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Synthesis of 2-Nitro 1,3-Dienes. Useful Intermediates in the Preparation of Unsaturated 1,4-Dicarbonyl Compounds

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Abstract. 2-Nitro 1,3-dienes have been obtained from conjugated dienes via a nitroselenation-elimination sequence. The elimination of the selenium moiety is catalyzed by base. Several of the 2-nitro 1,3-dienes were isolated, whereas others were generated *in situ* and used for further reaction. They were found to react readily with enol ethers to give nitronic esters, which subsequently were transformed to unsaturated 1,4-dicarbonyl compounds.

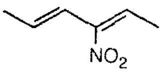
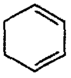
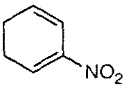
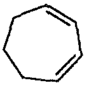
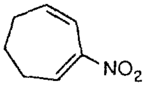
The utility of electron-deficient conjugated dienes as building blocks in organic synthesis has recently been demonstrated.[1-4] The synthetic importance of these dienes is increased if the electron-withdrawing group allows further functionalization and/or can be removed, as is the case for arylsulfonyl[1] and nitro[5] groups. While there are many examples of the use of sulfonyldienes,[1,2] only a limited amount of work has been done on nitrodienes.[3]

We now report the synthesis of 2-nitro 1,3-dienes by means of a sequence that involves the nitroselenation of the corresponding conjugated dienes[3e] followed by a base-catalyzed elimination of the phenylseleno group. When the resulting nitrodiene was not highly reactive towards dimerization, its isolation and purification was accomplished. The more reactive nitrodienes were generated *in situ* and used directly in the appropriate reaction. In this communication we describe the cycloaddition of these 2-nitro 1,3-dienes with enol ethers and the subsequent transformation of the nitronate cycloadducts to 1,4-dicarbonyl compounds. The latter compounds constitute potential precursors for the synthesis of naturally occurring products.[6]

When the the nitroselenation adducts from conjugated dienes were treated with a catalytic amount of a base such as N,N-dimethylaminopyridine (DMAP), a mild elimination of the phenylseleno group took place. This elimination, which is facilitated by the electron-withdrawing nitro group, produces PhSeH but the latter is oxidized *in situ* by air to give PhSePh.[7] Table I shows some nitrodienes which were isolated and characterized. However, in several other cases it was not possible to isolate the corresponding 2-nitro 1,3-diene due to rapid dimerization.

Nitroalkenes have been shown to react with electron-rich olefins such as enamines, allylsilanes, enolates, and silyl enol ethers to give nitronates.[8,9] Usually, these reactions were performed in the presence of a Lewis

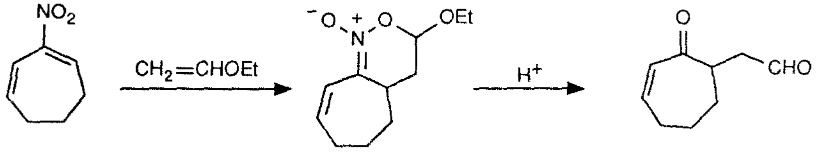
Table I. Synthesis of 2-nitro-1,3-dienes.[a]

Diene	Reaction time[b] (h)	Nitrodiene[c]	Yield[d] (%)
	20		45
	2.5		38
	1		75

[a] In a typical reaction, 1 mmol of the diene was nitroselenated as previously described.[3e] The crude extract was dissolved in 2 mL of methylene chloride and 5 mg of DMAP were added. The mixture was stirred and when the reaction was complete (followed by t.l c.) the solvent was evaporated and the nitrodiene purified by Kugelrohr distillation [b] Starting from the nitroselenation adduct. [c] Characterized by ^{1}H NMR and ^{13}C NMR [d] Isolated yield based on the starting diene.

acid catalyst in order to enhance the electrophilicity of the nitroalkene Reaction of nitrodiene **3** with ethyl vinyl ether in methylene chloride afforded the nitronate **4** in almost quantitative yield Hydrolysis of **4** under the usual Nef conditions[10] gave the aldehyde **5** (Scheme I).

Scheme I

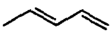
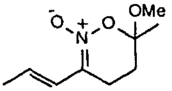
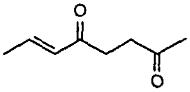
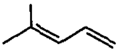
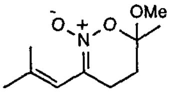
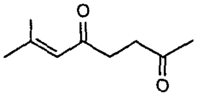
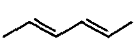
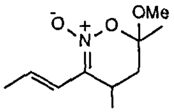
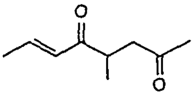
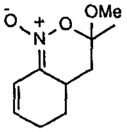
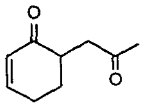
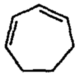
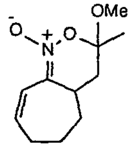
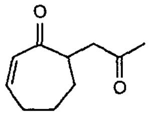
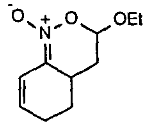
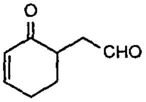
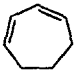
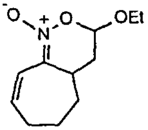
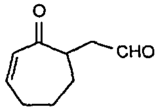


3 **4** **5**

Because of problems with the isolation of some of these 2-nitro 1,3-dienes we decided to study their *in situ* generation in the presence of the enol ether. In most cases, this actually gave a better yield of the nitronate (from the diene) Table II shows the results obtained in the synthesis of unsaturated dicarbonyl compounds with a series of representative dienes as starting materials and Scheme II summarizes the experimental method as exemplified by entries 4 and 6

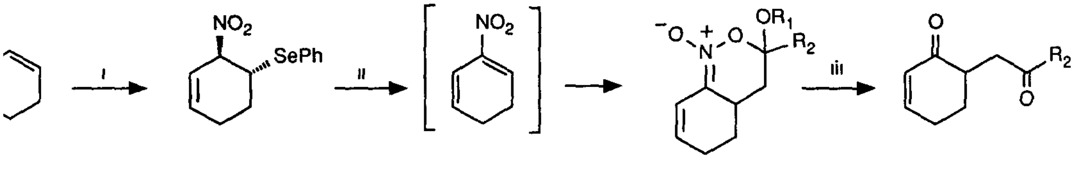
The synthesis of 1-nitro 1,3-dienes has been reported,[3a] but procedures for the preparation of the corresponding 2-nitro 1,3-dienes have involved unsatisfactory reaction conditions.[3b] Recently, Barco et al [3c,3d] described the preparation of some nitroalcohols that act as precursors for 2-nitro 1,3-dienes The present procedure via nitroselenation seems to be the more general one for these synthetically useful compounds.

Table II. Preparation of unsaturated 1,4-dicarbonyl compounds.

Entry	Diene	Reaction time[a] (h)	Nitronate[b,c]	Yield[d] (%)	Dicarbonyl compound[c]	Yield[e] (%)
1		8		45		95
2		48		57		90
3		48		53		96
4		18		38		95
5		18		50		50
6		9		42		93
7		8		62		30

[a] From the nitroselenyl adduct. [b] Entries 1-5: Obtained by reaction with $CH_2{=}CH(OMe)CH_3$; entries 6 and 7: Obtained by reaction with $CH_2{=}CHOEt$. [c] Characterized by IR, ^1H NMR and ^{13}C NMR. [d] Isolated yield after flash chromatography based on the corresponding diene. [e] Based on the nitronate.

Scheme II



6

R_1 = Me, Et; R_2 = Me, H

agents. i. PhSeBr, $HgCl_2$, $AgNO_2$; ii. DMAP, $CH_2{=}CH(OMe)CH_3$ (or $CH_2{=}CHOEt$); iii. 10% HCl

In a *typical procedure*, the crude extract obtained from the nitroselenation of 1 mmol of the appropriate diene[3e] was dissolved in methylene chloride (2 mL). To this solution were added 5 mg of DMAP and 1 mL of the appropriate enol ether. The solution was stirred under reflux and after the necessary reaction time (monitored by t.l c) the solvent was evaporated and the residue purified by flash chromatography on silica gel to give the nitronic ester. A solution of this nitronate in methylene chloride (1 mL) was hydrolyzed with 0 5 mL of 10% hydrochloric acid under reflux during 2 hours. The organic layer was washed with brine and water, dried ($MgSO_4$), and the solvent evaporated *in vacuo* yielding the dicarbonyl compound.

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