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γ-Selectivity in the Ceric Ammonium Nitrate Promoted Oxidative Addition of Silyl Dienol Ethers to Silyl Enol Ethers

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Key Words: Cerium(IV) Ammonium Nitrate; Oxidative Addition; Trimethylsilyl dienol ethers; Trimethyl silyl enol ethers; α,β-unsaturated carbonyl compounds.

Abstract: *Trimethylsilyl dienol ethers are easily oxidized by ceric ammonium nitrate to give α-carbonylallyl radicals which are able to add to enolic carbon-carbon double bonds with very high γ regioselectivity, allowing the method to be applied to the synthesis of 6-oxo-α,β-unsaturated carbonyl compounds.*

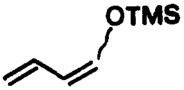
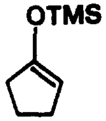
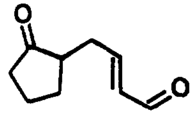
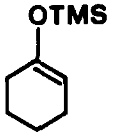
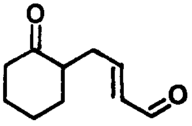
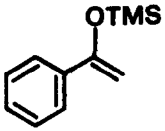
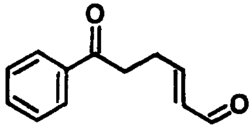
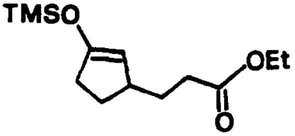
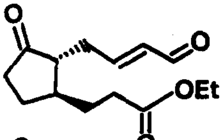
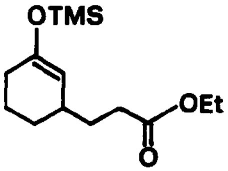
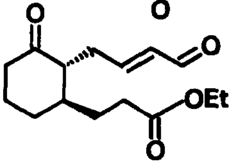
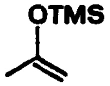
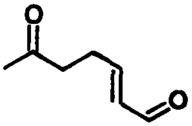
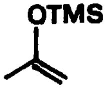
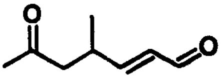
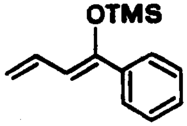
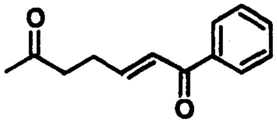
Oxidative addition of enolizable carbonyl compounds to alkenes promoted by one-electron metal oxidants has received considerable attention in the last few years, becoming a valuable tool in carbon-carbon bond formation.[1] On this subject, we have previously reported that ceric ammonium nitrate (CAN) is an efficient one-electron oxidant in generating α-ketoalkyl radicals from trimethylsilyl enol ethers. Oxidative addition of the resulting ketoalkyl radical to electron rich carbon-carbon double bonds allows the access to variety of polyfunctionalized carbonyl compounds such as unsaturated ketones, 1,4-diketones[2] and 4-oxoaldehydes.[3] As a useful extension of the above procedure, we report now on the CAN promoted oxidative addition of silyl dienol ethers to silyl enol ethers.

We have found that when a mixture of trimethylsilyl dienol ether and trimethylsilyl enol ether is treated with CAN in acetonitrile at 0°C, a very efficient cross-coupling occurs to give an unsaturated dicarbonyl compound in fairly good yield. Some results are reported in the Table.

Interestingly, the reaction exhibits a very high regioselectivity, practically only products derived from the attack to the carbon farther from the silyloxy group are observed, even when an alkyl substituent is present in this position (entry 7 in the Table) allowing the method to be successful applied to the synthesis of 6-oxo-α,β-unsaturated carbonyl compounds. Moreover, on the basis of ^{1}H-NMR coupling constants and IR spectra, a trans structure for the conjugated carbon-carbon double bond has been assigned which is in line with previous observations concerning free radical addition to conjugated dienes.[4]

In a typical experiment, to a mixture of trimethylsilyl dienol ether (1.8 mmol), trimethylsilyl enol ether (2.5-10 mmol) and pulverized calcium carbonate (10 mmol)[5], cooled at 0°C, a solution of CAN (3.1 mmol) in acetonitrile (15 mL) was added dropwise in 5 min. During the addition, the red colour of the CAN solution

Table 1. *6-Oxo-α,β-Unsaturated Carbonyl Compounds from CAN Promoted Oxidative Addition of* Trimethylsilyl Dienol Ethers to Trimethylsilyl Enol Ethers in Acetonitrile at 0°C.

	Trimethylsilyl dienol ether[a]	Trimethylsilyl enol ether	6-Oxo-α,β-unsaturated carbonyl compound	Yield, %[b]
1.				34 (67[c])
2.				62
3.				69
4.				44
5.				51
6.				77[d]
7.				47[d]
8.				67[d]

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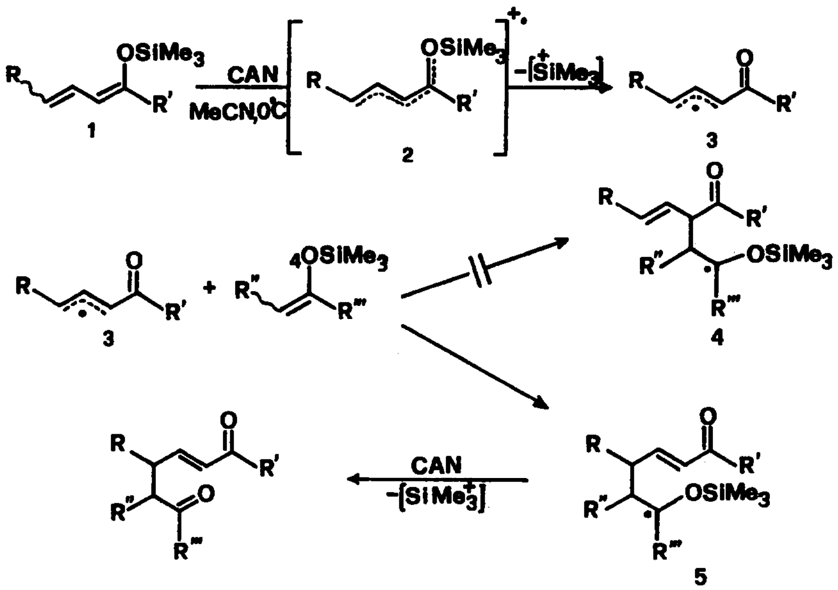
[a] CAN:Dienol ether:enol ether = 2:1:2-4. [b] Yield of isolated product. [c] Gas-chromatographic yield. [d] CAN:dienol ether:enol ether = 2:1:10.

instantaneously disappears. After addition was completed, the resulting white mixture was filtered on celite, the filtrate was poured into a 20% aqueous NH_4Cl solution (30 mL) and extracted with diethyl ether (3 x 50 mL). The collected organic phases were dried with sodium sulphate and the solvent was evaporated at reduced pressure (15 mmHg). The residual yellow oil was chromatographied on silica gel by eluting with petroleum ether- diethyl ether mixtures, to isolate the pure α,β-unsaturated carbonyl compound. All products had the expected ^{1}H-NMR, IR, MS spectra and correct C, H analyses.

The success of the method probably rest on the much easier oxidizability of the trimethylsilyl dienol ether with respect to the silyl enol ether. Accordingly, CAN should preferencially react with the former to generate an electrophilic α-carbonylallyl radical 3, probably through a transient radical cation 2 (see Scheme). Attack of 3 to the electron rich enolic double bond of the silyl enol ether gives radical 5, now a nucleophilic species, which is rapidly oxidized by CAN to the final product.



Scheme

The above mechanistic hypothesis is supported by the fact that a significant excess (from 2 to 4:1) of the 1,2-disubstituted silyl enol ether and a larger excess of the less reactive 1-substituted silyl enol ether (10:1) has to be used in order to avoid some homocoupling involving almost exclusively the silyl dienol ether.

The observed high regioselectivity might be rationalized considering that attack at the γ position of 3 leads to the most stabilized carbonyl conjugated α-silyloxy radical 5, probably formed through a transition state less energetic than that leading to the unconjugated α-silyloxy radical 4, assuming the addition step to possess a substantial product like character, as it should be the case.[6] Supporting this suggestion, a similar behaviour has been also observed in the alkoxy radical catalyzed autoxidation of 1,4-dienes, where the pentadienyl radical, showing some analogy with 3, generated by hydrogen abstraction from the bis-allylic carbon, reacts with oxygen to give exclusively conjugated dienylperoxy radicals.[7]

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4. See for example Oswald, A.A.; Griesbaum, K.; Thaler, W.A.; Hudson, Jr.B.E., *J.Am.Chem.Soc.* **1962**, *84*, 3897-3904.
5. In the absence of calcium carbonate extensive solvolysis of the trimethylsilyl dienol ether occurs caused by nitric acid produced by CAN in each oxidation step.
6. *Ab initio* AM1 MO calculations[8] have shown that in 3 the difference in the SOMO coefficients at C2 and C4 (c_2 = 0.669; c_4 = 0.685) as well as in the spin density (0.649 at C2; 0.667 at C4) is too small to justify such high regioselectivity. On this basis, a direct attack of the radical cation **2** to the enolic carbon-carbon double bond could be also envisaged, since, in **2**, both SOMO coefficient and spin density at C4 (c_4 = 0.653; s.d. at C4 = 0.576) are remarkably higher than at C2 (c_2 = 0.524; s.d. at C2 = 0.339), although the well known electrofugal ability of the trimethylsilyl group from a silane radical cation in acetonitrile[9] make most unprobable the attack of **2** occurring faster than the oxygen-silicon bond cleavage.
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