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Chemoselective Reactions of Anthrone with α,β-Unsaturated Ketones

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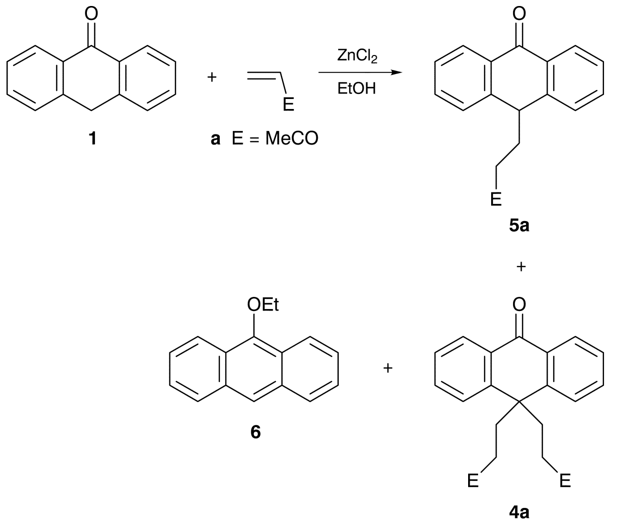
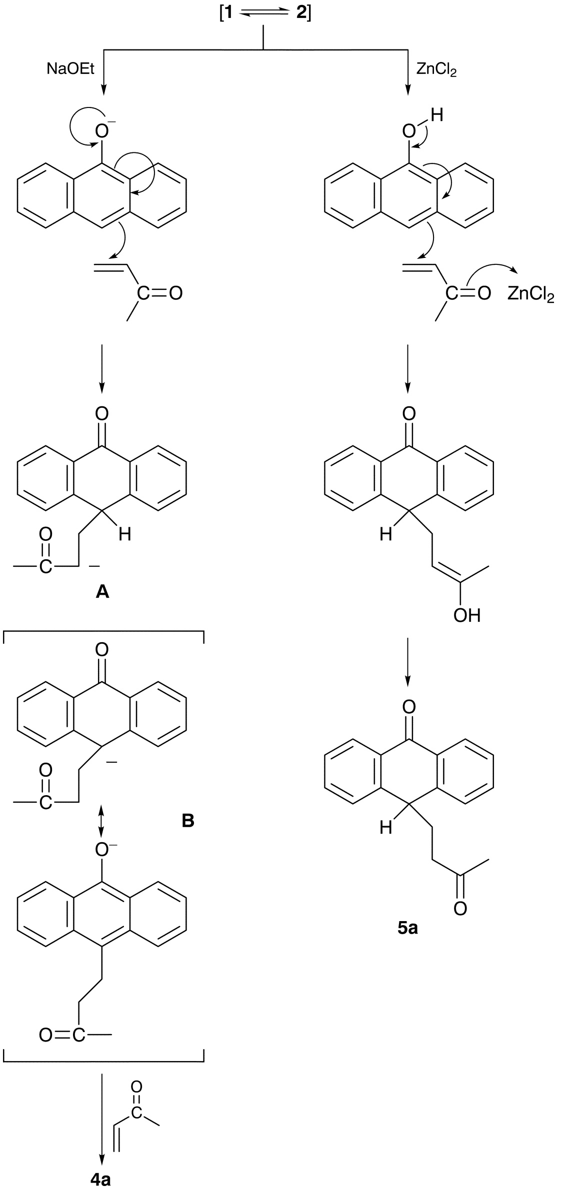
In the presence of $ZnCl_2$, 1,4-conjugated addition of anthrone with α,β-unsaturated ketones proceeded to give mono-Michael adducts, whereas in basic solution it gave bis-Michael adducts.

The conjugate addition reaction of anthrone with α,β-unsaturated carbonyl compounds in the presence of base is of the Michael type, which gives the bis-Michael adducts **4**.[6] These similar consecutive double Michael reactions are observed with substrates containing active methylene groups, such as indanone, fluorene or acetophenone.[7] In view of the importance of selective mono-Michael adducts in organic synthesis, the search for new reagents to effect the mono-Michael addition is worthwhile. There is currently no direct method available for the preparation of mono-Michael adducts with anthrone.

We now wish to report a new Lewis-acid-catalysed reaction of anthrone with a variety of α,β-unsaturated ketones. Surprisingly, in the presence of a catalytic amount of $ZnCl_2$ (0.03 equiv.), anthrone reacted with methyl vinyl ketone to give mono 10-substituted anthrone **5a** in a yield of 89% when the reaction was carried out in EtOH at reflux. By varying the amount of $ZnCl_2$, the yields and ratio of products were not influenced. Using mineral acid or toluene-*p*-sulfonic acid instead of $ZnCl_2$, it was found that in ethanol the known O-alkylated adduct 9-ethoxyanthracene **6**, was the major product, which is formed when anthrone is boiled under reflux in ethanol in the presence of H_2SO_4 without alkene.[4a]



We have extended the mono-Michael reaction of anthrone to a variety of α,β-unsaturated ketones. In all cases, mono-Michael adducts were obtained in reasonable yields, even with substituted α,β-unsaturated ketones such as cyclohexenone or cyclopentenone. It is rather surprising that the chemoselective Michael reactions of anthrone were performed by changing the catalyst. In fact, limited examples of α,β-unsaturated compounds, such as acrylonitrile,[6a] methylacrylate[6b,c] and methyl vinyl ketone,[8] have been reported in the base-catalysed Michael reactions of anthrone. A variation of alkenes and other reaction conditions were not reported at all. In an attempt to compare the reactivities of anthrone under two distinctive conditions we have examined a series of α,β-unsaturated ketones under basic conditions. We found that the conjugate addition reaction proceeded using both catalytic (0.02 equiv.) and stoichiometric amounts of $NaOCH_3$ to produce the bis-Michael adducts **4** in similar yields. For enones with no β-substituents, small amounts (< 5%) of mono 10-substituted



Scheme

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Table 1 Conjugated addition reaction of anthrone under acidic conditions at reflux

		Conditions		Product	
Entry	Alkene	Lewis acid (equiv.)	Solvent	Time (*t*/h)	Yield (%)[a]
1	Methyl vinyl ketone, **a**	$ZnCl_2$ (0.03)	EtOH	3, **5a**	89
2	Methyl vinyl ketone, **a**	$ZnCl_2$ (1.1)	EtOH	2, **5a**	81
3	Methyl vinyl ketone, **a**	ZnI_2 (0.1)	EtOH	10, **5a**	35
4	Methyl vinyl ketone, **a**	$AlCl_3$ (0.1)	EtOH	12 Mixture	
5	Methyl vinyl ketone, **a**	H_2SO_4 (0.1)	EtOH	12, **6**	45
6	Methyl vinyl ketone, **a**	pTSA (0.2)	EtOH	12, **6**	45
7	Ethyl vinyl ketone, **b**	$ZnCl_2$ (0.07)	MeOH	2, **5b**	67
8	*trans*-4-Methoxybut-3-en-2-one, **c**	$ZnCl_2$ (0.14)	MeOH	2, **5c**	22
9	Cyclopentenone, **d**	$ZnCl_2$ (0.05)	DMSO	7, **5d**	77
10	Cyclohexenone, **e**	$ZnCl_2$ (0.07)	MeOH	3, **5e**	86
11	Phenyl vinyl ketone, **f**	$ZnCl_2$ (0.14)	MeOH	2, **5f**	47

anthrones **5** were observed independent of the amounts of α,β-unsaturated ketones and $NaOCH_3$. On the other hand, β-substituted α,β-unsaturated ketones, such as cyclohexenone, cyclopentenone or *trans*-4-methoxybut-3-en-2-one, gave mono-Michael adducts, as for the $ZnCl_2$-catalysed Michael reaction. The steric hindrance of the enone terminus was found to be the most critical factor in the base-catalysed mono-Michael reaction of anthrone.

$$\mathbf{1} + \text{Alkene} \xrightarrow{\text{NaOMe}} \mathbf{4} + \mathbf{5}$$

Alkene	% Yield **4**	% Yield **5**
Methyl vinyl ketone	89	5
Ethyl vinl ketone	88	Trace
trans-4-Methoxybut-3-en-2-one	Trace	Trace
Cyclopentenone	Trace	85
Cyclohexenone	Trace	80
Phenyl vinyl ketone	50	None

The success of the mono-Michael reaction with $ZnCl_2$ may be explained by the equilibrium position between the tautomers anthrone (**1**) and anthracenol (**2**) lying towards the enol form in acidic media. Thus, the favorable formation of anthracenol **2** reacts with methyl vinyl ketone to give the mono-Michael adduct **5a**. Subsequent enolisation of **5a** would be less favorable and therefore the successive bis-Michael reaction would be disfavoured (Scheme). Meanwhile, under basic conditions the anthracenolate ion reacts with methyl vinyl ketone to give the corresponding carbanion **A**. This may then undergo a proton shift to give the more stable anthracenolate ion **B** (it may be the case that the C10 proton of the anthrone part in **A** is more acidic than the α hydrogen of the ketone part). Therefore, the resulting anthracenolate ion **B** is readily reacted with the alkene to give the bis-Michael adduct **4a** (see the Scheme on opposite page).

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Techniques used: H NMR, ^{13}C NMR, IR and mass spectrometry

References: 8

Schemes: 3

Table 2: Conjugated addition reaction of anthrone under basic conditions at reflux

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