



PROBLEM 54

[SUPPL Problem 54 # 4]

Arabic compound numbers in TAPSOC,
Roman numerals in Supplementary material

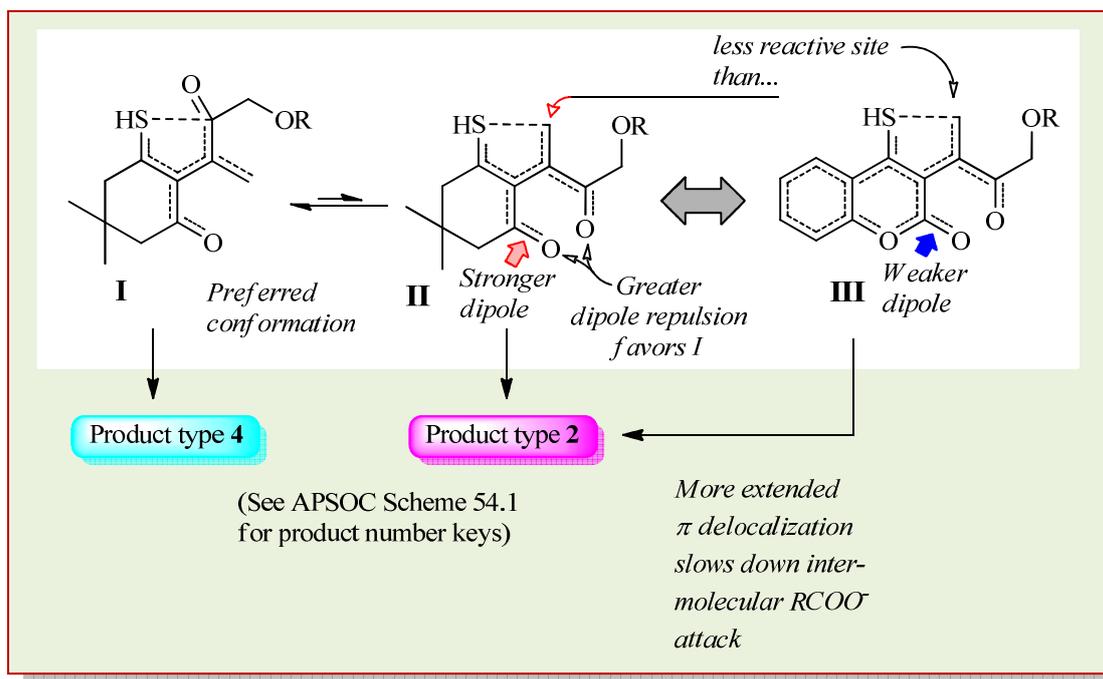
On the question of regioselectivity differences between 1 → 2 vs. 3 → 4.

This particular issue boils down to the competition between two nucleophiles (intramolecular RSH and intermolecular *m*-chlorobenzoate), and two electrophilic carbons in **16** vs **19**. The subject, which encompasses the useful criteria packed in the Swain-Scott nucleophilicity parameters, is not trivial (authors of the original work do not comment) and continues to attract the attention of the physical organic chemistry community [1].

Beyond theoretical considerations not accessible to this workbook, one might argue that, in addition to differences in the π MO extension in transition states **I** and **II**, conformations required for sulfur attack on the α,β -unsaturated ketone are also influenced by dipolar repulsion as depicted in Scheme SP54.4.1 (following page)

REFERENCE

[1] See, for example: Chamorro E, Duque-Noreña M, Notario R, Pérez P. J. Phys Chem. 2013;117:2636-2643, and references cited.



SCHEME SP54.4.1