

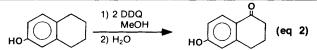
more than an oxidizin

DDO (2,3-dichloro-5,6-dicyano-1,4-benzoquinone), a quinone of high oxidation potential, is a versatile reagent with proven applications in synthesis. It is often the reagent of choice for dehydrogenation and selective oxidation. Thus, DDQ effects the dehydrogenation of the methano-bridged hexahydronaphthalene 1 to give the $10-\pi$ -electron annulene 2 in excellent yield.2

DDQ has recently been employed in the synthesis of diolepoxides of benz[a]anthracene, indicating its potential use in the synthesis of diolepoxides of other polynuclear aromatic hydrocarbons. These metabolites are currently of intense interest because of the proven muta- and carcinogenicity of a diolepoxide of benzo[a]pyrene.3

The dehydrogenation of 3-ketosteroids is only one example of the extensive use of DDQ in the steroid field.4 Saturated 3-ketosteroids (3) give the corresponding $\Delta^{1,4}$ derivatives (4).5,6 Δ^4 -3-Ketosteroids (5) yield the same $\Delta^{1,4}$ product under aprotic conditions, but $\Delta^{4,6}$ -dienes (6) in the presence of hydrogen chloride⁷ or p-toluenesulfonic acid.⁶

Many of the useful synthetic reactions of suitably substituted phenols with **DDQ** can be rationalized as proceeding through an intermediate quinone methide. Thus, mesitol is oxidized in methanol to the corresponding p-carboxaldehyde by two equivalents of **DDQ** (eq 1),8 and 6-hydroxy-



tetralin gives the tetralone (eq 2).9 Similarly, 3-alkylindoles are converted to 3-acylindole derivatives (eq 3).10

Upon treatment with **DDQ**, 2-(3,3-dialkylallyl)phenols undergo oxidative cyclization to 2,2-dialkylchromenes (eq 4).11 Phenols with o-allyl groups unsubstituted in the 3-position undergo oxidation to coumarins.12

DDQ also functions as a component in cycloaddition reactions. Thus, DDQ and 8-substituted heptafulvenes yield 3substituted 1,2-dicyanoazulenes, a result which can be rationalized as an $(8\pi + 2\pi)$ cycloaddition.¹³

DDQ has also been employed as a spray reagent in the tlc analysis of carbazoles.14

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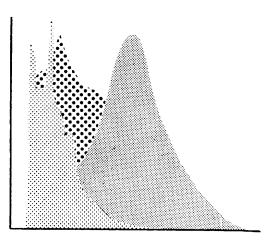
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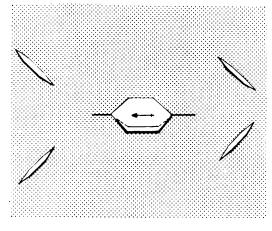
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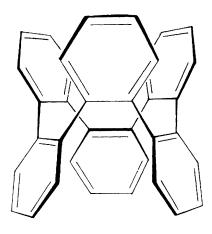
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