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Selective Conjugate Reduction of α,β-Unsaturated Esters and Amides via SmI_2-Promoted Electron Transfer Process

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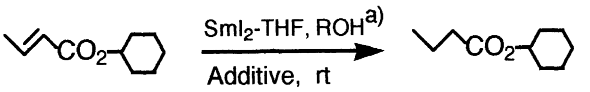
α,β-Unsaturated esters and amides were rapidly and selectively reduced to the corresponding saturated ones under mild conditions without affecting coexisting isolated double or triple bonds by using the reduction system, SmI_2–N,N-dimethylacetamide (DMA)–proton source.

The selective reduction of double bonds conjugated with ester groups is a useful reaction in organic synthesis and has been achieved by using $[(PPh_3)CuH]_6$,(1) Mg/MeOH,(2) $[PhSiH_3, Mo(CO)_6]$,(3) Zn-$NiCl_2$ under ultrasound radiation,(4) or NaHTe(5) as reagents. A SmI_2-promoted reduction of ethyl cinnamate has also been reported.(6) However, the method does not seem to have a general applicability because, for example, cyclohexyl crotonate was hardly reduced. In this paper we report the remarkable effect of additives on the above reaction and the particular system, SmI_2–DMA–proton source, which can be generally and effectively used for the conjugate reduction of a wide range of α,β-unsaturated acid derivatives.(7)

As shown in Table 1, the examination of additives on the reduction of cyclohexyl crotonate with SmI_2 has revealed very interesting facts; (1) the addition of basic polar compounds largely accelerated the electron transfer process and DMA was found to be most promissing for the conjugate reduction while the reductive dimerization was best promoted by the addition of HMPA(8) and (2) the use of bidentate ligands such as 1,2- or 1,3-diamine derivatives was also effective but in the presence of a tridentate chelating agent, N,N,N',N'',N''-pentamethyldiethylenetriamine, by which the coordination sphere of samarium might be completely occupied, no reaction took place at all, which strongly indicates that the coordination of substrates to samarium(II) is crucial for the present electron transfer reaction.

Table 1. Effect of Additives on the Reduction

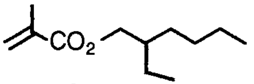
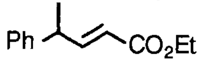
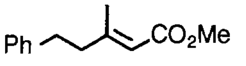
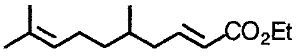
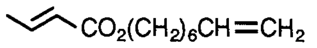
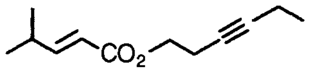
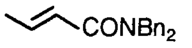
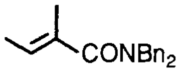


Run	Additive b)	Time	Yield/%
1	none	72 h	trace
2	DMF	5 min	67
3	DMA	2 min	92
4	TMU c)	15 min	45
5	NMP d)	15 min	10
6	HMPA	<1 min	7 e)
7	$Me_2N(CH_2)_3NMe_2$	6 h	82
8	$Me_2N(CH_2)_2NMe_2$	24 h	61
9	$[Me_2N(CH_2)_2]_2NMe$	24 h	N.R.

a) *t*-BuOH or cyclohexanol. b) 10–15 molar equiv.
c) Tetrametylurea. d) 1-Metyl-2-pyrrolidinone.
e) See the text.

Thus, under the optimized conditions, variously substituted α,β-unsaturated esters and amides were rapidly and selectively reduced without affecting coexisting isolated double or triple bonds. (Table 2)

Table 2. Selective Conjugate Reduction by Using SmI_2-DMA System[a)]

Entry	Conjugated ester or amide	Proton source	Time/min	Yield[b)]/%
1		*t*-BuOH	15	78
2		EtOH	12	96
3		MeOH	10	86
4		EtOH	2	97
5	Cholestery crotonate	*t*-BuOH	15	84
6		*t*-BuOH	2	92
7		*t*-BuOH	2	99
8		*t*-BuOH	5	30[c)]
9		*t*-BuOH	15	87
10		*t*-BuOH	3	99

a) To a solution of substrates (0.2 mmol) and proton sources (0.4 mmol) in THF (2-5 ml) was added successively a SmI_2-THF solution (0.1 mol dm^{-3}, 5 ml) and DMA (0.5 ml) under nitrogen. b) Isolated yield. c) The hydrodimer was isolated in 50% yield as a single isomer; see Ref. 8.

When the reduction of metyl cinnamate was carried out in the presence of CD_3OD as a "proton" source, deuterium was incorporated on both the carbons. This observation indicates that the reaction proceeds via a sequence of one electron reduction-protonation process transferring totally two electrons and two protons.

References

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