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

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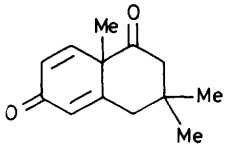
4-Benzoyl-4-methylcyclohexa-2,5-dienone and its 4-(4-chlorobenzoyl) and 4-(4-methoxybenzoyl) analogues (**2a**—**c**) have been isolated as the first simple examples of an elusive class of compounds, and their reactivities towards nucleophiles have been investigated.

Numerous attempts to prepare 4-acylcyclohexa-2,5-dienones have failed because of the extreme sensitivity of these compounds towards nucleophiles.[1—5] The simplest isolated representative of the class is the bicyclic compound (**1**), in which the main pathways for decomposition were suppressed or retarded.[4,5] We argued that 4-benzoylcyclohexa-2,5-dienones should be more stable than the previously sought 4-acetyl[4,5] and 4-formyl[1,2] analogues. Nucleophilic fragmentation of the vinylogous 1,3-dicarbonyl function, by attack at the benzoyl group, should be slowed down, as are the alcoholysis and hydrolysis reactions of benzoyl halides relative to acetyl halides.[6,7] Intramolecular migrations should be slowed also, for similar reasons. We now report the preparations of the compounds (**2a**—**c**)† as shown in Scheme 1, and some of their properties.

The steps from Danishefsky's diene (**3**)[8] to the acyl cyclohexenones (**7**; R = H) parallel those used by Danishefsky and his coworkers,[1—3,8] and by ourselves.[4,5] The parent compound (**7a**; R = H) was converted into a mixture of diastereoisomeric phenylselenyl ketones (**7a**; R = equatorial SePh, *cis* or *trans* to the benzoyl group). This was oxidised, and the derived selenoxide decomposed under a variety of conditions, including those which allowed the isolation of (**1**).[4,5] The products were 4-methylphenol and its benzoate, sometimes accompanied by inseparable amounts of the dienone. However, dehydrosilylation by palladium salts of the derived trimethylsilyl enol ethers (**8**)[9—11] (characterised by ^{1}H n.m.r. spectroscopy, but not purified), with a non-aqueous work-up, was successful. The dienones (**2a**), m.p. 111—113 °C, (**2b**), m.p. 115—118 °C, and (**2c**), m.p. 109—112 °C (from hexane), were obtained as colourless crystalline solids, having consistent i.r., ^{1}H and ^{13}C n.m.r., and mass spectra. They are stable towards storage and boiling in dry benzene. All the cyclohexadienones react in aqueous solutions, to give 4-methylphenol and the appropriate benzoic acid, with minimum background rate constants due to reaction with water, between 10^{-3} and 4×10^{-4} s^{-1} at 25.0 °C (half-lives 12—38 min). Reaction in even dilute aqueous acid and alkali is much faster, but gives the same products.

Rate–pH profiles and buffer studies have allowed the mechanism of the reactions in acids to be defined as A-1, with specific acid catalysis. This behaviour parallels the route established for dienone–phenol rearrangements,[12,13] and suggests that protonaton occurs rapidly and reversibly on the dienone carbonyl group, followed by rate-determining cleavage to form an incipient benzoyl cation. In accordance with this view, the rates of the acid-catalysed reactions are correlated by the Hammett equation against σ with a ρ value close to -2.0: *i.e.*, cleavage is aided by an electron-donating substituent in the benzoyl ring. The reactions in neutral to basic solutions are subject to general base catalysis, but appear to follow more than one mechanism, which will be the subject of future reports. Cleavage by alcohols, or much faster by alkoxides, gives the phenol and the alkyl benzoates. Surpris-



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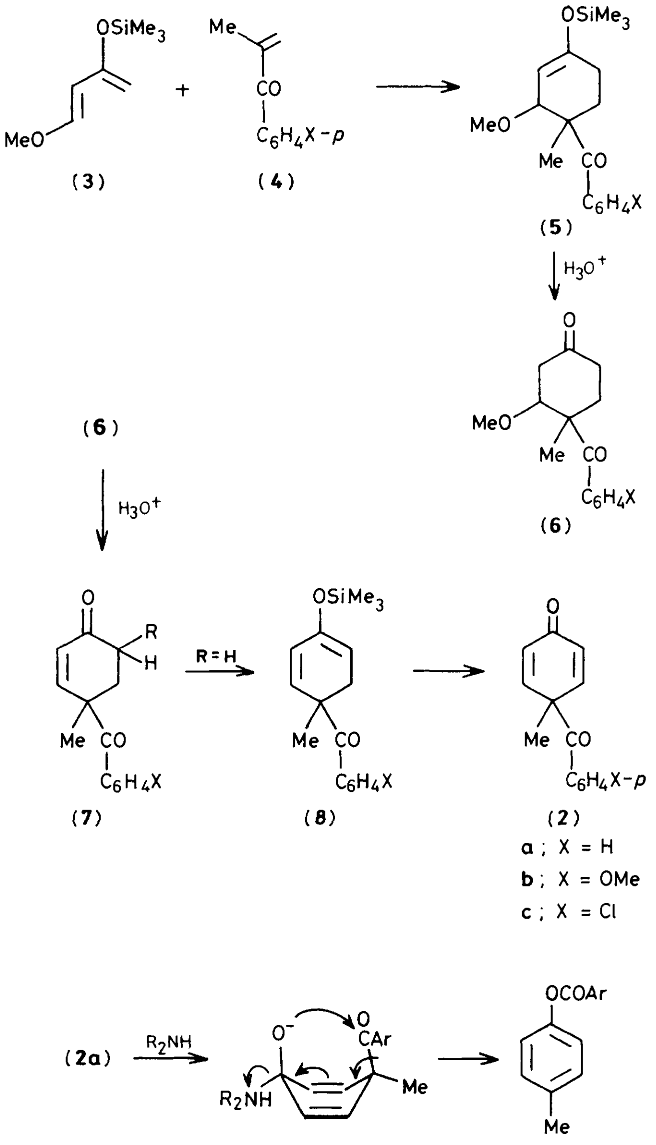

Scheme 1

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† Satisfactory microanalytical and spectroscopic data have been obtained for compounds (**6b**), (**7a**—**c**; R = H), (**7a**; R = SePh), (**2a**—**c**), and (**7**; X = 4-NO$_2$). Compound (**7a**; R = H) was first made by G. Harissis and A. J. Waring (1981, unpublished work).

ingly, although dimethylamine in ethanol produces *N,N*-dimethylbenzamide, some 4-methylphenyl benzoate is also found. Diethylamine and pyrrolidine give similar results, which have been shown to be due to initial formation of 4-methylphenyl benzoate (by a process first-order in both dienone and amine), and its subsequent aminolysis. We suggest a pathway (Scheme 1) which is being subjected to further scrutiny.

In non-aqueous acids, such as 2% trifluoroacetic acid in CD_2Cl_2 at −10 °C, the dienone (**2a**) rearranges completely within 100 s to 4-methylphenyl benzoate. This represents the rearrangement step of a retro-Fries reaction, which clearly is a very rapid process. Studies have been made of the rearrangement of (**2a**) in the presence of varying amounts of 3,5-dimethylphenol, induced by boron trifluoride–diethyl ether in benzene. The yields of 4-methylphenyl- and 3,5-dimethylphenylbenzoates suggest that the reaction follows partly intra- and partly inter-molecular pathways, probably *via* an acylium ion–phenol pair in a solvent cage from which limited escape is possible.

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