

Photoactive Catalysts

Presentation Catalyst Workshop

Sink or Swim Meeting Akron University May, 2006

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Photoactive Catalysts

Generate Catalysts

Improved Potlife

Fast Cure Response

Catalyze Non-Free Radical Reactions

Lithographic Applications

Photobase-Photoacid Catalysts

Photoactive Catalyst Applications

Photoacid

Amino Resin

Phenol Resins

Lithography

– Photoresist

Photobase

Epoxy

Isocyanate

Addition reactions

Lithography

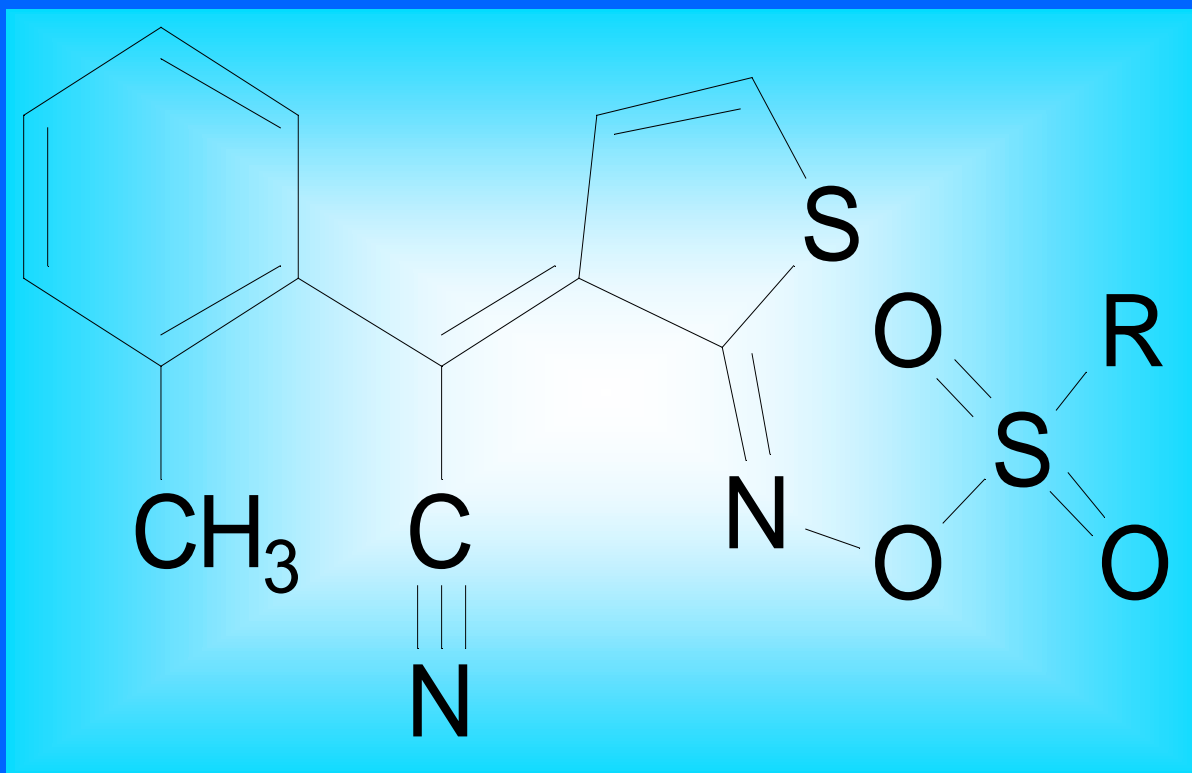
Adhesive

Coatings

Composite

Photoacid Catalysts

– Oxime ester



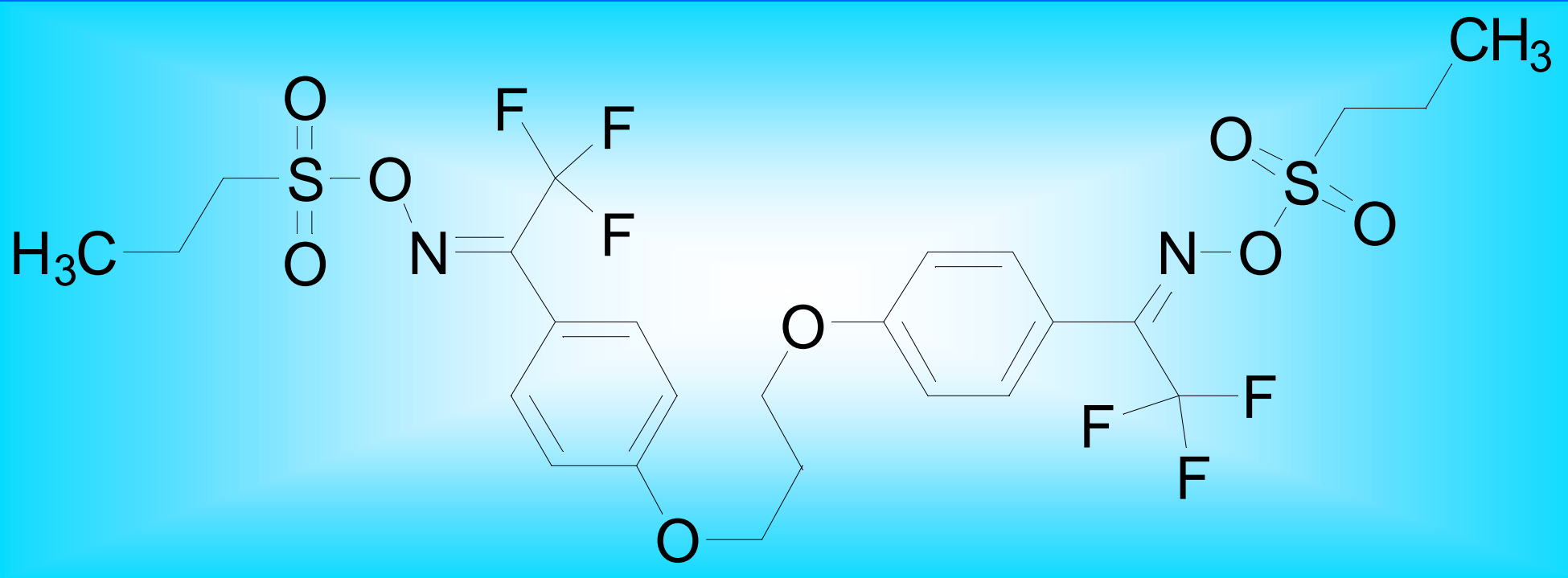
Non-ionic halogen free
Temperature stable <140°C
Wide range of light sources

Ciba® IRGACURE® PAG 1XX Family - Ciba Specialty Chemicals

Photoacid Catalysts

– Oxime ester

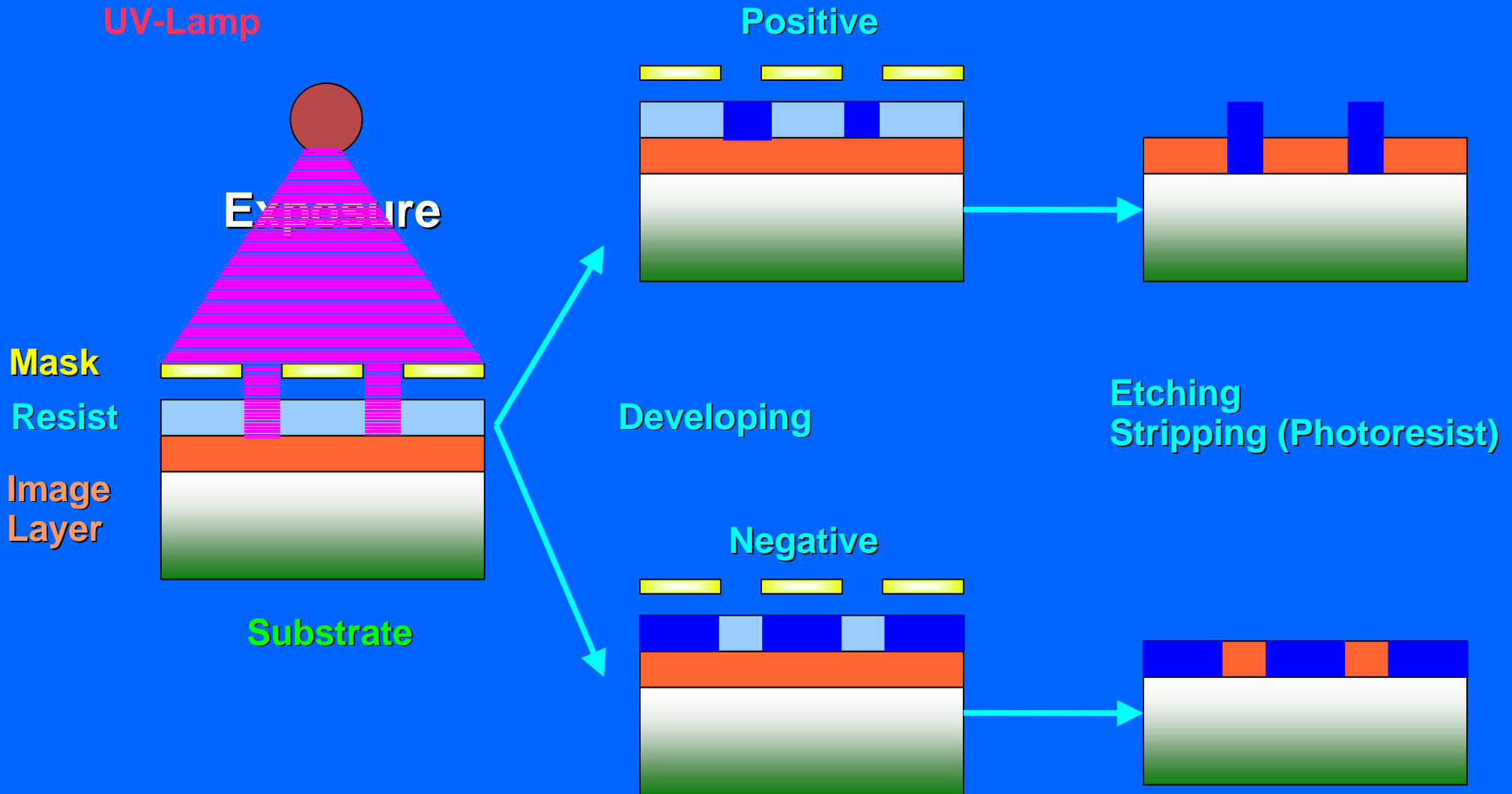
Non-ionic Deep UV
Temperature stable <188°C
High Sensitivity 248 nm



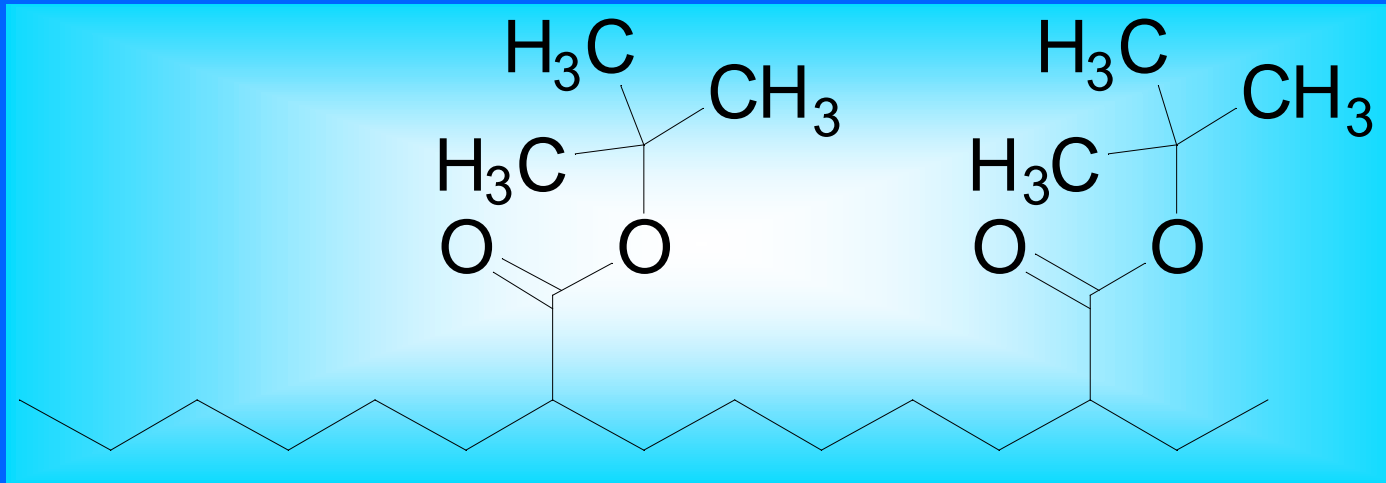
Ciba® IRGACURE® PAG 263 - Ciba Specialty Chemicals

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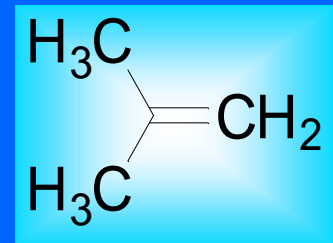
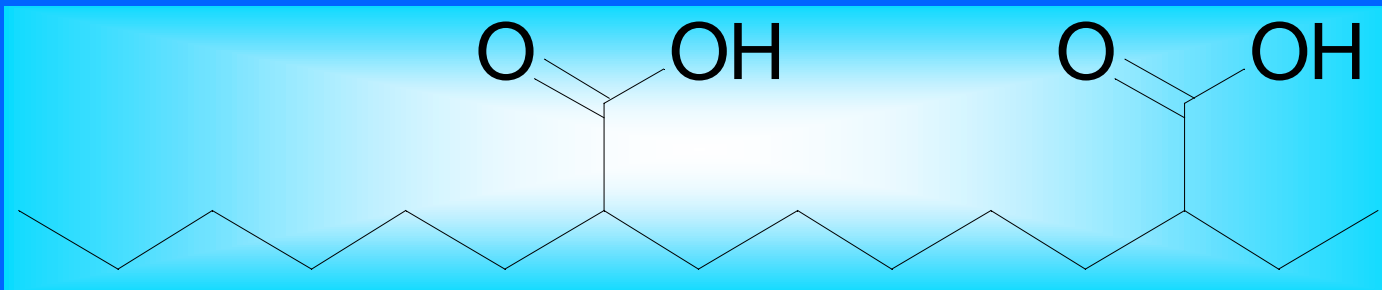
Photoresist Technology



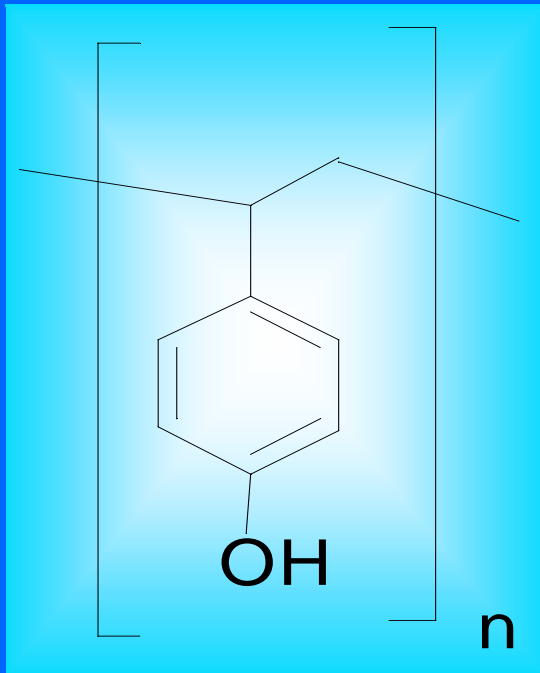
Photoresist positive



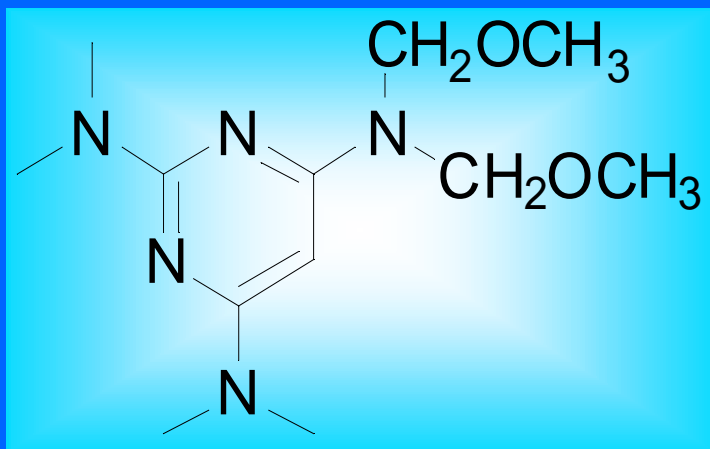
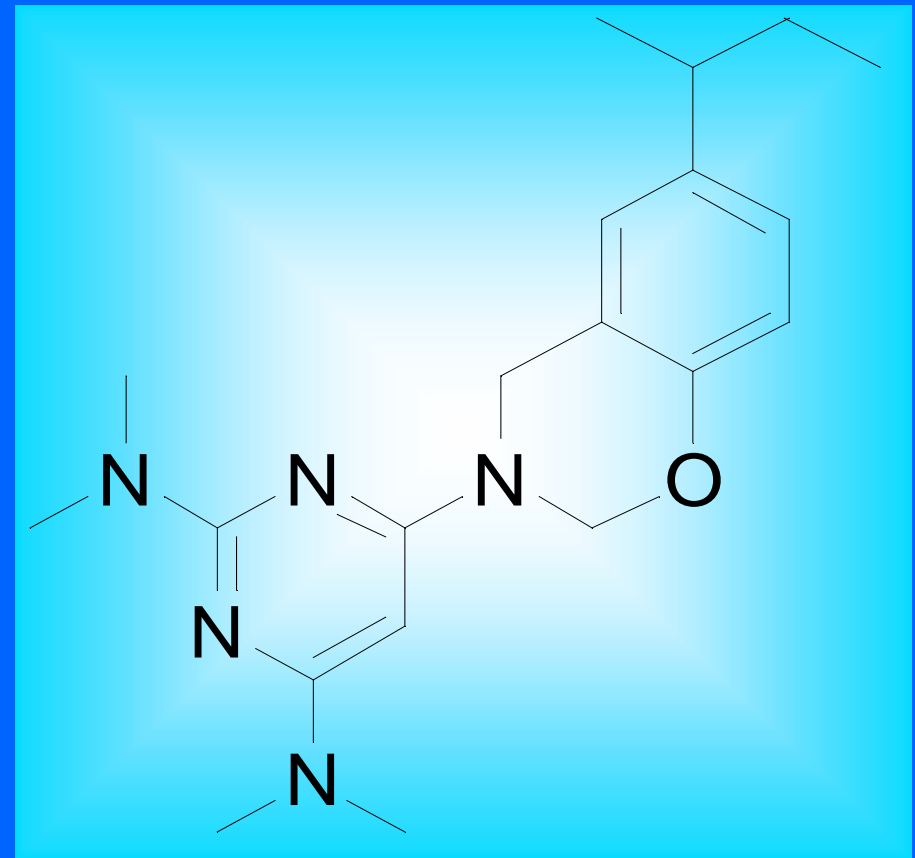
UV Exposure
H⁺



Photoresist negative

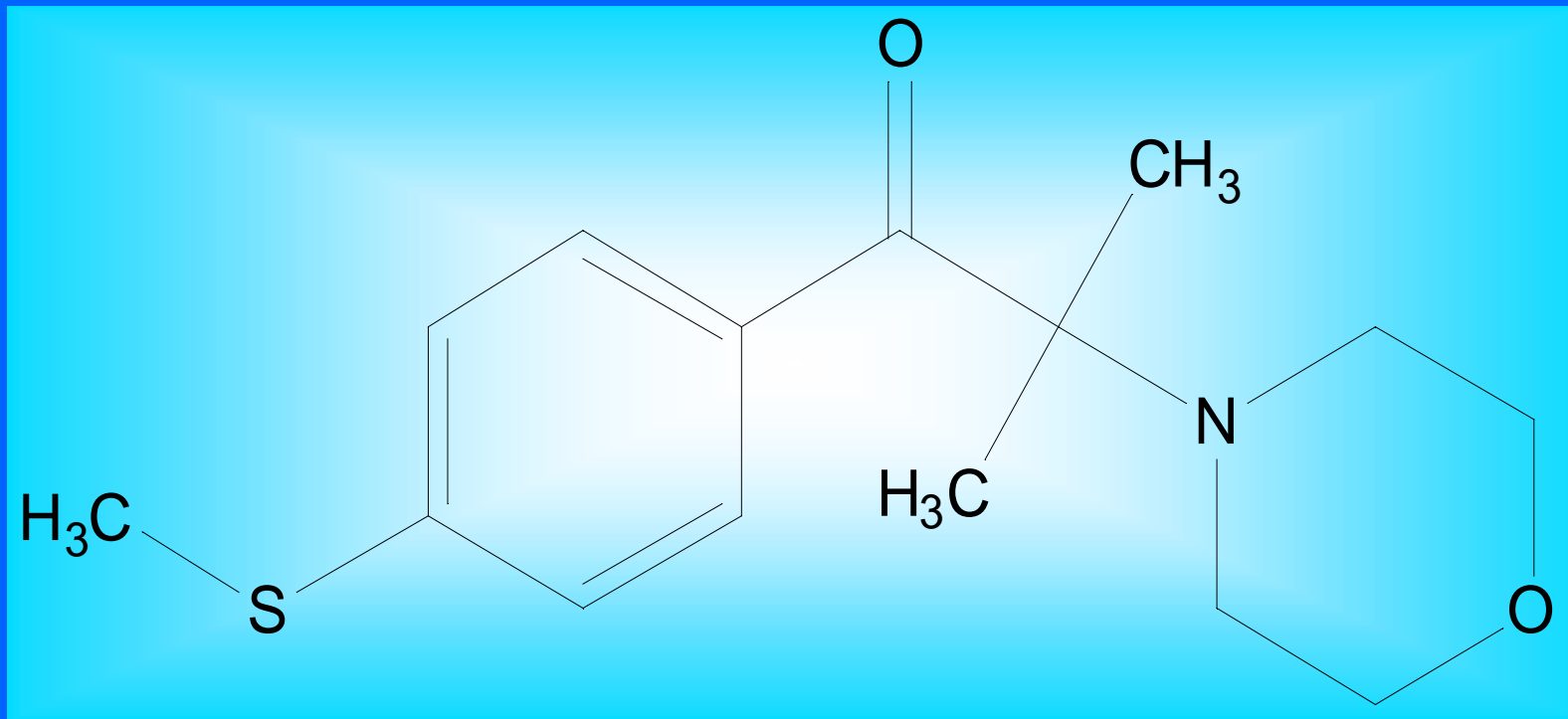


UV-Exposure
 H^+



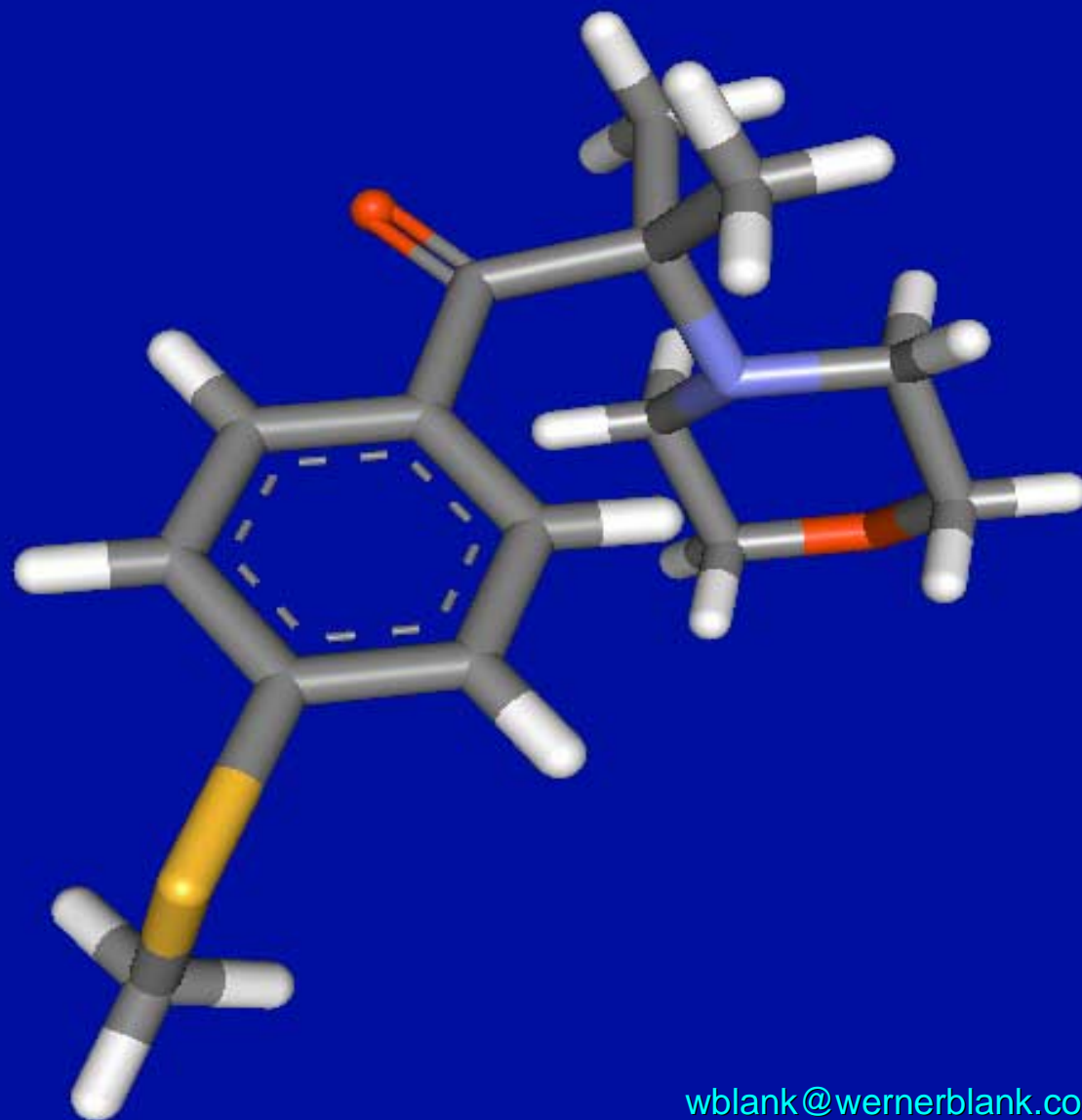
Photobase

Photoinduced Steric Release



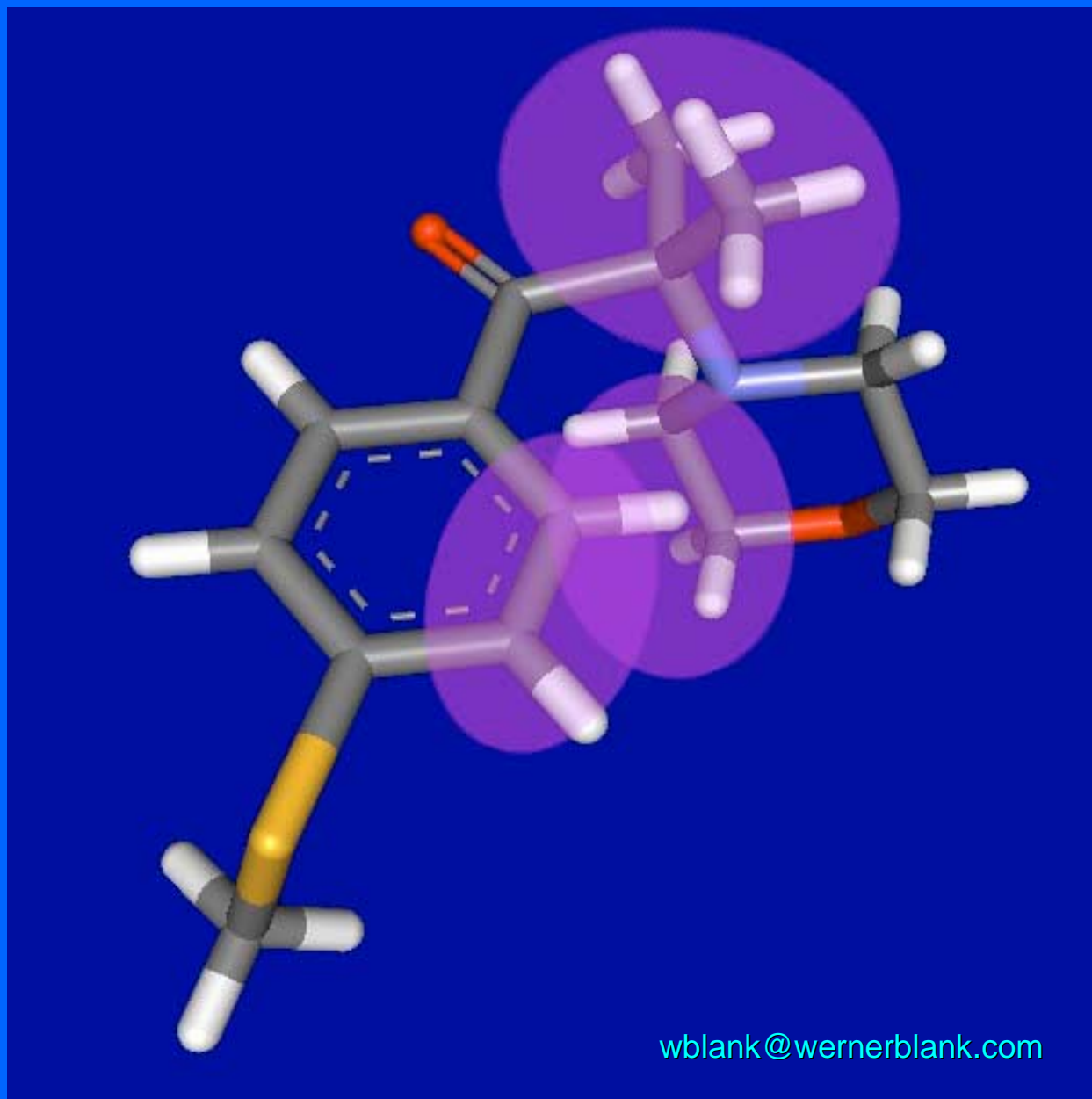
Ciba® IRGACURE® 907 - Ciba Specialty Chemicals

Photobase

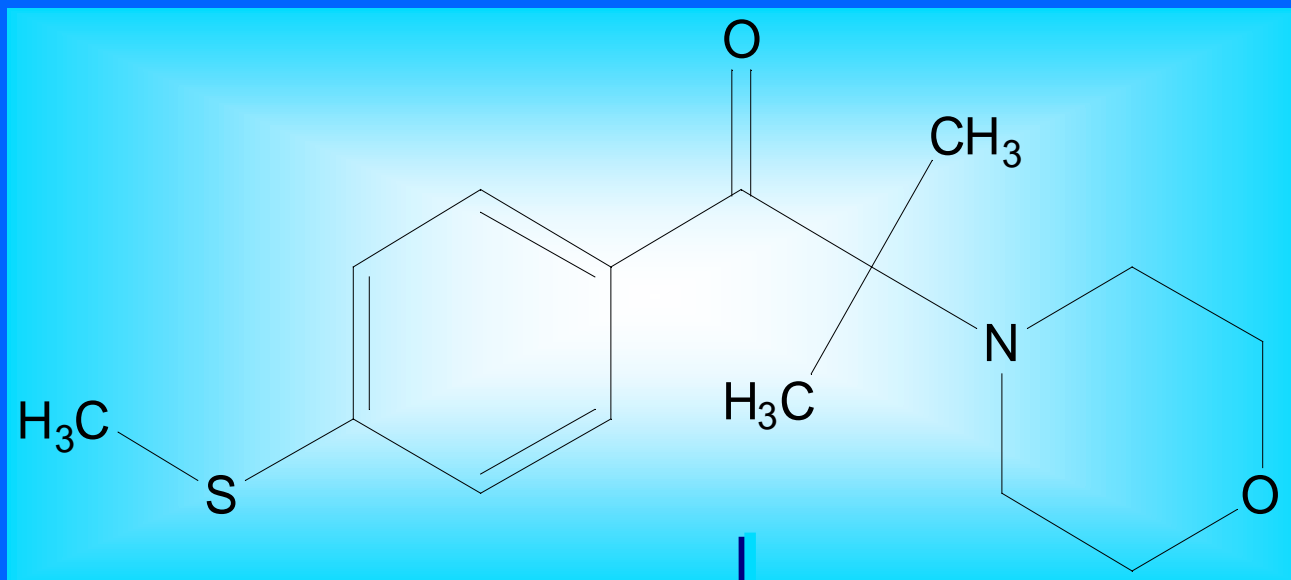


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Photobase Shielding



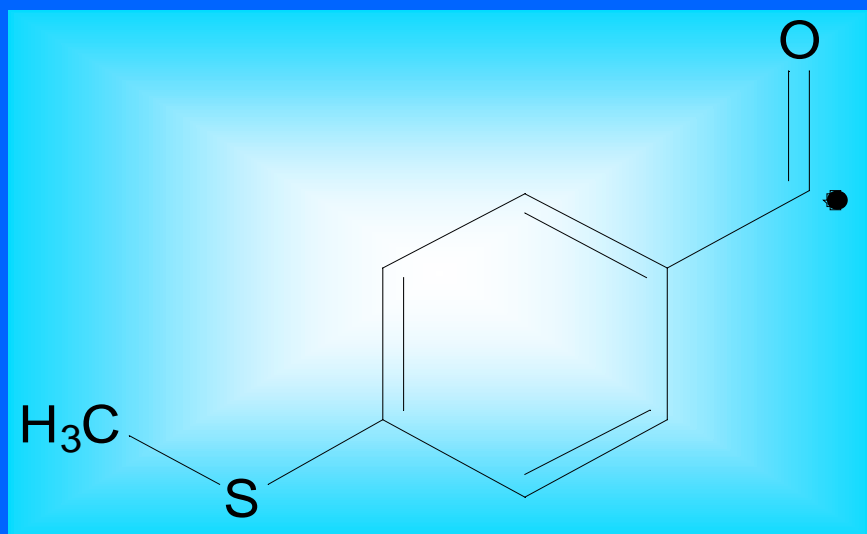
Photochemical Release of Active Amine



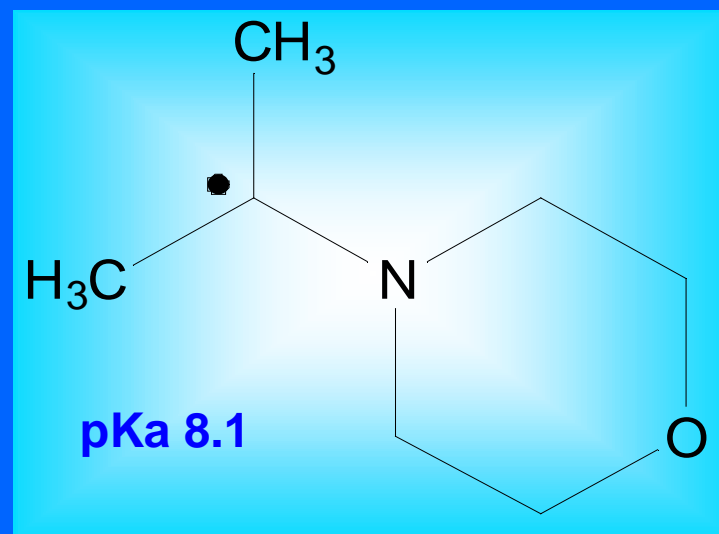
pKa 5.76

$h\nu$

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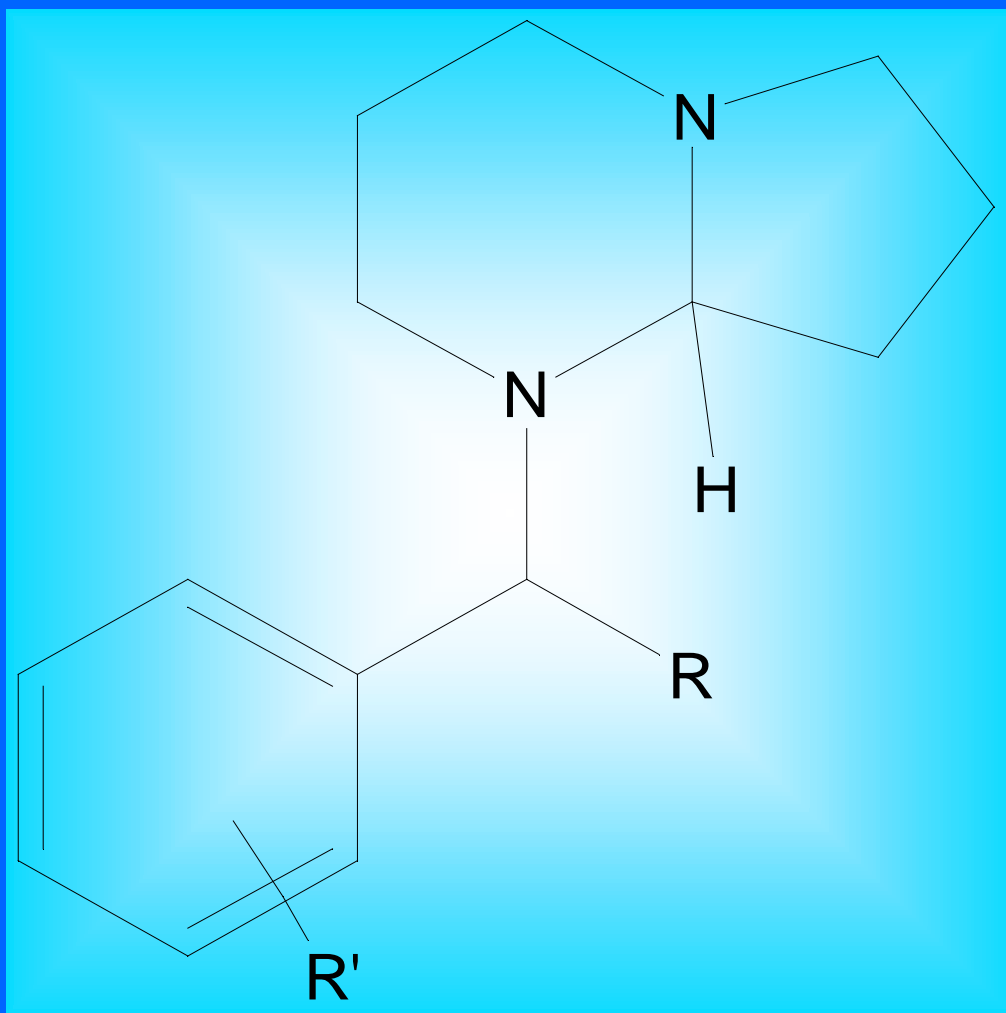


+



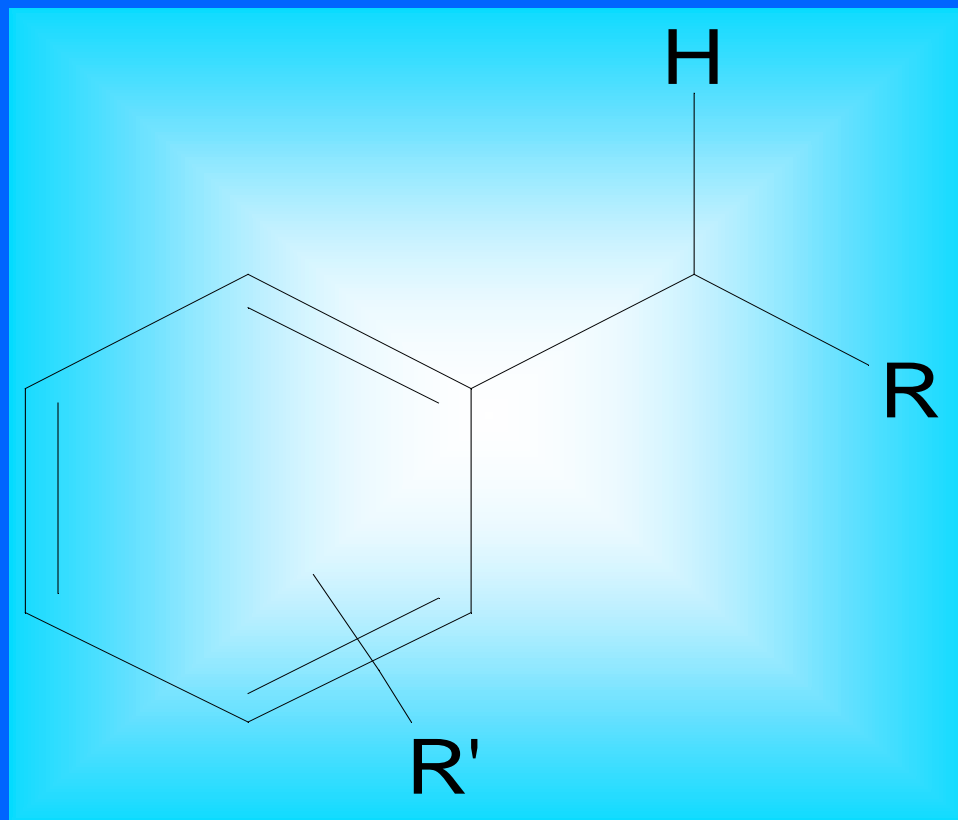
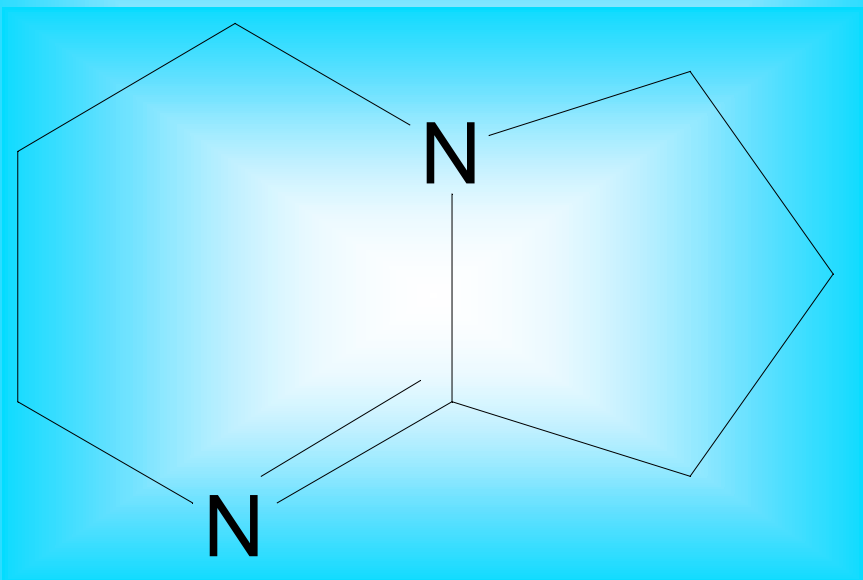
pKa 8.1

Photoinduced oxidative introduction of an amidine double bond



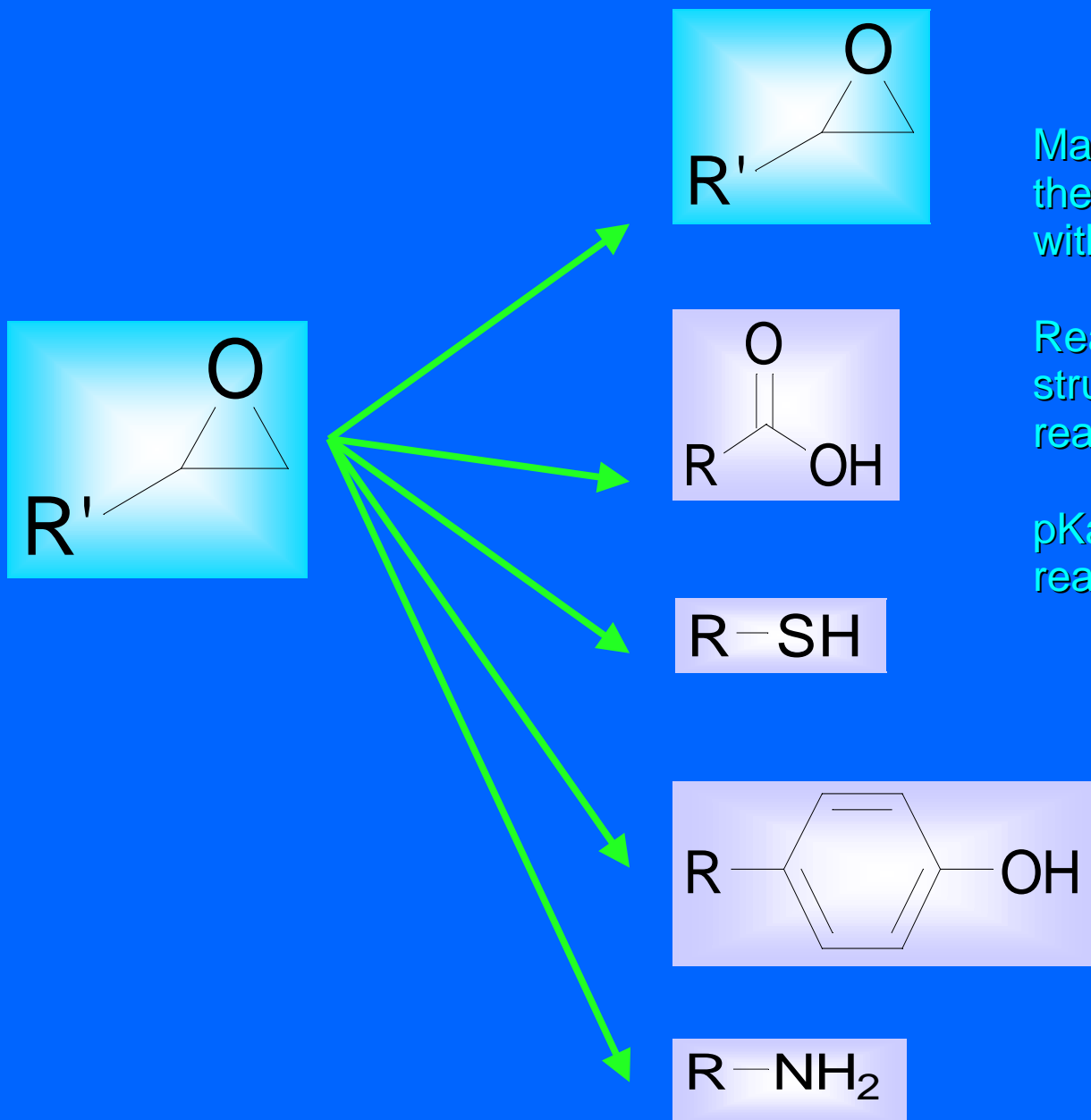
Ionic Form = L
pKa[HL/L+H; 2] = 8.96 ± 0.20
pKa[H₂L/HL+H; 5] = 1.68 ± 0.20
ACD ChemSketch pKa calculator

DBN release



$\text{pK}_a = 12.7$

Base Catalyzed Epoxy Reactions

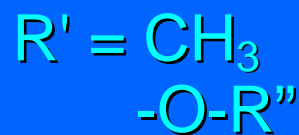
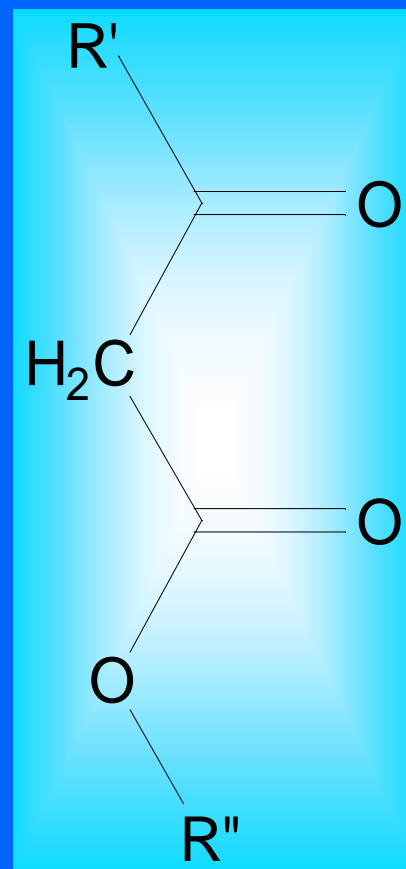
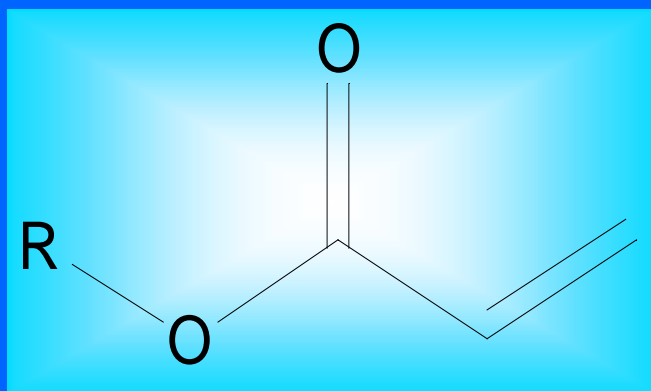


Many bases can catalyze the reaction of an epoxy group with a functional group

Reaction rate depends on the structure of the epoxy, the reactant and the amine catalyst.

pKa value does not determine reaction rate.

Base Catalyzed Michael Addition Reactions



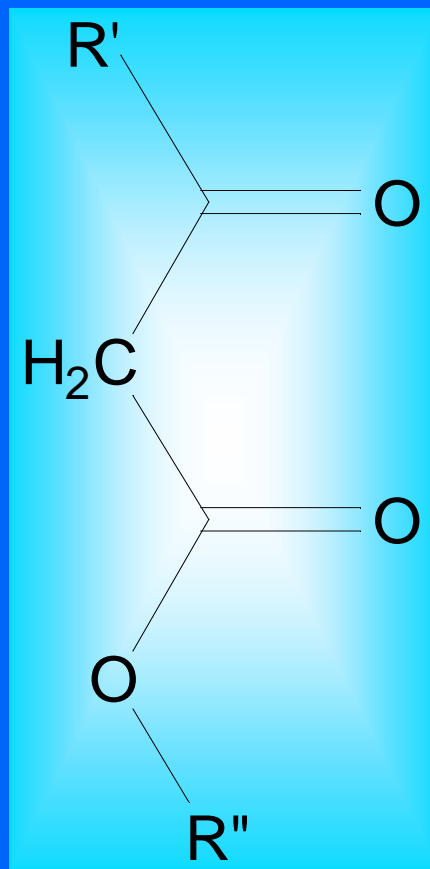
pKa 10.7
pKa 13.0



pKa 10.5

Base Catalyzed Isocyanate Reactions

R-NCO



R' = CH₃
-O-R''

pKa 10.7
pKa 13.0

R-OH pKa 17.0

R-SH pKa 10.7

H-OH pKa 15.7

References

First Commercial Photolatent Base Catalyst for UV-A Clearcoat Applications Kurt Dietliker, Tunja Jung, Johannes Benkhoff, Eugene Sitzmann Ciba Specialty Chemicals Inc., CH-4002 Basel, Switzerland, 8th Nürnberg Congress European Coatings Show 2005

Photolatent Amines: New Opportunities in Radiation Curing; Dietliker, K.; Jung, T.; Benkhoff, J. e!5 2004 (RadTech USA), Technical Conference, Proceedings, May 2-5, 2004.

Photoacid Generators for Microlithography; Ciba Specialty Chemicals, Product literature e-10/2006

157 nm University Resist Materials Research Project (LITJ102) International SEMATECH, Technology Transfer # 00073978A-ENG

Photobase Generation from Amineimide Derivatives and Their Use for Curing an Epoxide/Thiol System, SHIGEKI KATO, MASAMI YUSA Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 40, 4045–4052 (2002) ©2002 Wiley Periodicals, Inc.

New developments in catalysis. Blank, Werner J. (King Industries, Inc., Norwalk Ct 06897, USA). Macromolecular Symposia, 187(Quo Vadis-Coatings ?), 261-270 (English) 2002 Wiley-VCH Verlag GmbH.