Electrophilic Substitution by a Phenonium Ion Derived from 1-Chloro-2,3-dimethylbenzene: Arylation of Mesitylene and Formation of a Biphenyl

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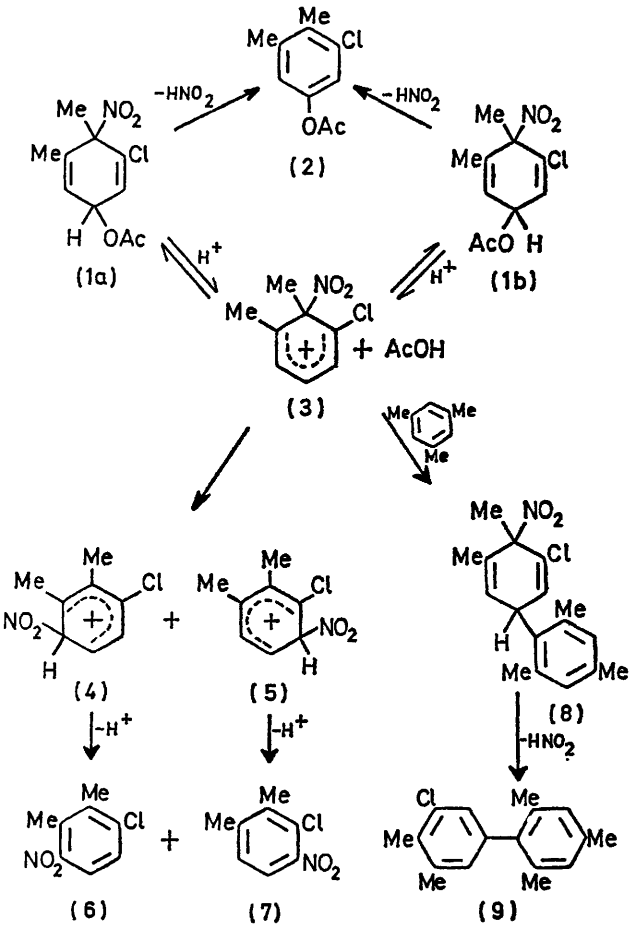
Summary Reaction of 1-chloro-2,3-dimethylbenzene with nitric acid in acetic anhydride gives 3-chloro-4,5-dimethyl-4-nitro-1,4-dihydrophenyl acetate; the adduct reacts with mesitylene in the presence of trifluoroacetic acid to form 3′-chloro-2,4,4′,5′,6-pentamethylbiphenyl.

ADDUCTS obtained in the nitration of suitably substituted aromatic substrates undergo a variety of rearomatization reactions, giving rise to unexpected 'nitration' products, in which there is continuing current interest.[1] We report here the formation of a biphenyl derivative in the course of such a rearomatization.

Nitration of 2,3-dimethylchlorobenzene in acetic anhydride gave the pair of diastereoisometic adducts (**1**) as well as the expected nitro-substitution products. The n.m.r. spectrum of each isomer showed two 3—4 Hz couplings between the ring protons, and is clearly consistent with structure (**1**) and not with the alternative structure in which the nitro-group has attacked the other methyl-substituted position, that *meta* to the chlorine. Reaction of either (**1a**) or (**1b**) with acetic acid at 50° resulted in epimerization accompanied by the slow 1,4-elimination of nitrous acid to form the acetate (**2**), a normal reaction of adducts which are secondary acetates.[2] When decomposition was carried out in 20% trifluoroacetic acid in chloroform at 25° rapid epimerization occurred but compounds (**6**) and (**7**) were obtained. In an attempt to distinguish between a denitration–renitration mechanism and one involving an intramolecular 1,3-nitro-shift,[3] mesitylene was introduced into the reaction mixture in order to trap any nitrating species formed. However, neither nitromesitylene nor the chlorodimethylnitrobenzene were observed but the biphenyl (**9**) was obtained. Precise mass measurement of the molecular ion established the molecular formula and n.m.r. spectroscopy confirmed the structure (**9**).

We interpret these observations in the following way. The phenonium ion (**3**) is formed from either (**1a**) or (**1b**) by acid-catalysed loss of acetate. In acetic acid cation (**3**) is rapidly recaptured by the solvent species and reverts to a mixture of (**1a**) and (**1b**). The equilibrium concentra-



tion of cation (**3**) is very low, because acetic acid is a weak acid and also because of the mass-law effect, and 1,4-elimination of nitrous acid from compounds (**1**) competes effectively with the further reaction of cation (**3**). In the stronger trifluoroacetic acid the equilibrium concentration of cation (**3**) should be greatly increased and the conversion of cation (**3**) into the phenonium ions (**4**) and (**5**) is more rapid than the elimination of nitrous acid from compounds (**1**). Thus the chlorodimethylnitroxylenes (**6**) and (**7**) are formed in preference to the acetate (**2**). When mesitylene is added it traps the phenonium ion(**3**) before the latter is converted into (**4**) and (**5**), giving the adduct (**8**), which undergoes 1,4-elimination of nitrous acid to form the biphenyl (**9**).

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