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

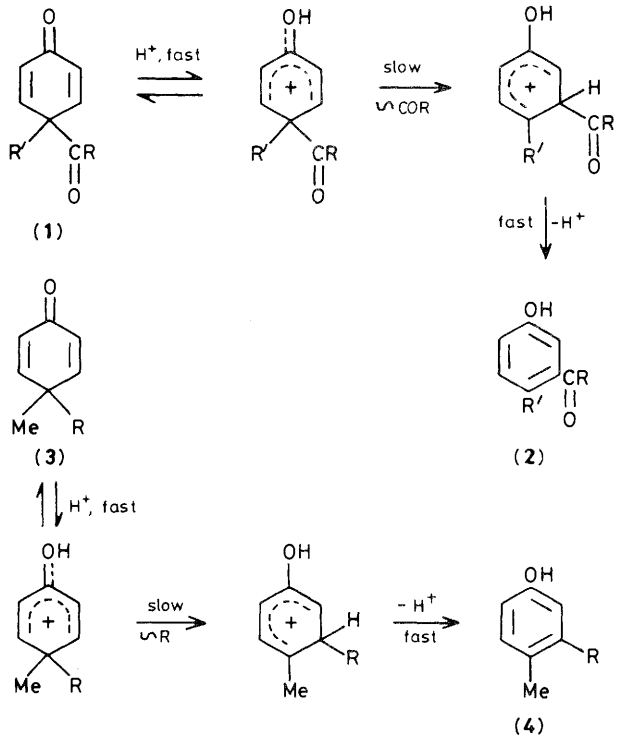
**Anthony John Waring* and Javid Hussain Zaidi**
*Department of Chemistry, University of Birmingham, P.O. Box 363, Birmingham B15 2TT*

The synthesis is reported of 3,4-dihydro-3,3,8a-trimethylnaphthalene-1,6(2*H*,8a*H*)-dione (**11**; R = Me). This is the first isolated 4-acylcyclohexa-2,5-dienone, a class of compounds postulated particularly as intermediates in the Fries and photo-Fries rearrangements. The dienone undergoes very easy acyl cleavage in the presence of bases or dilute acids, to form a phenolic acid (**18**). Similar cleavage, or a retro-Fries migration of the acyl group from the 4-position to the dienone ring oxygen, has prevented isolation of 4-acetyl-4-methylcyclohexa-2,5-dienone. Concentrated aqueous sulphuric acid causes rearrangement of the dienone to 3,4-dihydro-8-hydroxy-3,3,5-trimethylnaphthalen-1(2*H*)-one (**13**; R = Me), *via* recyclisation of (**18**). In trifluoroacetic acid solutions the same product (**13**; R = Me) is formed from the dienone by direct, formal dienone–phenol rearrangement.

4-Acylcyclohexa-2,5-dienones have been little studied because of their low stability. They have been postulated as unstable intermediates in the photo-Fries rearrangement of the carboxylate esters of phenols. For example, (**1**; R = Me, R′ = H) is believed to be an intermediate in the photo-rearrangement, with acyl migration to C-4, of phenyl acetate,[1-3] and (**1**; R = R′ = Me) in that of 4-methylphenyl acetate.[4] Similarly, the dienone (**1**; R = Ph, R′ = H) would be involved in the formation of 4-hydroxybenzophenone from phenyl benzoate.[1,5] The 4-acylcyclohexadienones are implicated as intermediates in the thermal, acid-induced Fries rearrangement equilibria between aryl carboxylates and 4- and 2-acyl-phenols.[6] They represent the products of *ipso*-acylation of 4-substituted phenols, and could also formally be produced by 4-alkylation of 4-acylphenols. (For many analogous substitutions, see ref. 7.) They have also been sought as intermediates in synthetic studies, reference to which will be made later.

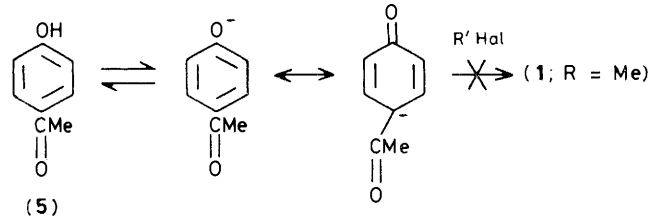
A major impetus for our interest was the hope that 4-acyl-4-alkylcyclohexadienones might be excellent compounds for measuring the migratory aptitudes (migration tendencies) of acyl groups in carbonium ion rearrangements. We hoped to measure the rates of the reaction sequence (**1**) to (**2**), in which the rate-determining step should be the acyl migration, particularly when the group R′ which is left behind is methyl. This would allow quantitative comparison with other migrating groups which we have studied previously, using the reactions (**3**) to (**4**).[8,9]

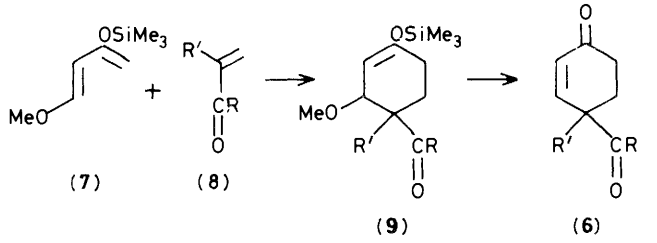
*Attempted Syntheses.*—A number of superficially attractive approaches to (**1**; R = Me, R′ = methyl or allyl) were based on the 4-alkylation of 4-hydroxyacetophenone (**5**). These have extensive analogy in the cyclohexadienone series,[7] but will not be described in detail. The high instability of the products towards bases (see later, and ref. 10), and competing ether formation, rendered this approach useless. We were led, therefore, to routes based on dehydrogenation of the cyclohexenones (**6**). These compounds are available using Danishefsky's method,[11] which uses a Diels–Alder addition of the eponymous diene (**7**) to α,β-unsaturated ketones (**8**), and then hydrolysis/elimination of the adducts (**9**). We first made 4-acetyl-4-methylcyclohexenone.[12] Various attempts to isolate the dienone (**1**, R = R′ = Me) by dehydrogenation failed, but all gave evidence that it had been formed and decomposed. Thus, reaction of the enone with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), which is believed to dehydrogenate ketones by abstracting hydride ion from the 3-position of their (1,2)-enol form,[13] gave 4-methylphenyl acetate. Treatment of the enone with benzeneseleninic anhydride, which is believed to form unsaturated ketones and dienones *via* a concerted elimination of benzeneseleninic acid from intermediate α-phenylselenoxy-ketones,[14] gave the same result. Oxidation using selenium dioxide in t-butyl alcohol, another standard route to cyclohexadienones,[7] which also succeeds in the preparation of 4-alkyl-4-ethoxycarbonylcyclohexa-2,5-dienones,[15] gave only 4-methylphenol. We believe that these reactions, which use a variety of mechanistically different pathways, give the desired dienone (**1**; R = R′ = Me), which then reacts further, as discussed later.

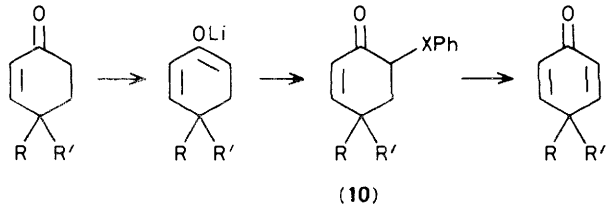


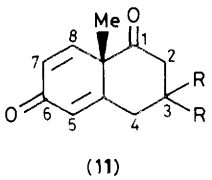

In order to achieve milder dehydrogenation conditions we tried routes employing α-phenylsulphinyl- and α-phenylselenoxy-ketones. Many ketones have been converted, *via* their

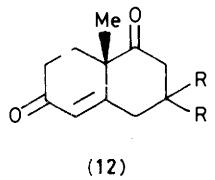
† Preliminary report: J. H. Zaidi and A. J. Waring, *J. Chem. Soc., Chem. Commun.*, 1980, 618.



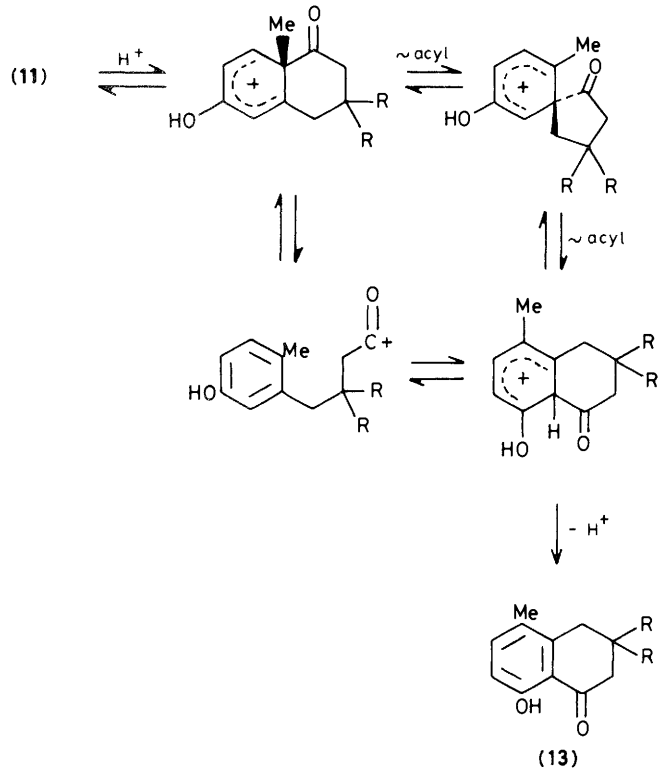




α-phenylthio derivatives, into α-phenylsulphinyl ketones, which easily lead to α,β-unsaturated ketones by elimination of benzenesulphenic acid.[16] The closest analogies at the time were the efficient conversions of 2-methyl- and 2,6-dimethyl-cyclohexanone into 6-methyl-and 2,6-dimethyl-cyclohexenone.[16] Clearly, the conversions of many cyclohex-2-enones into cyclohexa-2,5-dienones are more complex, because regiospecific enolate anion formation is required at C-6. Our 4-acetyl-4-methylcyclohexenone (**6**; R = R′ = Me) also has the enolisable acetyl group. We thought the former ambiguity was unlikely to be a problem, because Conia's group had shown that the enolates from cyclohex-2-enones are formed, under kinetic control, preferentially or exclusively at C-6.[17] We tried 4,4-dimethylcyclohex-2-enone as a model. The lithium enolate (lithium di-isopropylamide in THF) was quenched with diphenyl disulphide to give a product assumed, from its $^1$H n.m.r. spectrum, to be 4,4-dimethyl-2,5-bis(phenylthio)-cyclohexanone, formed by Michael addition of the phenylthio anion to 4,4-dimethyl-6-phenylthiocyclohex-2-enone (**10**; R = R′ = Me, X = S). Oxidation, followed by pyrolysis, gave some of the desired dienone. However, similar treatment of 4-acetyl-4-methylcyclohex-2-enone gave no trace of the corresponding dienone (**1**; R = R′ = Me). An alternative approach, used very successfully by Danishefsky and his co-workers,[18] employs the Diels–Alder addition of Danishefsky's diene (**7**) to a β-phenylsulphinyl-α,β-unsaturated ketone. The adduct readily loses benzenesulphenic acid, and with dilute aqueous acid suffers hydrolysis of the silyl enol ether and elimination of methanol. We made 3-methyl-4-phenylthiobut-3-en-2-one from 2-methylbutane-1,3-dione (3-formylbutan-2-one) and benzenethiol. Oxidation with sodium periodate gave the corresponding sulphoxide which was heated with diene (**7**) under the conditions used by Danishefsky.[18] However, the reaction mixture after work-up showed no evidence ($^1$H n.m.r.) of the desired dienone (**1**; R = R′ = Me), but only of recovered sulphoxide. We assume that the additional steric hindrance at C-3 in our sulphoxide, compared with those used before,[18] is responsible for the failure of the Diels–Alder addition.

Given the failure of the reactions described so far, we turned to seleno-ketones, which allow very mild and general introduction of α,β-unsaturation.[19] The best route from the acetyl-enone (**6**; R = R′ = Me) to its 6-phenylseleno derivative used auto-acid-catalysed enolisation, effected by heating the enone with benzeneselenenyl chloride in ethyl acetate. This method, which was developed by Plieninger and Gramlich for their synthesis of disodium prephenate[20] gave formation of the conjugated 1(6),2(3)-dienol, and selenylation at C-6, rather than at the acetyl group. A mixture of almost equal amounts of the two diastereoisomers of (**10**; X = Se, R,R′ = Me, COMe) was formed: analysis by n.m.r. spectroscopy showed that both have an equatorial phenylseleno group, and the 4-acetyl group is *cis* or *trans* to it. Oxidation of the mixture using 30% aqueous hydrogen peroxide and dichloromethane (2-phase system) at 0—25 °C gave a quantitative yield of 4-methylphenol as the sole detectable product. Oxidation using an equivalent of ozone in dry ether at −78 °C, then warming to 20 °C, similarly gave 4-methylphenol. Ozonation in dichloromethane at −78 °C, then warming and rapid aqueous work-up, gave a mixture of 4-methylphenol and its acetate. We ascribe these results to formation of the desired dienone (**1**; R = R′ = Me), with subsequent de-acetylation or migration of the acetyl group as discussed later. Comparable results were obtained by Danishefsky's group when they tried to make 4-formylcyclohexa-2,5-dienones.[21]

It is clear from the foregoing results that the dienone (**1**; R = R′ = Me) is unstable towards a variety of reagent types. We therefore sought an analogous group of compounds in which some of the instability could be suppressed. We first aimed for (**11**; R = H), in which acyl migration to the dienone oxygen is prevented. Oxidation of the Wieland–Miescher ketone (**12**; R = H) with DDQ in boiling benzene gave only 8-hydroxy-5-methyl-1,2,3,4-tetrahydronaphthalen-1-one (**13**; R = H), which is assumed to arise from the desired dienone (or its precursor cation) by migration of the acyl group, either by one 1,3-migration or by two successive 1,2-shifts as shown in Scheme 1. This unwanted result at least shows that the acyl group migrates more readily than does the methyl group under these conditions.* Protection was therefore sought for the acyl function until after the dienone ring had been formed. Borohydride reduction of (**12**) gave the known alcohol (**14**; R = R′ = H). Acetylation or trifluoroacetylation, by the acid anhydrides and pyridine, gave the known acetate (**14**; R = H, R′ = Ac)[22,23] and the trifluoroacetate (**14**; R = H, R′ = $COCF_3$). Dehydrogenation using DDQ in benzene, or more satisfactorily using benzeneseleninic anhydride (BSA),[14] gave the known acetoxy-[23] and the new trifluoroacetoxy-dienone (**15**; R = H, R′ = Ac and $COCF_3$, respectively). Attempts were then made to cleave the acetate and trifluoracetate ester functions, preparatory to mild neutral oxidation to form (**11**; R = H). Bell had previously hydrolysed the acetate, but under vigorous conditions which produced a rearranged product,

* It should be noted that methyl migration from C-8a to C-8 would leave behind an α-keto-carbenium ion which, although possible, would be unfavourable. Alkyl migration in the second step of a 2-step process (see Scheme 1) would also give such a cation.

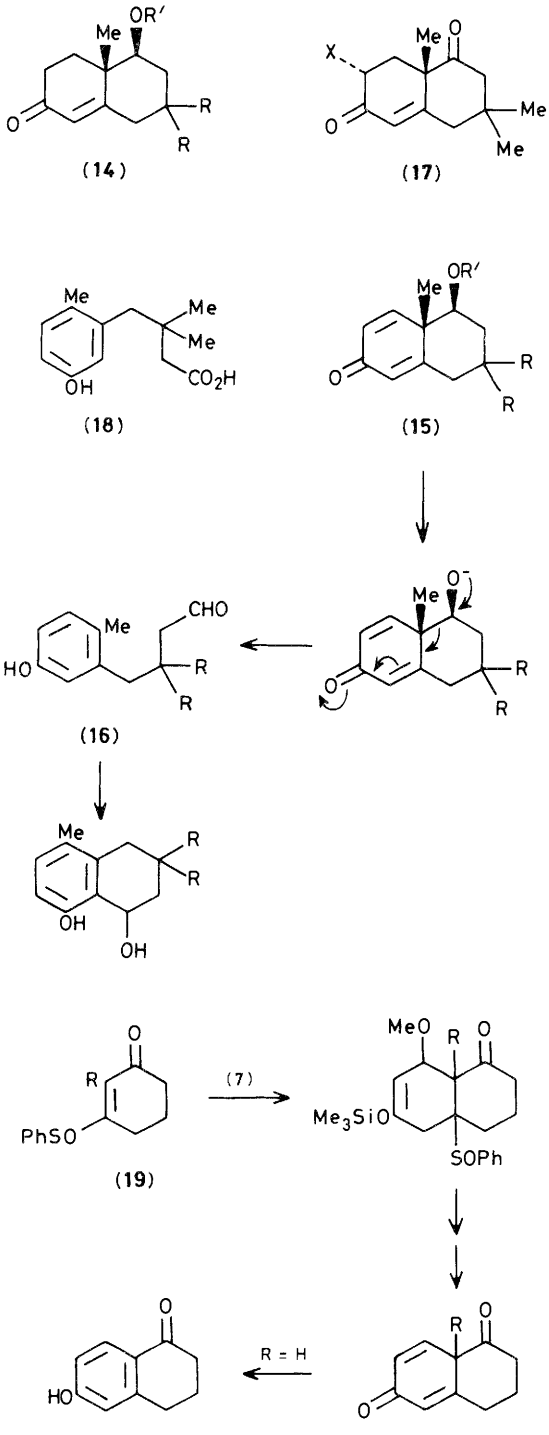


Scheme 1.

8-hydroxy-5-methyl-1,2,3,4-tetrahydronaphthalen-1-ol.[23] The hydroxy-ketone (**14**; R = R′ = H) is also known to fragment in a similar manner under alkaline conditions.[22,24] We found very mild conditions, such as treatment of the acetate with catalytic amounts of $10^{-2}$M alcoholic potassium hydroxide, or with an equivalent of $9 \times 10^{-3}$M alcoholic potassium carbonate, or of the trifluoroacetate with the latter, gave only 4-(5-hydroxy-2-methylphenyl)butanal (**16**) as a fragmentation product. This phenolic aldehyde cyclises to the 8-hydroxy-5-methyl-1,2,3,4-tetrahydro-1-naphthol under more strongly alkaline conditions. None of the desired hydroxy dienone (**15**; R = R′ = H) was detected. We also briefly investigated acid-sensitive protecting groups for the acyl function, but found the tetrahydropyranyl ether of the alcohol (**14**; R = R′ = H),[25] for example, to be completely decomposed by reaction with DDQ. Other cases were also unsuccessful.

An alternative potential route to (**11**; R = R′ = H) (Scheme 2) was based on Danishefsky's addition of the diene (**7**) to the phenylsulphinyl ketone (**19**; R = H), which led ultimately to 6-hydroxy-1,2,3,4-tetrahydronaphthalen-1-one, the phenolic tautomer of a dienone.[18] The same approach has been applied more recently also.[26] We prepared 2-methyl-3-phenylthiocyclohex-2-enone, which was oxidised incompletely to the sulphoxide (**19**; R = Me). All our attempts to achieve Diels–Alder addition led only to slow decomposition of the diene (**7**), with recovery of the sulphoxide, and no detectable dienone formation. As before we ascribe this failure to the additional steric hindrance introduced by the 2-methyl group in the dienophile.

The evidence so far was that the reactivity of the non-dienone ring needed to be reduced further, particularly towards nucleophilic attack at the acyl group. The bicyclic enone (**12**; R = H), a vinylogous β-diketone having a fully alkylated α-carbon atom, is known to be very susceptible to alkaline cleavage.[27–29] We therefore made known bicyclic enone (**12**; R = Me) from dimedone.[30] In accord with our parallel study



Scheme 2.

of (**12**; R = H), DDQ oxidation of this enone gave the hydroxytrimethyltetralone (**13**; R = Me), whose structure was studied critically (see Experimental section). Again, it seems that the desired dienone is formed, but that it undergoes a dienone–phenol rearrangement, formally as shown in Scheme 1. Our next aim was to produce a lithium enolate from the enone (**12**; R = Me). The kinetically controlled enolate formation would be expected to occur on the α′-side of the α,β-unsaturated ketone function, as is found for monocyclic cyclohexenones,[17] a tendency which should be reinforced by the presence of the gem-dimethyl group. When (**12**; R = Me) was added to a slight

excess of lithium di-isopropylamide in THF at —78 °C, then warmed to 5 °C and treated with an excess of bromine in dichloromethane, no evidence was found of the expected[17,31] α-bromo-ketone (**17**; X = Br). Only the starting enone was recovered. Grieco and his co-workers have subsequently reported that the Wieland–Miescher ketone (**12**; R = H) and its 4α-methyl derivative both form the enolates of the saturated ketone function under the same conditions.[32] It seemed then that formation of the desired α-phenylseleno-ketone from the enolate in this way would fail. However, treatment of the enone (**12**; R = Me) with benzeneselenenyl chloride in ethyl acetate[20,33] gave the stable phenylseleno-ketone (**17**; R = α-SePh), as white crystals. Oxidation with aqueous hydrogen peroxide at 0 °C, which served in the preparation of disodium prephenate,[20] caused fragmentation to the acid (**18**), which will be met again later. Oxidation with *m*-chloroperbenzoic acid in dichloromethane at −10 °C gave the dienone, but adequate purification proved impossible. However, the use of a molar equivalent of ozone in ether at −78 °C, followed by warming of the selenoxide solution [**17**; X = Se(O)Ph] to 20 °C to effect elimination, gave the dienone (**11**; R = Me), eventually as a white crystalline solid after a critical purification.

*Properties of the Cyclohexadienone* (**11**; R = Me).—The pure dienone is thermally stable; it does not (<0.1%) decompose on being heated at reflux in benzene, under nitrogen during 72 h. It is, however, very sensitive towards acids and bases. In 5 × $10^{-3}$M aqueous sulphuric acid at 25 °C it has a half-life of 90 s. Rate constants for its decomposition are given in the Experimental section. Preparative reactions in aqueous acids or alkalis gave the cleavage product (**18**), a phenolic acid. In $10^{-4}$M sodium hydroxide the dienone's half-life is 490 s: in $10^{-3}$M hydroxide the value is a few seconds. A different product is formed when the dienone is treated with concentrated sulphuric acids. In 78.0% aqueous sulphuric acid at 25 °C the hydroxytetralone (**13**; R = Me) is the sole product. The same compound is given from the cleaved acid (**18**) under the same conditions and, most importantly, at the same rate. The same held true in 68% acid. However, in 50% acid the dienone gave only the cleaved acid (**18**) which did not react further within 24 h. We conclude that the dienone cleaves very rapidly to (**18**), which is stable in less than about 50% sulphuric acid, but cyclises to give the hydroxytetralone in more concentrated acid. Under these conditions, this seems to be the sole route to the tetralone.

In attempts to observe true acyl migrations which might convert the dienone into (**13**; R = Me) *via* the sequence shown in Scheme 1, we investigated rearrangements induced by trifluoroacetic acid. Marx and his co-workers had observed clean migration of the ethoxycarbonyl group from C-4 to C-3 of 4-alkyl-4-ethoxycarbonylcyclohexadienones, at a convenient rate, when neat trifluoroacetic acid was used as the solvent.[15] When our dienone was injected into the neat acid at −10 °C in an n.m.r. tube, rapidly mixed, and the spectrum recorded immediately, the dienone was found to be completely converted into the tetralone (**13**; R = Me). The same was found using 15% w/w trifluoroacetic acid in deuteriated dichloromethane at −20 °C. However, reaction in 2.1% w/w acid in this solvent at −10 °C proceeded at a measurable rate (half-life 315 s), and again gave only the tetralone. No intermediate could be detected. Separate experiments showed that the open-chain acid (**18**) does not react under these conditions: in particular, it does not cyclise to the tetralone.

## Discussion

It is clear from this work that 4-acylcyclohexa-2,5-dienones can be made, but that they are sensitive in a number of ways. First, they are readily cleaved by nucleophiles. This type of reactivity will be discussed in detail in a later report, but it is in accord with the dienones being vinylogues of 2,2-disubstituted 1,3-diketones, which have the same property,[34] with the additional driving force of aromatisation. This severely restricts the methods available for preparing the dienones, and explains the failure of previous attempts.[21,26] The analogous 4-alkoxycarbonyl-4-alkylcyclohexadienones are much more stable and can be made by relatively vigorous procedures.[15,21]

The second type of sensitivity of the acyl dienones is towards acids. The cleavage in dilute acid was not studied in detail, but the profile of a plot of $\log_{10}$ (rate constant) against pH is parallel to those obtained in more extensive studies on pure, isolated 4-acylcyclohexa-2,5-dienones.[10] We believe, therefore, that the cleavage is by an *A*1 process, in which the dienone is protonated, rapidly and reversibly, at the dienone carbonyl oxygen, and then suffers rate-determining cleavage of the dienone-to-acyl bond.[10] The next type of reaction in acidic media is the easy acyl migration from C-4 to the carbonyl oxygen atom shown up in some of our preparative work. Subsequent studies on simpler, isolated 4-acyl-4-alkylcyclohexa-2,5-dienones have shown this reaction to be general.[10] Formally it is a reversal of the well known Fries rearrangement. The closest analogy we know is the reversible conversion of a number of 2- and 4-benzoyl-phenols into the corresponding phenyl benzoates.[6] This was effected by strong heating in the presence of trifluoromethanesulphonic acid, which is clearly needed to effect *ipso* protonation of the acyl phenols, and gives the dienone tautomer which then rearranges. In one case studied[6a] it was found that the benzoyl group of a 4-benzoylphenol migrated relatively rapidly to the dienone oxygen atom, to form the phenyl benzoate, but that benzoyl migration from oxygen, or from the 4-position, to C-2, is much slower. The 2-benzoylphenol is the most stable isomer, and Effenberger has given evidence for a dissociation/recombination process.[6a] The rearrangement of the acyl dienone (**11**; R = Me) to the hydroxytetralone (**13**; R = Me) presents mechanistic difficulties, which we are studying with the help of other compounds. The overall process is of a 1,3-acyl migration, from the 4- to the 2-position of the potential phenol ring. If this were to occur by an intramolecular process, by two successive 1,2-migration steps (Scheme 1), it would be similar to many dienone rearrangements known in steroidal and related compounds.[7,35] The calculation of a migration tendency for the acyl group would then be possible, in principle. If, however, the migration were to occur by a dissociation/recombination process, as also shown in Scheme 1, this concept would have little validity. We hope to be able to give evidence on this matter shortly.

## Experimental

*4-Acetyl-4-methylcyclohex-2-enone* (**6**; R = R′ = Me).[12]—3-Methylbut-3-en-2-one (methyl isopropenyl ketone)[36] (7.0 g) and 1-methoxy-3-trimethylsilyloxybuta-1,3-diene (**7**)[11] (12.32 g) were mixed in dry benzene (40 $cm^3$) and the mixture was stirred at reflux under nitrogen during 14 h. The residue obtained after the mixture had been cooled and evaporated under reduced pressure was mixed with hydrochloric acid (40 $cm^3$; 0.1M) and THF to render the mixture homogeneous, and it was stirred for 1 h at 20 °C. After dilution with water (30 $cm^3$), extraction with ether, washing of the extracts (saturated aqueous sodium hydrogen carbonate, then water), and evaporation, the crude title compound was obtained as a yellow oil. Spinning-band distillation gave pure enone (2.7 g, 25%) as a pale yellow oil, $\nu_{max.}$($CCl_4$) 2 970, 2 930, 1 710, and 1 680 $cm^{-1}$; δ($CCl_4$) 1.35 (3 H, s, 4-Me), 2.18 (3 H, s, acetyl), 5.89 (1 H, d, *J* 11 Hz, 2-H), and 6.91 (1 H, d, *J* 11 Hz, 3-H) (Found: C, 71.3; H, 8.1. Calc. for $C_9H_{12}O_2$: C, 71.0; H, 7.9%).

*Oxidation of* 4-*Acetyl*-4-*methylcyclohex*-2-*enone*.—(a) *With DDQ*. The preceding enone (0.20 g) was added to DDQ (0.30 g, 1.0 mol equiv.) in dry benzene (10 $cm^3$) and the mixture heated at reflux under nitrogen, with g.l.c. monitoring (25% XF1150 column at 180 °C). After 85 h and 180 h additional DDQ (0.30 g each time) was added. After 220 h, at 90% conversion, the mixture was cooled, filtered, and concentrated under reduced pressure. The solid residue was extracted with boiling ether (4 × 15 $cm^3$), and the extracts were washed successively with aqueous sodium sulphite and water, and dried. The product after concentration (0.1 g, 35%) was identical (i.r., $^1H$ n.m.r. g.l.c.) with an authentic sample of 4-methylphenyl acetate.

(b) *With benzeneseleninic anhydride* (*BSA*). The enone (0.1 g) was dissolved in dry benzene (10 $cm^3$), BSA[37] (0.24 g, 1 mol equiv.) was added, and the mixture was treated at reflux under nitrogen, with monitoring as above. Additional BSA (0.24 g) was added after 36 h, and all starting material was used up by 48 h. After being cooled, diluted with ether, and washed (aqueous sodium hydrogen carbonate, then water), the dried solution was concentrated to a yellow mass. Chromatography [15 cm silica column; light petroleum (40—60 °C)] gave only diphenyl diselenide and 4-methylphenyl acetate (0.03 g).

(c) *With selenium dioxide*. The enone (0.1 g) was heated at reflux, under nitrogen, with freshly sublimed selenium dioxide (74 mg, 1 mol equiv.) in t-butyl alcohol (10 $cm^3$) and a little glacial acetic acid during 18 h. Analysis by g.l.c. showed 95—98% conversion into 4-methylphenol. Work-up as in ref. 38 gave 4-methylphenol.

*Sulphenylation, and Attempted Dehydrosulphenylation of* 4-*Acetyl*-4-*methylcyclohex*-2-*enone*.—The enone (0.50 g, 3.3 mmol) was dissolved in dried THF (5 $cm^3$) and the solution was added to lithium di-isopropylamide (from 3.56 mmol of n-butyllithium), with 2,2′-bipyridyl as indicator, under nitrogen, at −78 °C. After being warmed, and kept at 0—5 °C for 15 min, the solution was heated with diphenyl disulphide (0.776 g, 3.56 mmol) and was stirred at 20 °C overnight. The mixture was diluted with ether, washed successively with 10% hydrochloric acid, aqueous sodium hydrogen carbonate, and brine, and dried. Evaporation gave the sulphenylation product (0.95 g) as a yellow solid. This was dissolved in methanol (30 $cm^3$) and oxidised[39] at 0 °C with saturated aqueous sodium periodate (0.55 g in 20 $cm^3$). A thick white precipitate formed within 5 min, and the mixture was stirred overnight at 20 °C. It was then diluted with water, extracted ($CHCl_3$), the extracts washed with brine, dried, and the solvent evaporated off. The residue was heated at reflux overnight in sodium-dried toluene (25 $cm^3$). The residue obtained after concentration showed no evidence of the dienone (**1**; R = R′ = Me) by n.m.r. analysis.

*Sulphenylation and Dehydrosulphenylation of* 4,4-*Dimethylcyclohex*-2-*enone*.—The cyclohexenone[36] (0.50 g, 3.3 mmol) was treated as above. The product, a pale yellow solid, had δ($CCl_4$) 8.8 (6 H, s, gem dimethyl), 2.75 (m, 2 Ph), and a complex methylene absorption, but no olefinic peaks. We assume the product to be 4,4-dimethyl-2,5-bis(phenylthio)cyclohexanone, formed by Michael addition of phenylthio anion to an initially formed 6-phenylthiocyclohex-2-enone. Pyrolysis as above gave as product a compound with g.l.c. behaviour identical with that of authentic 4,4-dimethylcyclohexa-2,5-dienone.

3-*Methyl*-4-*phenylthiobut*-3-*en*-2-*one*.—2-Methyl-3-oxobutanal[40] (6.0 g, 0.06 mol) was heated with benzenethiol (6.2 g, 0.061 mol) and toluene-*p*-sulphonic acid (0.60 g) in benzene, under nitrogen, with removal of water using a Dean–Stark head.[41] After 8 h, water (1.3 $cm^3$) had collected, and the mixture was cooled, poured into 1% aqueous sodium hydroxide, and extracted with ether (5 × 25 $cm^3$). The extract was washed successively with 25% aqueous potassium hydroxide, water, and brine. After the extract had been dried the solvent was evaporated off, and the brown oil was distilled using a spinning-band column, to give the *thio-enol ether*, a yellow oil, b.p. 120—125 °C at 0.1 mmHg, $\nu_{max.}$($CCl_4$) 3 058, 2 920, 1 660, 1 580, and 690 $cm^{-1}$; δ($CCl_4$) 1.85 (3 H, s, 3-Me), 2.28 (3 H, s, 1-$H_3$), and 7.37—7.08 (6 H, 4-H and Ph) (Found: C, 68.7; H, 6.2; S, 17.0. $C_{11}H_{12}OS$ requires C, 68.7; H, 6.3; S, 16.7%).

*Oxidation to* 3-*Methyl*-4-*phenylsulphinylbut*-3-*en*-2-*one, and attempted Diels–Alder Addition to the Diene* (**7**).—The foregoing sulphide (1.0 g) was oxidised as described above[39] to give a yellow oil (0.95 g), δ($CCl_4$) 1.84 (3 H, s, 3-Me), 2.12 (3 H, s, 1-$H_3$), and 7.6—7.15 (6 H, m, 4-H and Ph), whose microanalysis suggested it to be mainly the title sulphoxide, contaminated with unchanged starting sulphide. This mixture (0.5 g) was heated with the diene (**7**) (0.73 g) in anhydrous toluene (20 $cm^3$), under nitrogen, for 50 h. Analysis by g.l.c., and work-up of the product, showed no reaction to have taken place: the sulphoxide was recovered.

4-*Acetyl*-4-*methyl*-6-*phenylselenocyclohex*-2-*enone* (**10**; R,R′ = Me,COMe, X = Se).—4-Acetyl-4-methylcyclohex-2-enone (**6**; R = R′ = Me) (0.5 g) was dissolved in freshly dried, distilled ethyl acetate (15 $cm^3$) and the solution was stirred vigorously while benzeneselenenyl chloride (0.63 g) was added at 20 °C. The reaction was monitored by t.l.c. [silica; benzene–ether (4:1)]. After 4 h the mixture was washed successively with water and brine, dried, and evaporated to give a crude yellow oil. This was subjected to a preliminary purification by rapid chromatography on Merck Kieselgel 60 (70—230 mesh, 30 × 3 cm) using benzene (*ca.* 100 $cm^3$) to elute fast running side-products. The residue on the column was removed with ether, the eluate was rapidly evaporated in the cold, and the residue was re-chromatographed carefully on a similar column (40 × 3 cm), using benzene–ether (4:1) as eluant, to give the *seleno-ketone* as a mixture of two diastereoisomers, in the ratio 55:45, $\nu_{max.}$($CCl_4$) 1 720 and 1 692 $cm^{-1}$; δ($CCl_4$) (major isomer) 1.27 (s, 4-Me), 2.05 (s, acetyl), 4.20 (d of d, *J* 12 and 6 Hz, 6-H), 5.95 (d, *J* 10 Hz, 2-H), and 6.75 (d of d, *J* 10 and 1—2 Hz, 3-H); (minor isomer) 1.25 (s, 4-Me), 2.17 (s, acetyl), 4.02 (d of d, Σ *J* 13 Hz, 6-H), 5.92 (d, *J* 10 Hz, 2-H), and 6.85 (d, *J* 10 Hz, 3-H): both isomers have δ 1.9—2.8 (2 H, m, 5-H) and 7.2—7.5 (m, SePh) (Found: C, 58.3; H, 5.2. $C_{15}H_{16}O_2Se$ requires C, 58.6; H, 5.2%).

*Oxidation of* 4-*Acetyl*-4-*methyl*-6-*phenylselenocyclohex*-2-*enone* (**10**; X = Se, R,R′ = Me,COMe).—(a) *By hydrogen peroxide*. The preceding mixture (0.20 g) in dry dichloromethane (10 $cm^3$) was stirred at 0 °C whilst 30% aqueous hydrogen peroxide (0.18 $cm^3$) was added. After 2 h at 0 °C the mixture was warmed to 20 °C, diluted with water, and extracted repeatedly with dichloromethane. Evaporation of the dried extracts gave a quantitative yield of an oil, shown by g.l.c. and n.m.r. spectroscopy to be 4-methylphenol.

(b) *By ozone in ether*. The seleno-ketone mixture (0.12 g) in stirred dry ether (15 $cm^3$) was kept at −78 °C and dry ozone was passed in slowly until no further white precipitate formed. After warming to 20 °C the mixture was rapidly washed successively with saturated aqueous sodium hydrogen carbonate and brine, and dried. Analysis by g.l.c., i.r., and n.m.r. spectroscopy showed the product (42 mg, 100%) to be 4-methylphenol.

(c) *As in* (b), *with addition of acid before warming*. In order to ensure rearrangement, the seleno-ketone mixture (0.10 g) was treated as in (b), except that after the ozone had been passed in there was added trifluoracetic acid (1 drop), and the mixture was warmed and treated as above. The product was again 4-methylphenol (30 mg, 85%).

(d) *By ozone in dichloromethane.* The seleno-ketone mixture (0.16 g) in freshly dried and distilled dichloromethane was treated with ozone until the solution just became blue. Oxygen was bubbled in to expel excess of ozone, and the solution was warmed to 20 °C during 1.5 h. Work-up as above gave an oil shown by i.r. and n.m.r. spectra and g.l.c. to be a mixture of 4-methylphenol and its acetate.

8a-*Methyl*-3,4,7,8-*tetrahydronaphthalene*-1,6(2H,8aH)-*dione* (**12**; R = H).—2-Methylcyclohexane-1,3-dione[42] was treated with but-3-en-2-one (methyl vinyl ketone),[43] to give the title compound, m.p. 45—50 °C (lit.,[43] 47—50 °C).

*Oxidation of Compound* (**12**; R = H) *with DDQ.*—The preceding enone (4.0 g) was added to a solution of DDQ (5.08 g, 1 mol equiv.) in benzene (100 $cm^3$) and the mixture was heated at reflux under nitrogen. The reaction was followed by g.l.c. (20% NGS column at 230 °C). After 90 and 180 h further DDQ (2.54 g) was added. At 240 h almost all the enone had been consumed. The mixture was cooled, filtered, and concentrated. The residue was extracted with boiling light petroleum (b.p. 40—60 °C; 6 × 25 $cm^3$), and the combined extracts were washed successively with aqueous sodium sulphite and water, and dried. Concentration gave 8-hydroxy-5-methyl-1,2,3,4-tetrahydronaphthalen-1-one (**13**; R = H) (0.77 g, 20%), m.p. 48—50 °C (lit.,[29] 47—48.5 °C), with i.r., u.v., and $^1H$ n.m.r. spectra in excellent agreement with published data.[29]

cis-5-*Acetoxy*-4a-*methyl*-5,6,7,8-*tetrahydronaphthalene*-2(4aH)-*one* (**15**; R = H, R′ = COMe.—*cis*-5-Hydroxy-4a-methyl-3,4,5,6,7,8-hexahydronaphthalene-2(4a*H*)-one (**14**; R = R′ = H) was made by borohydride reduction of the preceding ketone.[44] The derived acetate[44] (0.1 g) in dried, distilled chlorobenzene was treated with benzeneseleninic anhydride (0.16 g) and the mixture was heated at reflux, under nitrogen, for 30 min. The residue obtained after evaporation was diluted with ether, and the solution was washed successively with aqueous sodium hydrogen carbonate and water, dried, and evaporated to give a yellow mass. Chromatography on a silica column [light petrol (b.p. 40—60 °C), then ether] gave the dienone (70 mg, 70%), m.p. 82—84 °C, identical with a sample made in lower yield by DDQ oxidation following ref. 23.

*Hydrolysis of* cis-5-*Acetoxy*-4a-*methyl*-5,6,7,8-*tetrahydronaphthalene*-2(4aH)-*one* (**15**; R = H, R′ = COMe).—(a) *Using potassium carbonate in methanol.* The preceding acetoxy-dienone (30 mg) was stirred with potassium carbonate (18.85 mg) in methanol (15 $cm^3$) at 20 °C. After 24 h, when reaction was complete, water was added and the mixture was extracted with dichloromethane. Evaporation of the dried extract gave an oil identical with that described next.

(b) *Using potassium hydroxide in methanol.* Hydrolysis of the acetoxy-dienone (100 mg) in 0.01M methanolic potassium hydroxide (44 $cm^3$) for 5 h at 20 °C, and work-up as above, gave an oil (85 mg), *ca.* 98% pure (g.l.c. on a 20% NGS column at 230 °C), $\nu_{max.}(CHCl_3)$ 3 600 (phenolic OH), 2 940, 2 870, 2 730, 1 725 (CHO), and 1 620 (aryl) $cm^{-1}$; $\delta(CDCl_3)$ 1.86 (2 H, quin., *J* 8 Hz, 3-$CH_2$), 2.20 (3 H, s, 2′-Me), 2.48 and 2.57 (each 2 H, each t, *J* 8 Hz, benzylic $CH_2$ and $CH_2CHO$), 5.2 (1 H, br, OH), 6.55 (1 H, d, *J* 10 Hz, 4′-H), 6.60 (1 H, s, 6′-H), 6.96 (1 H, d, *J* 10 Hz, 3′-H), and 9.75 (1 H, s, CHO). These data suggest that the compound is 4-(5′-hydroxy-2′-methylphenyl)butanal (**16**; R = H), formerly suggested as the intermediate in the hydrolytic rearrangement of (**15**; R = H, R′ = COMe) to 8-hydroxy-5-methyl-1,2,3,4-tetrahydro-1-naphthol.[23] A satisfactory elemental analysis was not obtained for the aldehyde.

cis-4a-*Methyl*-5-*trifluoroacetoxy*-3,4,5,6,7,8-*hexahydronaphthalene*-2(4aH)-*one* (**14**; R = H, R′ = $COCF_3$).—To a solution of *cis*-5-hydroxy-4a-methyl-3,4,5,6,7,8-hexahydronaphthalene-2(4a*H*)-one (**14**; R = R′ = H) (0.5 g) in pyridine (2.5 $cm^3$) was added trifluoroacetic anhydride (0.5 $cm^3$). After being kept at 20 °C overnight the mixture was diluted with ether, washed with water, and dried. Evaporation of the solvent gave the *trifluoroacetate* (0.35 g, 46%) as white crystals, m.p. 54—56 °C [from light petrol (b.p. 40—60 °C) at −78 °C], $\nu_{max.}(CCl_4)$ 1 790 (trifluoroacetate), 1 690, 1 630, and 1 156—1 176 (CF) $cm^{-1}$; $\delta(CCl_4)$ 1.33 (3 H, s, 4a-Me), 4.92—4.66 (1 H, m, 5-H), 5.73 (1 H, br s, 1-H), and 1.7—2.5 (10 H, m, $CH_2$ groups) (Found: C, 56.2; H, 5.8. $C_{13}H_{15}F_3O_3$ requires C, 56.5; H, 5.5%).

cis-4a-*Methyl*-5-*trifluoroacetoxy*-5,6,7,8-*tetrahydronaphthalene*-2(4aH)-*one* (**15**; R = H, R′ = $COCF_3$).—(a) *Using benzeneseleninic anhydride.* To a solution of the preceding enone (0.1 g) in dry benzene (10 $cm^3$) was added benzeneseleninic anhydride (0.13 g) and the mixture was heated under reflux (nitrogen). The reaction was followed by g.l.c. (25% XF1150 at 200 °C). Further BSA (0.13 g) was added at 36 h. At 72 h conversion was complete. Work-up as in the oxidation of (**6**; R = R′ = Me), with chromatography on silica, gave the *dienone* (60 mg, 60%) as an oil, $\nu_{max.}(CCl_4)$ 1 790, 1 675, 1 640, 1 615, and 1 150—1 180 $cm^{-1}$; $\delta(CCl_4)$ 1.39 (3 H, s, 4a-Me), 4.81—4.58 (1 H, m, 5-H), 6.08 (1 H, s, 1-H), 6.17 (1 H, d, *J* 9 Hz, of d, *J* 2 Hz, 3-H), and 6.73 (1 H, d, *J* 9 Hz, 4-H).

(b) *Using DDQ.* The enone (0.20 g) was added to a solution of DDQ (0.164 g) in benzene (15 $cm^3$) and the mixture was heated at reflux, as described for (**6**; R = R′ = Me). After 48 h a further portion (0.164 g) of DDQ was added. After 72 h the mixture (95% converted) was worked up as described above to give the same dienone (60 mg, 95—96% pure).

*Hydrolysis of the Dienone* (**15**; R = H, R′ = $COCF_3$).—Hydrolysis of the preceding dienone (30 mg) with potassium hydrogen carbonate (12 mg) in methanol (15 $cm^3$) for 2 h at 20 °C gave complete conversion into 4-(5-hydroxy-2-methylphenyl)butanal (**16**; R = H), identical with the sample obtained earlier.

2-*Methyl*-3-*phenylthiocyclohex*-2-*enone.*—Benzenethiol (3.6 g) and toluene-*p*-sulphonic acid (0.40 g) were added to a solution of 2-methylcyclohexane-1,3-dione (4.0 g) in benzene (100 $cm^3$), and the reaction was allowed to proceed as described earlier for the preparation of 3-methyl-4-phenylthiobut-3-en-2-one. Work-up gave the *thio compound*, white crystals (3.8 g, 54%), m.p. 96—98 °C (from ethanol); $\nu_{max.}(CCl_4)$ 2 950, 2 865, 1 670, 1 600, and 690 $cm^{-1}$; $\delta(CCl_4)$ 1.90 (3 H, t, *J* 1.7 Hz, 2-Me), 2.38—1.84 (6 H, 4-, 5-, and 6-$H_2$), and 7.42—7.39 (5 H, Ph) (Found: C, 71.8; H, 6.4; S, 15.0. $C_{13}H_{14}OS$ requires C, 71.5; H, 6.5; S, 14.7%).

2-*Methyl*-3-*phenylsulphinylcyclohex*-2-*enone* (**19**; R = Me), *and Attempted Addition to* (**7**).—The preceding compound (1.0 g, 4.59 mmol) dissolved in stirred methanol was oxidised with aqueous sodium periodate (containing 1.58 g, 6.86 mmol)[39] during 5 min at 0 °C. A thick white precipitate formed almost immediately. The mixture was then stirred at 20 °C overnight, and the mixture was diluted with water and extracted with chloroform. The washed (brine) and dried extracts were concentrated to give pale yellow crystals. Recrystallisation from hexane gave white crystals (0.92 g, 85%), m.p. 45—50 °C, which from their microanalysis and n.m.r. spectra appeared to be a mixture of the phenylsulphinyl ketone and the starting material. This was used for attempted addition to 1-methoxy-3-trimethylsilyloxybuta-1,3-diene (**7**)[11] following the procedures described earlier. Monitoring by g.l.c. and final work-up showed

there to be no reaction within 50 h, apart from decomposition of (7).

3,3,8a-*Trimethyl*-3,4,7,8-*tetrahydronaphthalene*-1,6(2H,8aH)-*dione* (**12**; R = Me).—2,5,5-Trimethylcyclohexane-1,3-dione was made from dimedone, and converted by Heathcock's group's procedure[30] into the bicyclic enone.

*Reaction of Compound* (**12**; R = Me) *with DDQ*.—The preceding enone (0.5 g) was added to a solution of DDQ (0.55 g) in dried benzene (15 $cm^3$), and the mixture was heated under reflux (nitrogen), with monitoring by g.l.c., as described for the reaction of (**6**; R = R′ = Me). Further DDQ (0.30 g) was added at 60 h. Work-up, as before, after 75 h gave 8-*hydroxy*-3,3,5-*trimethyl*-3,4-*dihydronaphthalene*-1(2H)-*one* (**13**; R = Me) (0.273 g, 55%) as slightly yellow crystals, m.p. 74—76 °C [from light petroleum (b.p. 40—60 °C)]; $\nu_{max.}$($CCl_4$) 3 400—3 070w, br (hydrogen-bonded OH), 1 645 (hydrogen-bonded carbonyl), and 1 615 $cm^{-1}$; $\lambda_{max.}$(EtOH) 214, 261, and 345 nm (log ε 4.11, 3.96, and 3.51), in excellent agreement (position, shape, and intensity) with that of (**13**; R = H); δ($CCl_4$) 1.12 (6 H, s, gem-dimethyl), 2.17 (3 H, s, 5-Me), 6.62 (1 H, d, *J* 8.5 Hz, 7-H), 7.14 (1 H, d, *J* 8.5 Hz, 6-H), and 2.63 and 2.44 (4 H, 2 s, benzylic $CH_2$ and $COCH_2$) (Found: C, 76.5; H, 8.0. $C_{13}H_{16}O_2$ requires C, 76.4; H, 7.9%). Measurements at low and high concentrations showed no change in the relative intensities of the hydroxyl and carbonyl peaks in the i.r. spectrum, and indicate the proximity of these groups (thus excluding the 5-hydroxy-1-tetralone structure). This parallels the behaviour of (**13**; R = H).

*Reduction of Compound* (**12**; R = Me).—The ketone (**12**; R = Me) (1.0 g, 4.85 mmol) was reduced with sodium borohydride (47 mg, 1.27 mmol) in ethanol (75 $cm^3$) at 0 °C during 2 h. Excess of borohydride was destroyed by acetic acid, the solvent was removed under reduced pressure, and the residue was taken up in chloroform, and the extract was washed and dried. Analysis by g.l.c. (20% NGS at 230 °C) showed the mixture to contain equal parts of starting material and a new product. Acetylation by reaction with acetic anhydride–pyridine, and work-up as described for (**14**; R = H, R′ = $COCF_3$), gave a crystalline product [m.p. 75—80 °C, from light petroleum (b.p. 40—60 °C)], identified as *cis*-6-acetoxy-3,3,8a-trimethyl-2,3,4,6,7,8-hexahydronaphthalene-1(8a*H*)-one. This had formed by reduction of the enone carbonyl group to hydroxyl. The compound has spectra incompatible with a structure analogous to (**14**; R = Me, R′ = COMe): δ($CCl_4$) 0.76 (3 H, s, 8a-Me), 1.08 and 1.28 (each 3 H, 2 s, gem-dimethyl), 1.96 (3 H, s, acetate), 5.2 (1 H, m, 6-H), and 5.35 (1 H, br, 5-H); $\nu_{max.}$($CCl_4$) 2 962, 2 880, 1 740, and 1 720 $cm^{-1}$ (unconjugated ketone). Similar reduction using sodium borohydride (0.185 g, 5.0 mmol) gave crystalline 1,6-*dihydroxy*-3,3,8a-*trimethyl*-1,2,3,4,6,7,8,8a-*octahydronaphthalene*, m.p. 162—164 °C [from chloroform–ethyl acetate (1:1)]; $\nu_{max.}$(Nujol) 3 500—3 100 $cm^{-1}$, with no carbonyl absorption; δ[$(CD_3)_2SO$] 0.78 (3 H, s, 8a-Me), 0.91 (6 H, s, gem-dimethyl), and 5.25 (1 H, br, 5-H) (Found: C, 73.9; H, 10.7. $C_{13}H_{22}O_2$ requires C, 74.2; H, 10.5%).

3,3,8a-*Trimethyl*-7-*phenylseleno*-3,4,7,8-*tetrahydronaphthalene*-1,6(2H,8aH)-*dione* (**17**; X = SePh).—A solution of the enone (**12**; R = Me) (1.0 g, 4.85 mmol) in freshly dried and distilled ethyl acetate (45 $cm^3$) was treated with benzeneselenenyl chloride (1.05 g, 5.35 mmol) and vigorously stirred at 20 °C. The reaction was monitored by t.l.c. After 7 h the mixture was washed with water, and the dried organic phase was concentrated to a yellow oil. This was twice chromatographed, as described for the preparation of (**10**; R = R′ = Me, COMe, X = Se), and the crystalline *seleno-ketone* washed with ether–light petroleum at 0 °C to give white crystals, m.p. 97—99 °C, $\nu_{max.}$($CCl_4$) 2 970, 1 720, and 1 685 $cm^{-1}$; δ($CCl_4$) 0.78 (3 H, s, 8a-Me), 1.13 and 1.36 (each 3 H, 2 s, gem-dimethyl), 2.06—2.78 (6 H, m, 2-, 4-, and 8-$H_2$), 4.22 (1 H, X part of ABX pattern, $J_{AX}$ + $J_{BX}$ = 19 Hz, axial 7-H), 5.90 (1 H, d, *J* 1.5 Hz, 5-H), and 7.20—7.68 (5 H, m, SePh) (Found: C, 62.9; H, 6.1. $C_{19}H_{22}SeO_2$ requires C, 63.2; H, 6.1%).

*Oxidation of Compound* (**17**; X = SePh), *and Cleavage to* 4-(5′-*hydroxy*-2′-*methylphenyl*)-3,3-*dimethylbutanoic Acid* (**18**).—A solution of the preceding seleno-ketone (0.20 g) in ethyl acetate (10 $cm^3$), cooled and stirred at 0 °C, was treated with 30% aqueous hydrogen peroxide (0.15 $cm^3$) slowly, and was stirred for 2 h further. After being warmed to 20 °C the mixture was diluted with water, extracted repeatedly with ethyl acetate, and the dried extract was evaporated to an oil (90 mg). The n.m.r. spectrum, δ($CDCl_3$) 1.05 (6 H, s, gem-dimethyl), 2.32 (3 H, s, 2′-Me), 2.21 (2 H, s, $CH_2CO_2H$), 2.67 (2 H, s, benzylic $CH_2$), 7.02 (1 H, d, *J* 8 Hz, 3′-H), 6.62 (1 H, d, *J* 8 Hz, 4′-H), and 6.68 (1 H, s, 6′-H), is identical with that of the acid (**18**) discussed later.

*Oxidation of Compound* (**17**; X = SePh) *by Ozone: Formation of* 3,3,8a-*Trimethyl*-3,4-*dihydronaphthalene*-1,6(2H,8aH)-*dione* (**11**; R = Me).—A solution of the recrystallised seleno-ketone (**17**; X = SePh) (0.20 g) in sodium-dried ether (20 $cm^3$) was cooled at −78 °C whilst ozonised oxygen was bubbled slowly through it. When no further white precipitate formed, ozone-free oxygen was passed through for a few seconds, and the mixture was warmed to 20 °C and stirred for 1.5 h. The solution, after being washed in turn with saturated aqueous sodium hydrogen carbonate (15 $cm^3$), water, and brine, was dried and concentrated, and the residue was chromatographed on a silica column (25 × 1.2 cm; $CHCl_3$). Elution with 10% ether–light petroleum (b.p. 40—60 °C) gave the *dienone* (70 mg, 62%), m.p. 71—73 °C; $\nu_{max.}$($CCl_4$) 2 960, 2 938, 2 878, 1 720, 1 675, 1 640, and 1 615 $cm^{-1}$—a typical cyclohexa-2,5-dienone pattern;[7] $\lambda_{max.}$ (95% EtOH) 255 and 223 nm (log ε 3.961 and 3.973). The n.m.r. spectrum in $CCl_4$, and in $C_6D_6$ (given in brackets), has δ 0.84 [0.37] (3 H, s, 8a-Me), 1.22 and 1.55 [0.62 and 0.89] (each 3 H, 2 s, 3-Me groups), 2.16 and 2.30 [1.57 and 0.80] (each 1 H, d, *J* 14 Hz, of d, *J* 2.5 Hz, 4-$CH_2$), 2.68 and 2.82 [1.94 and 2.14] (each 1 H, d. *J* 14 Hz, 2-$CH_2$), 5.99 [6.04] (1 H, t, *J* 1.8 Hz, 5-H), 6.19 [6.24] (1 H, d, *J* 10 Hz, of d, *J* 1.8 Hz, 7-H), and 7.28 [7.12] (1 H, d, *J* 10 Hz, 8-H), fits the dienone structure (**11**; R = Me) in all respects, including solvent-assisted shifts.[36] (Found: C, 75.3; H, 7.2—7.9%; $M^+$, 204.108. $C_{13}H_{16}O_2$ requires C, 76.4; H, 7.9%; *M*, 204.115). An acceptable microanalysis could not be obtained, owing to slight decomposition prior to analysis, and the mass spectrum had to be recorded within a few hours of preparation. The fragmentation pattern was also consonant with the proposed structure.

*Oxidation of the Seleno-ketone* (**17**; X = SePh) *by* m-*Chloroperbenzoic Acid*.—A solution of the seleno-ketone (0.20 g) in dichloromethane (1.0 $cm^3$) was stirred at −10 °C, and a slight excess of recrystallised, standardised *m*-chloroperbenzoic acid was added. After 15 min the mixture was stirred at 20 °C for 1.5 h, then insoluble *m*-chlorobenzoic acid was removed by filtration, and the filtrate was diluted with more dichloromethane, washed successively with saturated aqueous sodium hydrogen carbonate and brine, and dried. Evaporation gave a crude product which was filtered through a silica column [(15 cm; light petroleum (b.p. 40—60 °C)]. The n.m.r. spectrum showed peaks due to the preceding dienone, a little enone precursor (**12**; R = Me), and *m*-chlorobenzoic acid which could not be removed. The g.l.c. (20% NGS at 230 °C) showed rearrangement of the dienone to the tetralone (**13**; R = Me).

*Reactions of Dienone* (**11**; R = Me).—(a) *In dilute aqueous sulphuric acid.* The dienone (125 mg) was shaken with aqueous sulphuric acid (5 $cm^3$; 5 × $10^{-3}$M) at 25 °C for 60 min, a time known from kinetic measurements to be 6—7 half-lives. Ice was added, the mixture was extracted with ether, and the extracts were washed successively with saturated aqueous sodium hydrogen carbonate (15 $cm^3$) and brine, dried, and evaporated to afford a crystalline mass of 4-(5′-*hydroxy*-2′-*methylphenyl*)-3,3-*dimethylbutanoic acid* (**18**), m.p. 98—99 °C [from 10% ether–light petroleum (b.p. 40—60 °C)] (90 mg, 66%), with i.r. and n.m.r. data as given earlier; $\lambda_{max.}$(EtOH) 280 nm (log ε 3.204) (Found: C, 70.0; H, 8.4. $C_{13}H_{18}O_3$ requires C, 70.2; H, 8.2%).

(b) *In sodium hydroxide solutions.* The solutions used for kinetic measurements were kept at 25 °C until reaction was complete (constant u.v. spectrum). This was about 60 min in $10^{-4}$M base, but less than 5 s in $10^{-2}$M sodium hydroxide. The final spectra were identical with those of the cleaved acid (**18**) in the same base (*e.g.* in $10^{-2}$M NaOH the 'dienone' has $\lambda_{max.}$ 295 and 235 nm (log ε 3.412 and 3.841), and the acid has $\lambda_{max.}$ 295 and 235 nm (log ε 3.402 and 3.837). We conclude that the dienone is quantitatively converted into the acid (**18**), as its salt.

(c) *In conc. sulphuric acids.* The solutions used for kinetic measurements in 78.0% and in 68.1% sulphuric acid were kept in the u.v. spectrometer until no further change in spectrum occurred. The spectra were identical in all respects with those of the tetralone (**13**; R = Me) in the same acids: *e.g.* in 78.0% acid, $\lambda_{max.}$ is 298 and 400 nm (log ε 4.078 and 3.346). A sample of the dienone (20.0 mg) was kept in 78.0% sulphuric acid at 25 °C for 120 min (*ca.* 15 half-lives). After the reaction had been quenched with ice, the mixture extracted with dichloromethane (4 times), and the extracts washed successively with saturated aqueous sodium hydrogen carbonate and water, then dried and evaporated, pale yellow crystals (15.0 mg) were obtained. I.r. and n.m.r. spectroscopy and g.l.c. (20% NGS at 230 °C) showed the product to be the tetralone (**13**; R = Me), identical with the sample given by DDQ oxidation of (**12**; R = Me).

*Kinetics of Reactions of Dienone* (**11**; R = Me).—Stock solutions of the dienone were made up freshly in 95% ethanol (e.g. 1.0854 mg in 1.00 ml), in which they were stable over periods much longer than required for the kinetic runs, and thermostatted at 25 °C. Kinetics were measured by u.v. spectroscopy, as described before.[35] The kinetics were accurately first order in dienone, and gave the rate-constants (analytical wavelength normally 256 nm) in the Table. The rates in 5 × $10^{-2}$ and 5 × $10^{-1}$M sulphuric acids, and in $10^{-2}$M sodium hydroxide, were too fast for us to measure (half-life < 5 s). The rate constants for reaction in conc. sulphuric acids at 25 °C are: in 78.0% acid (300 nm), 1.51 × $10^{-3}$ $s^{-1}$; in 68.1% acid (274 and 294 nm), 1.83 × $10^{-5}$ $s^{-1}$.

*Kinetics of Reaction of the Acid* (**18**) *in Conc. Sulphuric Acids.*—A thermostatted stock solution of the acid (**18**) was added to the sulphuric acid in the u.v. cell. Rate constants, from observations at 274 and 296 nm, were: in 78.0% acid, 1.63 × $10^{-3}$ $s^{-1}$; in 65.8% acid, 5.0 × $10^{-4}$ $s^{-1}$. There is a linear relationship, of gradient −1.2, between $\log_{10}$ of these rate constants (and those given above for the dienone) and Hammett's acidity function, similar to that found for many other dienone rearrangements (see refs 35 and 45, and others cited there). The final u.v. spectra were quantitatively identical with those of the tetralone (**13**; R = Me) in the same acids. Complete spectra were also used to observe the changes in 65.8% acid: both the acid (**18**) and the dienone gave identical behaviour at all times, and a consistent rate constant was gained at a number of wavelengths. The tetralone (**13**; R = Me) was stable (less than 2% change) in 78.0% $H_2SO_4$ at 25 °C, showing this to be the thermodynamically controlled product. When the acid (**18**) was taken in 50% $H_2SO_4$, it gave an unchanging spectrum identical to that given by the 'dienone' (**11**; R = Me) in the same acid. This is evidence for the view that the dienone cleaves rapidly to the acid (**18**) in all these media, and is stable in 50% sulphuric acid, but cyclises to the tetralone in the more concentrated sulphuric acids.

**Table.**

| Sulphuric acid (a) [sodium hydroxide (b)] concentration | $k/s^{-1}$ |
|---|---|
| 5 × $10^{-3}$M (a) | 7.95 × $10^{-3}$ |
| 5 × $10^{-4}$M (a) | 1.47 × $10^{-3}$ |
| 5 × $10^{-5}$M (a) | 1.78 × $10^{-4}$ |
| 1 × $10^{-4}$M (b) | 1.42 × $10^{-3}$ |
| 1 × $10^{-3}$M (b) | 5.5 × $10^{-2}$ |

*Reactions of the Dienone* (**11**; R = Me) *in Trifluoroacetic Acid Solutions.*—The dienone (25 mg) in an n.m.r. tube, cooled at −10 °C, was treated with cold trifluoroacetic acid (0.5 $cm^3$) and a drop of dichloromethane (as internal standard). The spectrum, run immediately at −10 °C, was identical with that of the tetralone (**13**), and did not change further. Isolation confirmed the structure of the product. Similar results were obtained with a 15% (w/w) solution of trifluoroacetic acid in $CD_2Cl_2$ at −20 °C. When the dienone dissolved in $CD_2Cl_2$ at −10 °C, and a solution of trifluoroacetic acid in the same solvent was added to give a final concentration of this acid of 2.1% (w/w), the conversion into the tetralone (**13**; R = Me) could be monitored over a period of time of about 45 min. Kinetic points were gained, at 3 min intervals, which measured the decrease of each dienone methyl peak, and the increase of each tetralone methyl peak. The rate constants for dienone loss and tetralone gain were identical, at (2.2 ± 0.1 $s^{-1}$, half-life *ca.* 310 s), for a clean first-order process, with no other absorbances or emissions visible down to the 2—3% level. Work-up again gave the tetralone in good yield and purity. The open-chain acid (**18**) did not change under these conditions. It is therefore not an intermediate in the rearrangement of dienone (**11**; R = Me) to tetralone (**13**; R = Me) in this acid.

## Acknowledgements

We thank the British Council for a Scholarship to J. H. Z.

## References

1 J. C. Anderson and C. B. Reese, *J. Chem. Soc.*, 1963, 1781.
2 C. E. Kalmus and D. M. Hercules, *Tetrahedron Lett.*, 1972, 1575.
3 S. M. Beck and L. E. Brus, *J. Am. Chem. Soc.*, 1982, **104**, 1805.
4 V. P. Pathak and R. N. Khanna, *Synthesis*, 1981, 882.
5 For reviews, see D. Bellus and P. Hrdlovic, *Chem. Rev.*, 1967, **67**, 599; D. Bellus, *Adv. Photochem.*, 1971, **8**, 109.
6 (*a*) F. Effenberger and R. Guttmann, *Chem. Ber.*, 1982, **115**, 1089; (*b*) F. Effenberger, H. Klenk, and P. L. Reiter, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 775.
7 A. J. Waring, *Adv. Alicyclic Chem.*, 1966, **1**, 129.
8 J. W. Pilkington and A. J. Waring, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1349.
9 J. D. Palmer and A. J. Waring, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1089.
10 L. B. Jackson and A. J. Waring, unpublished work.
11 S. Danishefsky and T. Kitahara, *J. Am. Chem. Soc.*, 1974, **96**, 7807, and later papers. For a review, see S. Danishefsky, *Acc. Chem. Res.*, 1981, **14**, 400.
12 J. D. Palmer, M.Sc. Thesis, University of Birmingham, 1978.
13 H. J. Ringold and A. Turner, *Chem. Ind. (London)*, 1962, 211.

14 D. H. R. Barton, D. J. Lester, and S. V. Ley, *J. Chem. Soc., Perkin Trans. 1*, 1980, 2209.
15 J. N. Marx, J. C. Argyle, and L. R. Norman, *J. Am. Chem. Soc.*, 1974, **96**, 2121.
16 For a review of available methods, see B. M. Trost, T. N. Salzmann, and K. Hiroi, *J. Am. Chem. Soc.*, 1976, **98**, 4887.
17 L. Blanco, P. Amice, and J. M. Conia, *Synthesis*, 1976, 194; P. Amice, L. Blanco, and J. M. Conia, *ibid.*, p. 196.
18 S. Danishefsky, R. K. Singh, and T. Harayama, *J. Am. Chem. Soc.*, 1977, **99**, 5810.
19 K. B. Sharpless, R. F. Lauer, and A. Y. Teranishi, *J. Am. Chem. Soc.*, 1973, **95**, 6137; H. J. Reich, J. M. Renga, and I. L. Reich, *ibid.*, 1975, **97**, 5434. For a review see D. L. J. Clive, *Tetrahedron*, 1978, **34**, 1049.
20 H. Plieninger and W. Gramlich, *Chem. Ber.*, 1978, **111**, 1944; W. Gramlich and H. Plieninger, *ibid.*, 1979, **112**, 1550, 1571.
21 S. Danishefsky, C. F. Yan, and P. M. McCurry, *J. Org. Chem.*, 1977, **42**, 1819; S. Danishefsky, C. F. Yan, R. K. Singh, R. B. Gammill, P. M. McCurry, N. Fritsch, and J. Clardy, *J. Am. Chem. Soc.*, 1979, **101**, 7001.
22 C. H. Heathcock and R. Ratcliffe, *J. Am. Chem. Soc.*, 1971, **93**, 1746.
23 K. H. Bell, *Austr. J. Chem.*, 1972, **25**, 1117.
24 J. D. Cocker and T. G. Halsall, *J. Chem. Soc.*, 1957, 3441.
25 E. Piers, W. D. Waal, and R. W. Britton, *J. Am. Chem. Soc.*, 1971, **93**, 5113.
26 S. Danishefsky, J. Morris, G. Mullen, and R. Gammill, *J. Am. Chem. Soc.*, 1982, **104**, 7591.
27 N. L. Wendler, H. L. Slates, and M. Tishler, *J. Am. Chem. Soc.*, 1951, **73**, 3816.
28 M. S. Newman and A. B. Mekler, *J. Am. Chem. Soc.*, 1960, **82**, 4039.
29 J. P. John, R. K. Natarajan, S. Swaminathan, and P. S. Venkataramani, *Can. J. Chem.*, 1968, **46**, 2320.
30 J. E. Ellis, J. S. Dutcher, and C. H. Heathcock, *J. Org. Chem.*, 1976, **41**, 2670; R. D. Clark, J. E. Ellis, and C. H. Heathcock, *Synth. Commun.*, 1973, **3**, 347.
31 P. L. Stotter and K. A. Hill, *J. Org. Chem.*, 1973, **38**, 2576.
32 P. A. Grieco, S. Ferrino, and T. Oguri, *J. Org. Chem.*, 1979, **44**, 2593.
33 D. L. J. Clive, *J. Chem. Soc., Chem. Commun.*, 1973, 695.
34 H. Stetter, in 'Newer Methods of Preparative Organic Chemistry,' ed. W. Foerst, Academic, New York, 1963, vol. 2, pp. 51 *et seq.*
35 A. J. Waring, J. H. Zaidi, and J. W. Pilkington, *J. Chem. Soc., Perkin Trans. 1*, 1454; *J. Chem. Soc., Perkin Trans. 2*, 1981, 935.
36 K. L. Cook and A. J. Waring, *J. Chem. Soc., Perkin Trans. 2*, 1973, 529.
37 G. Ayrey, D. Barnard, and D. T. Woodbridge, *J. Chem. Soc.*, 1962, 2089.
38 P. J. Kropp, *J. Am. Chem. Soc.*, 1964, **86**, 4053.
39 B. M. Trost and R. A. Kunz, *J. Org. Chem.*, 1974, **39**, 2648.
40 A. H. Tracy and R. C. Elderfield, *J. Org. Chem.*, 1941, **6**, 63.
41 R. E. Ireland and J. A. Marshall, *J. Org. Chem.*, 1962, **27**, 1615.
42 M. S. Newman and S. Swaminathan, *Tetrahedron*, 1958, **2**, 88.
43 S. Ramachandran and M. S. Newman, *Org. Synth.*, 1973, Coll. Vol. 5, p. 486.
44 C. B. C. Boyce and J. S. Whitehurst, *J. Chem. Soc.*, 1960, 2680.
45 A. J. Waring, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1029.

*Received* 24*th July* 1984; *Paper* 4/1289