Reaction of Nitro-alkenes with Iodotrimethylsilane: A New Method for the Conversion of Vinyl Nitrosteroids to Ketosteroids

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Iodotrimethylsilane generated *in situ* from chlorotrimethylsilane and sodium iodide effects the reduction of nitro-alkenes (**1a**—**e**) and (**5**) at −5 to 0 °C to furnish the ketones (**2a**—**e**) and (**6**) respectively as the major products.

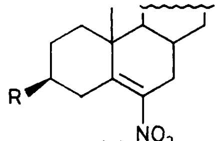
Since the trimethylsilyl cation (Me_3Si^+) is considered to be an equivalent of a proton in many of the reactions of halogenosilanes, it was argued that the reaction of chlorotrimethylsilane with 6-nitrocholest-5-ene (**1a**) would provide 5α-chloro-6-hydroxyiminocholestane as does the reaction of hydrochloric acid with (**1a**).[1] However, it failed to react with (**1a**) in refluxing dichloromethane, and bromotrimethylsilane was also unreactive towards (**1a**). The reaction of (**1a**) with iodotrimethylsilane generated *in situ* from Me_3SiCl/NaI provided a complex mixture of products at room temperature. However, the reaction of (**1a**) with Me_3SiCl/NaI at −5 to 0 °C for 10 min followed by aqueous work-up gave one major and two minor products (t.l.c.) which were isolated and identified as (**2a**), (**3a**),[2] and (**4a**) respectively by direct comparison with authentic samples. The stereochemistry of the oxime (**4a**) was established as *E* by n.m.r. analysis. This reaction was then studied with 3-substituted-Δ^5-6-nitrocholestanes (**1b**—**e**) and in each case the major product (70—85% yield) was the

Table 1. Reductions with Me_3SiCl/NaI.[a]

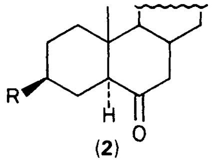
Substrate	Product[b] (% Yield)
(**1a**)	(**2a**) (75), (**3a**) (6), (**4a**) (8)
(**1b**)	(**2b**) (70), (**3b**) (8), (**4b**) (10)
(**1c**)	(**2c**) (80), (**3c**) (5), (**4c**) (6)
(**1d**)	(**2d**) (85), (**3d**) (2), (**4d**) (3)
(**1e**)	(**2e**) (77), (**3e**) (4), (**4e**) (8)

[a] In a typical experiment, a solution of (**1a**) (0.5 mmol) in dry CH_2Cl_2 (4 ml) was treated with NaI (2.0 mmol) and Me_3SiCl (1.0 mmol) with stirring at −5 to 0 °C for 10 min; the reaction was monitored by t.l.c. Aqueous work-up followed by t.l.c. on silica gel furnished (**2**—**4a**).

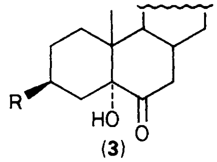
[b] All compounds were characterized by i.r., n.m.r., and mass spectroscopy, and by direct comparison with authentic samples.



(**1**)



(**2**)



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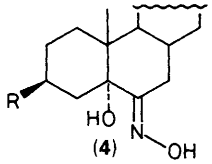

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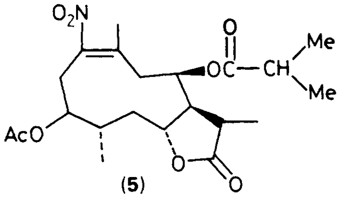
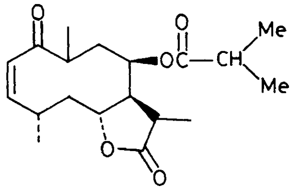


(**5**)



(**6**)

a; R = H
b; R = OAc
c; R = Cl
d; R = OMe
e; R = OH

corresponding 6-ketone (see Table 1). Similarly, 4-nitro-cholest-4-ene on treatment with Me_3SiCl/NaI gave cholestan-4-one (74%). Reaction of the nitro-alkene (**5**) prepared from the natural product tagitinin A[3], with Me_3SiCl/NaI furnished the ketone (**6**) in 78% yield.

Reaction of the oxime of (**2a**) with Me_3SiCl/NaI under the same conditions did not furnish the ketone (**2a**); starting material was recovered unchanged, thus indicating that oximes are not intermediates in the formation of ketones. Since the conditions are mild, this method could be a useful alternative to the standard method (Zn/AcOH)[4] for reducing the vinyl nitrosteroids to ketosteroids where refluxing conditions are required.

We have earlier reported[5] that hydrogen iodide generated *in situ* from trifluoroacetic acid and NaI could be an equivalent of Me_3SiI. The reaction of nitro compound (**1a**) with CF_3CO_2H/NaI did indeed furnish compounds (**2a**), (**3a**), and (**4a**) in 40, 20, and 25% yields respectively.

Olah *et al.*[6] have reported that the reaction of primary, secondary, and tertiary nitro compounds with Me_3SiI furnishes the corresponding cyanides, oximes, and iodides respectively, and that the reaction of 1-nitrocyclohexane with Me_3SiI yielded a complex mixture of products. We have obtained similar results.

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2 Hydroxy-ketones are also the byproducts in the nitration of alkenes: see, *e.g.*, C. R. Eck and B. Green, *J. Chem. Soc., Chem. Commun.*, 1972, 537, and references cited therein. Therefore, the purity of the nitro compounds used was fully ensured before use.

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