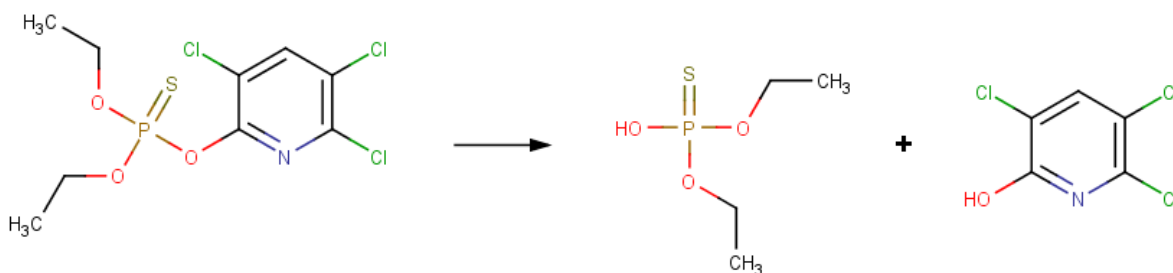
SCHEME:



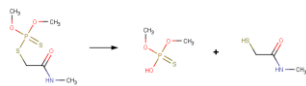
This scheme includes a selectivity rule to identify the most likely leaving group. Base-catalyzed cleavage favors P-L cleavage (where L is O, S, or N) at the L group that is attached to the most electron-withdrawing group (Larson and Weber, 1994). The selectivity rule specifies that the leaving group (labeled atom 3) is the attached the carbon atom (labeled atom 4) with the highest electrophilicity.

EXAMPLES:

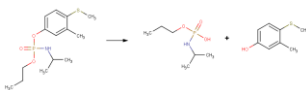
- Chlorpyrifos (Macalady and Wolfe, 1983)



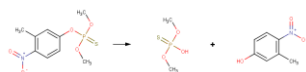
- Dimethoate (EFSA, 2005a)



- Fenamiphos (EFSA, 2005b)



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



Organophosphorus Ester Hydrolysis 2 (Neutral and Acid-Catalyzed)

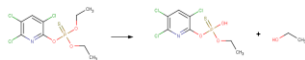
SCHEME:



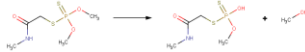
This scheme includes a selectivity rule to identify the most likely leaving group. Neutral and acid-catalyzed cleavage favors L-C cleavage (where L is O, S, or N), but not at the L group that is attached to the most electron-withdrawing group (Larson and Weber, 1994). The selectivity rule specifies that the leaving group (labeled atom 4) is the carbon atom with the lowest electrophilicity.

EXAMPLES:

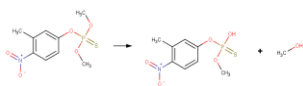
- Chlorpyrifos (Macalady and Wolfe, 1983)



- Dimethoate (EFSA, 2005a)



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



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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>.

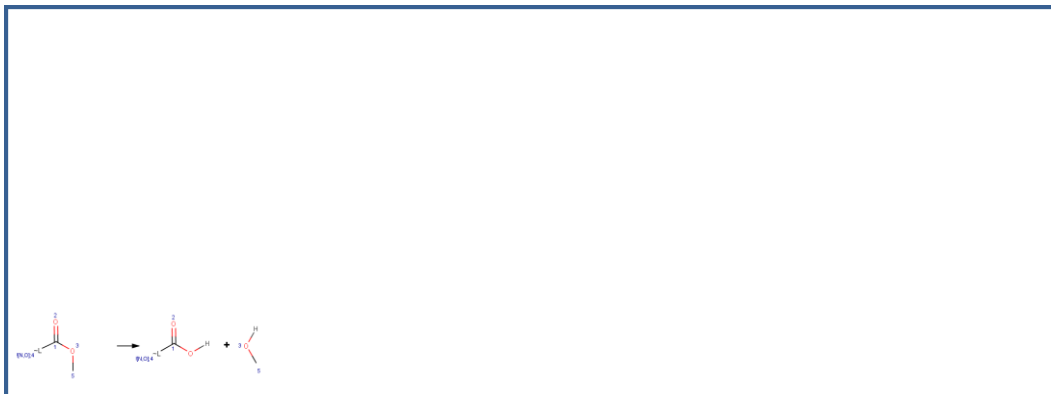
Greenhalgh, R. K.L. Dhawan and P. Weinberger. 1980. Hydrolysis of fenitrothion in model and natural aquatic systems. *Journal of Agricultural and Food Chemistry*. 28(1): 102-105.

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

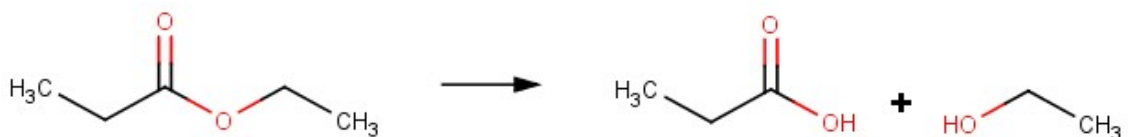
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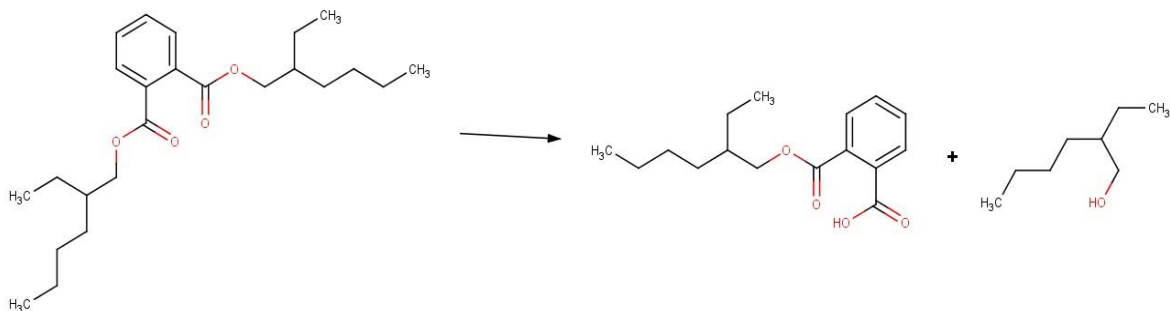
Two reactivity rules are included for this scheme. To distinguish this scheme from the Anhydride Hydrolysis scheme, the first reactivity rule specifies that atom 3 is not part of an anhydride structural fragment. To distinguish this scheme from the Lactone scheme, the second reactivity rule specifies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

EXAMPLES:

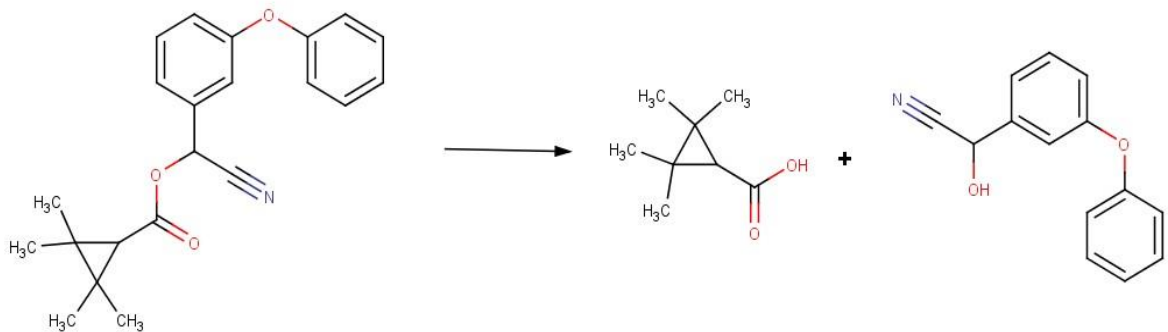
- Ethyl propanoate (McMurry, 2012)



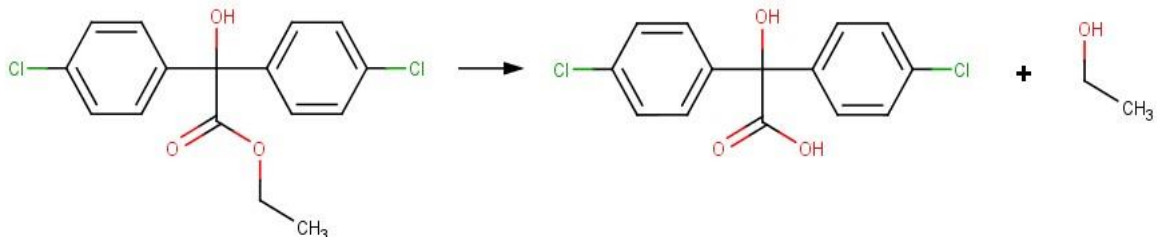
- Bis(2-ethylhexyl)phthalate (Larson and Weber, 1994)



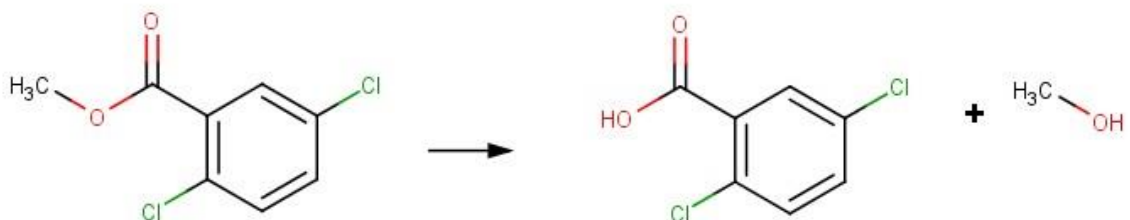
- Fenpropathrin (Larson and Weber, 1994)



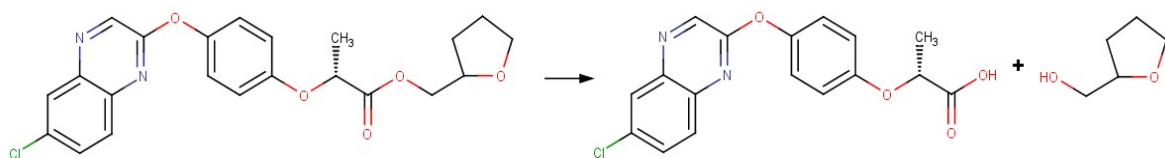
- Chlorobenzilate (Larson and Weber, 1994)



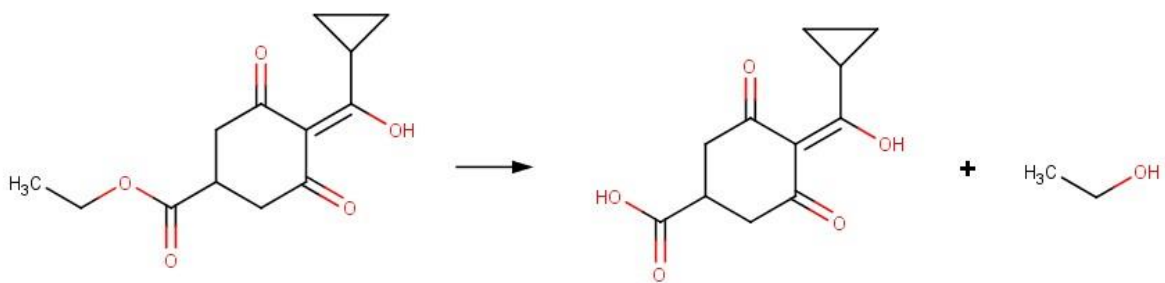
- 2,5-dichlorobenzoic acid methylester (EFSA, 2007a)



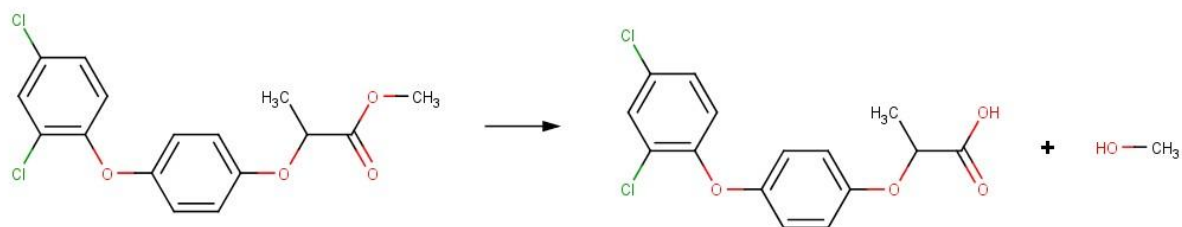
- Propaquizafop (EFSA, 2006)



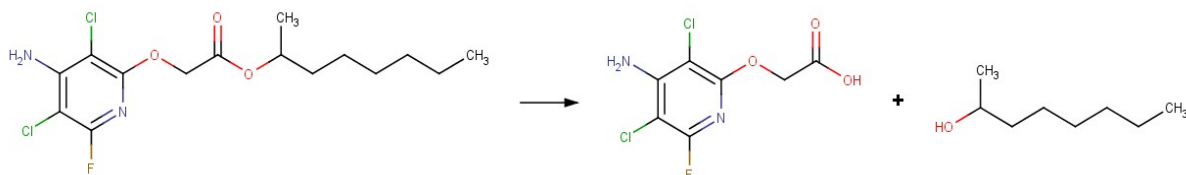
- Trinexapac (EFSA, 2005)



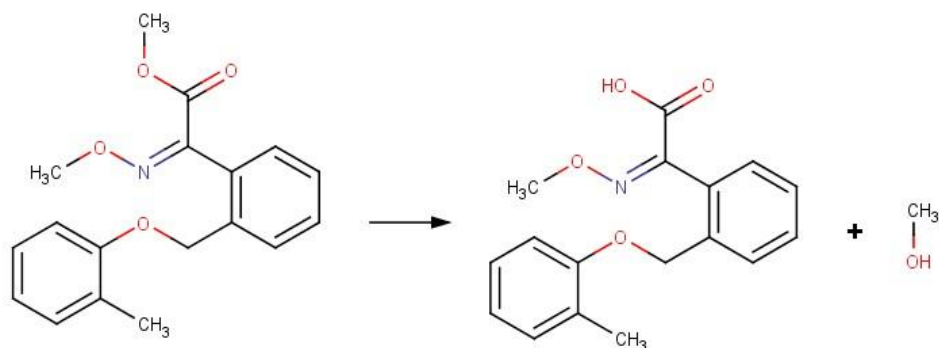
- Diclofop-methyl (EFSA, 2007b)



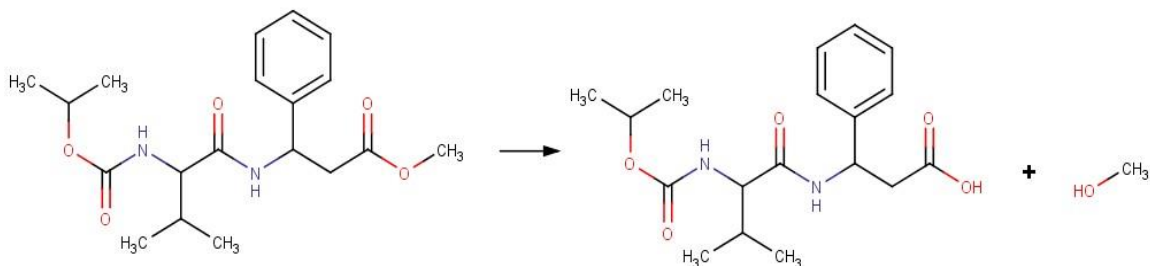
- Fluroxypyr (EFSA, 2009)



- 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*, 8th 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>.

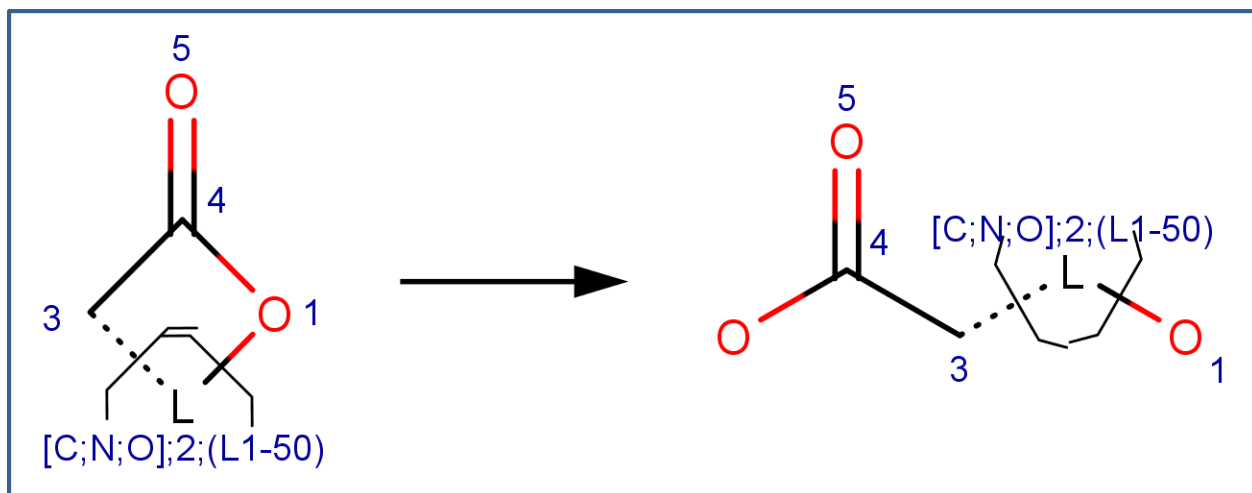
EFSA (European Food Safety Authority), 2009. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State Ireland for the existing active substance Fluroxypyr upon submission in the framework of the renewal of the inclusion of a first group of active substances in Annex I to Council 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

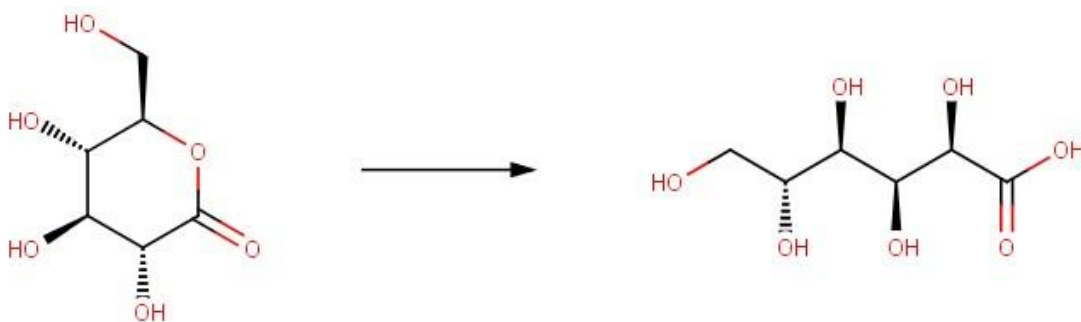
SCHEME:



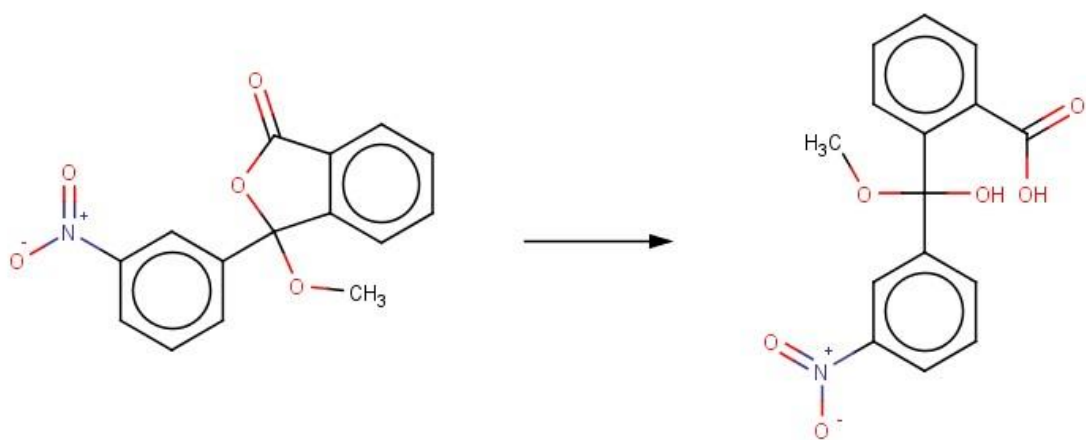
To distinguish this scheme from the Carboxylic Acid Ester scheme, the scheme includes a reactivity rule which specifies that atom 1 is a ring atom. Additionally, to distinguish this scheme from hydrolysis of cyclic anhydrides, the scheme includes a reactivity rule which specifies that atom 1 is not part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

EXAMPLES:

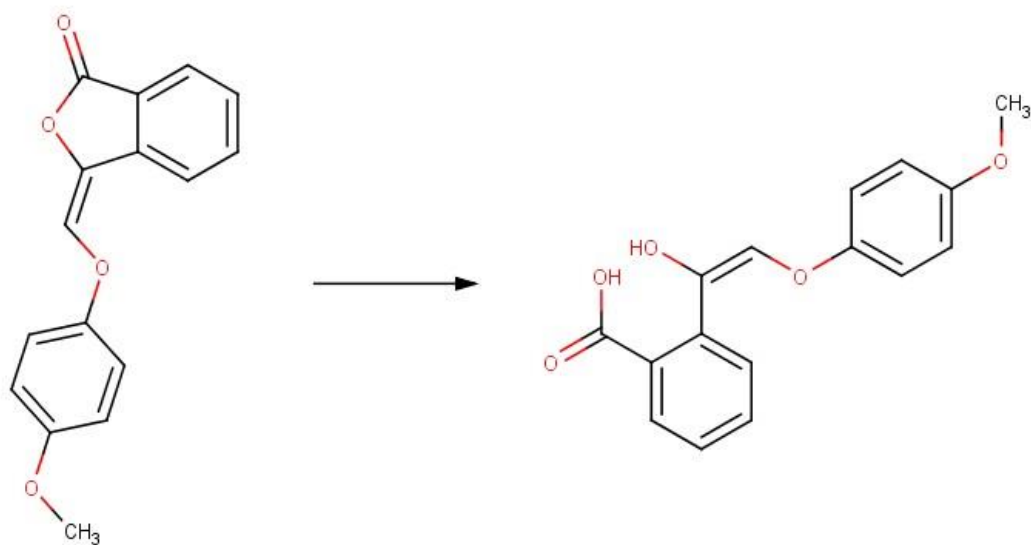
- Gluconolactone (Pocker and Green, 1973)



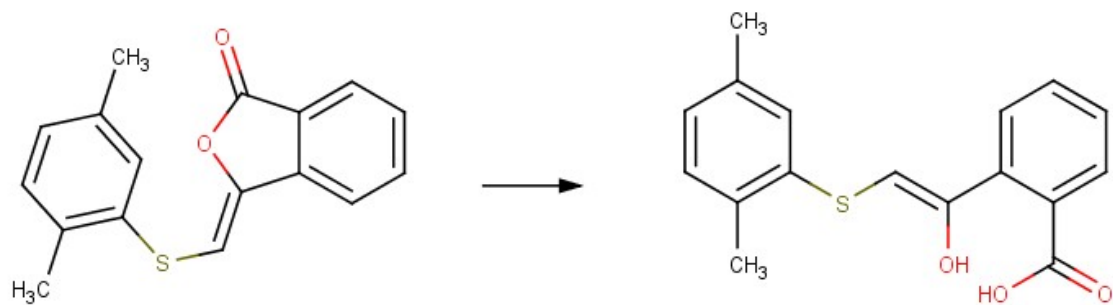
- 3-methoxy-3-(3-nitrophenyl)-2-benzofuran-1-one (Weeks and Whitney, 1981)



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



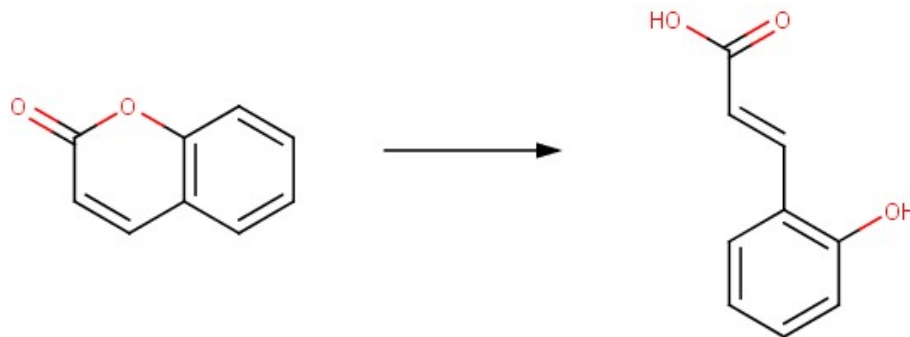
- (3Z)-3-[(2,5-dimethylphenyl)sulfanylmethylidene]-2-benzofuran-1-one (Bowden *et al*, 1998)



- 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 thiophenoxymethylene)-(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.

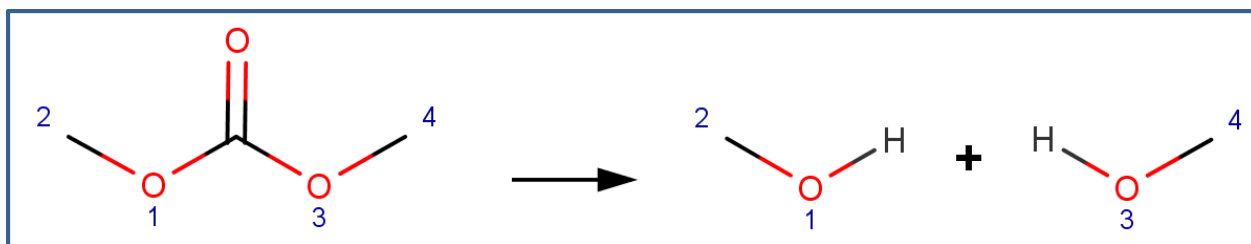
Olson, A.R. and P.V. Volue. 1951. The Hydrolysis of Beta-Butyrolactone. *J. Am. Chem. Soc.* 73: 2468-2471.

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

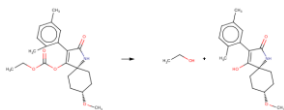
SCHEME:



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.

EXAMPLES:

- Spirotetramat (EFSA, 2008)

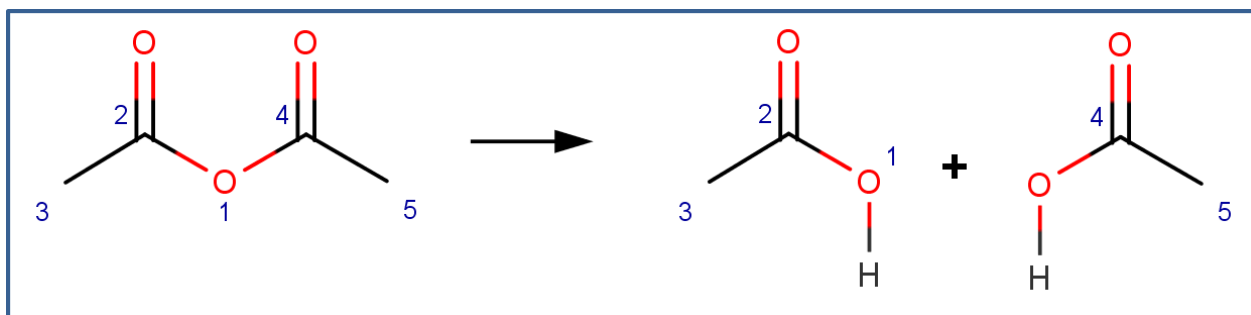


REFERENCES:

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>.

Anhydride Hydrolysis

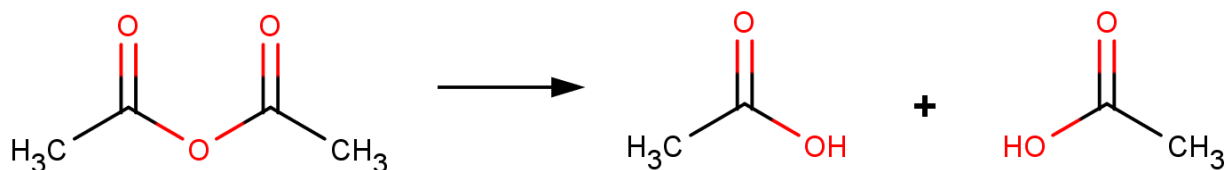
SCHEME:



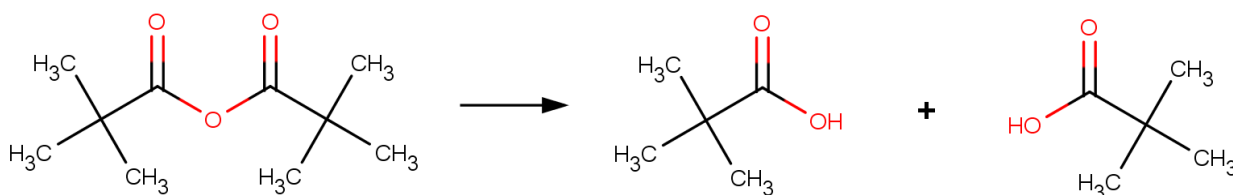
Note that a selectivity rule is included for this scheme to eliminate duplication of products. Specifically, to distinguish between the carbon atoms labelled 2 and 4, atom 2 is identified as the less sterically hindered atom.

EXAMPLES:

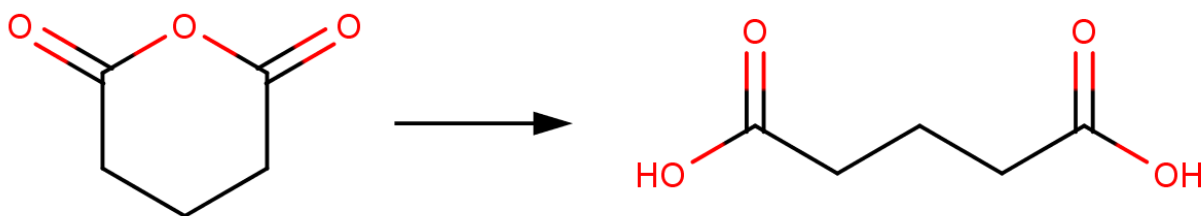
- Acetic anhydride (Bunton and Fendler, 1965)



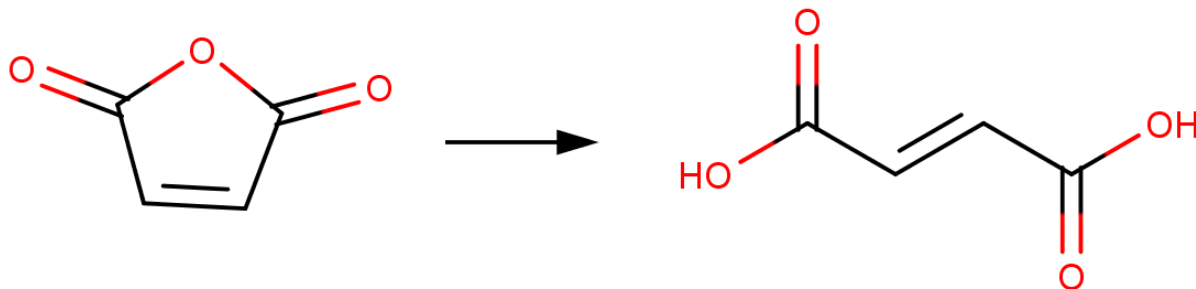
- Trimethylacetic anhydride (Bunton and Fendler, 1965)



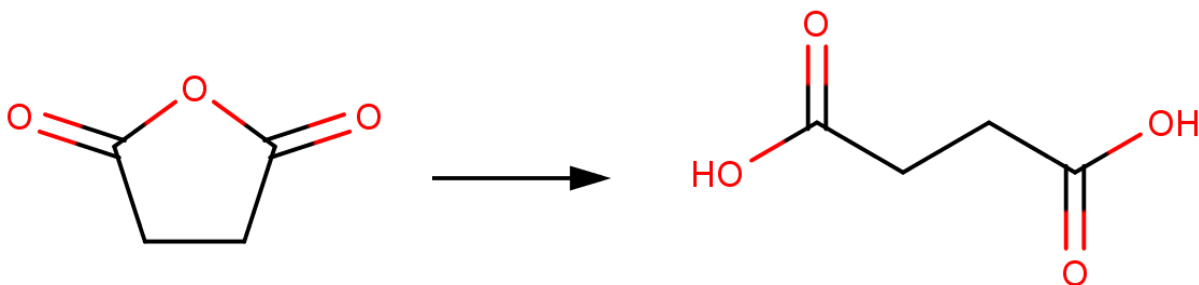
- Glutaric anhydride (Bunton *et al*, 1963)



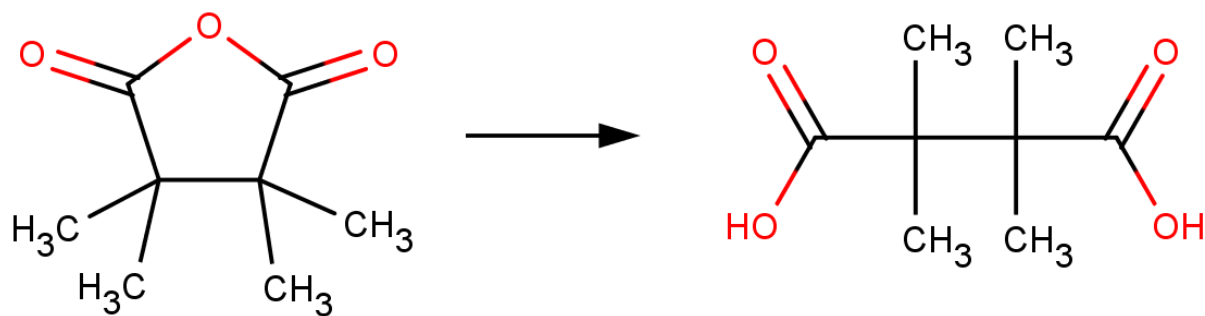
- Maleic anhydride (Bunton *et al*, 1963)



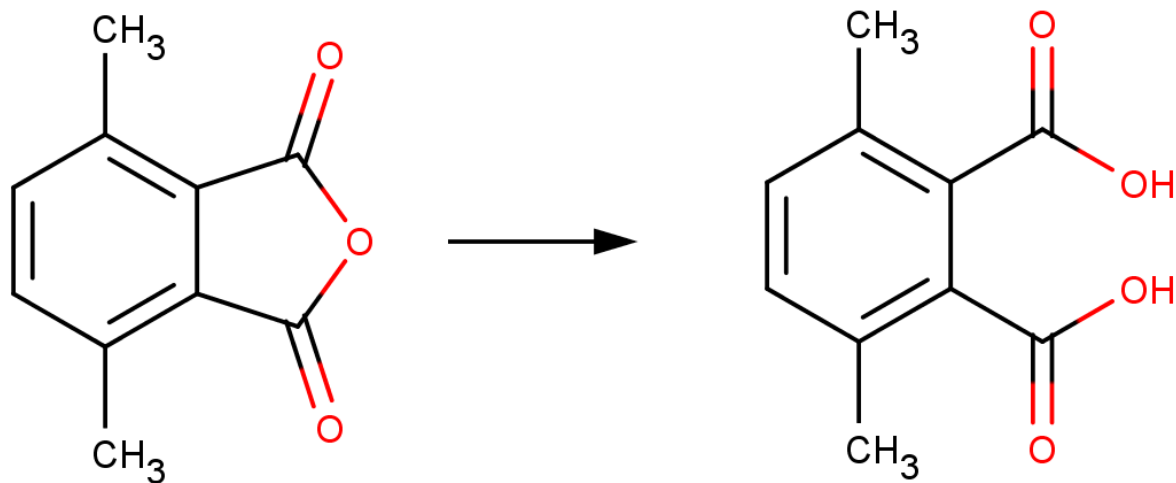
- Succinic anhydride (Bunton *et al*, 1963)



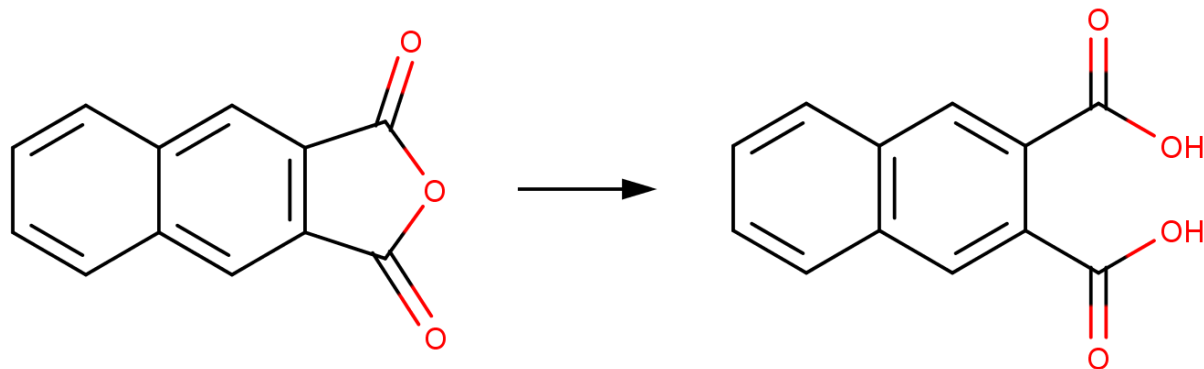
- Tetramethylsuccinic anhydride (Bunton *et al*, 1963)



- 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.

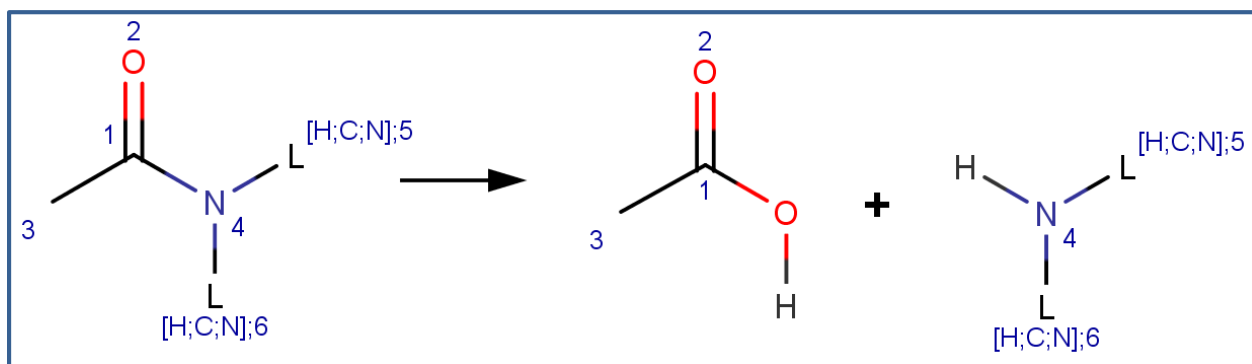
Bunton, C.A. and J.H. Fendler. 1965. The hydrolysis of carboxylic anhydrides. V. The acid hydrolysis of acetic and trimethylacetic anhydride. *Journal of Organic Chemistry*. 30(5): 1365-1371.

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. 1975. Hydrolysis of phthalic and 3,6-dimethylphthalic anhydrides. *Journal of the Chemical Society, Perkin Transactions 2*. 1975(4): 282-284.

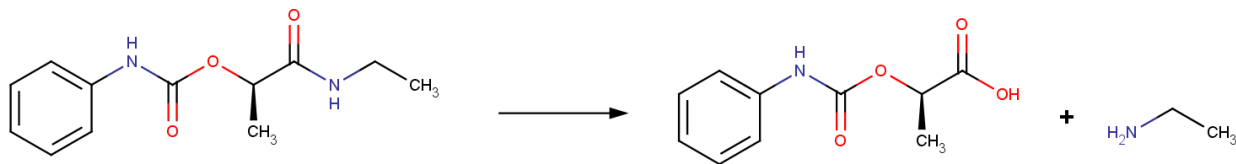
Hawkins M.D. 1975b. Hydrolysis of 2,2,2-trifluoroethyl hydrogen 3,6-dimethylphthalate. *Journal of the Chemical Society, Perkin Transactions 2*. 1975(4): 285-287.

Amide Hydrolysis

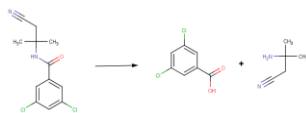


EXAMPLES:

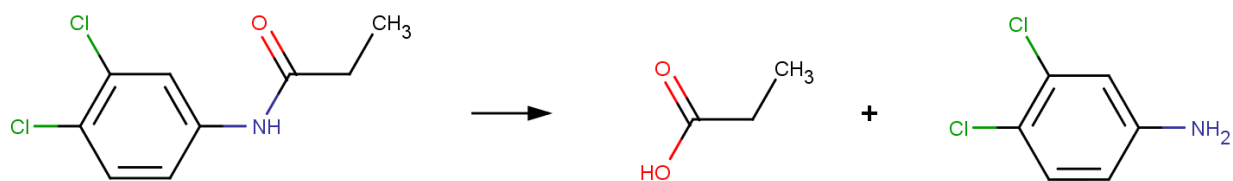
- Carbetamide (EFSA, 2006a)



- Pronamide (Larson and Weber, 1994)

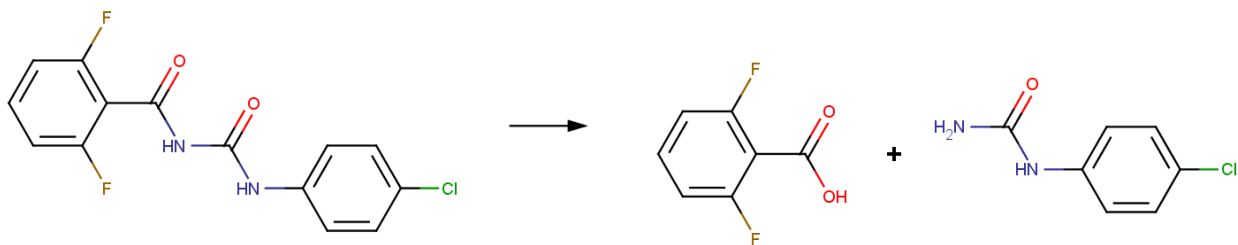


- Propanil (EFSA, 2008b)

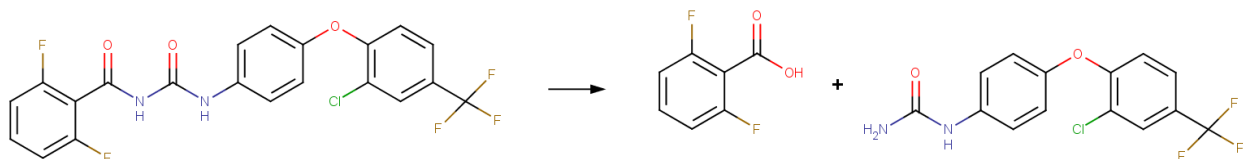


FORMYLUREA EXAMPLES: (Urea group adjacent to an amide group)

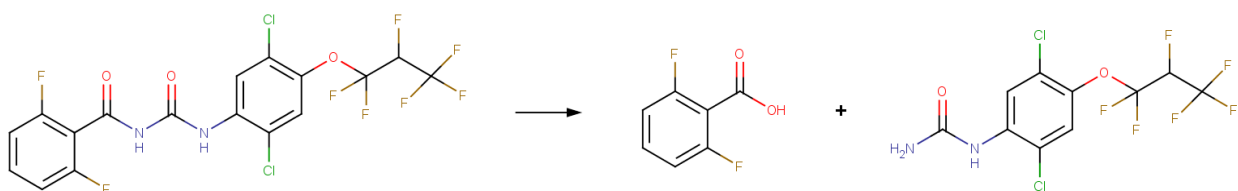
- Diflubenzuron (EFSA, 2006b)



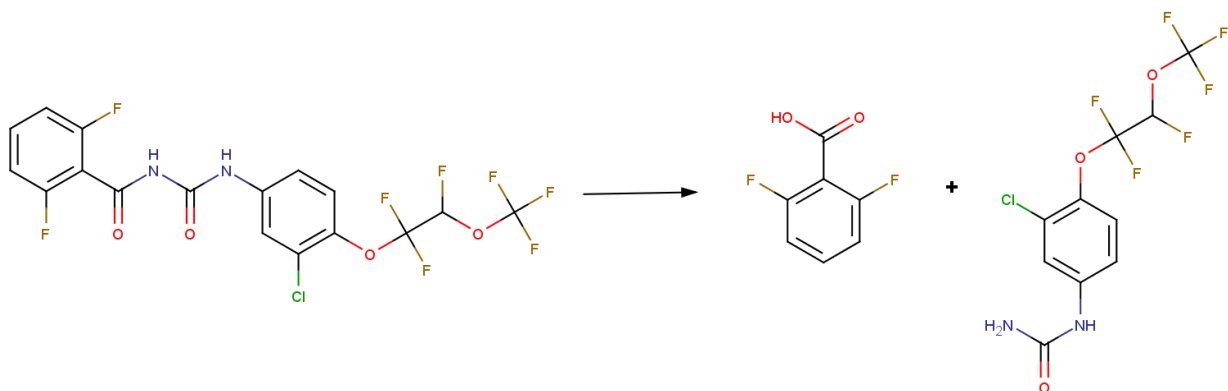
- Flufenoxuron (EFSA, 2008a)



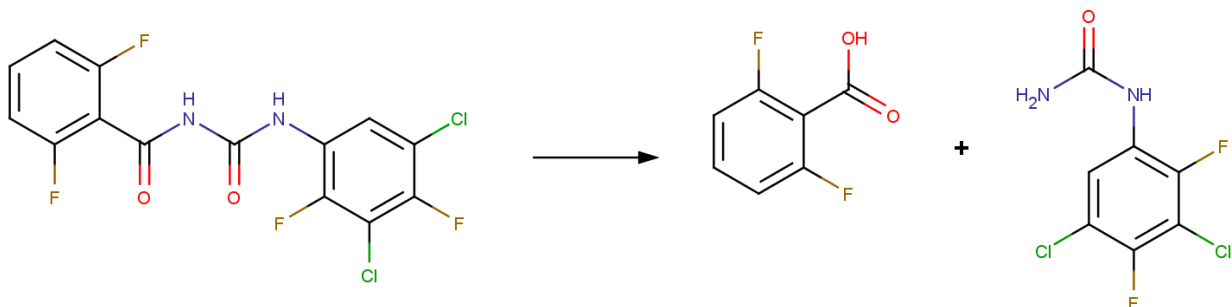
- Lufenuron (EFSA, 2007b)



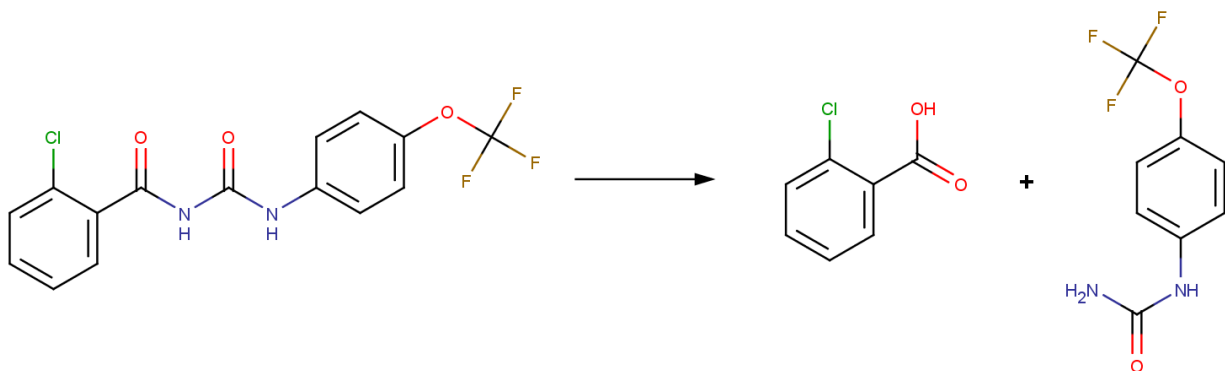
- Novaluron (EFSA, 2008c)



- 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>.

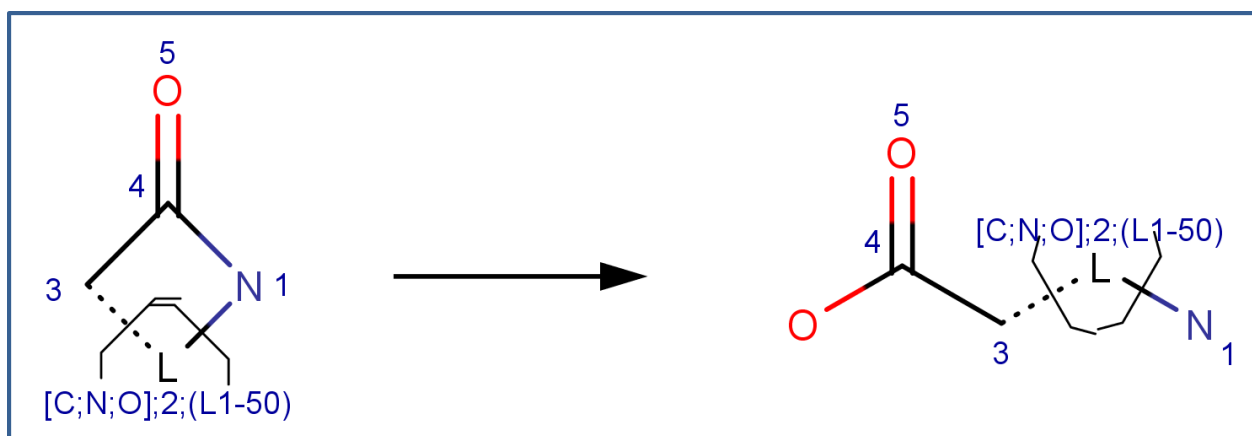
EFSA (European Food Safety Authority), 2008b. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State Italy for the existing active substance Propanil of the review programme referred to in Article 8(1) of Council Directive 91/414/EEC, Volume 3, Annex B, part 4, B.8. Available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

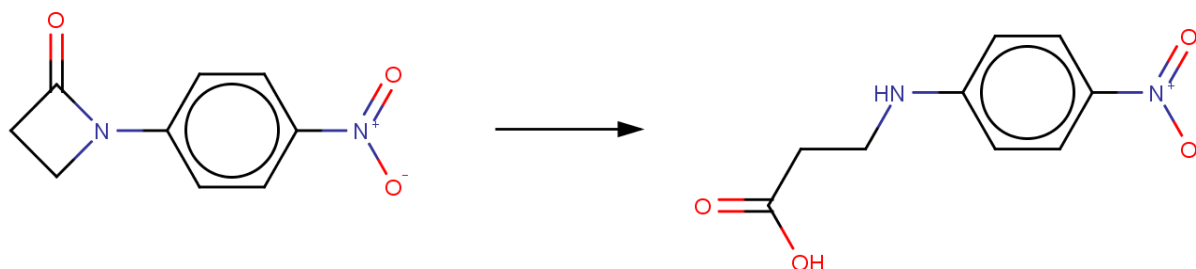


To distinguish this scheme from the Amide scheme, the scheme includes a reactivity rule which specifies that atom 1 is a ring atom. Additionally, to distinguish this scheme from hydrolysis of cyclic imides, the scheme includes a reactivity rule which specifies that atom 1 is not part of an imide structural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

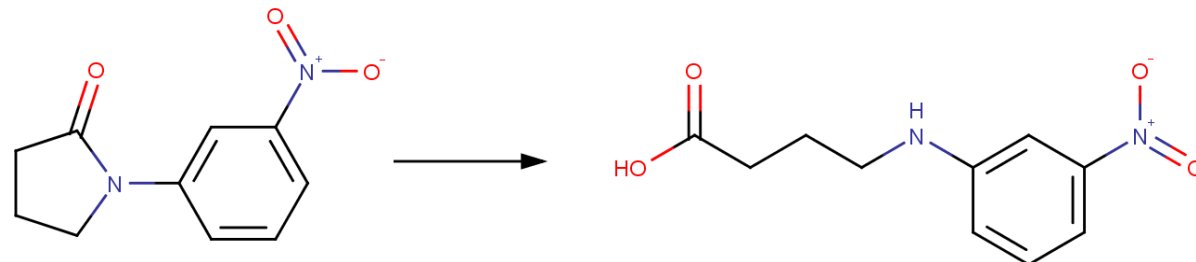
The lactam hydrolysis pathway is unlikely to be a significant transformation process under environmentally relevant conditions. In abiotic hydrolysis studies at 25°C, the products of the lactam hydrolysis pathway are generally not observed. However, at high temperature (> 50°C) and/or elevated concentrations of OH⁻, significant formation of the products of the lactam hydrolysis pathway has been observed (e.g., Abbas *et al*, 1996; Blackburn and Plackett, 1972; Bowden and Bromley, 1990). Additionally, 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).

EXAMPLES:

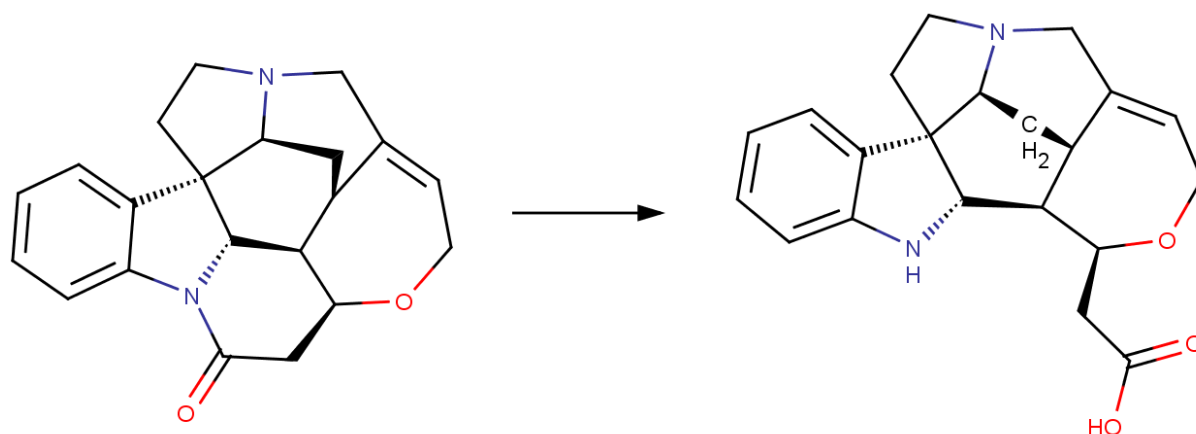
- 1-(4-Nitrophenyl)-2-azetidinone (Blackburn and Plackett, 1972)



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



- Strychnine (Abbas *et al*, 1996)

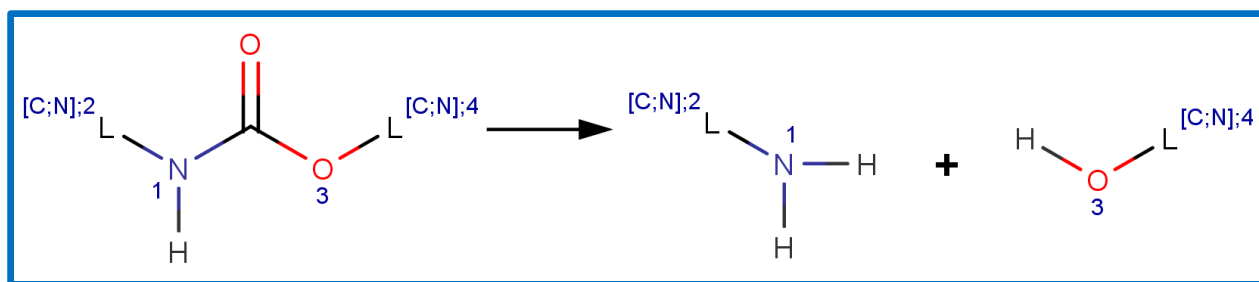


REFERENCES:

- 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

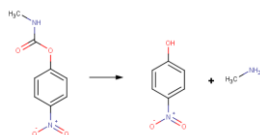
SCHEME:



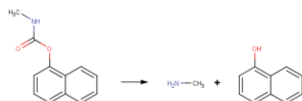
As is shown in the examples below, a number of N-alkyl and N-aryl carbamates have been observed to undergo the hydrolysis scheme shown above. The N,N-disubstituted carbamates (a.k.a. secondary carbamates) are resistant to hydrolysis (Aly and El-Dib, 1971; Christenson, 1964; EFSA, 2004c; Larson and Weber,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

EXAMPLES:

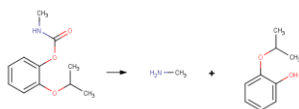
- 4-nitrophenyl N-methylcarbamate (Bender and Homer, 1965)



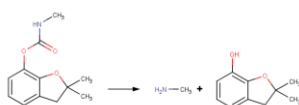
- Carbaryl (a.k.a. Sevin) (Aly and El-Dib, 1971; EFSA, 2005a; Wolfe *et al*, 1978b)



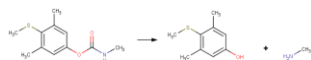
- Propoxur (a.k.a. Baygon) (Aly and El-Dib, 1971)



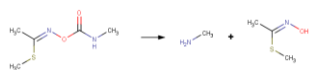
- Carbofuran (EFSA, 2004a; Ilesce *et al*, 2006)



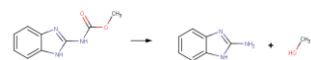
- Methiocarb (EFSA, 2005b)



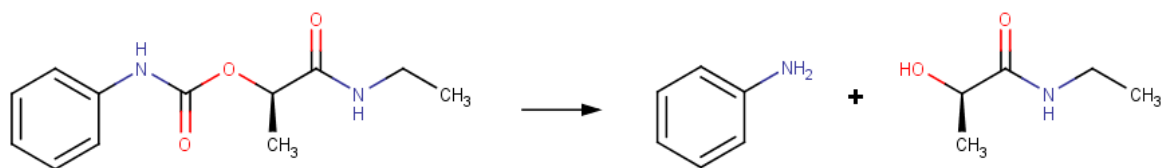
- Methomyl (EFSA, 2004b)



- 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.

EFSA (European Food Safety Authority), 2004a. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State Belgium for the existing active substance Carbofuran 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 7, B.8. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

EFSA (European Food Safety Authority), 2004b. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State United Kingdom for the existing active substance Methomyl 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.6. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

EFSA (European Food Safety Authority), 2004c. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State United Kingdom for the existing active substance Pirimicarb 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), 2005a. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State Spain for the existing active substance Carbaryl 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 United Kingdom for the existing active substance Methiocarb 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), 2006. 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), 2009. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State Germany for the existing active substance Carbendazim 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>.

Iesce, M.R., M. della Greca, F. Cermola, M. Rubino, M. Isidori and L. Pascarella. 2006. Transformation and Ecotoxicity of Carbamic Pesticides in Water. *Environmental Science & Pollution Research* 13(2): 105-109.

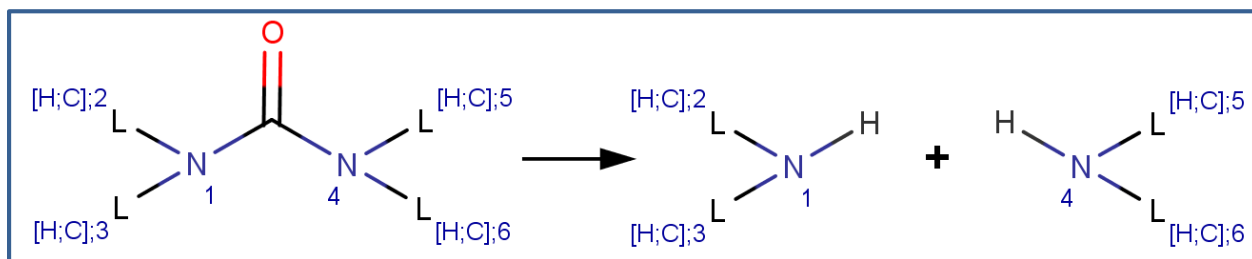
Larson, R.A. and E.J. Weber. *Reaction Mechanisms in Environmental Organic Chemistry*. Boca Raton: CRC Press, Inc., 1994.

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, Protham and Chlorprotham: A Comparison of the Rates of Hydrolysis and Photolysis with the Rate of Biolysis. *Water Research*. 12: 565-571.

Urea Hydrolysis

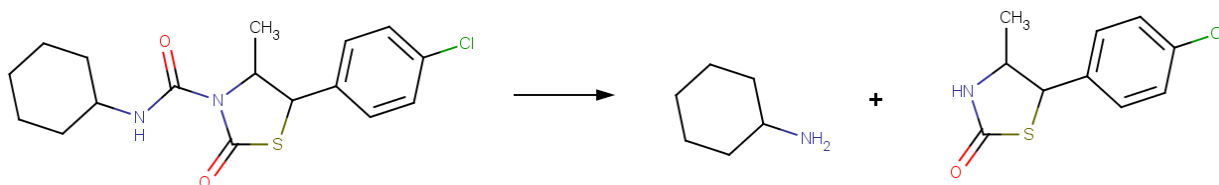
SCHEME:



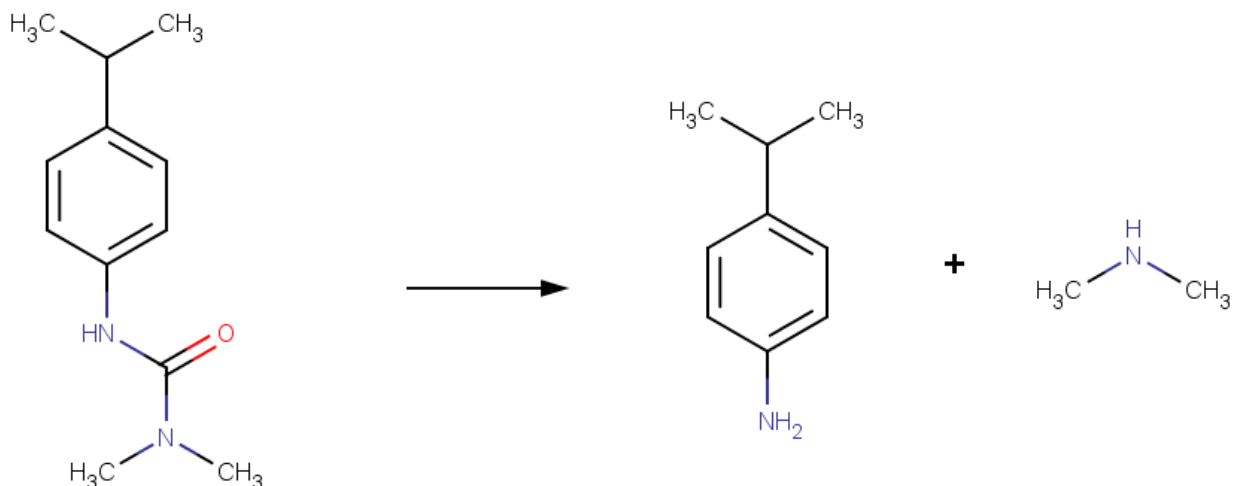
The urea hydrolysis pathway is unlikely to be a significant transformation process under environmentally relevant conditions. In abiotic hydrolysis studies at 25°C, the products of the urea hydrolysis pathway are generally either minor products (<3%) or not observed at all. For example, in molecules with a urea group adjacent to an amide group, hydrolysis is 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). Additionally, the urea hydrolysis pathway may occur through an enzyme-mediated process.

EXAMPLES:

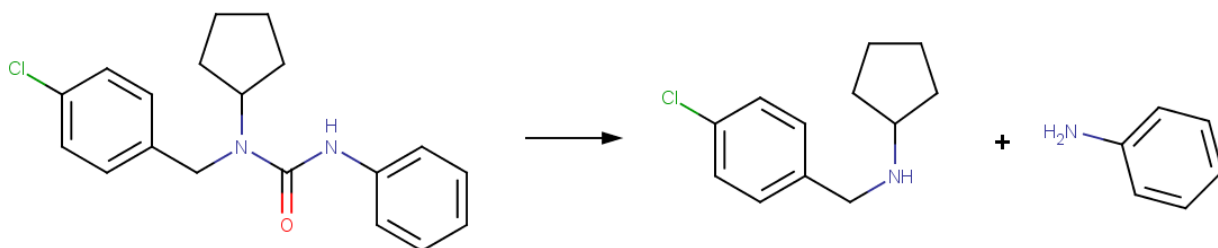
- Hexythiazox (EFSA, 2006a)



- 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>.

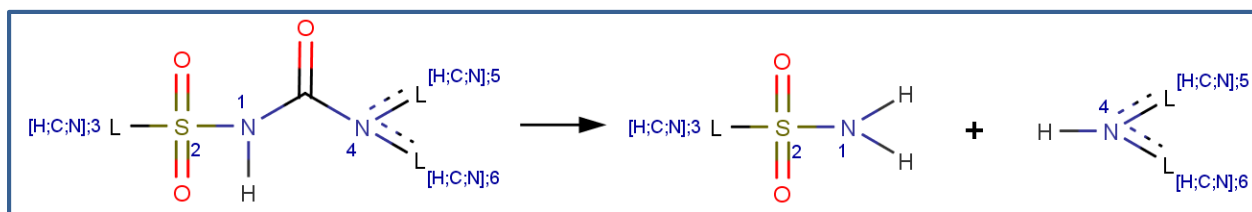
EFSA (European Food Safety Authority). 2006b. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State the Netherlands for the existing active substance Pencycuron of the third stage (part A) of the review programme referred to in Article 8(2) of Council Directive 91/414/EEC, 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.

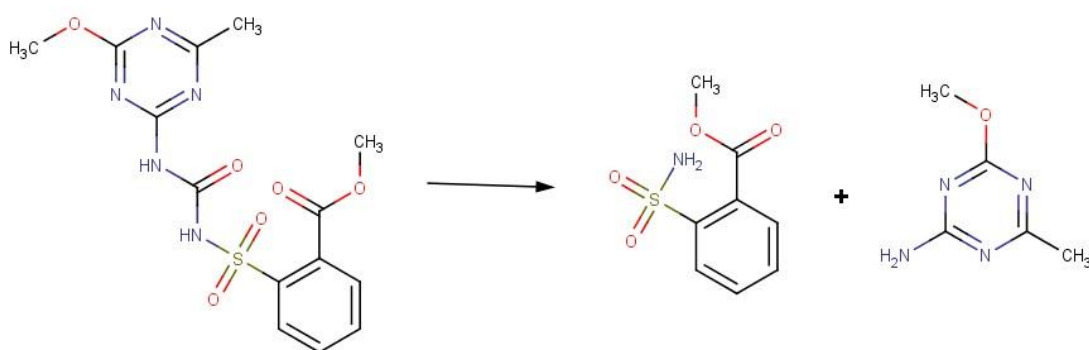
Sulfonylurea Hydrolysis

SCHEME:

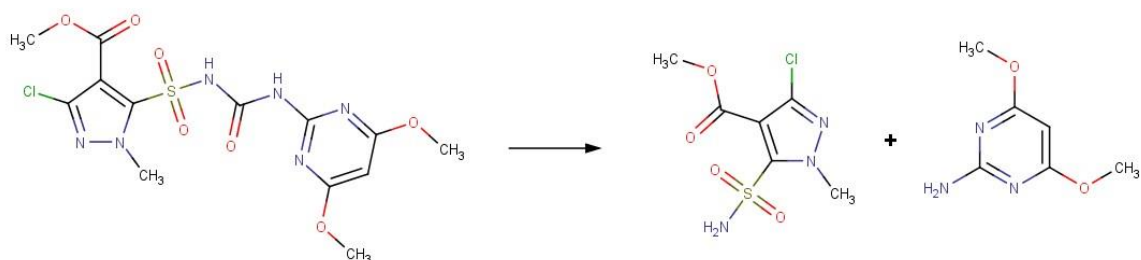


EXAMPLES:

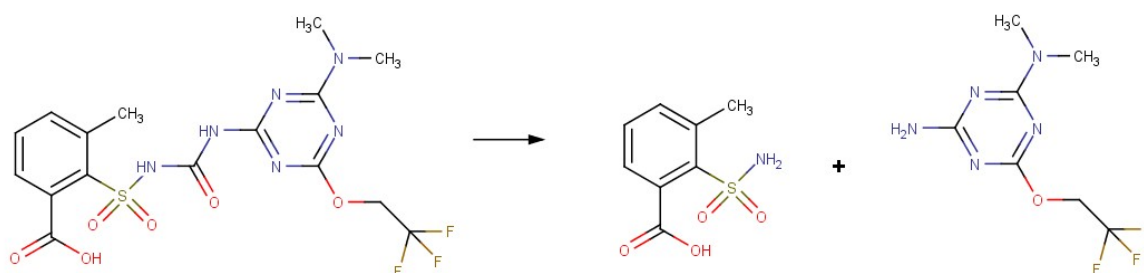
- Metsulfuron-methyl (EFSA, 2013)



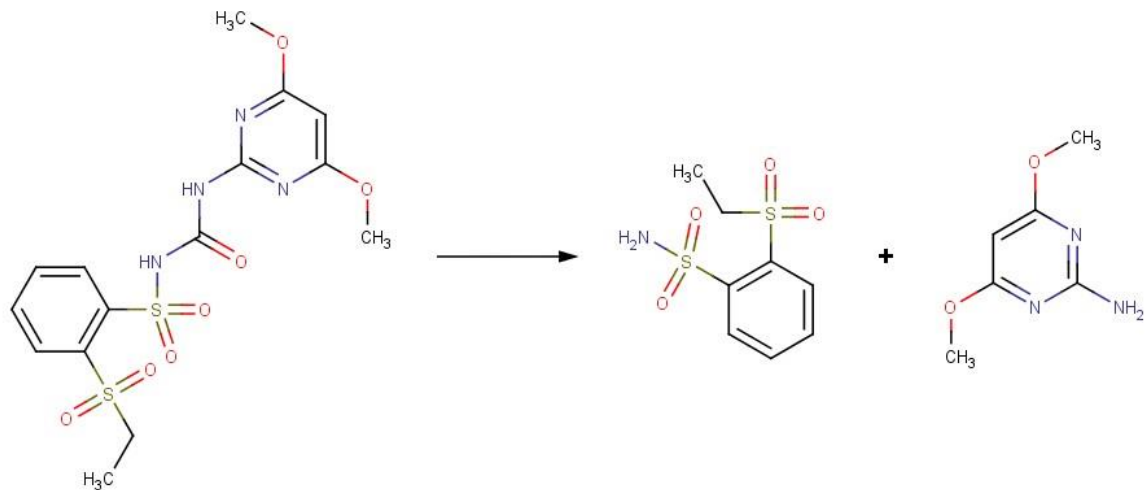
- Halosulfuron-methyl (EFSA, 2011)



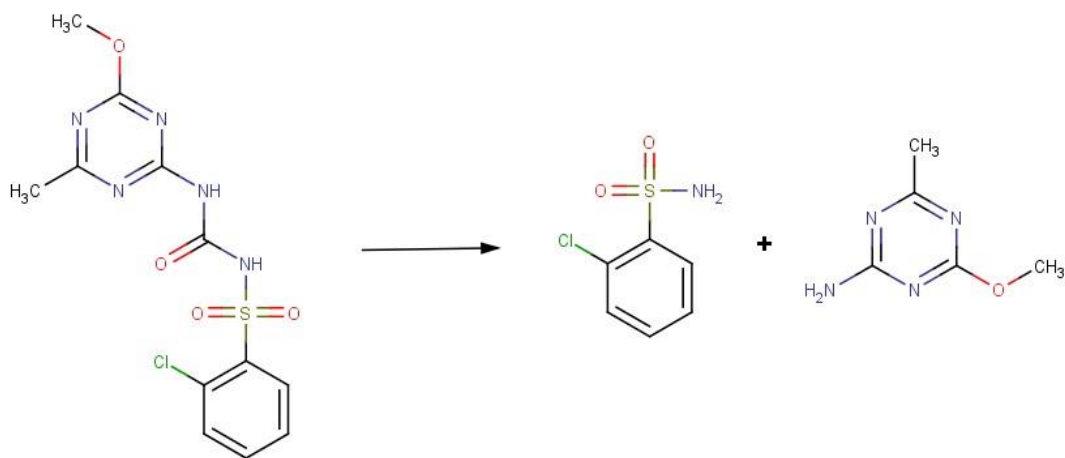
- Triflusulfuron-Methyl (EFSA, 2007a)



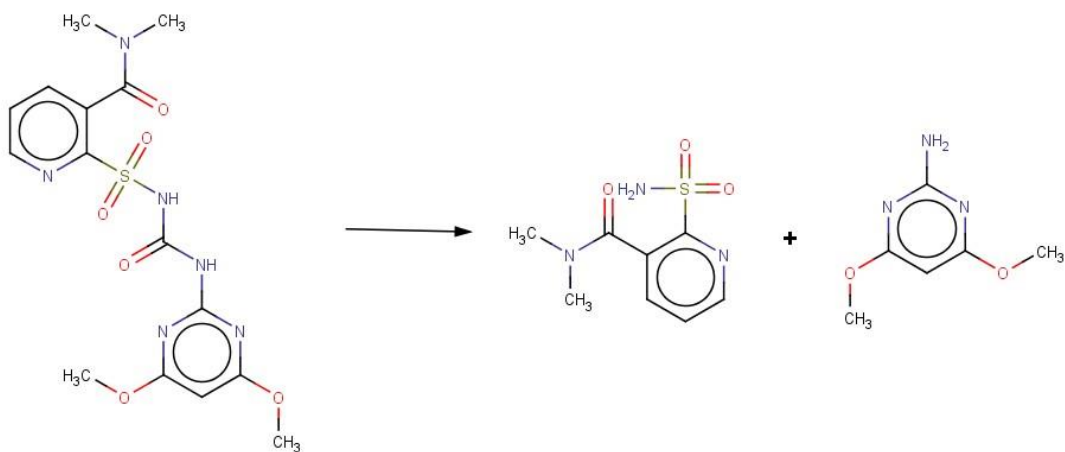
- Rimsulfuron (EFSA, 2005)



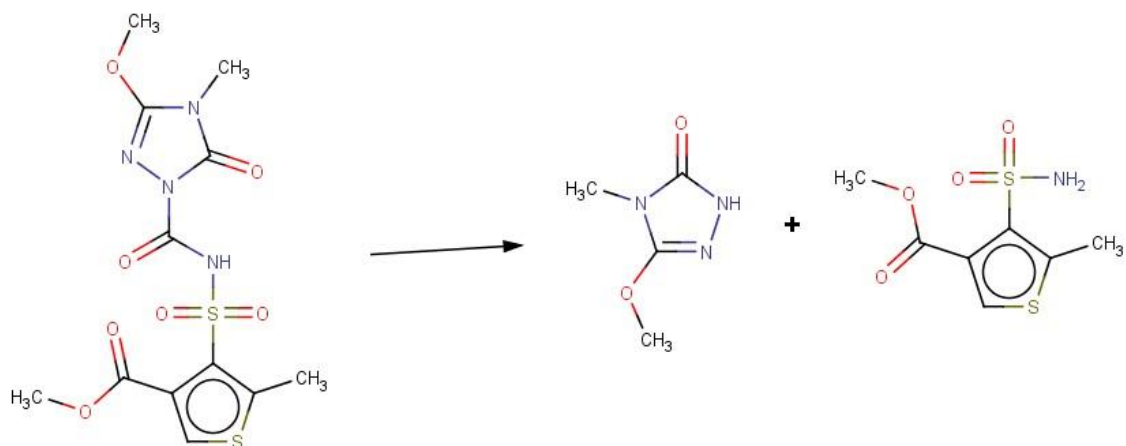
- Chlorsulfuron (EFSA, 2007b)



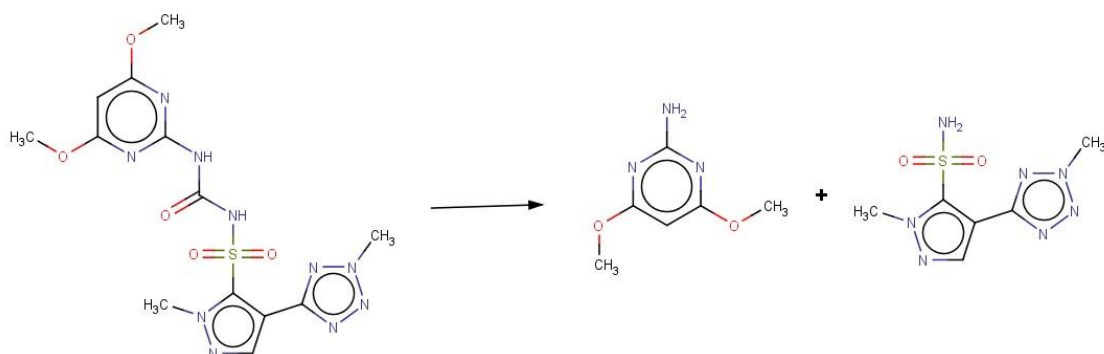
- Nicosulfuron (EFSA, 2006c)



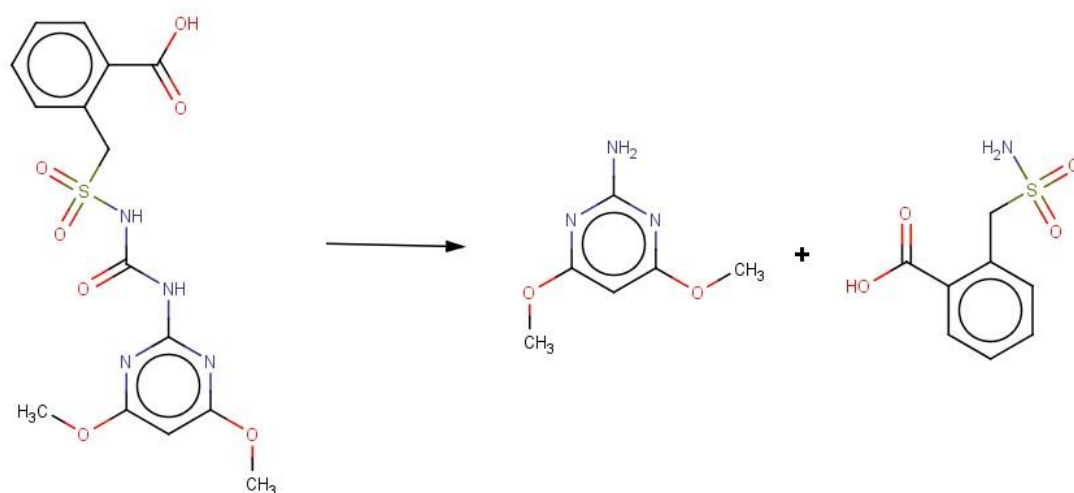
- Thiencarbazone-Methyl (EFSA, 2012).



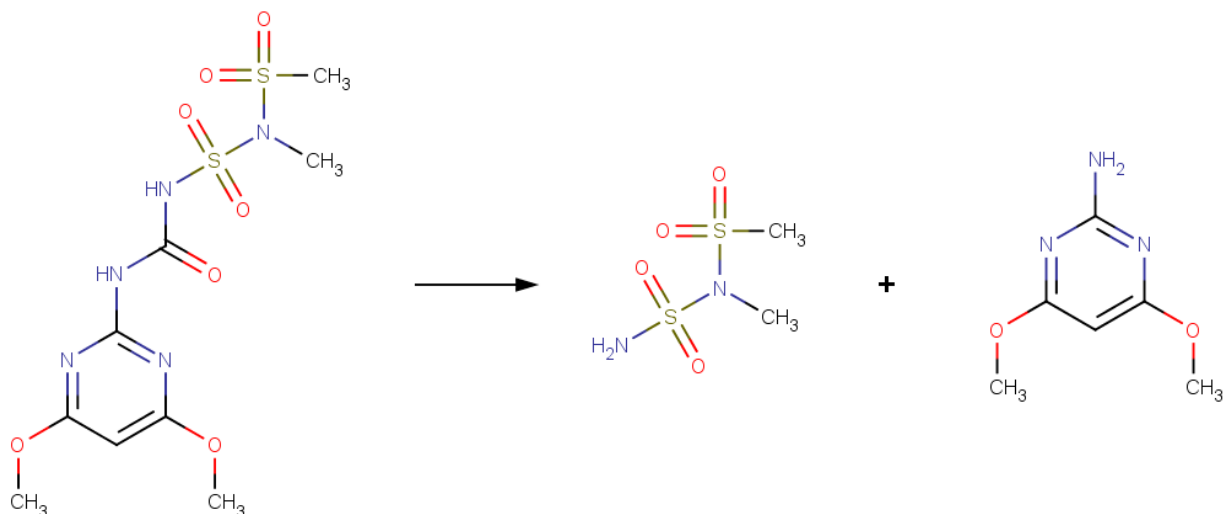
- Azimsulfuron (Boschin *et al*, 2007; EFSA, 2009)



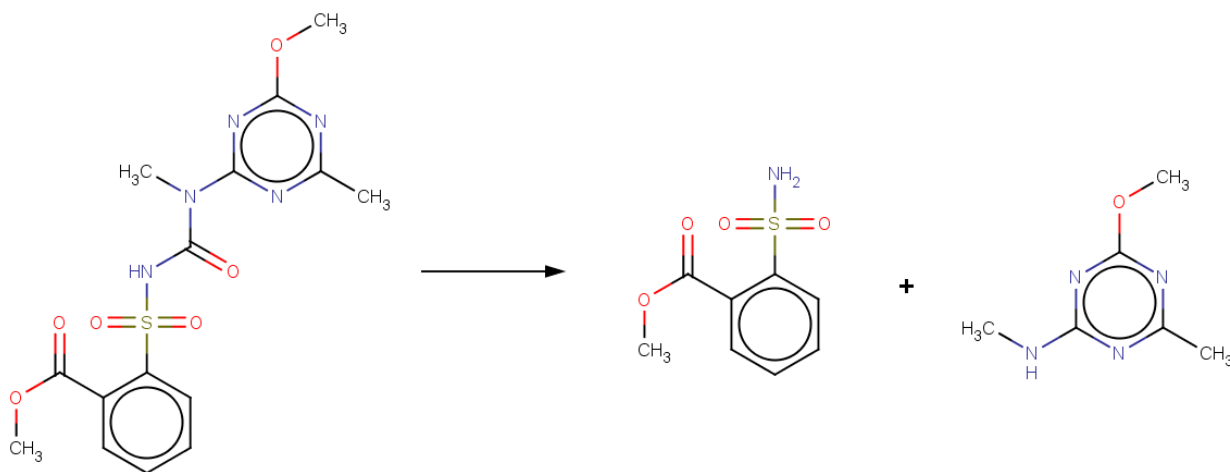
- Bensulfuron Methyl (EFSA, 2006b)



- Amidosulfuran (EFSA, 2006a)



- Tribenuron-methyl (EFSA, 2004)



REFERENCES:

Boschin, G., A. D'Agostina, C. Antonioni, D. Locati and A. Arnoldi. 2007. Hydrolytic degradation of azimsulfuron, a sulfonylurea herbicide. *Chemosphere*. 68: 1312-1317.

EFSA (European Food Safety Authority). 2004. Draft Assessment Report (DAR): Initial risk assessment provided by the rapporteur Member State Sweden for the existing active substance Tribenuron (based on the variant tribenuron-methyl) 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). 2005. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State Germany for the existing active substance Rimsulfuron 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). 2006a. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State Austria for the existing active substance Amidosulfuron 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. Monograph prepared by the Member State Italy in the context of the inclusion of the following active substance Bensulfuron Methyl in Annex I of Council Directive 91/414/EEC, Volume 3, Annex B.8. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

EFSA (European Food Safety Authority). 2006c. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State The United Kingdom for the existing active substance Nicosulfuron 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 France for the existing active substance Triflusulfuron-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). 2007b. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State Greece for the existing active substance Chlorsulfuron 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). 2009. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State Sweden and the co-rapporteur Member State Slovenia for the existing active substance Azimsulfuron upon submission in the framework of renewal of the inclusion of a first group of active substances in Annex I to Council Directive 91/414/EEC, Volume 3, Annex B.8. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

EFSA (European Food Safety Authority). 2011. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State Italy for the new active substance Halosulfuron-Methyl of the review programme referred to in Article 11(1) of Commission Regulation (EC) No 1107/2009, Volume 3, Annex B, B.8. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

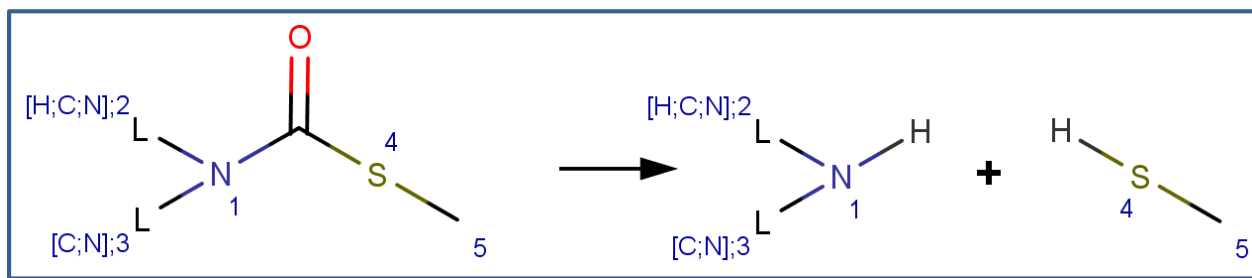
EFSA (European Food Safety Authority). 2012. Report and Proposed Decision of the United Kingdom made to the European Commission for Thiencarbazone-Methyl under Regulation 1107/2009 (Article 80 transitional measures), Volume 3, Annex B, B.8, part A. Available from <http://dar.efsa.europa.eu/dar-web/provision>.

EFSA (European Food Safety Authority). 2013. Renewal Assessment Report (RAR): Draft Re-Assessment Report Review provided by the Member State Slovenia and the co-rapporteur Member State Sweden for

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>.

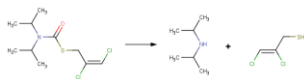
Thiocarbamate Hydrolysis

SCHEME:



EXAMPLES:

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

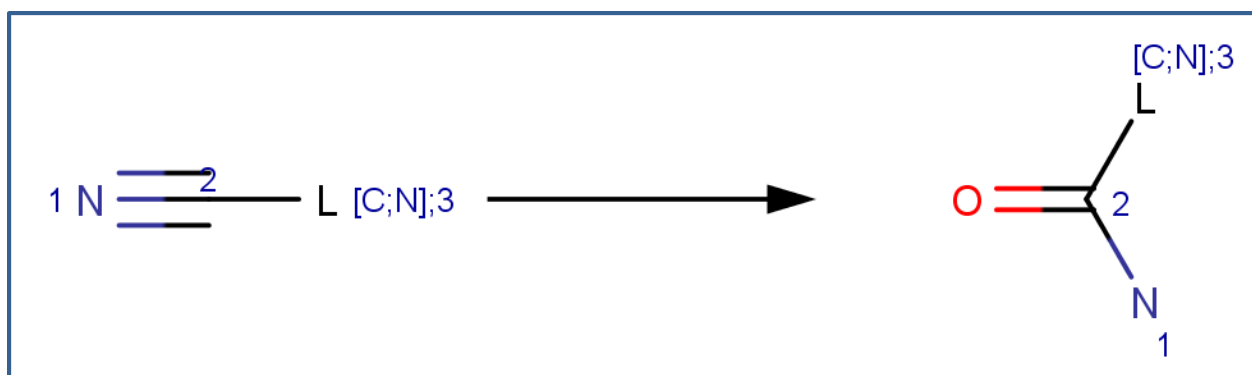


REFERENCES:

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.

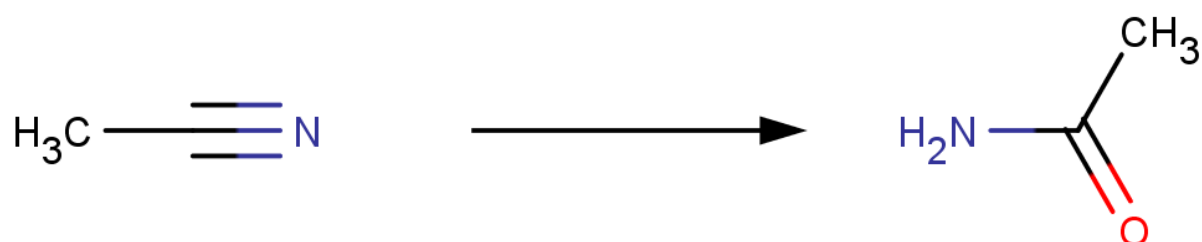
Nitrile Hydrolysis

SCHEME:

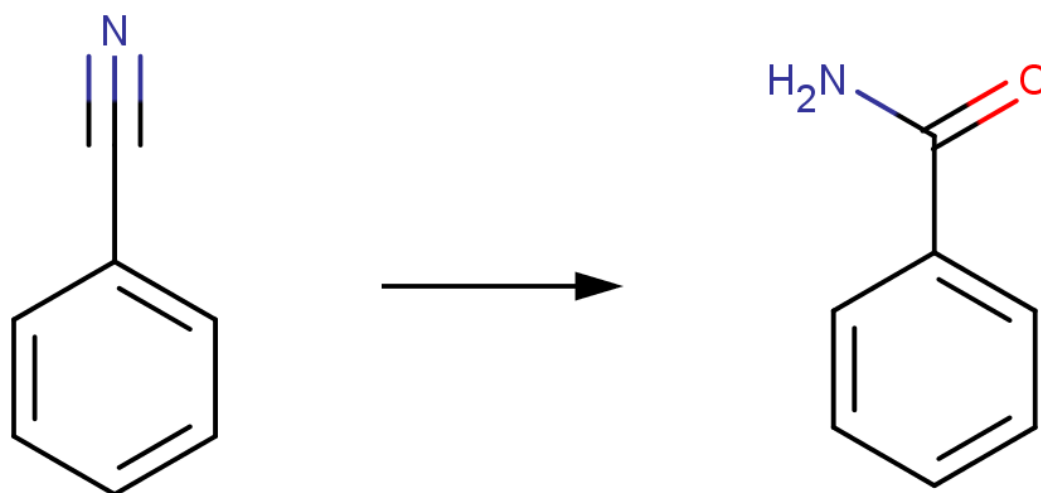


EXAMPLES:

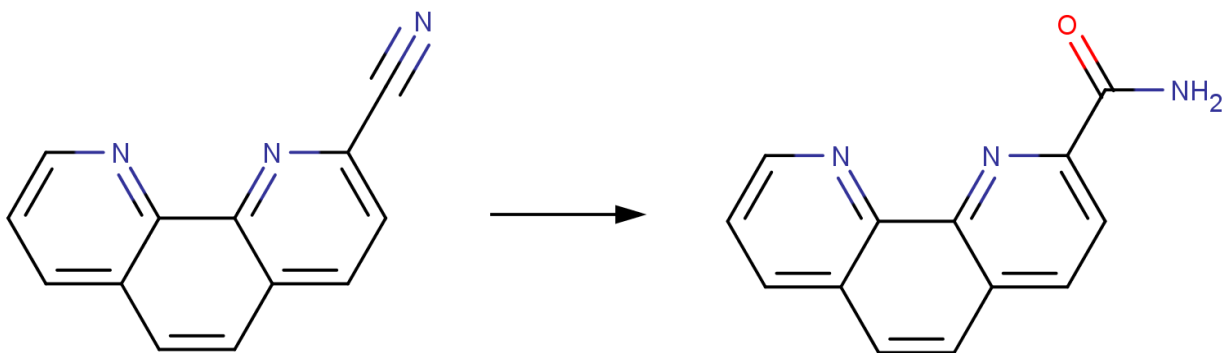
- Acetonitrile (Peskoff and Meyer, 1913; U.S. EPA, 1987)



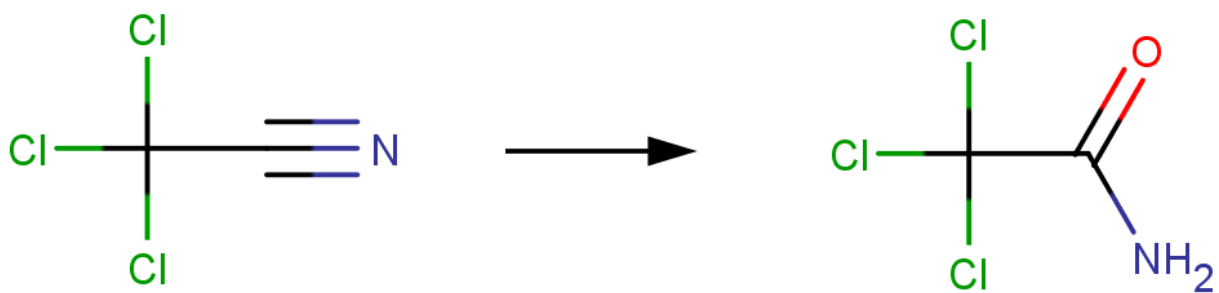
- Benzonitrile (Wiberg, 1955)



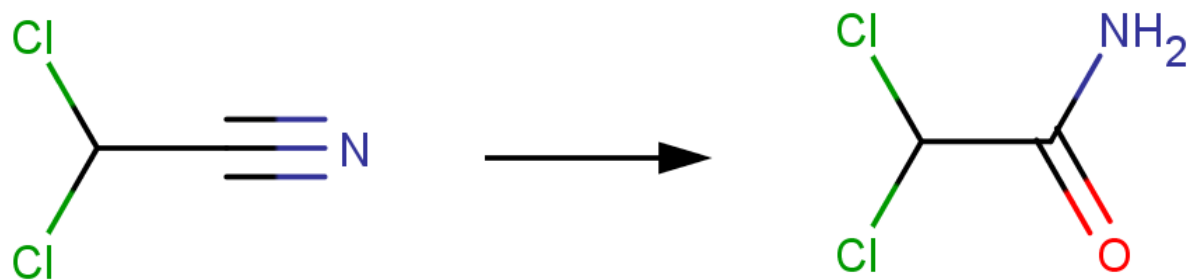
- 1,10-phenanthroline-2-carbonitrile (Breslow *et al*, 1967)



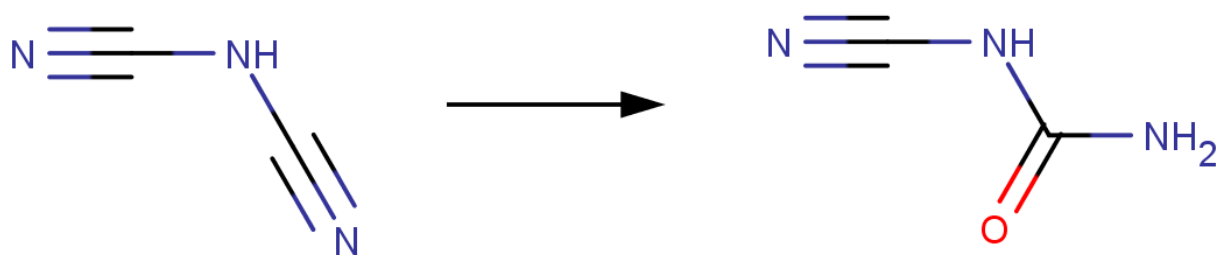
- Trichloroacetonitrile (Glezer *et al*, 1999)



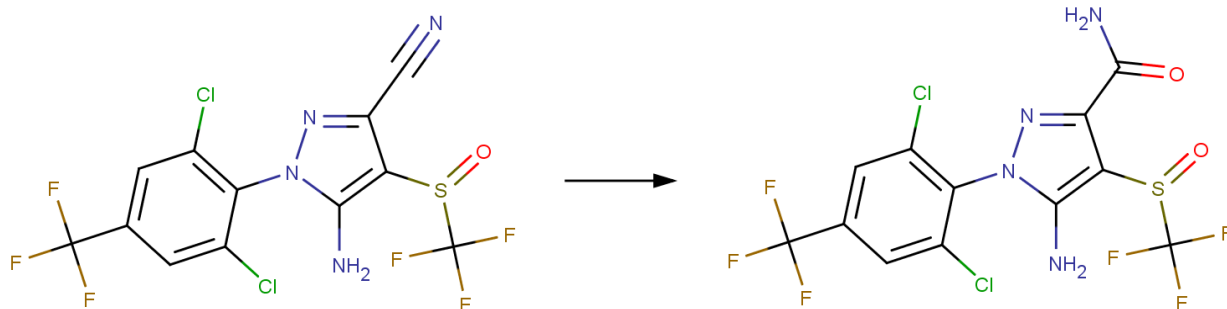
- Dichloroacetonitrile (Reckow *et al*, 2001)



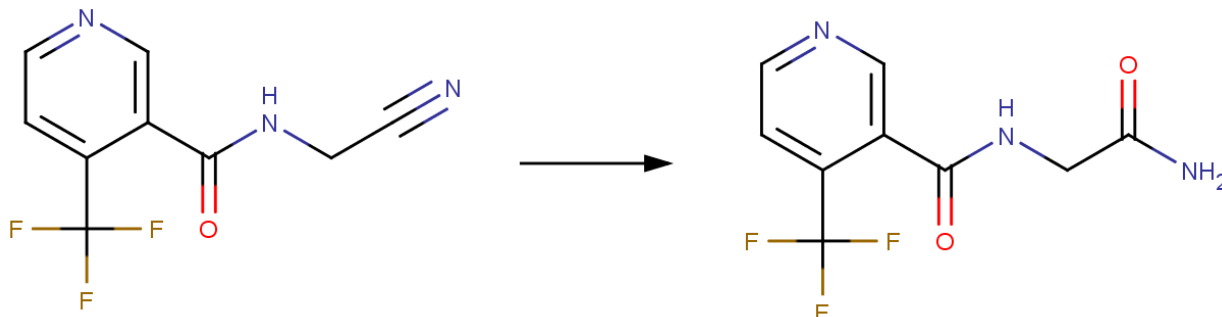
- Dicyanamide (Hill *et al*, 1984)



- Fipronil (EFSA, 2005a)



- Flonicamid (EFSA, 2005b)



REFERENCES:

Breslow, R., R. Fairweather and J. Keana. 1967. Metal-catalyzed hydration of phenanthroline nitrile. *Journal of the American Chemical Society*. 89: 2135-2138.

EFSA (European Food Safety Authority). 2005a. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State France for the existing active substance Fipronil 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). 2005b. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State France for the existing active substance Flonicamid 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>.

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.

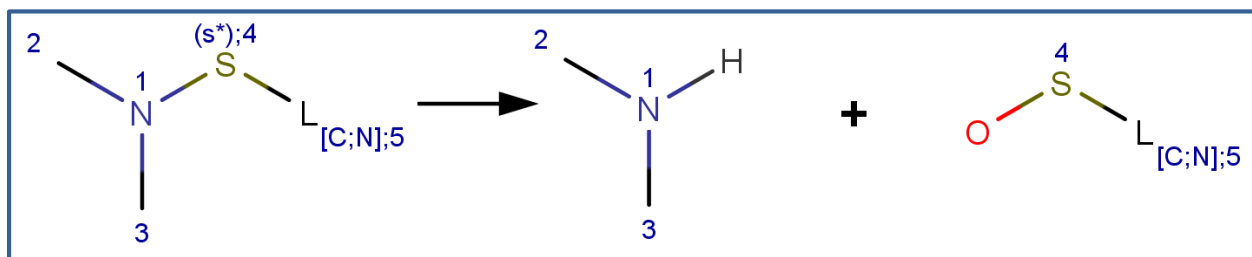
Reckow, D.A., T.L. Platt, A.L. MacNeill and J.N. McClellan. 2001. Formation and degradation of DCAN in drinking waters. *AQUA*. 50(1): 1-13.

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.

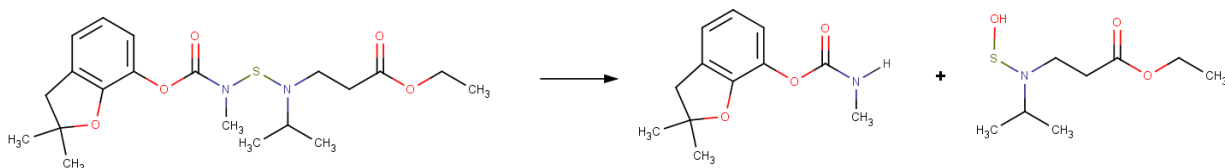
N-S Cleavage

SCHEME:

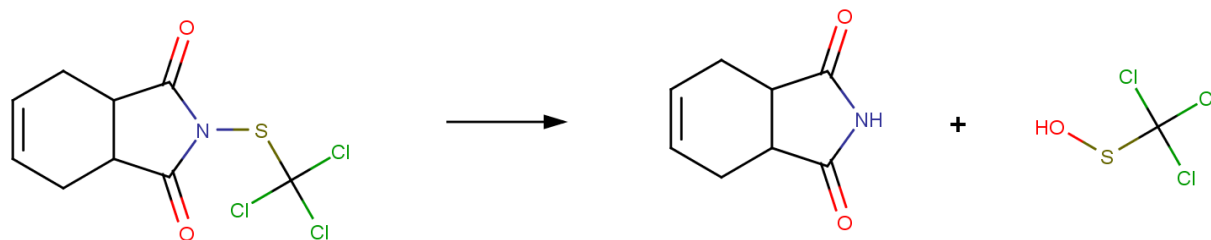


EXAMPLES:

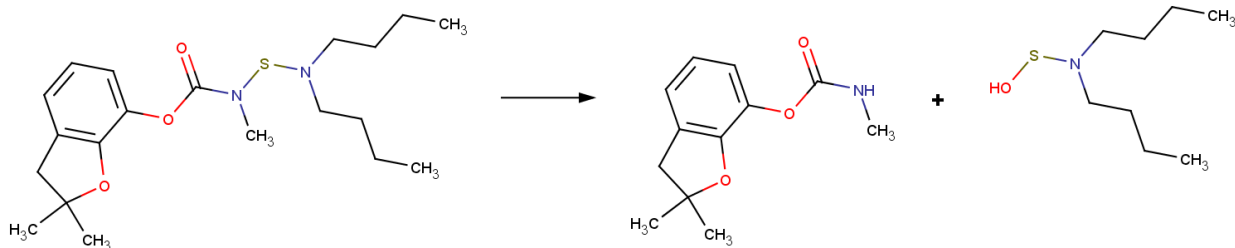
- Benfuracarb (EFSA, 2004a; Ilesce *et al*, 2006)



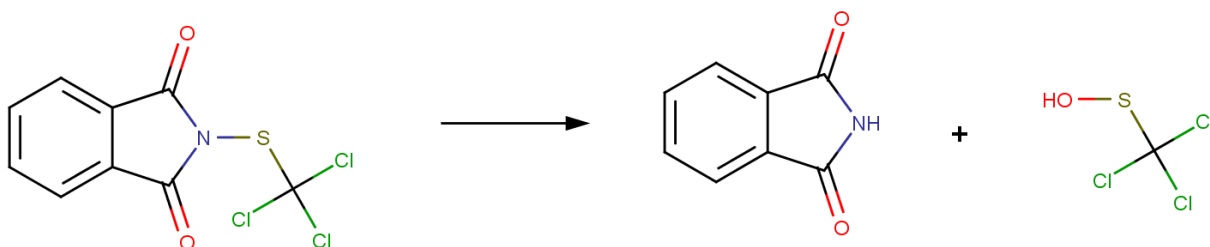
- Captan (EFSA, 2005a; Wolfe *et al*, 1976)



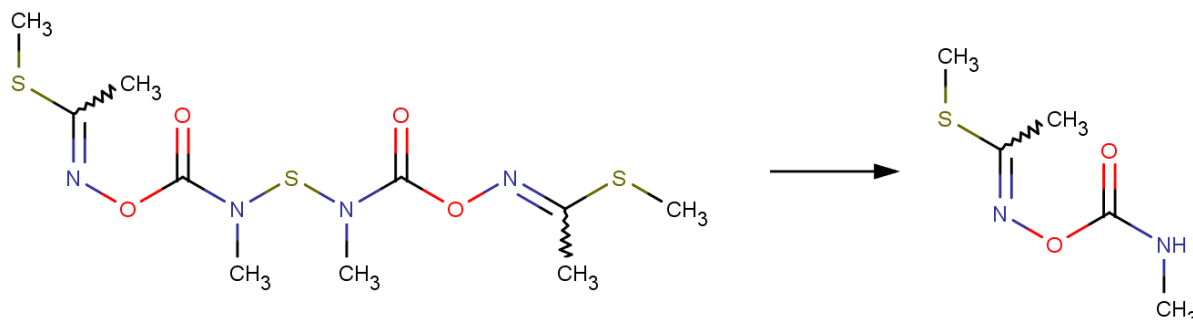
- Carbosulfan (de Melo Plesse *et al*, 2005; EFSA, 2004b; Ilesce *et al*, 2006; Umetsu *et al*, 1980)



- Folpet (EFSA, 2005b)



- Thiodicarb (EFSA, 2005c)



REFERENCES:

De Melo Plese, 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.

EFSA (European Food Safety Authority). 2004a. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State Belgium for the existing active substance Benfuracarb 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). 2004b. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State Belgium for the existing active substance Carbosulfan 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). 2005a. Draft Assessment Report (DAR): Initial risk assessment provided by the Member State Italy for the existing active substance Captan 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 Italy for the existing active substance Folpet 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 Thiodicarb 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>.

Iesce, M.R., M. della Greca, F. Cermola, M. Rubino, M. Isidori and L. Pascarella. 2006. Transformation and Ecotoxicity of Carbamic Pesticides in Water. *Environmental Science and Pollution Research*. 13(2): 105-109.

Umetsu, N., E. Kuwano and T.R. Fukuto. 1980. Nature of N-S bond cleavage of 2,3-dihydro-2,2-dimethyl-7-benzofuranyl (di-n-butylaminosulphenyl) (methyl)carbamate. *Journal of Environmental Science and Health B*. 15(1): 1-23.

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.