Dienone–Phenol Rearrangement of 4-Chloro-4-methylcyclohexadienones

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Summary 4-Chloro-4-methyl-, 4-chloro-3,4-dimethyl-, 4-chloro-2,4-dimethyl-, and 4-chloro-2,4,6-trimethylcyclohexa-2,5-dienones give the corresponding 3-chloro-4-methylphenols on reaction with trifluoromethanesulphonic acid.

Dienone–phenol rearrangement studies have been employed to measure the relative migratory aptitudes of substituent groups.[1–3] We now report that chlorine migrates in preference to methyl in such rearrangements.

When 4-chloro-4-methyl-, 4-chloro-3,4-dimethyl-, 4-chloro-2,4-dimethyl-, and 4-chloro-2,4,6-trimethylcyclohexa-2,5-dienones[4] were dissolved in neat trifluoromethanesulphonic acid and the temperature raised to 35 °C migration of the chlorine from the 4- to the 3-position occurred rapidly ($<$10 min) to give 3-chloro-4-methyl-, 5-chloro-3,4-

dimethyl-, 5-chloro-2,4-dimethyl-, and 3-chloro-2,4,6-trimethylphenols, respectively. The reactions were essentially quantitative and no isomeric phenols could be detected by n.m.r. spectroscopy (*ca.* 2% of isomeric phenols should have been detected).

In the series of 4-X-4-methylcyclohexa-2,5-dienones the substituents X = CO_2Et,[3,5] OCOMe,[6] Ph,[3] and Cl migrate in preference to Me, which migrates in preference to X = OH[7] and OMe.[1] Both the relative migration tendencies and the effect of the non-migrating group on the stability of the transition state are important in determining the outcome of the competitive migration of a pair of substituent groups.[1–3] Thus in the above sequence OH and OMe are particularly effective in dispersing the developing positive charge in the transition state. These groups thus stabilize the transition state and do not migrate in competition with Me. The CO_2Et group is destabilizing in this sense and thus migrates. The OCOMe and Ph groups are particularly effective in forming new bridging bonds (the OCOMe group forming a 5-membered ring through the carbonyl oxygen) and thus migrate in preference to Me. Chlorine, like OH and OMe, has a destabilizing inductive effect and a stabilizing electron-donating resonance effect. However, unlike the former, the inductive effect outweighs the resonance effect and hence it is destabilizing and thus migrates.

There is a striking contrast in the reactions of the 4-chloro-4-methylcyclohexadienones and of the 4-methyl-4-nitrocyclohexa-2,5-dienones. The latter rearrange very rapidly, even in non-acidic conditions, and give the corresponding 4-methyl-2-nitrophenols.[8,9] A radical dissociation–recombination reaction has been proposed for non-acidic and weakly acidic conditions[9] and, for strongly acidic conditions,[9,10] reversion of the conjugate acid of the nitrodienone to the phenol–nitronium ion encounter pair followed by recombination at the *ortho* position has been suggested.[10] No 1,2 shift products (3-nitro-4-methylphenols) are formed. Fission of the C–N bond in nitromethane is 97 kJ mol^{-1} less endothermic than fission of the C–Cl bond in methyl chloride.[11] It is therefore understandable why a radical dissociation–recombination pathway exists for 4-methyl-4-nitrocyclohexadienones but not, apparently, for 4-chloro-4-methylcyclohexadienones. Unimolecular expulsion of a nitronium ion from the conjugate acid of a 4-nitro-4-methylcyclohexadienone apparently occurs readily but loss of the chlorine from the conjugate acid of a 4-chloro-4-methylcyclohexadienone requires a bimolecular attack by a good nucleophile.[12] Thus neither of the pathways available for the dissociative rearrangement of 4-methyl-4-nitrocyclohexadienones are readily accessible to the 4-chloro-4-methylcyclohexadienones, which are therefore constrained to undergo intramolecular migration of the chlorine by a 1,2 shift.

Formation of 3-chloro-4-methylphenols on rearrangement of 4-chloro-4-methylcyclohexa-2,5-dienones contrasts with an earlier claim that 4-chloro-3,4-dimethylcyclohexa-2,5-dienone gives 3,4-dimethylphenol and 2-chloro-4,5-dimethylphenol in acetic acid.[13] In our hands a solution of the dienone in acetic acid was stable over a period of a week.

Formation of a 4-chloro-4-methylcyclohexa-2,5-dienone[4] followed by acid-catalysed rearrangement to a 3-chloro-4-methylphenol provides an indirect method of chlorination of a 4-methylphenol at the 3-position, in good yield. Direct (mono) chlorination at the *meta* position of a phenol does not occur.

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