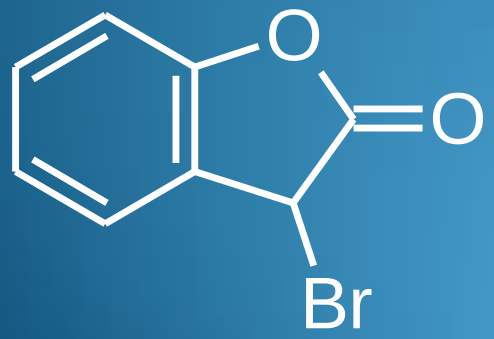
University Pardubice

Faculty of Chemical Technology

Institute of Organic Chemistry and Technology

SYNTHESIS AND REARRANGEMENT OF SUBSTITUTED S-(1-BENZOFURAN-2(3*H*)-ONE-3-YL) ISOTHIURONIUM-BROMIDES

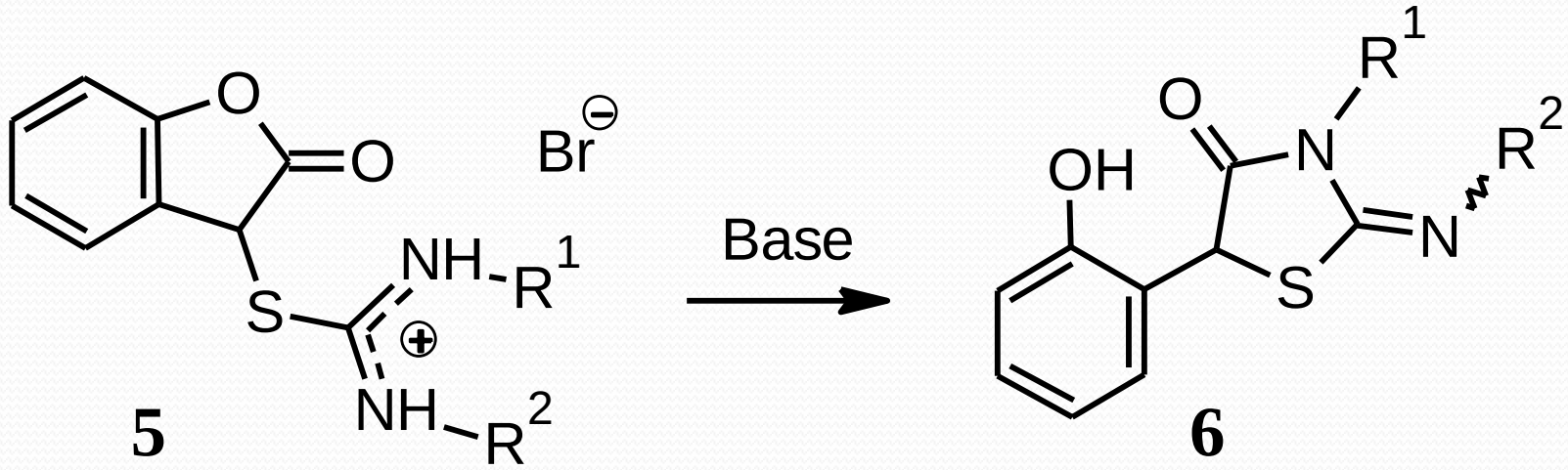


Ing. Richard Kammel

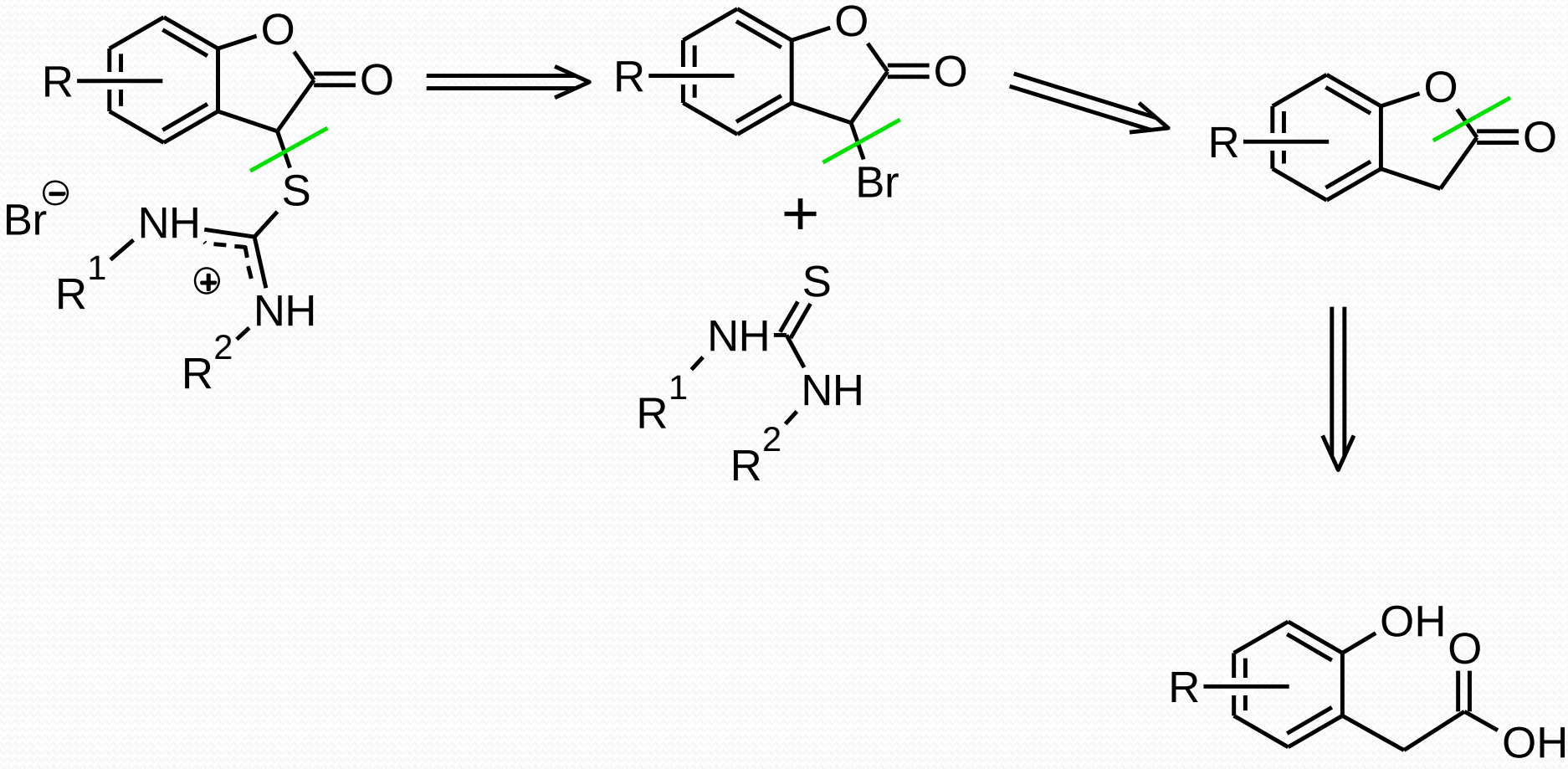
doc. Ing. Jiří Hanusek, Ph.D.

Goals of the thesis

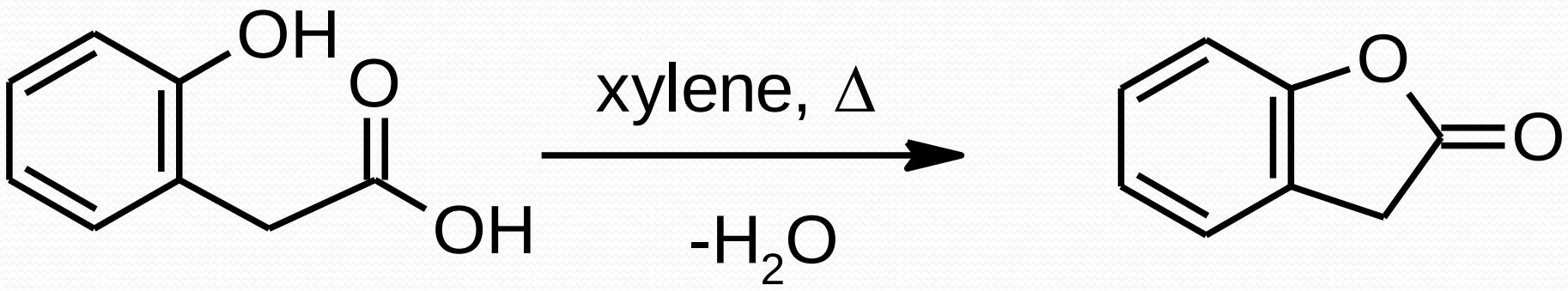
- Preparation of isothiuronium salts
- Preparation of transformation products of these salts
- The mechanism study of selected salt transformation



Retrosynthetic analysis



Lactonization (2-hydroxyphenyl)acetic acid



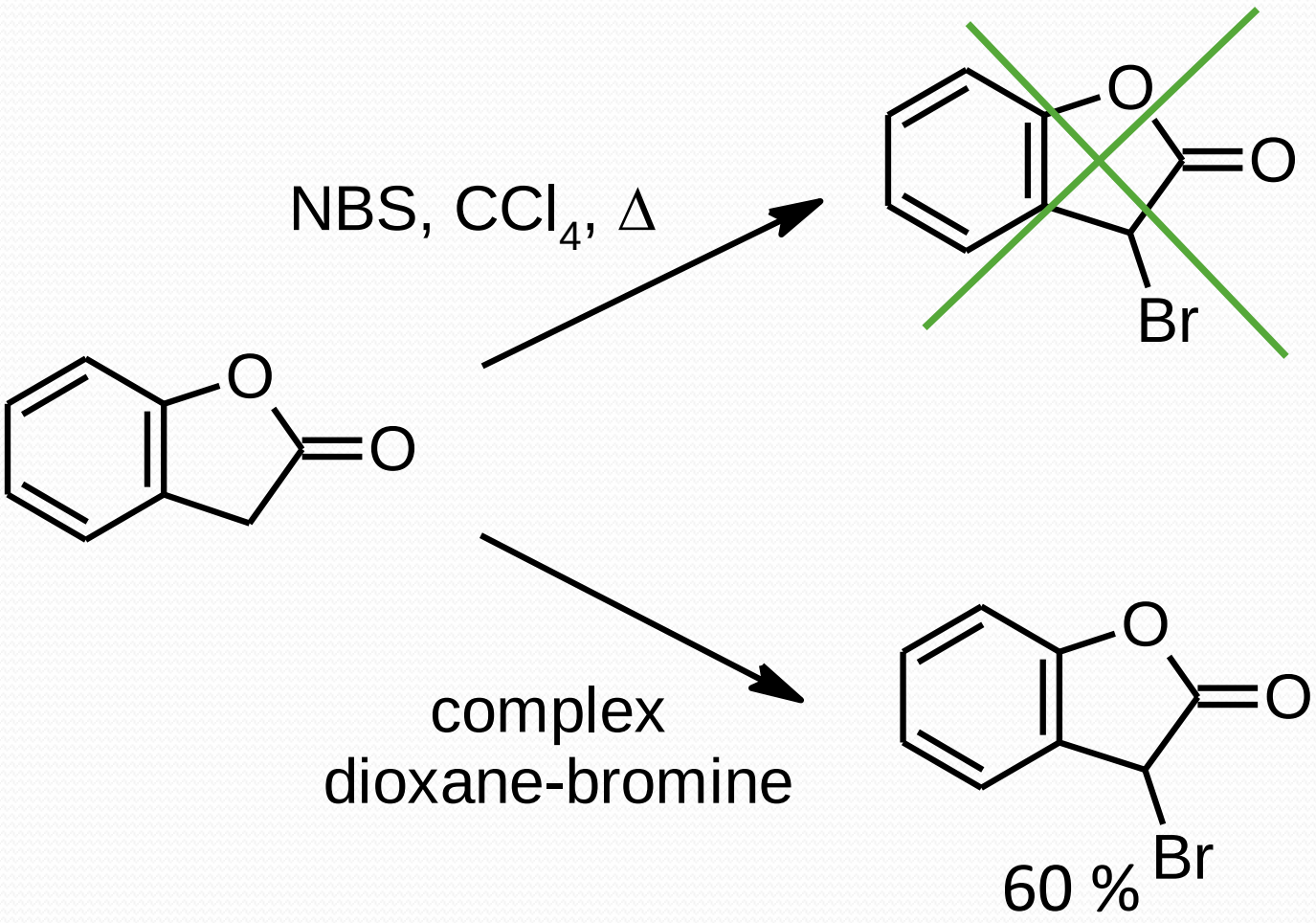
4 **5**

83 %

Kadin S. B.: *J. Med. Chem.* **1972,** *15,* 551-552

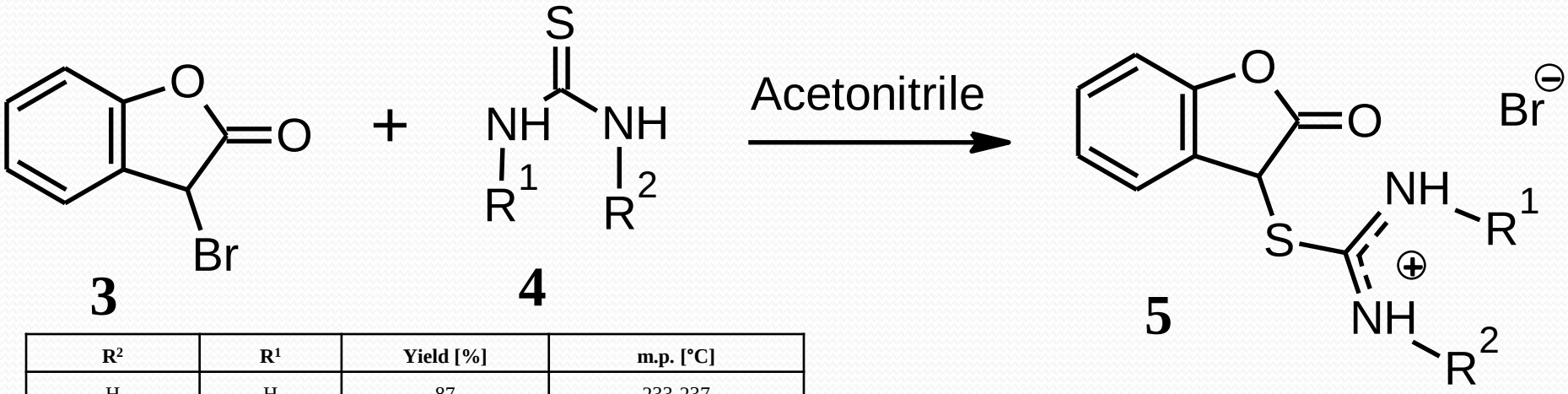
Kotten I. A.; Sauer R. J.: *Org. Synth.* **1973**, *Coll. Vol. 5*,145; **1962**, *Vol. 42*, 26.

Lactone bromination



Kotten I. A.; Sauer R. J.: *Org. Synth.* **1973**, *Coll. Vol. 5*,145; **1962**, *Vol. 42*, 26.
Abramenko P. I., Zhiryakov V. G.: *Chem. Heterocycl. Comp.* **1977**, *13*, 1194-119

Preparation of isothiuronium salts

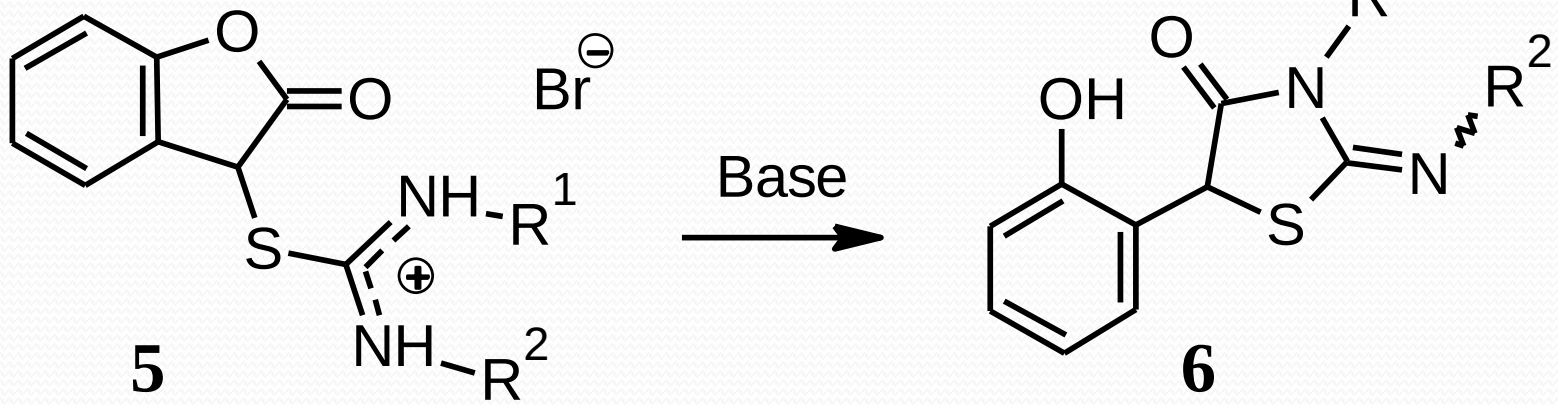


R²	R¹	Yield [%]	m.p. [°C]
H	H	87	233-237
CH_3	H	83	181-183
$CH(CH_3)_2$	H	83	223-233
$C(CH_3)_3$	H	67	207-219
Ph	H	65	209-213
4-CH_3Ph	H	71	215-233
4-CH_3OPh	H	85	211-232
4-BrPh	H	85	199-222
4-(CH_3CO)Ph	H	62	208-223
Py(2)	H	82	166-169
Bz	H	51	191-206
CH_3	CH_3	87	231-238
CH_2CH_3	CH_2CH_3	80	195-210
Ph	Ph	65	219-224
4-CH_3OPh	CH_3	58	175-207
CH_2	CH_2	88	181-185

51-87 %

Characterization : ^{1}H, ^{13}C NMR, elemental analysis, m.p., HRMS

Rearrangement of isothiuronium salts[1]

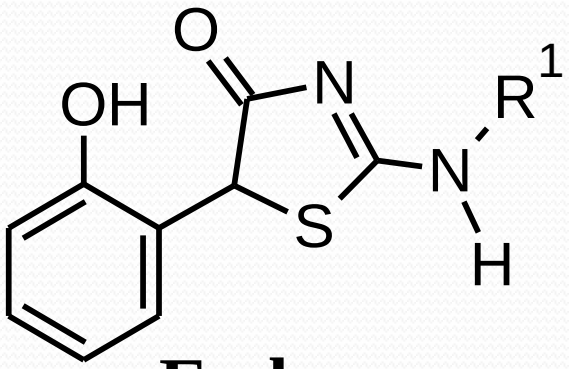


R²	R¹	Yield [%]	m.p. [°C]
H	H	83	212-214
CH_3	H	68	155-156
$CH(CH_3)_2$	H	68	200-201
$C(CH_3)_3$	H	95	210-212
Ph	H	82	203-205
4-CH_3Ph	H	91	197-201
4-CH_3OPh	H	86	166-168
4-BrPh	H	88	138-142
4-(CH_3CO)Ph	H	73	179-181
Py(2)	H	75	219-222
Bz	H	93	196-198
CH_3	CH_3	80	139-161
CH_2CH_3	CH_2CH_3	86	140-143
Ph	Ph	88	217-219
4-CH_3OPh	CH_3	69	216-219
CH_2	CH_2	70	126-129

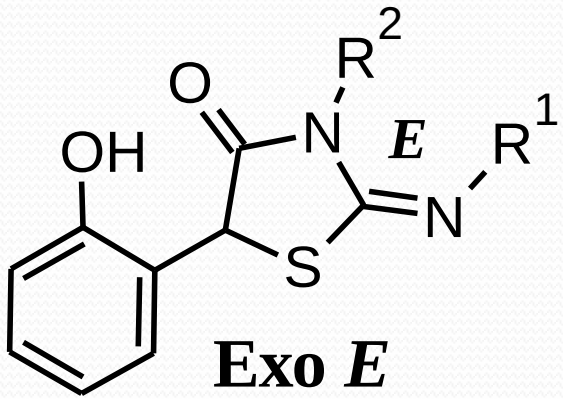
69-95 %

Characterization : ^{1}H, ^{13}C NMR, elemental analysis, m.p., HRMS

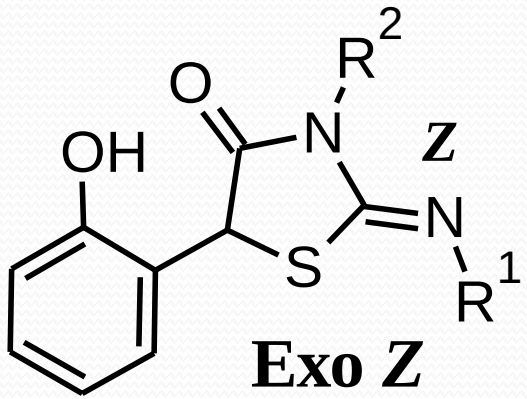
Tautomerism



Endo



Exo *E*



Exo *Z*