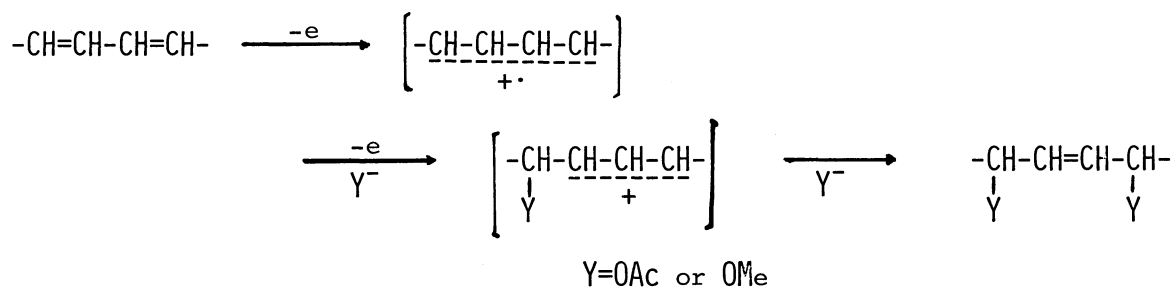


ANODIC ACETOXYLATION OF SUBSTITUTED CYCLOPENTADIENES
AND NOVEL SYNTHESIS OF ALLETHROLONE ¹⁾

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The anodic oxidation of substituted cyclopentadienes in acetic acid brought about the facile introduction of acetoxy group into 1,4-positions in relatively good yields. A novel synthesis of allethrolone starting from 2-methyl-3-allylcyclopentadiene was achieved using this unique electrochemical process as a key step.

In our recent study on the electrooxidation of carbon-carbon double bond, it was found²⁾ that the anodic oxidation of 1,3-diene in acetic acid or methanol gave mainly the product formed by the electron transfer from the unsaturated system to the anode.

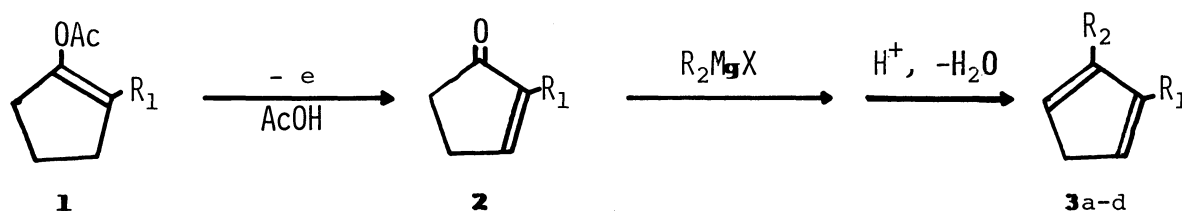


For instance, the oxidation of cyclopentadiene in methanol containing tetraethylammonium tosylate gave 1,4- and 1,2-dimethoxy-2-cyclopentenes in the yield of 51% and 6%, respectively.

In the present study, we wish to report a general synthesis of 1,4-diacetoxy-2-cyclopentenes through the anodic acetoxylation of substituted cyclopentadienes, and a novel synthesis of allethrolone.

The starting 2,3-disubstituted cyclopentadienes (**3a-d**) were prepared through the

Grignard reaction of 2-substituted-2-cyclopentenones (**2**) followed by the dehydration.³⁾ The cyclopentenones (**2**) were readily obtained by the anodic oxidation⁴⁾ of 2-substituted cyclopentenyl acetates (**1**) in acetic acid containing tetraethylammonium tosylate. The isolated yield of **3a-d** from **1** was 36-45%. The monosubstituted cyclopentadienes (**3e,f**) were prepared by the usual alkylation reaction of cyclopentadienyl anion with alkyl halide.⁵⁾



The anodic oxidation of **3a-g** in acetic acid using triethylamine as a supporting electrolyte gave 1,4-diacetoxy-2-cyclopentenones (**4a-g**) in relatively good yields (Table 1). All of the products (**4a-g**) were identified by spectroscopic and elemental analyses. The formation of the corresponding 1,2-diacetoxy compounds was less than 2-3%. This electrochemical direct 1,4-introduction of acetoxy group into cyclopentadienes is clearly superior to the hitherto known usual method⁶⁾ in its facility and generality.

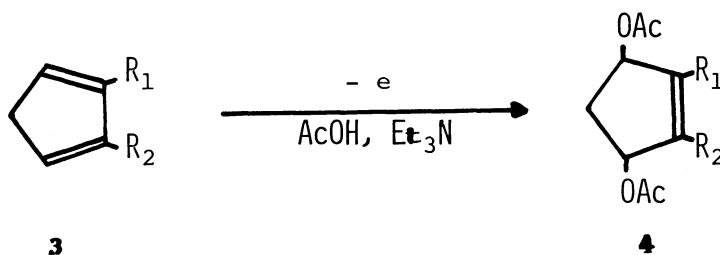
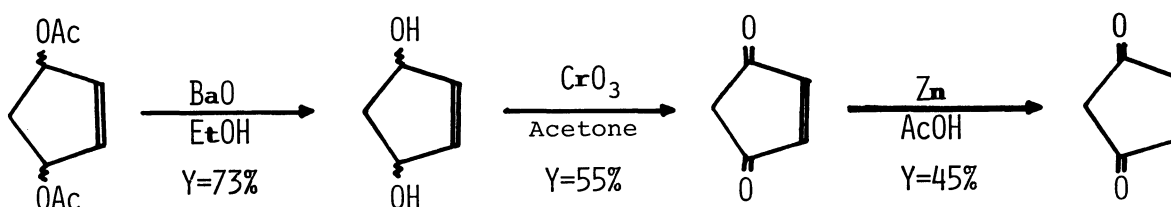


Table 1

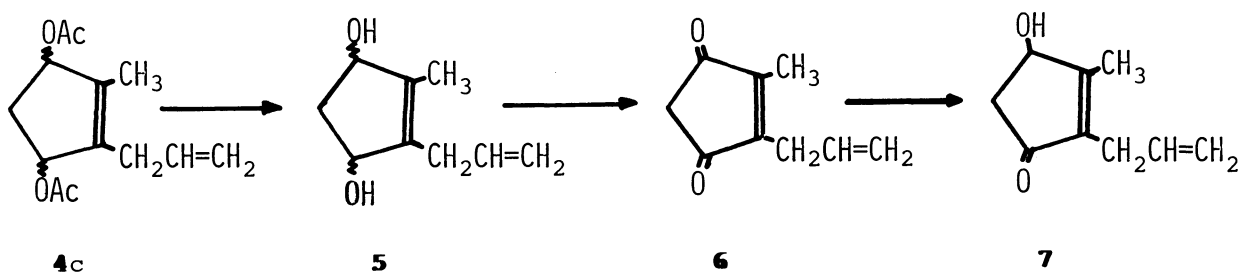
3	R ₁	R ₂	yield (%) of 4 ^{*)} , ^{**))}
a	Me	Me	43
b	Me	i-Pr	61
c	Me	CH ₂ CH=CH ₂	46
d	Me	n-Pr	57
e ^{**))}	H	CH ₂ CH=CH ₂	40
f ^{**))}	H	i-Pr	57
g	H	H	45 ^{*)} ^{**))}

- *) The electrolysis was carried out at room temperature using carbon rod electrode until 2F/mole of electricity was passed.
- **) The mixture (1:1) of cis and trans isomers.
- **) 1,2-Diacetoxycyclopentene-3 was also formed in a 6% yield.
- **) The starting cyclopentadienes were the equilibrium mixture (1:1) of 1- and 2- substituted isomers at room temperature.⁴⁾

1,4-Diacetoxy-2-cyclopentene (**4g**) was able to be transformed readily to 1,3-cyclopentadione according to the known procedures.⁶⁾



As one of the interesting applications of this unique synthetic method involving the anodic acetoxylation as a key step, a novel synthesis of allethrolone (**7**)^{7),8)} was performed through the following reaction route starting from 1,3-diacetoxy-3-allyl-2-methylcyclopent-2-ene (**4c**). The corresponding 1,3-diol **5** was obtained in a 83% yield by the reduction of **4c** with lithium aluminium hydride and subsequent oxidation of **5** with Jones' reagent gave the cyclopent-2-ene-1,3-dione **6** in a 66% yield. Selective reduction of the dione **6** with zinc in a mixed solvent of acetic acid and methylene chloride yielded the desired allethrolone **7**. The total yield of **7** from **4c** was 50%.



This method would possess much potentiality in the general syntheses of 4-hydroxycyclopentenones such as rethrolones.

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