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ON CYCLOPENTADIENONE-KETALS AND THEIR DIMERS.
A NOVEL REARRANGEMENT OF α,β-UNSATURATED KETONE DIALKYL KETALS

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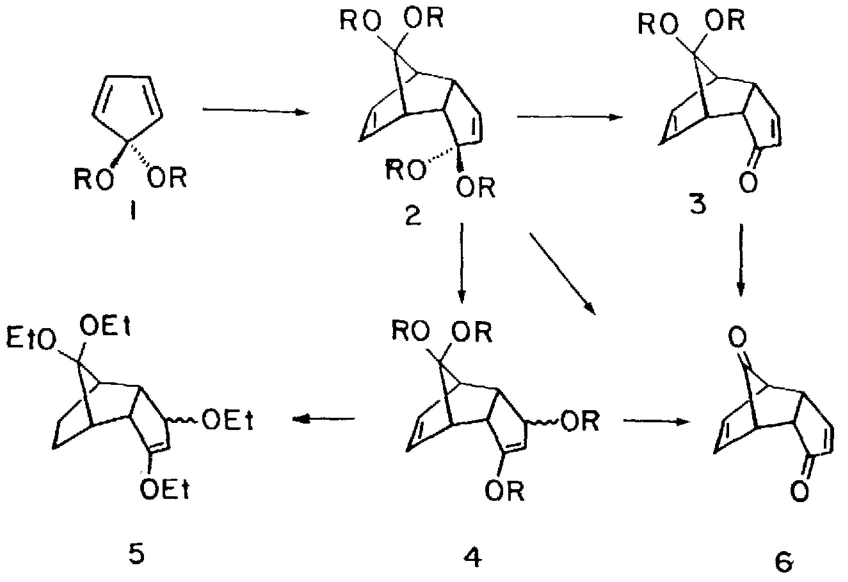
Abstract. The dimers(2a & b) of dimethyl- and diethylcyclopentadienone ketals(1a & b) undergo a novel 1,3-alkoxy-rearrangement to 4(a & b). Mild hydrolysis of 2 or 3 gives the monoketones (3a or b). On strong acid catalysed hydrolysis 2, 3 or 4 afford the cyclopentadienone-dimer(6)

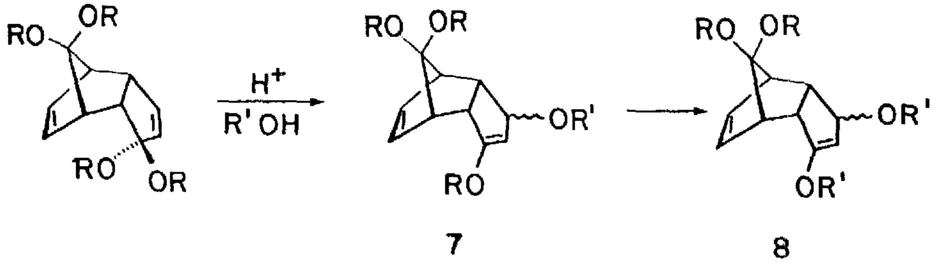
In contrast to the notorious elusiveness of cyclopentadienone, its ketals (1) had been prepared[1-3] and in particular the approach of Eaton and Hudson[3] provided a ready way to achieve cycloaddition products of cyclopentadienone with a variety of dienophiles.[4-8] The admittedly sensitive procedure has been explored to a certain extent[3,4,7,8] but nobody probed into what actually happens in the reaction mixture before, along with or instead of the cycloaddition reactions. We followed carefully this chain of events and report now the surprising and interesting results.

Cyclopentadienone-dimethyl- and diethyl ketals (1a & b) were obtained as described[3,4] and dimerized, each at its known rate,[3,8] to 2 (a & b). These dimers had been invoked[3,8] but were, peculiarly, never isolated and characterized. We were able to isolate the dimers 2 by carefully handling their solutions in petroleum-ether (PE), always over anhydrous K_2CO_3 and at low to moderate temperatures. They can be conveniently distilled (over K_2CO_3) e.g. 2b at 107°/0.5 torr. Any trace of aqueous acid, however, or treatment with silica gel/water[9], readily converts them to the monoketals (3).[10] The MS, IR and NMR spectra (including double irradiations) are completely in accord with the described structures.

Prolonged warming of 2(a or b) in PE, gradually converts it into a new isomeric compound, the formation of which is greatly enhanced by anhydrous acid. These products can also be purified by distillation and their spectral data (MS, IR and NMR + double irradiations) enabled us to assign them structure 4 (e.g. 4b: b.p. 130°/0.1 Torr; ν_{max}(neat) 1640 cm^{-1} (RO-C=C); δ(90 MHz, C_6D_6/TMS) 5.96 (m, $2H_{8,9}$), 4.59 (m, $1H_4$), 3.90 (m, $1H_5$), 3.37 (m, 9H) 3.0 (m, 3H), 1.1 (m, 12H); m/e 308 (M^+). Found: C 69.88, H 9.23; calc. for $C_{18}H_{28}O_4$: C 70.10, H 9.15%.

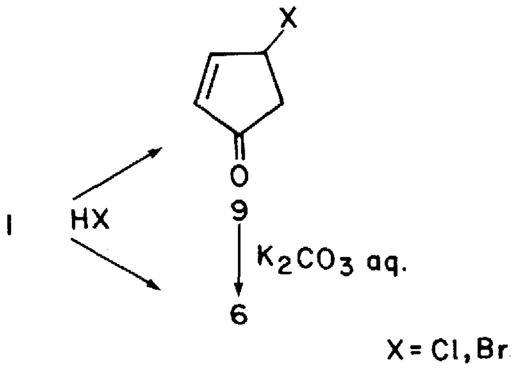
Our assignment gained further support from chemical quarters. Thus, hydrogenation of 4b over Pd/C/K_2CO_3 (anh.), provided one out of two possible dihydro diethoxy ketals (5). However, the most compelling evidence was obtained by dissolving 2 (a or b) in dry R'OH containing a catalytic amount of TFA, whereby 7 was formed in the primary stage and 8 was the ultimate product, obviously following active solvent participation.





	a	b
R	Me	Et
R'	Et	Me

Finally, strong acid catalysed hydrolysis of both 2 and 3 as well as of 4 leads to the known and versatile diketone 6.[1,2,11] Similar treatment of the monomers 1a & b (at -30°C) results also in the formation of 6 accompanied by 9 as the major product. While the latter survives acid treatment, it is readily transformed by base into 6.



There are a number of contexts for evaluation of the above results. We had wondered why the dimeric ketals (2) do not readily undergo thermal dissociation to the monomers (1), in analogy to, say, dicyclopentadiene itself. The reason lies, in part at least, with the above described, facile 2 ⟶ 4 rearrangement. We can also now understand, why this rearrangement had been overlooked in previous instances: any fraction of 1 that is not intercepted by an added dienophile, ultimately winds up as the ubiquitous diketone (6), following acid hydrolysis of itself or via 3 or 4.

The most interesting aspect, however, is the nature of the novel α,β-unsaturated ketal (2) to 3-alkoxyenolether (4) rearrangement. Surprisingly, this 1,3 shift is, to our knowledge, not documented in the vast literature covering α,β-unsaturated ketones and their ketals.[12] It is, however, well known that the latter are relatively unstable. Thus, dialkyl ketals of α,β-unsaturated ketones are very rare and ethylene ketal formation is often accompanied by migration of the α,β-double bond to the β,γ-position.[13] It stands to reason that we deal with geometry-dependent 1,3-dialkoxy vs. alkoxy-double bond interactions. With this premise, we are presently investigating the scope and mechanism of such rearrangements.

References and Notes

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