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SYNTHESIS OF HIGHLY ALKYLATED FUNCTIONALIZED CYCLOPENTADIENES

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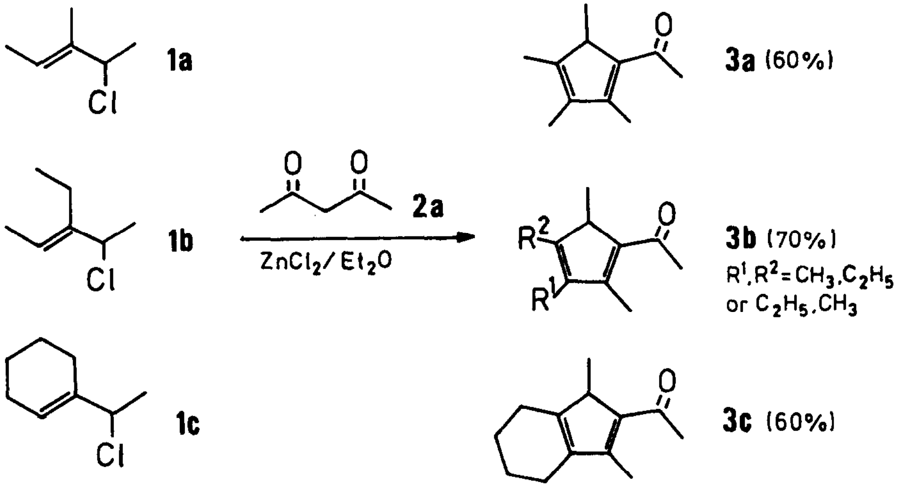
Abstract. Tetra- and pentaalkylated cyclopentadienyl ketones and carboxylic acids are prepared by electrophilic allylation of enolizible 1,3-dicarbonyl compounds and successive acid catalyzed cyclisation.

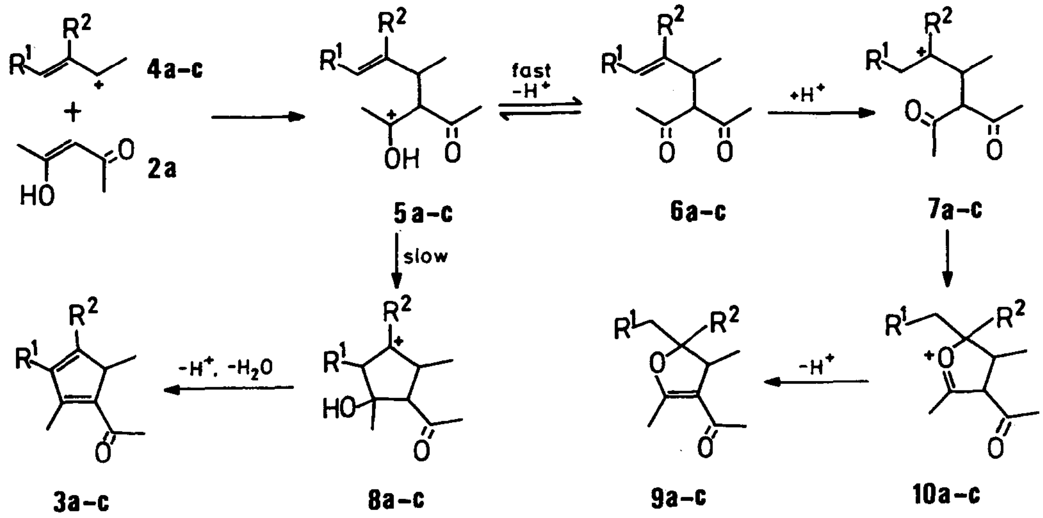
The pentamethylcyclopentadienyl group is an important ligand in organometallic chemistry, and various synthetic approaches to pentamethylcyclopentadiene and its derivatives have been developed.[1] We report now a novel and straightforward access to highly alkylated acetyl- and alkoxycarbonylcyclopentadienes, which employs the $[3^+ + 2]$ strategy, previously developed for the synthesis of cyclopentenes by Lewis acid catalyzed reaction of allyl chlorides with alkenes[2] or alkynes.[3]



When the allylic chlorides **1a-c** (25 mmol in 50 ml of CH_2Cl_2) were added dropwise to a solution of acetylacetone **2a** (33 mmol) and $ZnCl_2/Et_2O$[4] (52 mmol) in CH_2Cl_2 (350 ml) at -20°C and kept at -20°C for 1 d and at 4°C for 2 d, the cyclopentadienes **3a-c** were isolated in 60-70% yield after workup with aqueous ammonia and chromatographic removal[5] of small amounts of the dihydrofurans **9a-c**. As expected, traces of isomers (< 5%) with different orientation of the endocyclic double bonds were detectable in the NMR spectra of **3a,b**.

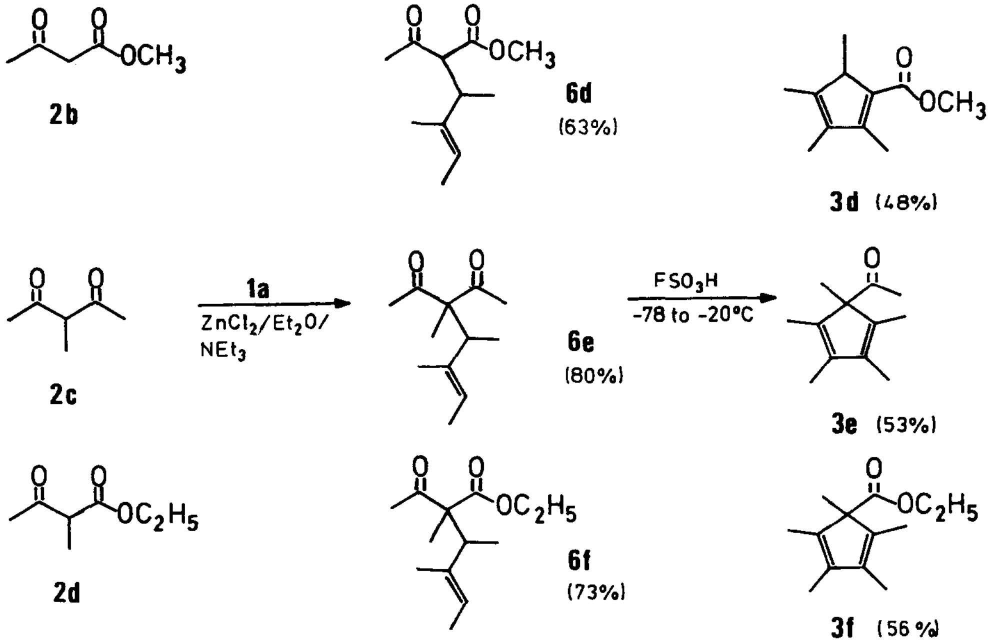
The reactions are suggested to proceed via the allylated dicarbonyl compounds **6a-c**, (Scheme) which are isolated as the only products when the reactions are carrried out at -78°C.[6] Treatment of **6a-c** with $ZnCl_2/Et_2O/HCl$ in CH_2Cl_2 at -20°C yields the cyclopentadienes **3a-c** (60-70%) accompanied by small amounts of the dihydrofurans **9a-c** (3-20%). These heterocycles are isolated as the major products, when **6a-c** are treated with dry HCl in CH_2Cl_2 at 0°C. As shown in the Scheme, the formation of the dihydrofurans **9a-c** is rationalized by protonation of the CC-double bond of **6** to give the carbenium ion **7** which attacks at the lone pair of the carbonyl group.

Scheme



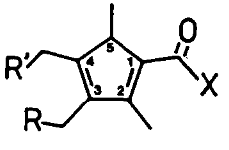
4-10: a: $R^1 = R^2 = CH_3$; b: $R^1, R^2 = CH_3, C_2H_5$; c: R^1-R^2 = $-(CH_2)_4-$

When the trimethylallyl chloride **1a** was reacted with the dicarbonyl compounds **2b-d** under the conditions described above, a complex mixture of compounds was produced, probably because of self-condensation reactions of **1a**. The corresponding cyclopentadienes **3d-f** are generated, however, when the acyclic products **6d-f**, which are formed from **1a** and **2b-d** in presence of $ZnCl_2/Et_2O/Et_3N$, are treated with one equivalent of FSO_3H in CH_2Cl_2.

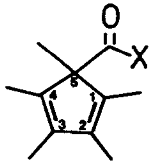


We are presently exploring the scope of this reaction. Until now, we have not yet succeeded to obtain cyclopentadienes from allyl chlorides, which are unsubstituted in the central allylic position[7] or which carry two alkyl groups at the same allylic terminus.

Table. ^{13}C NMR Chemical Shifts of the Cyclopentadienes 3a-f[8]



3a-d



3e-f

	R	R'	X	C-1	C-2	C-3	C-4	C-5	1-C	2-C	3-C	4-C	5-C	X,R,R'
3a	H	H	CH_3	142.6	154.9	135.7	150.1	49.7	194.3	14.5	10.7	12.4	14.9	30.4
$3b_1$	CH_3	H	CH_3	143.0	154.4	141.9	149.9	49.7	194.2	14.3	18.3	12.1	15.0	30.4, 14.1*
$3b_2$	H	CH_3	CH_3	142.8	154.7	135.1	156.1	47.4	194.3	14.5	10.6	19.8	14.8	30.4, 14.3*
3c	CH_2-CH_2		CH_3	142.8	154.0	138.6	153.4	48.5	194.4	13.9	22.4*	22.6*	14.8	30.4, 22.7*, 23.9*
3d	H	H	OCH_3	131.8	156.7	135.2	149.3	49.6	165.5	13.8	10.6	12.3	14.7	50.5
3e	H	H	CH_3	137.0	139.4	139.4	137.0	71.4	10.2	11.4	11.4	10.2	14.5,	207.9, 22.7
3f	H	H	OC_2H_5	136.5	137.6	137.6	136.5	63.6	10.3	11.3	11.3	10.3	18.4,	174.0, 60.3, 14.3

* may be interchanged

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8) The IR and ^{1}H NMR spectra of the previously prepared compounds **3e,f** agree with literature reports.[1]

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