HETEROCYCLIC SYSTEMS VIA FUNCTIONALLY SUBSTITUTED VINYL CARBANIONS

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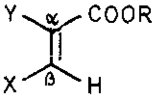
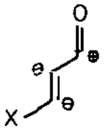
Highly selective reactions of polyfunctional systems are of great importance in synthetic organic chemistry. Direct ß- and/or α-C-lithiation of ß-functionally substituted acrylates 1 yields versatile building units without previous protection of the carboxylic functionality. This means that the generation of stable vinyl lithium derivatives prevails over the expected 1.2- or 1.4-addition of the lithiating agent to the acrylate system. The possible twofold lithiation offers a preparative versatility, which for structural reasons is not accessible to aryl- and hetaryl systems.



1

Y = H, alkyl, aryl, RO, R_2N
X = RO, R_2N, RS, ROOC



2

Butenolides, tetronates, cyclopentenones and derivatives, which are portions of many natural products, are easily accessible by applying this reaction principle[1]. A wide variety of substituents are compatible with this lithiation: alkyl-, aryl-, and electron donating substituents in α-position or for instance an electron withdrawing ester group in ß-position. Besides, lithiation of aminomethylene malonitrile derivatives led to a new azafulvene.

New extensions and applications of this valuable synthon 2 for highly functionalized heterocyclic syntheses will be discussed.

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1) R.R. Schmidt, J. Talbiersky and R. Betz, Chem.Ber. 115, 2674 (1982); O. Miyata and R.R. Schmidt, Angew.Chem. 94, 651 (1981); Angew.Chem.Int.Ed.Engl. 21, 775 (1982); and ref.