Synthesis of 3,4-Dihydro-3,3,8a-trimethylnaphthalene-1,6(2*H*,8a*H*)-dione, a 4-Acylcyclohexa-2,5-dienone

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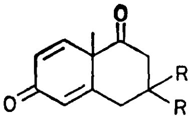
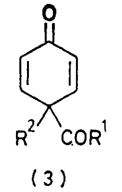
Summary The synthesis is reported of the first simple geminal acyl-substituted cyclohexadienone, which is shown to undergo very easy deacylation with formation of a phenolic ring; similar cleavage, or a formal retro-Fries rearrangement, have so far prevented isolation of the analogous 4-acetyl-4-methylcyclohexa-2,5-dienone.

We report the synthesis and properties of 3,4-dihydro-3,3,8a-trimethylnaphthalene-1,6(2*H*,8a*H*)-dione (**1**) which is of interest as the first simple 4-acylcyclohexa-2,5-dienone. This type of compound, of general structure (**3**; R^1,R^2 = alkyl) represents the product of *ipso* acylation of a 4-substituted phenol. A recent attempt to prepare the formyl compound (**3**; R^1 = H, R^2 = Me) failed because of its ready deformylation.[1] In contrast, a number of 4-alkoxycarbonyl dienones have been made. The lactones (**4**; R^1 = OEt, R^2 = CO_2Et,[2] and R^1 = OMe, R^2 = CO_2Me[3]) are sensitive intermediates in syntheses of disodium prephenate, and the lactones (**4**; R^1 = R^2 = H, and R^1 = H, R^2 = CO_2Et)[4] and the more stable esters [**5**; R^1 = Me or Et, and R^2 = Me, Et, Pr^i, CH_2Ph, Ph, CH_2CO_2Et, and $CH_2C(OMe)_2CO_2Me$] have been reported.[1–7]

Our initial target was 4-acetyl-4-methylcyclohexa-2,5-dienone (**3**; R^1 = R^2 = Me). Attempts to prepare this by dehydrogenating the corresponding 4-acetyl-4-methylcyclohex-2-enone† with selenium dioxide in t-butyl alcohol[8] gave only 4-methylphenol. With 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)[8] or benzeneseleninic anhydride[9] in non-polar solvents the product was 4-methylphenyl acetate. Because these types of dehydrogenation involve different types of reactions we believed that the only reasonable common intermediate was the desired dienone. The conversion into 4-methylphenyl acetate represents the formal reversal of a Fries rearrangement. To avoid this type of reaction we turned to bicyclic compounds.

The Wieland–Miescher ketone (**6**; R = H) and its analogue (**6**; R = Me) upon heating with DDQ or benzeneseleninic anhydride in benzene‡ gave only the phenols (**9**; R = H)[10] and (**9**; R = Me),† presumably, in one reaction at least, by dienone–phenol rearrangement of (**1**) and (**2**). We therefore prepared selectively§ the α-phenylseleno ketone (**8**; R = Me) from (**6**; R = Me) and phenylselenyl chloride.[2,4,11] Oxidation by ozone in dry ether at −78 °C to form the phenylselenoxy ketone, and warming at room temperature led to the desired dienone (**1**), purified by column chromatography on silica.¶† Oxidation of (**8**) by hydrogen peroxide, which succeeds in the preparations of 4-alkoxycarbonylcyclohexa-2,5-dienones,[1,2,4] failed to give (**1**) owing, we believe, to its ready cleavage (*vide infra*).


(1) R = Me
(2) R = H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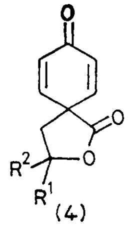
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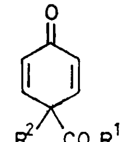
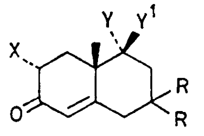
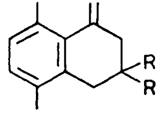
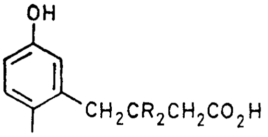
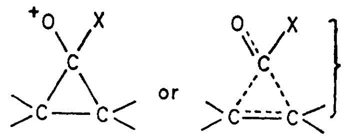

(5)


(6) X = H; YY^1 = O
(7) X = Y = H; Y^1 = OCOZ
(8) X = SePh; YY^1 = O


(9)


(10)


(11)

The dienone (**1**)† is a white crystalline solid, m.p. 71—73 °C. When pure it is thermally stable in boiling benzene (< 2% reaction in 80 h), but it is highly unstable in acidic or alkaline solution. Nucleophilic attack on the 1-ketone group of the vinylogous β-diketone function allows aromatisation of the dienone ring and cleavage of the other ring. In 5×10^{-5}, 5×10^{-4}, and 5×10^{-3} M aqueous H_2SO_4 at 25 °C its half-lives, for clean 1st order conversion into the acid (**10**; R = Me),† are 3000, 350, and 75 s, respectively. In 10^{-4} and 10^{-3} M aqueous NaOH the half-lives at 25 °C for cleavage to the anion of (**10**; R = Me) are 490 and < 6 s, respectively. In concentrated aqueous sulphuric acids the dienone (**1**) rearranges rapidly to the phenol (**9**; R = Me),† but not directly. Rapid cleavage ($t_{1/2} < 2$ s) gives the acid (**10**; R = Me) which then cyclises relatively slowly by a Friedel–Crafts type of acylation. This step, (**10**; R = Me)→ (**9**; R = Me) has half-lives in 79 and 69% H_2SO_4 of 490 s and 10 h, respectively, at 25 °C, and has precedent in the literature conversion of (**10**; R = H) into (**9**; R = H).[10]

The dienones (**5**; R^1 = Et, R^2 = Me and Et) rearrange to phenols *via* 1,2-ester migration, with $t_{1/2}$ in CF_3CO_2H at 38·5 °C of 120 and 277 min, respectively.[6] In contrast, our

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† New compounds gave satisfactory microanalytical and/or mass spectrometric data, and i.r., ^1H n.m.r., and u.v. spectra.

‡ These conditions allow excellent conversions of (**7**, R=H, Z=Me or CF_3) into the corresponding cyclohexadienones.

§ Similar selectivity was absent for reaction of (**6**; R=H).

¶ Similar attempts to prepare (**3**; R^1=R^2=Me) from 4-acetyl-4-methyl-6-phenylselenocyclohex-2-enone have so far given only 4-methylphenol and its acetate, in a ratio which varies with the reaction solvent. In contrast, all the alkoxycarbonyl dienones (**5**) were made from the cyclohexenones with SeO_2 or DDQ, or by a route involving final acid treatment.[5]

acyl dienone (**1**) is completely converted into (**9**; R = Me) and a minor side product in less than 3 min at −10 °C. In CD_2Cl_2 containing 2% of CF_3CO_2H at −10 °C the pseudo 1st order rate constant for (**1**)→(**9**; R = Me) is $2{\cdot}2 \times 10^{-3}$ s^{-1} (half-life 300 s). This reaction does not proceed *via* the acid (**10**; R = Me). A qualitative comparison of these rates with earlier data[6,12] implies that the migratory aptitude of the acyl group is considerably greater than that of an ethoxycarbonyl group. If the acyl migration in (**1**)→(**9**; R = Me) involves two successive concerted 1,2-shifts *via* a spiran intermediate[8] this result would be consistent with a transition state resembling (**11**). The mesomeric stabilisation of a migrating ethoxycarbonyl group would be wholly or partly lost on passing into (**11**; X = OEt), whereas an acyl group lacks this stabilisation throughout and should have a lower activation energy for migration. Our results cannot exclude the possibility that (**1**) leads to (**9**; R = Me) *via* a phenol-acylium ion complex similar to that presumably involved in the rearrangement of (**3**; $R^1 = R^2 =$ Me) to 4-methylphenyl acetate.

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