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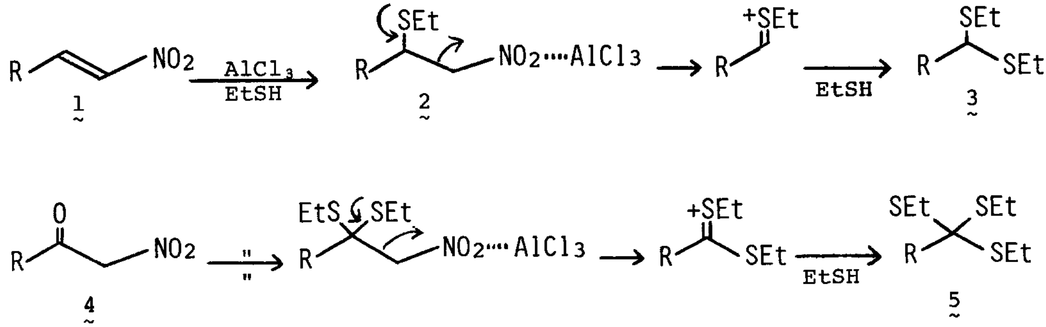
REDUCTIVE DISPLACEMENT OF THE NITRO GROUP INTO HYDROGEN IN PRIMARY *α*-NITROKETONES

Manabu Node, Takeo Kawabata, Masaru Ueda, Mayumi Fujimoto,
Kaoru Fuji,* and Eiichi Fujita
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

Summary: The nitrogroup in primary *α*-nitroketones is converted into hydrogen with aluminum chloride and ethanethiol.

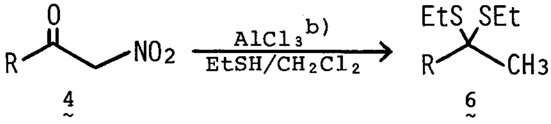
We have studied the synthetic utility of the combination system of a hard acid and a soft nucleophile. This reagent system has been shown to be effective for the cleavage of various carbon-oxygen bonds[1] and the reduction of functionalized polycyclic aromatics.[2] The activated carbon-carbon double bonds such as nitroolefin 1 could be cleaved to give the dithioacetal 3 as shown in Scheme 1.[3] α-Nitroketones 4 should give the orthothioester 5 under the same reaction conditions if the same type of mechanism is operative. Unexpectedly however, the attempted reaction of 4(R=C_6H_5) with aluminum chloride and ethanethiol afforded a 78% yield of the dithioacetal 6(R=C_6H_5), where the nitro group was replaced by the hydrogen atom. Though several methods for the reductive transformation of the nitro group into hydrogen have been reported,[4] none of them could be applied to primary nitro compounds. Thus, it is worth studying the generality of this reductive displacement. Primary α-nitroketones 4 listed in the Table were converted into the corresponding dithioacetals 6 in acceptable yield.

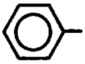
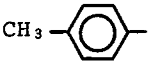
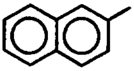
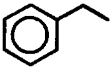
Scheme 1.



In contrast to the reported one electron transfer process for the reductive displacement of the nitro group into hydrogen,[4] the nitro group-hydrogen exchange using the present system seems to be specific to primary nitro compounds, which suggests the possible mechanism involving the ionic process as shown in Scheme 2. This process was supported by the fact that dithioacetal **7** and vinyl sulfide **8** synthesized through the definite route gave **6**($R=C_6H_5$) under the same reaction conditions employed for **4**($R=C_6H_5$). The formation of diethyl disulfide (**9**) is another proof for this process. To our knowledge, this is the first report on the reductive displacement of the nitro group to the hydrogen atom in acidic media.

Table. Reductive displacement of the nitro group into hydrogen.a)



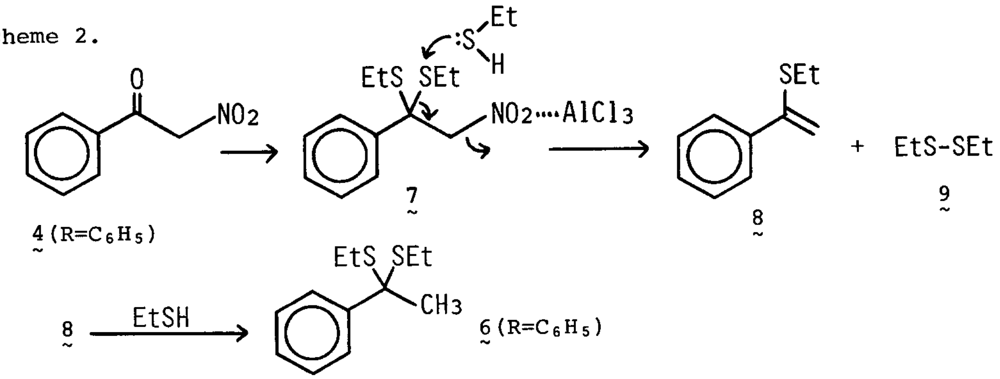
R	Mol eq. of $AlCl_3$	Temp.	Time (h)	Yield (%)
	3	r.t.	3.5	78
	3	r.t.	8	60
	3 + 2c)	r.t.	20	66
	3 + 2c)	0°-r.t.	8	60
$CH_3(CH_2)_5$-	3 + 2c)	0°-r.t.	8	57

a) All reactions were run in argon.

b) Purified by sublimation.

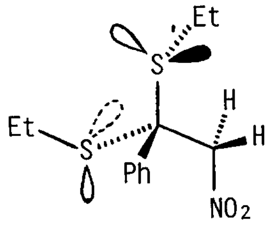
c) Additional 2 mol eq. of $AlCl_3$ was added after several hours. Use of 5 mol eq. of $AlCl_3$ from the beginning is to be avoided because the amount of the byproduct from the Nef-type side reaction is increased.

Scheme 2.

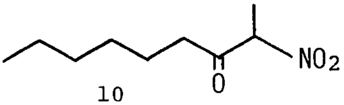


Different mode of the reaction between 2 and 7 could be attributed to the polarizability of the carbon-sulfur bond. Deslongchamps et al[5] have shown that in the most stable conformation of dithioacetals one of the lone pair orbitals on each sulfur atom should be oriented antiperiplanar to another carbon-sulfur bond. Application of this principle to dithioacetal 7 leads the conformation shown in Fig. 1 as a most plausible one. Thus, a carbon-sulfur bond of 7 is more susceptible to the attack of the ethanethiol than that of 2, bacause of the stereoelectronic assistance of the lone pair of the adjacent sulfur atom.

Fig. 1 The most plausible conformation of 7.



A synthetic utility of this transformation involves the use of nitromethane as a methyl anion equivalent, which can be used under the milder conditions than those required for the methyl anions such as methyl lithium or the methyl Grignard reagents, since α-nitroketones 4 was obtained from the reaction of carboxylic acids[6] or acyl cyanides[7] with nitromethane in the absence of the strong base.[8]



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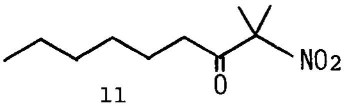

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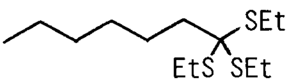

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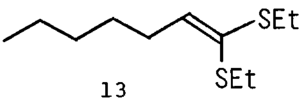

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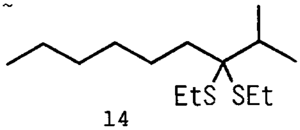

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In the case of secondary α-nitroketone **10**, the expected cleavage of the carbon-carbon bond occurred with aluminum chloride and ethanethiol in dichloromethane to give orthothioester **12** and ketene thioacetal **13** in 57% and 12% yield respectively. The same treatment of tertiary α-nitroketone **11** afforded **12** (40%) and **13** (23%) along with the dithioacetal **14** (18%), in which the nitro group was displaced by hydrogen. Studies of the difference of the reactivity of those α-nitroketones under these conditions are in progress.

References and Notes

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