Synthesis of 4-Benzoyl-4-methylcyclohexa-2,5-dienone and its Benzoyl Substituted Derivatives: Isolated 4-Acylcyclohexa-2,5-dienones†

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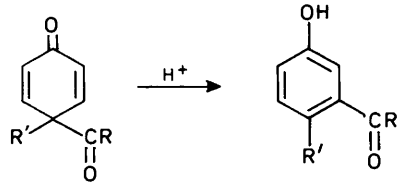
The syntheses are reported of 4-benzoyl-4-methylcyclohexa-2,5-dienone, and its 4-(4-chlorobenzoyl) and 4-(4-methoxybenzoyl) analogues. These are the first isolated 4-acylcyclohexa-2,5-dienones containing the dienone function in a monocyclic ring system. All are sensitive to nucleophilic attack at the benzoyl carbonyl group, being cleaved to 4-methylphenol and derivatives of the appropriate substituted benzoic acid. Treatment with acids failed to give the desired dienone–phenol rearrangement, with a [1,2]benzoyl migration from C-4 to C-3, but instead gave 4-methylphenyl benzoate or its derivatives, by a reversal of a Fries rearrangement with C-4 to O- aroyl migration.

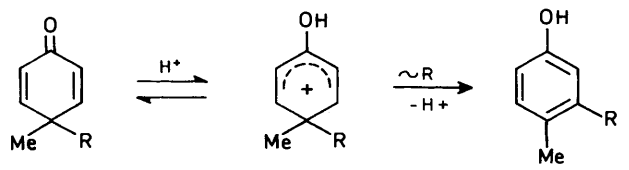
4-Acylcyclohexa-2,5-dienones are compounds of low stability. They have been postulated as unstable intermediates in the photo-Fries rearrangement of carboxylate esters of phenols. For example, u.v. irradiation of phenyl acetate is believed to give the 4-acetyl dienone (**1**; R=Me, R′=H) as the intermediate in its rearrangement to 4-acetylphenol.[1–3] Similarly, the 4-acetyl-4-methyl analogue (**1**; R=R′=Me) has been postulated as the intermediate in the photorearrangement of 4-methylphenyl acetate.[4] However, our own studies of this rearrangement



(**1**) (**2**)

did not give the claimed photoproduct, 4-acetyl-3-methylphenol, which might be formed from this intermediate.[4] Instead, we obtained 2-acetyl-4-methylphenol as the (*ortho*) rearrangement product well established in an earlier study.[5] The 4-benzoyl dienone (**1**; R = Ph, R′ = H) would be involved in the formation of 4-hydroxybenzophenone from phenyl benzoate.[1,6] The 4-acylcyclohexadienones are similarly implicated as reactive intermediates in acid-induced, thermal Fries rearrangement equilibria between aryl carboxylates and 2- and 4-acylphenols.[7,8] They have also been sought as intermediates in synthetic studies, to which reference will be made later.

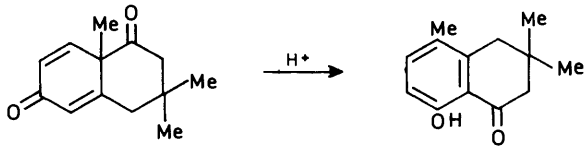
We were particularly interested in 4-acyl-4-alkylcyclohexa-2,5-dienones which, we hoped, might offer excellent compounds for measuring the migratory aptitudes of acyl groups in carbonium ion rearrangements. We hoped to measure the rates of the acyl migration shown in (**1**)→(**2**), in which a methyl



(**3**) R = Me, Et, Pr, Bu[S] (**4**)

group, R′, is left behind, and to compare these with the rates we found earlier for other migrating groups using the reactions (**3**)→(**4**).[9,10]

We have reported previously our attempts to prepare 4-acetyl-4-methylcyclohexa-2,5-dienone by a number of routes.[11] All failed, but a number gave evidence that the dienone had been formed, and then underwent very easy retro-Fries rearrangement to 4-methylphenyl acetate. Other reactions gave 4-methylphenol, presumably by easy de-acetylation of the dienone, with 4-methylphenol or 4-methylphenoxide ion as an aromatically stabilised leaving group.[11] Danishefsky and his co-workers had obtained phenols in a similar manner when they tried to synthesize 4-formylcyclohexa-2,5-dienones[12,13] and a 4-acyl-4-aryl dienone.[14] We had been able to prepare the bicyclic dienone (**5**), in which the attack by nucleophiles on the 4-acyl substituent of the dienone ring is hindered by the *gem*-dimethyl group, and retro-Fries rearrangement is prevented by the non-dienone ring. Unfortunately, useful measurements of the migratory aptitude of the acyl group in the dienone–phenol rearrangement of (**5**)→(**6**) were impractical because of the high rate of this reaction.[11] It is known, however, that 4-alkyl-4-

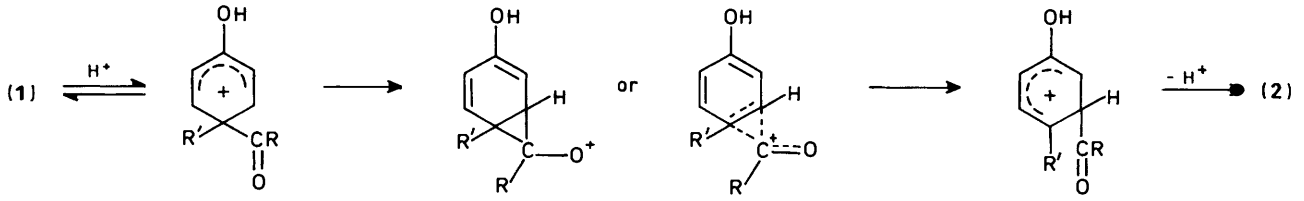


(**5**) (**6**)

ethoxycarbonylcyclohexa-2,5-dienones can be prepared using relatively harsh reactions, that they are quite stable, and that the ethoxycarbonyl group migrates in dienone–phenol rearrangements at a conveniently measurable rate.[15]

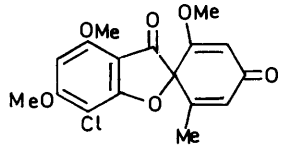
We suggested previously[16] a reason why an acyl group should apparently undergo much faster 1,2-migration than an alkoxycarbonyl group in the dienone-phenol rearrangement (or, indeed, in other cationic shifts). The transition state for migration (**7**) can be represented in a number of ways, one of which has positive charge on the 'old' carbonyl oxygen, and another which resembles an acylium ion–phenol complex. The alkoxycarbonyl group itself [see (**1**)→(**7**)→(**2**), R = OAlkyl] has stabilising delocalisation of electrons which is lost in the first representation of the transition state, whereas an acyl group never has this sort of stabilisation. This contrast is similar to that involved in the formation of tetrahedral intermediates in the S_N2 substitution reactions of acyl chlorides *vs.* alkyl chloroformates, for example. Similarly, the acylium ion

† Preliminary communication; L. B. Jackson and A. J. Waring, *J. Chem. Soc., Chem. Commun.*, 1985, 857.



(7)

formulation resembles the intermediates involved in the S_N1 reactions of these substrates. It is known that alkaline hydrolyses of benzoyl chloride are appreciably slower than those of acetyl chloride, and that ethyl chloroformate hydrolyses more slowly still, under conditions believed to give S_N2 reactions. The same reactivity order applies to alcoholysis reactions.[17,18] We have been unable to find satisfactory comparative data for the related S_N1 reactions. However, this general sort of reactivity consideration led us to believe that attempts to prepare 4-alkyl-4-benzoyl- or substituted benzoyl-cyclohexa-2,5-dienones might be successful. This hope was realised, and we now report the isolation and some of the chemistry of these, the first 4-acylcyclohexa-2,5-dienones in which the dienone ring is part of a monocyclic system. In our previous work[11,16] it was part of a bicyclic system, for the reasons outlined earlier. It is perhaps worth pointing out that compounds such as dehydrogriseofulvin (**8**) also have the



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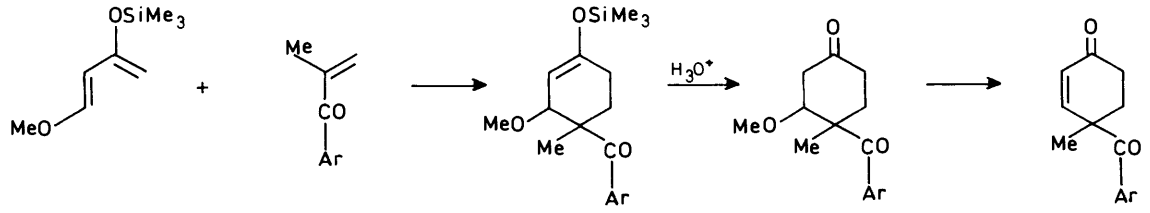
dienone ring in a polycyclic system,[19] and that they are 4-acyl-4-alkoxy substituted cyclohexadienones.

Attempted Syntheses.—The obvious synthetic route, in the light of our previous studies, involves the intermediacy of appropriate 4-alkyl-4-benzoylcyclohex-2-enones, which were unknown compounds. We chose to prepare these following the general route developed by Danishefsky and his co-workers,[20,21] which required the Diels–Alder addition of Danishefsky's diene (**9**) to 2-benzoylpropene (**10**; Ar = Ph) or its ring-substituted derivatives. The latter compounds are available from Mannich reactions of substituted propiophenones, with concomitant elimination to form the desired α-methylene ketones (Scheme 1). Some preparations were unreliable in our hands.[22] The method of Sugita and his co-workers[23] was developed satisfactorily, but required different reaction times for different substituents in the propiophenones. The preparation of 2-(4-nitrobenzoyl)prop-2-ene was particularly troublesome; this has since been made reliable[24] although, as in some of the other cases, still not high-yielding. The method of preparing α-methylene ketones developed by Gras[25] is also quite satisfactory, but the extra expense of the method was not justified by the improved yields.

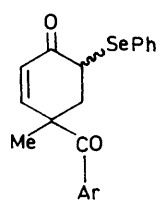
The Diels–Alder additions were effected by heating 2-benzoylpropene, or its ring-substituted analogues, with Danishefsky's diene[20] in benzene at reflux. The assumed initial adducts (**11**) were hydrolysed by heating with dilute aqueous HCl in THF, which usually also effects elimination of methanol from the 3-methoxycyclohexanone (**12**), to form the desired substituted cyclohex-2-enone (**13**). The yields of adducts were, however, rather disappointing. It appeared (from g.l.c. and n.m.r. analysis) that the slow addition reaction reached an equilibrium position, and that further heating failed to increase the amount of adduct. Indeed, because the diene slowly decomposed or polymerised, prolonged reaction reduced the yields. The use of boiling toluene instead of benzene as reaction solvent also gave poorer yields. Examples have recently appeared of Diels–Alder additions of analogues of Danishefsky's diene being catalysed by Lewis acids, including magnesium bromide,[26] zinc chloride,[27] and ethyl aluminium dichloride.[26] Our attempts to achieve catalysis by anhydrous zinc chloride, in the reaction of 2-(4-methoxybenzoyl)propene in refluxing dichloromethane, were unsuccessful. The product mixture from the Diels–Alder addition of the same dienophile in benzene was hydrolysed to give both 4-(4-methoxybenzoyl)-4-methylcyclohex-2-enone and the related 3-methoxy-4,4-disubstituted cyclohexanone [(**13**) and (**12**), respectively; Ar = 4-$MeOC_6H_4$].

Following earlier experiences,[11] we did not attempt to dehydrogenate the cyclohexenones with selenium dioxide or benzeneseleninic anhydride. Reaction of the 4-benzoyl-4-methylcyclohexenone with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) consumed the enone but produced no dienone detectable by n.m.r. spectroscopy. Dehydrogenation *via* the α-phenylseleno ketone had served well previously.[11,28] Accordingly, 4-benzoyl-4-methylcyclohexenone (**13**; Ar = Ph) was treated with benzeneselenenyl chloride in ethyl acetate, to give 4-benzoyl-4-methyl-6-phenylselenocyclohex-2-enone (**14**; Ar = Ph). The phenylseleno group was shown by n.m.r. spectroscopy to occupy an equatorial position, but its stereochemical relationship to the benzoyl group was not determined. We obtained the same phenylseleno ketone by treating the lithium dienolate of the cyclohexenone (LDA–THF, −78 °C) with



(9) (10) (11) (12) (13)

Scheme.



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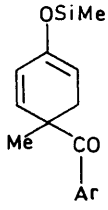

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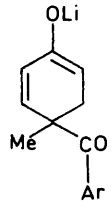

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benzeneselenenyl bromide, prepared *in situ*,[29] in THF. The yields of phenylseleno ketone were, however, inferior to those from the previous method. Again following the work of Zaidi,[11] we elected to oxidise this product to the phenylselenoxy ketone using ozone, with the expectation that elimination [29,30] would easily follow to produce the desired dienone. However, the use of a number of different procedures, both for the ozonation and for decomposition of the presumed selenoxide, generally failed to give evidence of the formation of the dienone. Some conditions (see Experimental section) did give a mixture containing 4-methylphenol and its benzoate, which had presumably been formed from the dienone, and in another experiment small peaks ascribed to the dienone were seen in the n.m.r. spectrum of the crude product. An attempt at oxidation–elimination using a two-phase aqueous hydrogen peroxide–ethyl acetate mixture gave benzoic acid as a product, again probably due to hydrolytic cleavage of the initially formed dienone. It was clear that milder conditions were necessary, and that they should not involve water or other nucleophilic solvents. We therefore prepared the trimethylsilyl enol ether of the parent cyclohexenone, and attempted to effect palladium(II)-assisted dehydrosilylation. This method, introduced by Ito and his co-workers [31] has been used, for example, to convert the silyl enol ether of a cyclohexanone into a cyclohex-2-enone,[32] and of a cyclopentanone into a cyclopent-2-enone.[33] Attempts to prepare the trimethylsilyl enol ether (**15**; Ar = Ph) by treating the cyclohexenone with chlorotrimethylsilane and triethylamine in dimethylformamide (DMF),[34] or by treating the dienolate anion (**16**; Ar = Ph, prepared using excess LDA in THF), with chlorotrimethylsilane and triethylamine,[34] gave the desired product in moderate yield. Far better was the mild and rapid procedure of Duboudin and her co-workers,[35] in which the cyclohexenone was treated with triethylamine and iodotrimethysilane, formed *in situ* from chlorotrimethylsilane and anhydrous sodium iodide, in acetonitrile at room temperature. Although moderate yields (> 50%) of the desired silyl ether were obtained when a rapid aqueous wash was used in the work-up, the preferred procedure used extraction of the product into pentane, removal of solvent, and immediate reaction of the crude silyl ether in acetonitrile with palladium(II) acetate. The desired dienone (**1**; R = Ph, R′ = Me) was obtained as a crystalline solid, whose spectroscopic properties were in accord with the structure.

The analogous cyclohexadienones containing a 4-methoxybenzoyl, or a 4-chlorobenzoyl group were prepared from the corresponding 4-aroyl-4-methylcyclohexenones in exactly the same way as described above. Both were obtained as colourless crystalline materials, which are stable towards storage for months below room temperature, and which show spectroscopic properties consistent with their structures. In the case of the 4-(4-chlorobenzoyl) dienone, solvent shifts in the ^{1}H n.m.r. spectrum were recorded, and were in accord with those measured for simpler cyclohexa-2,5-dienones.[36] It has been reported that ketones can be dehydrogenated to give their α,β-unsaturated derivatives using catalytic quantities of palladium(II) salts, although under much more vigorous conditions than would be survived by our dienones.[37] We tried the oxidation of 4,4-dimethylcyclohex-2-enone using a catalytic amount of palladium(II) acetate and a stoicheiometric amount of DDQ to re-oxidise the reduced palladium species, hoping to produce a catalytic cycle. No sign of the expected 4,4-dimethylcyclohexa-2,5-dienone was detected. The corresponding trimethylsilyl enol ether, 1-trimethylsilyloxy-4,4-dimethylcyclohexa-1,5-diene was, however, converted in satisfactory yield into the 4,4-dimethyl dienone by a stoicheiometric quantity of palladium(II) acetate. Attempts to prepare a pure sample of the 4-methyl-4-(4-nitrobenzoyl)cyclohexa-2,5-dienone *via* the silyl ether derived from the corresponding cyclohexenone were unsuccessful. The reaction product contained about 50% of the desired dienone, a little unchanged enone, and 4-methylphenol, detected by n.m.r. spectroscopy. We assume that the 4-methylphenol is formed by decomposition of the dienone, and all attempts at chromatographic purification gave cleavage to the phenol and 4-nitrobenzoic acid. Other purification methods failed.

The three pure dienones, (**1**; R′ = Me, R = Ph, 4-ClC_6H_4, and 4-$MeOC_6H_4$) are stable during storage at or below room temperature, and during heating at 80 °C. However, unless they are rigorously purified they darken during storage due, we believe, to slow decomposition of traces of palladium-containing impurities. All the dienones are sensitive towards cleavage by nucleophiles. The parent compound (**1**; R′ = Me, R = Ph) is completely cleaved within 3 h by treatment with water below 20 °C, giving 4-methylphenol and benzoic acid. Reaction with methanol is slower, converting 20% of the dienone into methyl benzoate and 4-methylphenol in 17.5 h at 25 °C. Detailed kinetic and mechanistic studies of this and other cleavages will be reported separately, but the net process is consistent with easy attack by the nucleophile at the benzoyl carbon atom, with expulsion of 4-methylphenoxide or 4-methylphenol as leaving group (see Experimental section).

Acid-induced reactions of the dienones (**1**; R′ = Me, R = Ph, 4-ClC_6H_4, 4-$MeOC_6H_4$) were studied, in the hope of effecting acyl migration from C-4 to C-3 [see (**1**)→(**2**)] in the manner typical of dienone–phenol rearrangements. If this could be achieved, measurements of the variation with acidity of the rate of rearrangement should allow the migratory aptitudes of the substituted benzoyl groups to be determined in the way used previously.[9,10,15] We believed at the outset of this work that the acyl groups would migrate more readily than an alkyl group. This is certainly true for migration of an ethoxycarbonyl group in (**3**; R = CO_2Et)→(**4**),[15] and seems to be found in the acyl migration in (**5**)→(**6**).[11] Much evidence is accumulating that acyl groups undergo 1,2-migrations in carbocations with considerable ease.[38–45] Reaction of the parent dienone (**1**; R′ = Me, R = Ph) in 10^{-2}M aqueous HCl gave only 4-methylphenol and benzoic acid. To reduce nucleophilic attack, we treated the dienone with dilute trifluororacetic acid in [^{2}H]dichloromethane, observing the reaction by ^{1}H n.m.r. spectroscopy. Similar conditions had allowed other rearrangements to be monitored[15] or observed.[11] However, reaction was complete by the time the first spectrum was observed, 50% of the dienone being cleaved to 4-methylphenol and the rest rearranged to 4-methylphenyl benzoate. The latter was shown not to arise from acylation under the conditions used, but by an intramolecular [1,5]migration of the benzoyl group from C-4 to the dienone oxygen atom. This process represents the reversal of a Fries rearrangement, in which esters of phenols rearrange under acidic conditions to 4- and 2-acylphenols.[7,8] Details of our studies of this rearrangement under other conditions, and the dienone cleavages in aqueous acids will be presented separately. The essential result, however, is that dienone–phenol rearrangement could not be observed under any of the conditions we tried, and our hopes of measuring rates, and migratory aptitudes for 1,2-shifts of benzoyl and substituted-benzoyl groups were thwarted.

Experimental

G.l.c analyses employed a Pye 104 instrument with flame-ionisation detector and glass columns (7 ft × $\frac{1}{4}$ in), packed with silicone gum (E30, 2%) or cyanoethyl silicone fluid (XF1150, 25%) on silanized Supasorb (60—80 mesh, B.D.H.). Silicia for column chromatography was Merck Kieselgel 60, 70—230 mesh, or for medium-pressure use, 230–400 mesh. ^{1}H N.m.r. spectra were recorded on Varian XL 100 or Perkin-Elmer R14 instruments at 100 MHz, and ^{13}C n.m.r. spectra on a JEOL FX60 instrument at 15.03 MHz (Me_4Si internal standard). I.r. spectra were recorded on Pye-Unicam SP1050 or SP3-100 instruments, calibrated using polystyrene film, and u.v. spectra on a Pye-Unicam SP8-100 spectrophotometer.

2-Benzoylpropene (**10**; Ar = Ph).—The method of ref. 23 was modified. Propiophenone, (20.34 g, 0.15 mol), fresh paraformaldehyde (5.20 g, 0.17 mol), dimethylammonium chloride (14.90 g, 0.18 mol), and *N*,*N*-dimethylformamide (DMF)(50 cm^3) were heated at reflux during 75 min, then water was added and the mixture steam distilled. The distillate was extracted with pentane, the extracts allowed to stand over anhydrous potassium carbonate for 30 min, and the solvent evaporated under reduced pressure to give the product (10.80 g, 48%), $\nu_{max.}$(film) 3 070, 2 980, 2 960, 2 930, 1 655, 1 628, 1 598, 1 580, 980, and 940 cm^{-1}; $\delta_H(CCl_4)$ 2.00 (3 H, s, Me), 5.53 and 5.80 (1 H, each a fine mult., CH_2), and 7.3—7.8 (5 H, m, aryl).

2-(4-Methoxybenzoyl)propene (**10**; Ar = 4-$MeOC_6H_4$).—4′-Methoxypropiophenone (22.90 g, 0.14 mol), paraformaldehyde (4.80 g, 0.16 mol), dimethylammonium chloride (13.80 g, 0.17 mol), and DMF (50 cm^3) were heated at reflux as above, but for 24 h. Steam distillation was followed by extraction of the distillate with light petroleum (b.p. 30—40 °C). Distillation (Kügelrohr, oven temperature 108—112 °C, at 0.5 mmHg) gave the ketone (3.29 g, 31%), $\nu_{max.}$(film) 2 980, 2 940, 1 655, 1 605, 1 575, 1 260, and 1 170 cm^{-1}; $\delta_H(CCl_4)$ 2.00 (3 H, s, Me), 3.85 (3 H, s, OMe), 5.45 and 5.78 (1 H, each a fine mult., CH_2), 6.90 (2 H, d, *J* 9 Hz, 3- and 5-H), and 7.77 (2 H, d, *J* 9 Hz, 2- and 6-H) (Found: C, 74.8; H, 7.0. $C_{11}H_{12}O_2$ requires C, 74.9; H, 6.8%). Use of the general method of Gras and his co-workers[25] gave yields of 21%.

2-(4-Chlorobenzoyl)propene (**10**; Ar = 4-ClC_6H_4).—From 4′-chloropropiophenone (5.80 g), the procedure used for 2-benzoylprop-1-ene gave the product (4.30 g, 69%), $\nu_{max.}(CCl_4)$ 2 930, 2 850, 1 660, 1 595, 980, and 940 cm^{-1}; $\delta_H(CCl_4)$ 2.00 (3 H, s, Me), 5.50 and 5.80 (1 H, each a fine mult., CH_2), 7.34 (2 H, d, *J* 9 Hz, 3- and 5-H), and 7.64 (2 H, d, *J* 9 Hz, 2- and 6-H).

2-(4-Nitrobenzoyl)propene (**10**; Ar = 4-$NO_2C_6H_4$).—4′-Nitropropiophenone[46] (10.0 g, 56 mmol), paraformaldehyde (3.25 g), dimethylammonium chloride (9.56 g), and DMF (20 cm^3) were treated as detailed for 2-benzoylprop-1-ene, except that the extraction was with light petroleum (b.p. 30—40 °C) to give the product (2.13 g, 20%), white crystals, m.p. 79—82 °C (lit.,[23] 81—82 °C); $\nu_{max.}(CCl_4)$ 2 960, 2 940, 2 860, 1 668, 1 605, 1 535, 1 350, and 862 cm^{-1}; $\delta_H(CCl_4)$ 2.09 (3 H, s, Me), 5.57 and 5.96 (1 H, each a fine mult., CH_2), 7.76 (2 H, d, *J* 9 Hz, 2- and 6-H), and 8.23 (2 H, d, *J* 9 Hz, 3- and 5-H).

4-Benzoyl-4-methylcyclohex-2-enone (**13**; Ar = Ph).—Following Harissis and Waring,[47] 2-benzoylprop-1-ene (7.53 g, 51 mmol), 1-methoxy-3-trimethylsilyloxybuta-1,3-diene,[20] and sodium-dried benzene (20 cm^3) were heated at reflux under nitrogen for 6 days. The cooled mixture was concentrated under reduced pressure, and stirred for 1 h with 0.1M HCl (25 cm^3) and sufficient THF to render the mixture homogeneous. The mixture was then poured into water (30 cm^3) and extracted with ether. The ether extracts were washed, with 5% aqueous sodium hydrogen carbonate (5 cm^3), dried ($MgSO_4$), and concentrated to give the crude product as a deep yellow oil. The addition of ether, and gentle cooling with liquid air gave the cyclohexenone as white crystals, m.p. 67—70 °C (lit.,[47] 63—64 °C); $\nu_{max.}(CCl_4)$ 2 970, 2 930, 1 680, 1 418, and 1 445 cm^{-1}; $\delta_H(CCl_4)$ 1.52 (3 H, s, Me), 1.8—2.7 (4 H, m, 5-and 6-CH_2), 5.85 (1 H, d, *J* 10 Hz, 2-H), 6.94 (1 H, d, *J* 10 Hz, 3-H), and 7.32—7.77 (5 H, m, ArH). $\delta_C(CDCl_3)$ 24.23 (CH_3), 33.46 (cyclohexenone CH_2-5), 34.57 (cyclohexenone CH_2-6), 49.31 (cyclohexenone C-4), 128.52 (C-2, -3, -5, and -6 of benzoyl), 132.29 (C-4 of benzoyl), 136.96 (C-1 of benzoyl), 152.95 (cyclohexenone C-3), 198.10 (cyclohexenone C-1), and 202.46 (benzoyl carbonyl). The cyclohexenone C-2 is expected to be at *ca.* 128 p.p.m., and to overlap the benzoyl signal at 128.52 p.p.m. (Found: M^+, 214.096. $C_{14}H_{14}O_2$ requires *M*, 214.099). Purification was also effected by column chromatography on silica (CH_2Cl_2).

4-(4-Methoxybenzoyl)-4-methylcyclohex-2-enone (**13**; Ar = 4-$MeOC_6H_4$).—2-(4-Methoxybenzoyl)prop-1-ene (1.50 g, 8.5 mmol), 1-methoxy-3-trimethylsilyloxybuta-1,3-diene (1.46 g, 8.5 mmol), and sodium-dried benzene (7.0 cm^3) were heated at reflux during 7 days. Further 1-methoxy-3-trimethylsilyloxybuta-1,3-diene (0.4 g, 2.3 mmol) was added to make up a deficiency shown by n.m.r. spectroscopy, and reflux continued for 7 days further. Work-up as above gave the crude product which was purified by chromatography on a short column of silica (CH_2Cl_2) under nitrogen pressure to give the *cyclohexenone* (552 mg, 26%) as white crystals, $\nu_{max.}(CCl_4)$ 2 970, 2 940, 2 840, 1 690, 1 675, 1 605, 1 255, 1 170, and 840 cm^{-1}; $\delta_H(CCl_4)$ 1.52 (3 H, s, Me), 1.85—2.83 (4 H, m, 2 × CH_2), 3.85 (3 H, s, OMe), 5.93 (1 H, d, *J* 10 Hz, 2-H), 7.07 (1 H, d, *J* 10 Hz, 3-H), 6.88 (2 H, d, *J* 9 Hz, 3- and 5-H of benzoyl), and 7.87 (2 H, d, *J* 9 Hz, 2- and 6-H of benzoyl) (Found: C, 73.4; H, 6.7%; M^+ 244.110. $C_{15}H_{16}O_3$ requires C, 73.7; H, 6.6%; *M*, 244.110). A second compound (**12**; Ar = 4-$MeOC_6H_4$, 160 mg) eluted from the column was shown to be *3-methoxy-4-(4-methoxybenzoyl)-4-methylcyclohexanone*, $\delta_H(CDCl_3)$ 1.60 (3 H, s, 4-Me), 1.85—2.66 (6 H, m, 2-, 5-, and 6-CH_2), 3.04 (3 H, s, 3- MeO), 3.85 (3 H, s, 4-methoxybenzoyl), 4.13 (1 H, m, 3-H), 6.93 (2 H, d, *J* 9 Hz, 3- and 5-H of benzoyl), and 7.72 (d, *J* 9 Hz, 2- and 6-H of benzoyl) (Found: C, 69.6; H, 7.0. $C_{15}H_{20}O_3$ requires C, 69.5; H, 7.3%). Reactions on a larger scale (*e.g.* using 4.20 g of the starting methoxybenzoylpropene) gave no higher percentage yield.

4-(4-Chlorobenzoyl)-4-methylcyclohex-2-enone (**13**; Ar = 4-ClC_6H_4).—2-(4-Chlorobenzoyl)propene (3.24 g, 18 mmol), 1-methoxy-3-trimethylsilyloxybuta-1,3-diene (3.07 g, 18 mmol), and sodium-dried benzene (10 cm^3) were heated under reflux (nitrogen atmosphere) for 6 days. Work-up as above, and chromatography on silica (CH_2Cl_2) gave the *cyclohexenone* (1.85 g, 41%) as pale yellow crystals, m.p. 50—53 °C; $\nu_{max.}(CCl_4)$ 2 980, 2 940, 1 685, and 1 590 cm^{-1}; $\delta_H(CCl_4)$ 1.51 (3 H, s, Me), 1.85—2.65 (4 H, m, 5- and 6-CH_2), 5.88 (1 H, d, *J* 10 Hz, 2-H), 6.91 (1 H, d, *J* 10 Hz, 3-H), 7.31 (2 H, d, *J* 8 Hz, 3- and 5-H of chlorobenzoyl), 7.72 (2 H, d, *J* 8 Hz, 2- and 6-H of chlorobenzoyl group) (Found: C, 67.4; H, 5.3. $C_{14}H_{13}ClO_2$ requires C, 67.6; H, 5.3%). The electron impact mass spectrum showed only a weak pair of peaks due to the cyclohexenone (M^+, 248,250) and a stronger pair (M^+, 246,248) which appeared, surprisingly, to be due to the dienone (Found: M^+, 246.043. $C_{14}H_{11}{}^{35}ClO_2$ requires *M*, 246.044).

4-Methyl-4-(4-nitrobenzoyl)cyclohex-2-enone (**13**; Ar = 4-$NO_2C_6H_4$).—2-(4-Nitrobenzoyl)propene (2.00 g, 10.5 mmol), 1-methoxy-3-trimethylsilyloxybuta-1,3-diene (2.00 g, 11 mmol), and sodium-dried benzene (10 cm^3) were heated for 6 days, and worked up as above to give, after chromatography on silica

(CH_2Cl_2), the *cyclohexenone* (1.40 g, 51%) as yellow crystals, m.p. 70—73 °C; $\nu_{max.}$ 2 960, 1 693, 1 605, 1 533, 1 350, 855, and 820 cm^{-1}; $\delta_H(CDCl_3)$ 1.60 (3 H, s, Me), 1.94—2.73 (4 H, m, 5-and 6-CH_2), 6.10 (1 H, d, *J* 10 Hz, 2-H), 7.07 (1 H, d, *J* 10 Hz, 3-H), 7.94 (2 H, d, *J* 8 Hz, 2- and 6-H of nitrobenzoyl), and 8.33 (2 H, d, *J* 8 Hz, 3- and 5-H of nitrobenzoyl) (Found: M^+, 259.084. $C_{14}H_{13}NO_4$ requires *M*, 259.084).

4-*Benzoyl*-4-*methyl*-6-*phenylselenocyclohex*-2-*enone* (**14**; Ar = Ph).—Following the general procedure of Gramlich and Plieninger,[28] as developed by Zaidi and Waring,[11] benzene selenenyl chloride (500 mg, 2.6 mmol) was added to 4-benzoyl-4-methylcyclohex-2-enone (510 mg, 2.4 mmol) in dried and freshly distilled ethyl acetate. The mixture was stirred at room temperature, under nitrogen, during 48 h. The solution was washed with water (5 cm^3), and brine (5 × 5 cm^3), and the aqueous washings were then extracted with ethyl acetate. The combined organic extracts were dried ($MgSO_4$) and concentrated to a dark yellow oil. Rapid chromatography on a wide silica column (hexane) removed the fast-running band of selenium-containing by-products. The residue was extracted from the column with CH_2Cl_2 and ether, and this extract was concentrated and re-chromatographed on another silica column (benzene, then chloroform) to give the crude *seleno ketone* (623 mg, 70%), as a pale yellow oil which on treatment with ether gave white crystals (46 mg, 6%) of pure material, m.p. 97—101 °C; $\nu_{max.}$ 3 070, 2 940, 2 860, 1 683, 1 600, and 1 580 cm^{-1}; $\delta_H(CDCl_3)$ 1.50 (3 H, s, Me), 2.33 (1 H, d of d, *J* 5 and 14 Hz, *eq* 5-H), 2.96 (1 H, d of d, *J* 10 and 14 Hz, *ax* 5-H), 4.26 (1 H, d of d, X part of ABX pattern, $J_{AX} + J_{BX}$ 15 Hz, *ax* 6-H), 6.09 (1 H, d, *J* 10 Hz, 2-H), 7.02 (1 H, d, *J* 10 Hz, 3-H), and 7.20—7.78 (5 H, m, aryl). This shows the phenylseleno group to be equatorial to the cyclohexenone ring (Found: C, 65.0; H, 5.2. $C_{20}H_{18}O_2Se$ requires C, 65.0; H, 4.9%).

4-*Benzoyl*-4-*methyl*-6-*phenylselenocyclohex*-2-*enone* (**14**; Ar = Ph).—Following the general method of Reich,[29] to dried di-isopropylamine (2.0 cm^3, 1.2 mmol), in dried THF (4.0 cm^3) under nitrogen at −78 °C, was added butyl-lithium[3] (0.58M; 2.0 cm^3, 1.2 mmol). A solution of 4-benzoyl-4-methylcyclohex-2-enone (214 mg, 1.0 mmol) in THF (0.4 cm^3) was added dropwise by syringe, and the solution stirred at −78 °C during 15 min. A solution of bromine (96 mg, 0.6 mmol) in THF (0.5 cm^3) was added to a solution of diphenyl diselenide (0.18 g, 0.6 mmol) in dried THF (1.0 cm^3), and the stirred mixture was added rapidly to the preceding enolate. The mixture was then poured onto 0.5M HCl (10 cm^3) and a 1:1 ether–pentane mixture (8 cm^3). The organic layer was washed with water, saturated aqueous sodium hydrogen carbonate, and brine, and then dried. Removal of solvent gave an oil which was purified by column chromatography (silica; hexane then chloroform) to give the crude seleno ketone (215 mg, 80% pure by n.m.r., with 20% of the starting enone: a 47% yield of the seleno ketone). Treatment with ether gave the pure crystalline seleno ketone as above.

Attempts to Prepare 4-*Benzoyl*-4-*methylcyclohexa*-2,5-*dienone by Oxidation–Elimination of the Seleno Ketone*.—The preceding seleno ketone (160 mg, 0.45 mmol) in redistilled dichloromethane (20 cm^3) at −78 °C was treated with ozonised oxygen, either until the solution became blue, after which the excess ozone was removed by further passage of oxygen, or had the calculated volume of a saturated solution of ozone in dichloromethane added. The solutions were then: (*a*) allowed to warm to room temperature; or (*b*) had a slight excess of diethylamine added and were then plunged into a hot oil-bath and allowed to boil at reflux for 1 min; or (*c*) heated rapidly to 25 °C by plunging into the hot oil-bath; or (*d*) poured rapidly into an excess of boiling dichloromethane or dichloromethane containing 1 equiv. of diethylamine. In each case the product was either, (*a*) washed with saturated (or alternatively 1% or 0.4%) aqueous sodium hydrogen carbonate and then water and brine, or (*b*) extracted rapidly with water at room temperature or with iced water, and then dried. In each case the products showed no n.m.r. evidence of the desired cyclohexadienone. In other experiments the pure seleno ketone (35.0 mg, 0.09 mmol) in redistilled ethyl acetate (5.0 cm^3) was treated with aqueous hydrogen peroxide (27% solution; 0.035 or 0.023 cm^3, 0.28 or 0.19 mmol) during 45 or 75 min at 25 °C. The mixture was washed rapidly with water, dried, and concentrated to give a yellow oil which was chromatographed on a silica column (dichloromethane), but without change in the spectra. The n.m.r. and i.r. spectra suggested that the products contained benzoic acid, and probably 4-methylphenyl benzoate and unchanged 4-benzoyl-4-methylcyclohex-2-enone.

4-*Benzoyl*-4-*methyl*-1-*trimethylsilyloxycyclohexa*-1,5-*diene*.—*Method* 1. Using a modification of House's[34] general method, 4-benzoyl-4-methylcyclohex-2-enone (0.25 g, 1.16 mmol), chlorotrimethylsilane (0.16 g, 1.45 mmol), triethylamine (0.29 g, 2.90 mmol), and DMF (0.5 cm^3) were heated at reflux, with stirring under nitrogen, during 23 h. The mixture was cooled in ice, poured into ice-cold pentane (30 cm^3), shaken with ice–water (1.0 cm^3), and the pentane solution dried (Na_2SO_4). Evaporation of the solvent under reduced pressure gave a yellow oil (139 mg), shown by its ^1H n.m.r. spectrum to comprise 50% of the desired silyl ether and 50% of the starting material.

Method 2. In a modification of another method of House,[34] a solution of lithium di-isopropylamide (1.17 mmol) in THF (1.10 cm^3), containing a crystal of 2,2′-bipyridyl was stirred under nitrogen at −78 °C. 4-Benzoyl-4-methylcyclohex-2-enone (0.25 g, 1.16 mmol) in THF (1 cm^3) was added dropwise by syringe, and the mixture stirred during 15 min at −78 °C, to form the enolate. A filtered quenching solution of triethylamine (52.0 mg, 0.5 mmol) and chlorotrimethylsilane (0.21 g, 1.9 mmol) in THF (2.0 cm^3) was injected, the mixture stirred during 15 min, and worked up using pentane as above. This gave a 2:1 mixture (268 mg) of silyl ether and starting cyclohexenone, the latter formed during the water washing, to which the silyl ether is sensitive.

Method 3. Using the general procedure of Duboudin and her co-workers,[35] dried sodium iodide (0.44 g, 2.95 mmol) in dry acetonitrile (3.0 cm^3) was added to a stirred mixture of triethylamine (0.30 g, 2.95 mmol), chlorotrimethylsilane (0.32 g, 2.95 mmol), and 4-benzoyl-4-methylcyclohex-2-enone (0.5 g, 2.33 mmol). After 45 min the mixture was poured into ice-cold pentane (50 cm^3), and the pentane washed with ice–water (1 cm^3) and then dried. Evaporation of the solvent under reduced pressure gave a light yellow oil (0.53 g), shown by n.m.r. to contain the starting ketone (30%) and the silyl ether; $\delta_H(CDCl_3)$ 0.18 (9 H, s, $OSiMe_3$), 1.33 (3 H, s, Me), 2.90 (2 H, d, *J* 5 Hz, 3-CH_2), 4.78 (1 H, br t, 2-H), 5.72—6.85 (2 H, m, 5- and 6-H), and 7.2—8.0 (5 H, m, ArH). Subsequent preparations omitted the aqueous wash, and the product was used for the next step immediately after removal of the solvent.

4-*Benzoyl*-4-*methylcyclohexa*-2,5-*dienone* (**1**; R = Ph, R′ = Me).—Following the general method of Ito and his co-workers,[31] palladium(II) acetate (393 mg, 1.74 mmol) was added to a stirred solution of 1-trimethylsilyloxy-4-benzoyl-4-methylcyclohexa-1,5-diene (**15**; Ar = Ph), (376 mg, 1.66 mmol, prepared as above) in dry acetonitrile (10.0 cm^3). Stirring was continued during 1 h at room temperature, after which the mixture was poured into ether (20 cm^3) and the palladium mirror and precipitate were washed with ether; the combined ether solutions were then washed quickly with ice–water (2.0

cm^3) and dried ($CaSO_4$). The oil (351 mg) remaining after evaporation of the solvent was shown by n.m.r. to contain 70% of the *dienone* (88% yield). Crystallisation from hexane–CCl_4 gave pure dienone, white crystals, m.p. 111—113 °C; $\nu_{max.}(CCl_4)$ 2 925, 2 850, 1 690, and 1 662 (dienone), 1 600, and 1 580 cm^{-1}; $\delta_H(CCl_4)$ 1.58 (3 H, s, Me), 6.34 (2 H, d, *J* 10 Hz, 2- and 6-H), 6.95 (2 H, d, *J* 10 Hz, 3- and 5-H), and 7.30—7.80 (5 H, m, ArH); $\delta_C(CDCl_3)$ 24.82 (Me), 54.97 (C-4 of cyclohexadienone ring), 128.52 (C-2, -3, -5, and -6 of benzoyl group), 129.69 (C-2 and -6 of dienone), 133.26 (C-4 of benzoyl ring), 137.36 (C-1 of benzoyl), 151.26 (C-3 and -5 of dienone), 184.85 (carbonyl of cyclohexa-2,5-dienone), and 196.61 (benzoyl carbonyl) (Found: M^+, 212.082. $C_{14}H_{12}O_2$ requires *M*, 212.084). Detailed modifications, including the use of the silyl ether–acetonitrile solution directly from the previous step, and extraction of the reaction mixture with boiling pentane and filtration of this solution through Celite, allowed the crystalline dienone to be obtained directly in up to 57% yield, upon evaporation of the solvent.

4-(4-*Methoxybenzoyl*)-4-*methylcyclohexa*-2,5-*dienone* (**1**; R = 4-$MeOC_6H_4$).—Following the procedure given above, sodium iodide (0.26 g, 1.73 mmol) in dry acetonitrile (4.0 cm^3) was added to a stirred mixture of triethylamine (0.19 g, 1.85 mmol), chlorotrimethylsilane (0.20 g, 1.81 mmol), and 4-(4-methoxybenzoyl)-4-methylcyclohex-2-enone (336 mg, 1.37 mmol). After 45 min at room temperature, the mixture was extracted with ice-cold pentane (50 cm^3) and the pentane layer dried, and evaporated. The 1-trimethylsilyloxy-4-(4-methoxybenzoyl)-4-methylcyclohexa-1,5-diene (**15**; Ar = 4-$MeOC_6H_4$) so formed was dissolved in dry acetonitrile (1.0 cm^3) and stirred with palladium(II) acetate (0.28 g, 1.22 mmol) in dry acetonitrile (3.0 cm^3) during 1 h. The mixture was treated with pentane, after which the solution was filtered through Celite, and the solvent evaporated to give the *dienone* (100 mg, 30%) as white crystals from hexane, m.p. 115—118 °C, $\nu_{max.}(CCl_4)$ 2 940, 2 860, 1 660, 1 605, 1 575 (cyclohexa-2,5-dienone), and 1 250 cm^{-1}; $\delta_H(CDCl_3)$ 1.57 (3 H, s, Me), 3.80 (3 H, s, OMe), 6.35 (2 H, d, *J* 10 Hz, 2- and 6-H of dienone ring), 7.05 (2 H, d, *J* 10 Hz, 3- and 5-H of dienone), 6.81 (2 H, d, *J* 10 Hz, 3- and 5-H of 4-methoxybenzoyl), 7.80 (2 H, d, *J* 10 Hz, 2- and 6-H of 4-methoxybenzoyl group) (Found: M^+, 242.093. $C_{15}H_{14}O_3$ requires *M*, 242.094).

4-(4-*Chlorobenzoyl*)-4-*methylcyclohexa*-2,5-*dienone* (**1**; R = 4-ClC_6H_4).—Following the procedures given above, 4-(4-chlorobenzoyl)-4-methylcyclohex-2-enone (342 mg, 1.37 mmol) gave 1-trimethylsilyloxy-4-(4-chlorobenzoyl)-4-methylcyclohexa-1,5-diene (300 mg) as a pale yellow oil. This was treated with palladium(II) acetate in acetonitrile to give the title *dienone* (135 mg, 39%) as pale cream crystals (from hexane), m.p. 109—112 °C; $\nu_{max.}(CCl_4)$ 2 940, 2 860, 1 660, and 1 590 cm^{-1}. To help reinforce the structure assignment, n.m.r. spectra were recorded in $CDCl_3$ and C_6D_6: the respective chemical shifts (δ values), and solvent shifts, $\delta(CDCl_3) - \delta(C_6D_6)$ are: 4-methyl group, 1.57, 1.14, 0.43; 2- and 6-H of cyclohexadienone ring, 6.45, 6.13, 0.32; 3- and 5-H of dienone ring, 6.99, 6.13, 0.86; 3-and 5-H of benzoyl group, 7.29, 6.65, 0.64; 2- and 6-H of benzoyl, 7.80, 7.39, and 0.41 (Found: M^+, 246.044. $C_{14}H_{11}ClO_2$ requires *M*, 246.044).

Attempts to Prepare 4-Methyl-4-(4-*Nitrobenzoyl*)*cyclohexa*-2,5-*dienone* (**1**; R = 4-$NO_2C_6H_4$).—Following the procedure given above, 4-methyl-4-(4-nitrobenzoyl)cyclohex-2-enone (250 mg, 0.96 mmol) gave a pale yellow oil, assumed to be 4-methyl-4-(4-nitrobenzoyl)-1-trimethylsilyloxycyclohexa-1,5-diene (280 mg, 87%). This was immediately subjected to palladium(II) acetate treatment to give a yellow oil (100 mg), whose n.m.r. spectrum showed the presence of the desired dienone (46%), 4-methylphenol (41%), and the starting cyclohexenone (13%). Attempts to effect purification by crystallisation, or preparative t.l.c. failed, the latter causing decomposition to 4-methylphenol and 4-nitrobenzoic acid.

Thermal Stability of 4-*Benzoyl*-4-*methylcyclohexa*-2,5-*dienone* [**1**; R = C_6H_4).—The dienone was heated at reflux in dried benzene during 3 h. Analysis by n.m.r. showed that no detectable change had occurred.

Hydrolysis of 4-*Benzoyl*-4-*methylcyclohexa*-2,5-*dienone* (**1**; R = C_6H_4).—(a) *In water.* The dienone (22.0 mg) was stirred with water (3.0 cm^3) during 3 h at room temperature (< 20 °C). The mixture was extracted with chloroform and the extract dried and evaporated to give a mixture shown by n.m.r. to comprise equivalent amounts of 4-methylphenol and benzoic acid.

(b) *In aqueous sodium hydroxide.* The dienone (5.2 mg) was shaken during 15 min with aqueous sodium hydroxide (1.0M; 1.0 cm) and spectroscopic ethanol (0.1 cm^3 to effect solution). The mixture was extracted with chloroform, and the extracts washed with brine, dried, and evaporated to give an oil shown by n.m.r. and g.l.c. analysis (E30 column at 125 °C) to comprise 4-methylphenol, benzoic acid, and 4-benzoyl-4-methylcyclohex-2-enone as an impurity present in the original dienone sample.

(c) *With sodium methoxide in methanol.* Reaction of the dienone with a 10 mol excess of sodium methoxide in methanol, during 10 min at 25 °C, was followed by quenching with ice and immediate extraction into chloroform. The aqueous layer was further extracted with ether, and the combined organic extracts were dried and evaporated, to give a quantitative yield of 4-methylphenol and methyl benzoate in an equimolar ratio (n.m.r. analysis).

(d) *With sodium* [$^2H_3$]*methoxide in* [$^2H_3$]*methanol.* The dienone(13.0 mg, 6.1 × 10^{-5} mol) was dissolved in [$^2H_4$]methanol (0.3 cm^3), and the n.m.r. spectrum recorded at −10 °C. This had δ_H 1.56 (3 H, s, Me), 6.44 (2 H, d, *J* 10 Hz, 2- and 6-H of dienone ring), 7.25 (2 H, d, *J* 10 Hz, 3- and 5-H), and 7.34—7.76 (5 H, m, aryl H). [$^2H_4$]Methanol (1.0 cm^3) was treated with sodium (7.0 mg), then cooled to −10 °C, and 0.20 cm^3 of the resulting solution was injected into the dienone solution to give 0.122M sodium [$^2H_3$]methoxide. The n.m.r. spectrum was recorded immediately, but the absence of the peak at δ 1.56 showed all dienone to have been already consumed. A number of subsequent spectra were all identical, having δ_H 2.17 (3 H, s, Me), 6.51 (2 H, d, *J* 8 Hz, 2- and 6-H) and 6.82 (2 H, d, *J* 8 Hz, 3- and 5-H) due to 4-methylphenol, and 7.25 − 8.60 (5 H, m, ArH) due to [$^2H_3$]methyl benzoate, in a 1:1 mol. ratio. Work-up with chloroform in the usual way gave an oil (15.0 mg), which was shown by i.r. spectroscopy (CCl_4) and g.l.c. analysis (XF1150 column at 150 °C) to contain only 4-methylphenol and [$^2H_3$]methyl benzoate.

(e) *With methanol.* The dienone (20.0 mg, 90 mmol) in methanol (10 cm^3) was held at 25 °C during 10 min. Rapid cooling in a bath at −20 °C was followed by evaporation of the solvent at 0.5 mmHg. The residue contained only the dienone. A similar solution, with identical quantities, was kept at 25 °C during 17.5 h, and the residue, after evaporation, was examined by n.m.r. spectroscopy. This showed methyl benzoate and 4-methylphenol to have been formed, by methanolysis of (17 ± 3)% of the dienone. Another solution of the dienone (20.0 mg) in methanol (2.0 cm^3) was treated in the same way, for 17.5 h: this was found to contain unchanged dienone, and (26 ± 3)% of methanolysis products. In an early experiment, the dienone was treated with methanol, and the product worked up by being poured onto ice, followed by rapid extraction with chloroform and drying of the extract in the usual way. Analysis by n.m.r. showed that methanolysis had occurred along with significant

hydrolysis during the work-up, so this procedure was abandoned.

Methanolysis of 4-(4-*Methoxybenzoyl*)-4-*methylcyclohexa*-2,5-*dienone* (**1**; R = 4-$MeOC_6H_4$).—The dienone (20.0 mg) was treated as above with methanol (0.5 cm^3) during 17.5 h at 25 °C. Cooling and evaporation of the solvent at 0.5 mmHg gave a residue shown by n.m.r. spectroscopy to contain unchanged dienone, and 4-methylphenol and methyl 4-methoxybenzoate corresponding to methanolysis of somewhat more than 60% of the dienone.

Hydrolysis of 4-*Benzoyl*-4-*methylcyclohexa*-2,5-*dienone in Dilute Acid.*—The dienone (5.0 mg) was treated with ethanol (0.1 cm^3) and 10^{-2}M aqueous HCl (2.5 cm^3), and held in an ultrasonic bath for 30 s. Chloroform was added, and the washed and dried solution evaporated to give a residue (5.0 mg) containing only 4-methylphenol and benzoic acid (g.l.c. on E30 column at 125 °C).

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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 M. R. Sandner, E. Hedaya, and D. J. Trecker, *J. Am. Chem. Soc.*, 1968, **90**, 7249.
6 For reviews, see D. Bellus and P. Hrdlovic, *Chem. Rev.*, 1967, **67**, 599; D. Bellus, *Adv. Photochem.*, 1971, **8**, 109.
7 F. Effenberger and R. Guttmann, *Chem. Ber.*, 1982, **115**, 1089.
8 F. Effenberger, H. Klenk, and P. L. Reiter, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 775.
9 J. W. Pilkington and A. J. Waring, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1349.
10 J. D. Palmer and A. J. Waring, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1089.
11 A. J. Waring and J. H. Zaidi, *J. Chem. Soc., Perkin Trans. 1*, 1985, 631.
12 S. Danishefsky, C. F. Yan, and P. M. McCurry, *J. Org. Chem.*, 1977, **42**, 1819.
13 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.
14 S. Danishefsky, J. Morris, G. Mullen, and R. Gammill, *J. Am. Chem. Soc.*, 1982, **104**, 7591.
15 J. N. Marx, J. C. Argyle, and L. R. Norman, *J. Am. Chem. Soc.*, 1974, **96**, 2121.
16 J. H. Zaidi and A. J. Waring, *J. Chem. Soc., Chem. Commun.*, 1980, 618.
17 E. K. Euranto, in 'The Chemistry of Carboxylic Acids and Esters,' ed. S. Patai, Wiley, New York, 1969, p. 575 *et seq.*
18 A. Kivinen, in 'The Chemistry of Acyl Halides,' ed. S. Patai, Interscience, New York, 1972, p. 172 *et seq.*
19 A. Mustafa, in 'Benzofurans,' vol. 29 of 'The Chemistry of Heterocyclic Compounds,' eds. A. Weissberger and E. C. Taylor, Wiley, New York, 1974, p. 370 *et seq.*
20 S. Danishefsky and T. Kitahara, *J. Am. Chem. Soc.*, 1974, **96**, 7807.
21 S. Danishefsky, *Acc. Chem. Res.*, 1981, **14**, 400.
22 E. B. Knott, *J. Chem. Soc.*, 1947, 1190; J. H. Burckhalter and R. C. Fuson, *J. Am. Chem. Soc.*, 1948, **70**, 4184.
23 K. Sugita, T. Kilp, and J. E. Guillet, *J. Polym. Sci., Polym. Chem. Ed.*, 1976, **14**, 1901.
24 G. Goodyear and A. J. Waring, unpublished work.
25 J. Gras, *Tetrahedron Lett.*, 1978, 2111.
26 T. Cohen and Z. Kosarych, *J. Org. Chem.*, 1982, **47**, 4005.
27 A. P. Kozikowski, K. Sugiyama, and J. P. Springer, *J. Org. Chem.*, 1981, **46**, 2426.
28 H. Plieninger and W. Gramlich, *Chem. Ber.*, 1978, **111**, 1944; W. Gramlich and H. Plieninger, *ibid.*, 1979, **112**, 1550, 1571.
29 H. J. Reich, J. M. Renga, and I. L. Reich, *J. Am. Chem. Soc.*, 1975, **97**, 5434.
30 Reviewed by D. L. J. Clive, *Tetrahedron*, 1978, **34**, 1049.
31 Y. Ito, T. Hirao, and T. Saegusa, *J. Org. Chem.*, 1978, **43**, 1011.
32 P. A. Wender and J. C. Lechleiter, *J. Am. Chem. Soc.*, 1980, **102**, 6340.
33 A. E. Greene, M. A. Teixeira, E. Barreiro, A. Cruz, and P. Crabbé, *J. Org. Chem.*, 1982, **47**, 2553.
34 H. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, 1969, **34**, 2324.
35 P. Cazeau, F. Moulines, O. Laporte, and F. Duboudin, *J. Organomet. Chem.*, 1980, **201**, C9.
36 K. L. Cook and A. J. Waring, *J. Chem. Soc., Perkin Trans. 1*, 1973, 529.
37 R. J. Thiessen, *J. Org. Chem.*, 1971, **36**, 752; S. Wolff and W. C. Augusta, *Synthesis*, 1976, 240.
38 H. O. House and G. D. Ryerson, *J. Am. Chem. Soc.*, 1961, **83**, 979, and references cited therein.
39 C. P. Falshaw, S. A. Lane, and W. D. Ollis, *J. Chem. Soc., Chem. Commun.*, 1973, 491.
40 V. Tortorella, L. Toscano, C. Vetuschi, and A. Romeo, *J. Chem. Soc., C*, 1971, 2422.
41 P. Bakuzis, G. C. Magalhaes, H. Martins, and M. L. F. Bakuzis, *J. Org. Chem.*, 1974, **39**, 2427.
42 E. Lee-Ruff and P. Khazanie, *Can. J. Chem.*, 1975, **53**, 1708.
43 Y. Sawaki and Y. Ogata, *J. Am. Chem. Soc.*, 1978, **100**, 856.
44 F. B. H. Ahmad, J. M. Bruce, J. Khalafy, V. Pejanović, K. Sabetian, and I. Watt, *J. Chem. Soc., Chem. Commun.*, 1981, 166; F. B. H. Ahmad, J. M. Bruce, J. Khalafy, and K. Sabetian, *ibid.*, 1981, 169.
45 R. D. Bach and J. M. Domagala, *J. Org. Chem.*, 1984, **49**, 4181; R. D. Bach and R. C. Klix, *ibid.*, 1987, **52**, 580, and references cited therein.
46 P. M. Kochergin and L. S. Blinova, *Zh. Prikl. Khim.*, 1968, **41**, 447; (*Chem. Abstr.*, 1968, **69**, 18 776s).
47 G. Harissis, M.Sc. Thesis, University of Birmingham, 1981.

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