Selective Ring Transformations of 1-[2-(Trimethylsilylmethyl)cyclopropylcarbonyl]imidazoles

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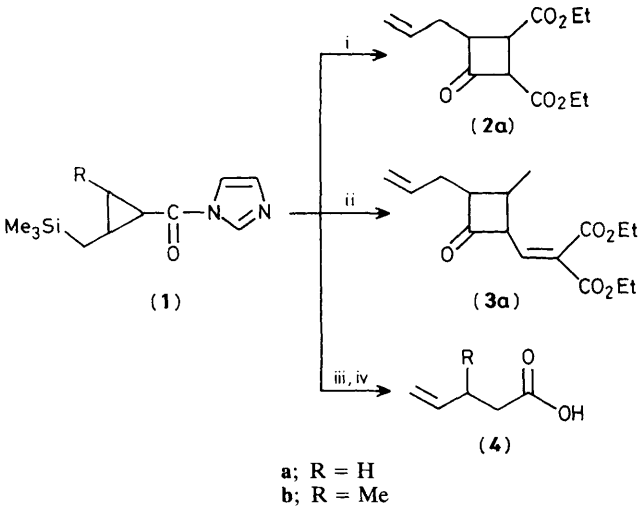
The title compounds underwent CsF- or $BF_3 \cdot Et_2$-induced selective ring-opening reactions leading to the cyclobutanone derivatives or γ,δ-unsaturated carboxylic acids, respectively.

The generation of a carbanion possessing an electrophilic centre provides potential synthetic intermediates. The high electrophilicity, however, prevents us from generating such a carbanion with bases. From this point of view, the fluoride-induced desilylation of trimethylsilylmethylisothiocyanate has been developed to give the isothiocyanato carbanion, which serves as a versatile building block for heterocyclic synthesis.[1] The present paper reveals that 1-[2-(trimethylsilylmethyl)cyclopropylcarbonyl]imidazoles (**1**) are candidates for this strategy.

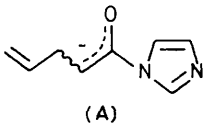
The 1-acylimidazoles (**1**) were directly prepared in high yields by the $Ni(CO)_4$-induced reductive carbonylation reac-



Scheme 1. *Reagents and conditions:* i, $EtO_2CCH{=}CHCO_2Et$ (6 equiv.), CsF (2 equiv.), MeCN, reflux, 6 h; ii, $MeCH{=}CH{-}CH{=}C(CO_2Et)_2$ (5 equiv.), $MeCH{=}C(CO_2Et)_2$ (1 equiv.), CsF (2 equiv.), MeCN, reflux, 5 h; iii, $BF_3 \cdot OEt_2$ (1 equiv.), CH_2Cl_2, room temp., 24 h; iv, H_2O.

tion of 1,1-dibromo-2-(trimethylsilylmethyl)cyclopropanes with imidazole.[2] Dropwise addition of (**1a**) to diethyl maleate in the presence of CsF in acetonitrile gave the 1:1 adduct (**2a**)† in 65% yield as the sole isolable product (Scheme 1). No reaction occurred in tetrahydrofuran (THF) or dichloromethane. The success of this transformation depends on the presence of the highly electrophilic 1-acylimidazole moiety probably assisting the attack of CsF on the silicon atom because benzyl 2-(trimethylsilylmethyl)cyclopropanecarboxylate did not undergo the ring-opening reaction under the conditions employed here.

A similar treatment with diethyl fumarate led to the same cyclobutanone (**2a**) in 58% yield as shown by comparison of spectral data. Thus, since the stereochemistry of the electrophile is lost, the stepwise mechanism involving the nucleophilic intermediate (A) seems to be operative. Another possible route to (**2a**) may involve the cycloaddition of allylketene [derived by removal of imidazolyl ion from (A)][3] with an olefinic compound and the subsequent equilibration of the adduct, but attempts to trap the ketene intermediate with cyclopentadiene were found to fail. The latter route is unlikely although the fast reversion of the ketene to (A) is undeniable.



(A)

In the reaction of (**1a**) with ethyl 2-ethoxycarbonyl-2,4-hexadienoate, the C–C bond formation occurred selectively at the γ,δ positions leading to the cyclobutanone (**3a**)† in 58% yield without detectable production of α,β-adducts. Curiously, the presence of ethylidene malonate is essential to achieve this transformation although the reason has not been clarified yet.

The combination of trimethylsilyl group and 1-acylimidazole moiety permits another selective conversion of (**1**) into the γ,δ-unsaturated carboxylic acids (**4**) on treatment with $BF_3 \cdot OEt_2$ [yields: (**4a**), 83%; (**4b**), 93%]. The acids (**4**) are formally regarded as the products of regioselective attack by the carboxycarbocation on allylsilanes because the preparation of (**1**) was initiated by the addition of dibromocarbene to allylsilanes. The reaction is also presumed to be facilitated by the presence of the silyl group.[4] With 1-(2-n-hexylcyclopropylcarbonyl)imidazole, no ring cleavage was observed.

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† Compound (**2a**): a mixture of stereoisomers, i.r. (neat) 1765—1715, 1645 cm^{-1}; ^1H n.m.r. (C_6D_6, 300 MHz) δ 0.8—1.2 (m, 6H), 2.5—2.7 (m, 2H), 2.9—3.2 (m, 2H), 3.4—3.6 (m, 1H), 3.8—4.2 (m, 4H), 5.0—5.2 (m, 2H), 5.6—5.9 (m, 1H); *m/z* 254 (M^+). Compound (**3a**): a mixture of stereoisomers, i.r. (neat) 1760—1710, 1690, 1650 cm^{-1}; ^1H n.m.r. ($CDCl_3$, 90 MHz) δ 1.1—1.4 (m, 9H), 2.0—2.5 (m, 2H), 2.7—3.1 (m, 3H), 4.0—4.4 (m, 4H), 4.9—5.2 (m, 2H), 5.5—6.1 (m, 1H), 6.5—6.6 (m, 1H); *m/z* 294 (M^+).

References

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