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REDUCTION OF α,β-UNSATURATED NITROCOMPOUNDS WITH TRIBUTYLTIN HYDRIDE[1].

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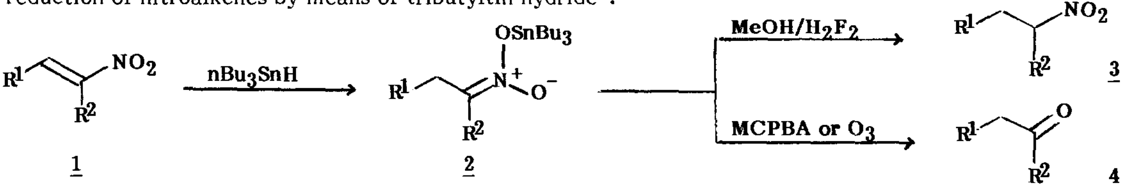
Abstract: Nitroalkenes upon treatment with tributyltin hydride in the absence of any catalyst provide a new method for the reduction of α,β-unsaturated nitrocompounds. Oxidative cleavage of the intermediate stannyl nitronates yielded carbonyl compounds in good yields.

In the preceding paper we described a convenient method for the preparation of carbonyl compounds via Nef reaction on trialkysilyl nitronates. In this communication we report our preliminary results on the reduction of nitroalkenes by means of tributyltin hydride[2].



The tin hydride reduction of unsaturated carbon-carbon bonds is well documented[3], however to our knowledge no reports have been described concerning reduction of α,β-unsaturated nitrocompounds promoted by tin hydrides[3,4]. Our new finding is that treatment of 1 with tributyltin hydride (1.2 equiv.) in methylene chloride at room temperature for 20-24h followed by work-up[3b] afforded the corresponding nitroalkane 3 in high yield. Some examples are given in the Table to illustrate this method. For primary nitroalkanes work-up involved treatment of the reaction mixture with methanol (2ml), evaporation of the solvent and dilution with methanol followed by addition of hydrofluoric acid (2N in MeOH). The precipitate tin compounds were filtered off and the nitrocompound was separated by column chromatography on silica gel and purified by Kugelröhr distillation. Under these conditions α-substituted tin nitronates afforded the expected secondary nitroalkanes together with the corresponding ketones. We observed that unsubstituted tin nitronates are very sensitive to moisture whereas the α-substituted ones are stable under the above work-up conditions and therefore a concomitant Nef reaction also takes place (Entries **b** and **h**). Of the solvents examined, methylene chloride, benzene and methanol were the most effective; acetonitrile, dimethoxyethane and tetrahydrofuran were found unsuitables for carry out reduction of nitroalkenes by means of tributyltin hydride. In benzene the reaction was extremely slow but it can be accelerated by the addition of methanol. Also, we have found that tributyltin trifluoromethanesulfonate[5] notably enhances tin hydride reduction of nitroalkenes in methylene chloride or benzene as solvents. Also, it is worth of note that under the conditions reported here no dimeric products were formed during tin hydride reduction of nitroalkenes[6].

Further applications of the present procedure can be illustrated in the high yield formation of ketones from stannyl nitronates in a single pot operation. For example when a β-methyl-β-nitrostyrene (5 equiv.) in methylene chloride (5ml) was subjected to treatment with tributyltin hydride (5.2 equiv.) overnight followed by addition of MCPBA (5.2 equiv.) in methylene chloride (10ml) the corresponding ketone was isolated in high yield. Attemps to prepare aldehydes from β-nitrostyrenes 1 (R^2=H) by MCPBA oxidation of the corresponding stannyl nitronates failed to give good results. This fact may be adscribed to an easy destannylation of the tin nitronate as we have mentioned above. However, we have found that treatment of tin nitronates with ozone afforded good yields in the expected aldehydes. For example when nitrostyrene was treated with tributyltin hydride under nitrogen atmosphere overnight and then the resulting mixture was subjected to reductive ozonolysis, phenylacetaldehyde was obtained in 72% isolated yield together with 1-phenyl-2-nitroethane in 10% isolated yield.

In conclusion we have found new applications of tributyltin hydride in organic synthesis. Importantly, the method allows reduction of nitroalkenes under mild reaction conditions without need any catalyst and therefore it could be used in selective reductions. Further investigations to explore the scope and limitations of the method as well as "in situ" utilization of the intermediate stannyl nitronate are in progress in our laboratory.

Table. Reaction of nitroalkenes 1 with nBu_3SnH.

	Compound 1[a]		Product 3[b]		Product 4[b]	
Entry	R^1	R^2	Yield, %[c]	b.p.°C/torr[d] or m.p.°C	Yield, %[c]	b.p.°C/torr[d] or m.p.°C
a	C_6H_5	H	90	92/0.05	72[e]	200/760
b	C_6H_5	CH_3	50[f]		97	115/20
c	$4\text{-}CH_3OC_6H_4$	H	80[g]	135/0.06	70[e]	105/0.05
d	$4\text{-}CH_3OC_6H_4$	CH_3	—	—	95	150/20
e	$3\text{-}O_2NC_6H_4$	H	80	59	—	—
f	$4\text{-}CH_3C_6H_4$	CH_3	—	—	99	120/17
g	$4\text{-}ClC_6H_4$	H	99	135/1.0	—	—
h	$4\text{-}NCC_6H_4$	CH_3	50[h]	150/0.5	95	72-73
i	CH_2CH_3	CH_3	—	—	72	105/760

a) These compounds were prepared by the method described by J. Bourguignon, G. Le Nard, G. Queguiner, Can. J. Chem., 63, 2354 (1985). b) All products exhibited physical and spectral characteristics in accordance with the assigned structures. c) Isolated yields. d) Reported boiling points are those observed during distillation with a Kugelröhr apparatus and are uncorrected. e) By reductive ozonolysis of the corresponding stannyl nitronate; 10% of the nitroalkane was also isolated. f) 50% of the ketone was isolated. g) 5% of the corresponding oxime was isolated. h) 45% of the ketone was isolated.

REFERENCES AND NOTES

1.- Reagents and Synthetic Methods 66. For part 65 see the preceding paper. The present work has been supported by Departamento de Investigación del Gobierno Vasco (Eusko Jaurlaritzako Hezkuntza Saila). A grant from Eusko Jaurlaritza to M.O. is gratefully acknowledged.

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