

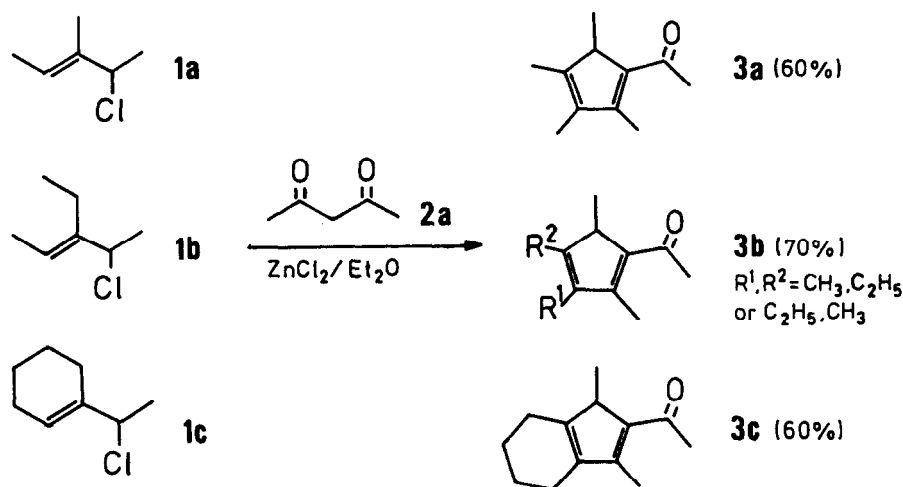
## SYNTHESIS OF HIGHLY ALKYLATED FUNCTIONALIZED CYCLOPENTADIENES

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**Abstract.** Tetra- and pentaalkylated cyclopentadienyl ketones and carboxylic acids are prepared by electrophilic allylation of enolizable 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.<sup>1</sup> We report now a novel and straightforward access to highly alkylated acetyl- and alkoxy-carbonylcyclopentadienes, which employs the [3<sup>+</sup> + 2] strategy, previously developed for the synthesis of cyclopentenes by Lewis acid catalyzed reaction of allyl chlorides with alkenes<sup>2</sup> or alkynes.<sup>3</sup>

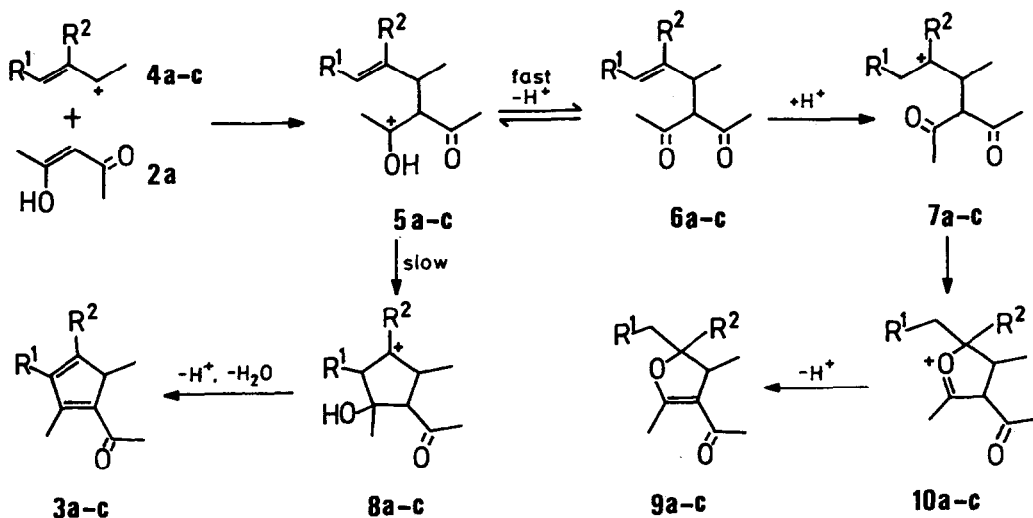


When the allylic chlorides **1a-c** (25 mmol in 50 ml of  $\text{CH}_2\text{Cl}_2$ ) were added dropwise to a solution of acetylacetone **2a** (33 mmol) and  $\text{ZnCl}_2/\text{Et}_2\text{O}^*$  (52 mmol) in  $\text{CH}_2\text{Cl}_2$  (350 ml) at  $-20^\circ\text{C}$  and kept at  $-20^\circ\text{C}$  for 1 d and at  $4^\circ\text{C}$  for 2 d, the cyclopentadienes **3a-c** were isolated in 60-70% yield after workup with aqueous ammonia and chromatographic removal<sup>5</sup> 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**.

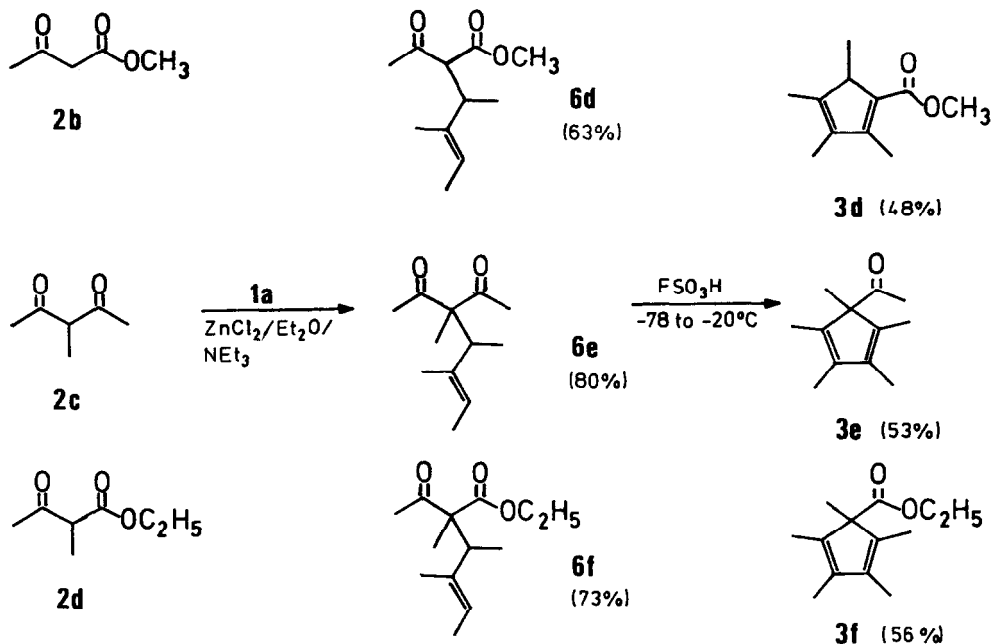
The reactions are suggested to proceed via the allylated dicarbonyl compounds **6a-c**, (Scheme) which are isolated as the only products when the reactions are carried out at  $-78^{\circ}\text{C}$ .<sup>6</sup> Treatment of **6a-c** with  $\text{ZnCl}_2/\text{Et}_2\text{O}/\text{HCl}$  in  $\text{CH}_2\text{Cl}_2$  at  $-20^{\circ}\text{C}$  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  $\text{HCl}$  in  $\text{CH}_2\text{Cl}_2$  at  $0^{\circ}\text{C}$ . 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



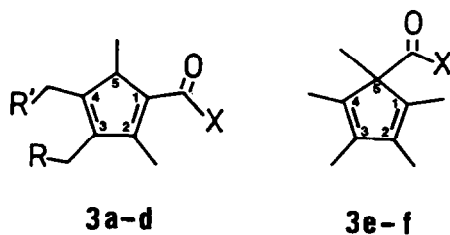
4-10: a:  $\text{R}^1=\text{R}^2=\text{CH}_3$ ; b:  $\text{R}^1,\text{R}^2=\text{CH}_3,\text{C}_2\text{H}_5$ ; c:  $\text{R}^1-\text{R}^2=-(\text{CH}_2)_4-$

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  $\text{ZnCl}_2/\text{Et}_2\text{O}/\text{Et}_3\text{N}$ , are treated with one equivalent of  $\text{FSO}_3\text{H}$  in  $\text{CH}_2\text{Cl}_2$ .



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<sup>7</sup> or which carry two alkyl groups at the same allylic terminus.

Table.  $^{13}\text{C}$  NMR Chemical Shifts of the Cyclopentadienes 3a-f<sup>a</sup>



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 <sub>3</sub>	142.6	154.9	135.7	150.1	49.7	194.3	14.5	10.7	12.4	14.9	30.4
3b <sub>1</sub>	CH <sub>3</sub>	H	CH <sub>3</sub>	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 <sub>2</sub>	H	CH <sub>3</sub>	CH <sub>3</sub>	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 <sub>2</sub> -CH <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>	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 <sub>3</sub>	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 <sub>3</sub>	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 <sub>2</sub> H <sub>5</sub>	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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- 5) In order to prevent decomposition of the products, NH<sub>3</sub>-saturated mixtures of hexane/ether have to be used for the chromatographic separations on silica.
- 6) Examples of other acid catalyzed alkylations of  $\beta$ -dicarbonyl compounds:  
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- 7) Cf: H. Mayr, H. Klein, G. Kolberg, *Chem. Ber.* **117**, 2555 (1984).
- 8) The IR and <sup>1</sup>H NMR spectra of the previously prepared compounds **3e,f** agree with literature reports.<sup>1</sup>

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