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Stannous Iodide–HCl in Tetrahydrofuran: A New System for the Reduction of various Nitro Compounds. Mild Conversion of 6-Nitro-Δ^5-Steroids to 6-Keto-steroids

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It has been shown that 6-nitro-Δ^5-steroids, nitrostyrene and saturated aliphatic nitro compounds in tetrahydrofuran are reduced efficiently with stannous iodide and a catalytic amount of concentrated hydrochloric acid to the corresponding 6-ketosteroids, oximes or hydroxylamine derivatives in good yields, respectively.

A literature survey indicates that stannous iodide has been exploited very little for chemical transformations.[1] Luche *et al.* have reported the formation of iodohydrins for the reaction of stannous iodide with epoxides.[2] However, there is no report on its application as a reducing agent for organic compounds. Nitro compounds, because of their high nucleophilicity and easy preparation, are valuable and occasionally superior precursors to a large number of target molecules as well as important intermediates in organic synthesis.[3] Since the conversion of the nitro functionality into another functional group, especially the carbonyl group, is an important transformation in organic synthesis[4] and becuse of our continuing interest in the development of efficient reducing agents for this type of transformation,[5] we decided to study the reduction of various nitro compounds with stanous iodide and the results are presented in this communication.

Reaction of 3-β-acetoxy-6-nitrocholest-5-ene **1b** with stannous iodide in tetrahydrofuran (THF) furnished the unchanged starting material after 24 h of stirring at room temperature. However, when the reaction was catalysed with two drops of concentrated HCl, 3β-acetoxycholestan-6-one **2b** was obtained in 80% yield. Similarly, the reaction of 6-nitrocholest-5-ene **1a**, 3β-chloro-6-nitrocholest-5-ene **1c**, 3β-methoxy-6-nitrocholest-5-ene **1d** and 3-nitro-5α-cholest-2-ene **3** with stannous iodide (catalyst HCl) furnished the corresponding ketones **2a**, **2c**, **2d** and **4** in 60–80% yield (see Table). Reaction of **1b** and **1c** with tin(II) chloride (catalyst HCl) was messy and gave a mixture of several products in each case.[5a]

Reaction of 1-nitro-1-cyclohexene **6** with stannous iodide (catalyst HCl) in THF furnished the cylohexanone oxime **7** in 95% yield. Reaction of β-nitrostyrene **8a** and β-methyl-β-nitrostyrene **8b** with the same reagent furnished the corresponding phenylacetaldehyde oxime **9a** and 1-phenylacetone oxime **9b**, respectively.†

Reaction of the nitro compounds **10** obtained from a natural product[6] and the compound **16** with SnI_2 (catalyst HCl) furnished the ketone **11** and triketone **17**, respectively, thus demonstrating the versatility of this reagent.

We have also studied the reaction of nitroalkane, 3β-chloro-6-nitrocholestane **5** with SnI_2 (catalyst HCl). The reaction was found to proceed very slowly in comparison to unsaturated analogue **2c** and after 24 h of stirring at room temperature, the ketone **2c** was isolated in 80% yield. When this reaction was stopped after 12 h, the oxime of ketone **2c** was isolated in 40% yield. However, no oxime of the ketone **2c** could be isolated (or detected while monitoring the reaction on TLC) during the reaction of **1c** with SnI_2. It is to be noted here that when oximes were treated with SnI_2 (catalyst HCl), the corresponding ketones are obtained in quantitative yield.[7] Oximes of aldehydes and ketones represent a series of derivatives for the classical identification of carbonyl compounds and also serve as intermediates for many reactions such as the preparation of amides by the Beckmann rearrangement.[8]

Reaction of 5-methyl-5-nitrohexan-2-one **12** with SnI_2 (catalyst HCl) furnished the pyrroline-1-oxide **13**. It is interesting to note that the reaction of 1-nitrodecane **14a** with this reagent combination gave only the corresponding hydroxylamine derivative **14b**. However, compound **13c** was detected

† For a comparison of this reaction with sodium stannite ($SnCl_2$–NaOH) reduction of nitroalkenes, see R. S. Verma, M. Verma and G. W. Kabalka, *Tetrahedron Lett.*, 1985, **26**, 6013.

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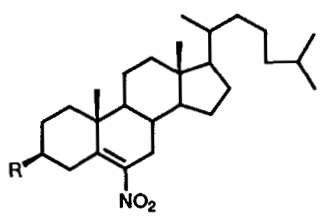

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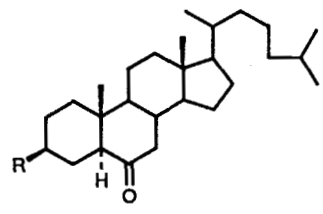

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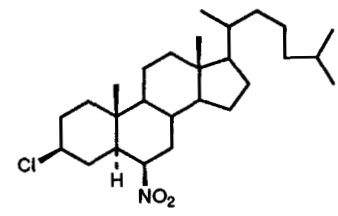

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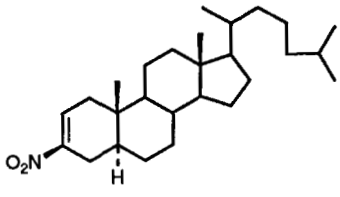
b R = OAc
c R = Cl
d R = OMe



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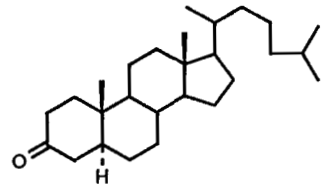

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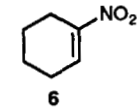

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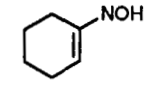

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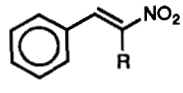

8

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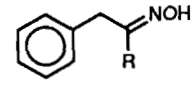
b R = Me



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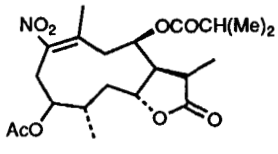

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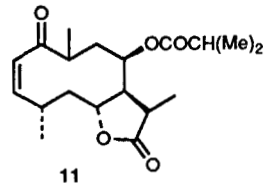

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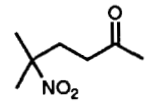

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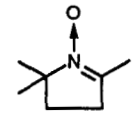


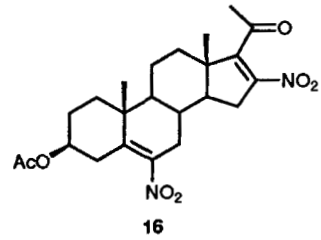
13

14

a R = NO_2
b R = NHOH
c R = CNO

15

a R^1 = H,NO_2 R^2 = CH_2COMe
b R^1 = NOH R^2 = CH_2COMe
c R^1 = H,NO_2 R^2 = Me
d R^1 = NOH R^2 = Me



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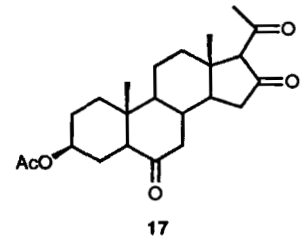

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Table 1 Reduction of nitro compounds with stannous iodide (catalytic HCl in THF).

Entry	Substrate	Product[b,c]	Time/h	Isolated yield (%)[d]
1	**1a**	**2a**	12	70
2	**1b**	**2b**	10	80
3	**1c**	**2c**	8	82
4	**1d**	**2d**	6	80
5	**3**	**4**	6	62
6	**5**	**2c**	24	80
7	**6**	**7**	2	95
8	**8a**	**9a**	2	85
9	**8b**	**9b**	2	85
10	**10**	**11**	8	60
11	**12**	**13**	22	75
12	**14a**	**14b**	7	90
13	**15a**	**15b**	6	95
14	**15c**	**15d**	6	95
15	**16**	**17**	10	90
16	Nitrobenzene	No reaction	24	—
17	*o*-Hydroxy-nitrobenzene	No reaction	24	—

[a] In a typical reaction, 1 mmol of the substrate in 5 ml of THF was treated with 2.50 mmol of stannous iodide with stirring at room temperature. Two drops of concentrated HCl (0.58 mmol HCl in 2.14 mmol water) were added after 5 min and the reaction was followed by TLC until the disappearance of the starting material. Dilution of the reaction mixture with water, followed by extraction with dichloromethane (4 × 75 ml) and washing successively with sodium thiosulfate solution and brine and evaporation of the dried solution furnished a crude material which was purified by preparative TLC. [b] All compounds were characterized by IR, NMR and mass spectroscopy and by direct comparison with authentic samples. [c] NMR spectral analysis of the oximes showed the formation of both *syn* & *anti* isomers in 60:40 ratio. [d] THF was found to be the best solvent for this reduction procedure. In case of entries 7, 8, 12–14 yield is determined by GLC.

in the reaction mixture and was found to convert into **14b** during the course of the reaction.

The difference between reaction of the steroidal nitroalkenes and compounds **6** and **8** to give the corresponding oxime is noteworthy. Aromatic nitro compounds are found to be resistant to this reducing system (entries 16 and 17 in Table 1). Thus, this simple and mild procedure for converting vinyl nitrosteroids to ketosteroids could be a useful addition to the existing methods, such as the standard method of Zn/acetic acid where refluxing conditions are invariably required.[9]

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