Tetrahedron Letters Vol. 22, pp 875 - 878
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0040-4039/81/0222-0875$02.00/0

CARBON-CARBON DOUBLE BOND CLEAVAGE
WITH A HARD LEWIS ACID AND ETHANETHIOL

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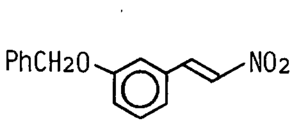
Summary: Double bonds activated by the electron withdrawing group(s) are cleaved with the reagent system consisting of a hard Lewis acid and ethanethiol to give dithioacetals.

A variety of carbon-oxygen bonds including alkyl ethers,[1-3] benzyl ethers,[4,5] methylenedioxy moiety,[2,3] esters,[6,7] and lactones[6] have been cleaved with the combination system of a hard acid and a soft nucleophile. All of those carbon-oxygen bond cleavage reactions have been accomplished by changing the balance between the pulling factor (the coordination of a hard acid with the oxygen atom) and the pushing factor (the nucleophilic attack of a soft nucleophile to the carbon atom). In the course of our investigation on the deblocking of benzyl ethers with the hard acid and soft nucleophile system, unexpected cleavage of carbon-carbon double bond of nitroolefin 1 with BF_3-etherate and ethanethiol to give 2 was observed.[5] Extention of this reaction has led to the development of a new type of the cleavage reaction of carbon-carbon double bond activated by the electron withdrawing group(s). The results of the cleavage of the styrene type double bonds are summarized in Table I. The order of the activity of metal halides (entries 5-8) corresponds to that of the reported hardness of them.[8]



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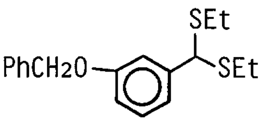

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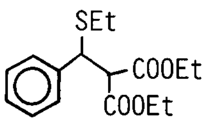

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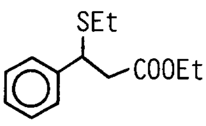

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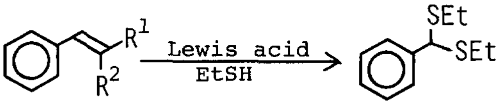
Table I. Double Bond Cleavage of 3



3 4

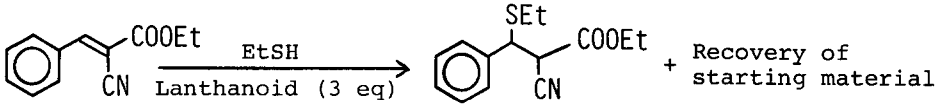
Entry	Compound 3		Conditions				Yield of 4, %
	R^1	R^2	Lewis acid	(eq)	Temp	Time, h	
1	NO_2	Me	$BF_3\cdot OEt_2$	(10)	r.t.a)	1.0	47.6
2	NO_2	Et	$BF_3\cdot OEt_2$	(10)	0°	0.5	51.6
3	COMe	COMe	$AlCl_3$	(3)	0°	0.28	87.3
4	COOEt	CN	$BF_3\cdot OEt_2$	(20)	r.t.	180	87.6
5	COOEt	CN	$ZnCl_2$	(3)	r.t.	72	13.3
6	COOEt	CN	$FeCl_3$	(3)	r.t.	96	69.9
7	COOEt	CN	$AlCl_3$	(3)	r.t.	0.5	84.0
8	COOEt	CN	$AlBr_3$	(3)	r.t.	0.28	94.3
9	COMe	COOEt	$AlCl_3$	(3)	0°	0.42	77.5
10	COOEt	COMe	$AlCl_3$	(3)	0°	0.33	82.7
11	CN	CN	$BF_3\cdot OEt_2$	(20)	r.t.	156	60.8
12	CN	CN	$AlCl_3$	(3)	0°	0.25	>99
13	COOEt	COOEt	$BF_3\cdot OEt_2$	(3)	r.t.	72	71.2b)
14	COOEt	COOEt	$AlCl_3$	(3)	0°	0.42	94.2
15	COOEt	H	$AlBr_3$	(3)	r.t.	2.5	0c)

a) Room temperature. b) The adduct 5 was obtained in 28.3% yield.

c) A 2:3 mixture of 6 and starting material (determined by ^{1}HNMR) was obtained.

Rare earth chlorides have been reported to be efficient catalysts for the acetalization of aldehydes.9) Some rare earth chlorides tested were shown to be uneffective for the double bond cleavage of 3 (R^1=COOEt, R^2=CN) and gave rise to the Michael adduct 7 in some cases (see Table II).

Table II. Lanthanoids as a Lewis Acid



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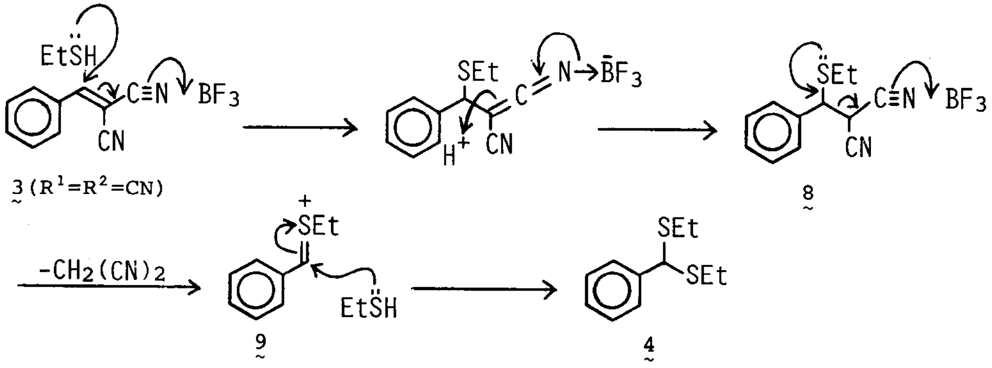
Lanthanoid	Reaction time (day)	Ratio of 7 : 3(R^1=COOEt,R^2=CN)
$YbCl_3 \cdot 6H_2O$	4	1 : 0
$LaCl_3 \cdot 7H_2O$	7	1 : 1
$CeCl_3$	2	0 : 1

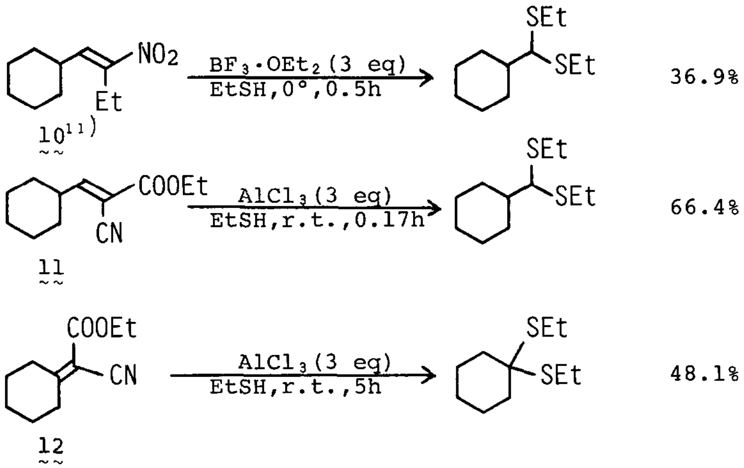
The possible mechanism of the double bond cleavage reaction is shown in Scheme 1. Thus, the Michael addition of ethanethiol takes place to afford the adduct 8 which is converted into the sulfonium species 9 by the loss of the active methylene moiety. Addition of another molecule of ethanethiol completes the overall transformation. Or another pathway involving the direct attack of ethanethiol on 8 in S_N2 sence giving 4 is also possible. The formation of the Michael adduct in the first stage was confirmed by the fact that the intermediate 8 prepared from 3 (R^1=R^2=CN) with ethanethiol afforded 4 in 91.0% yield with $AlCl_3$ (3 eq) in ethanethiol. The double bond cleavage reaction seems to proceed smoothly when the conjugate base of the active methylene compound is stable. A close inspection of Table I reveals that whether the reaction ceeses at the stage of the Michael addition or proceeds further to cleave the carbon-carbon bond depends upon the pKa-value of the leaving active methylene group. Those compounds which have the leaving group of smaller pKa-value than diethyl malonate (approximate pKa in water is 14)[10] can be cleaved with those reagent systems listed in Table I.

Scheme 1. The Possible Mechanism of Carbon-Carbon Double Bond Cleavage



Double bonds in the aliphatic compounds **10**, **11**, and **12** were also cleaved with the Lewis acid and ethanethiol system though the yields were fairly low (Table III).

Table III. Double Bond Cleavage of Aliphatic Compounds



10[11)] **11** **12**

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(Received in Japan 22 November 1980)