Diels–Alder Reactions of (Trimethoxymethyl)cyclopentadienes. Formation of Adducts derived from the 2-Substituted Tautomer

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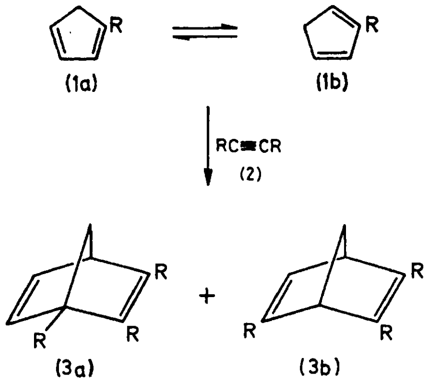
Summary The 1·2 : 1 tautomeric mixture of 2- and 1-(trimethoxymethyl)cyclopentadienes, when treated with dimethyl acetylenedicarboxylate, *p*-benzoquinone, and methyl propiolate, gave adducts derived largely from the 2-substituted tautomer; more reactive dienophiles gave 2 : 1 mixtures of adducts derived from the 2- and 1-substituted tautomers, respectively.

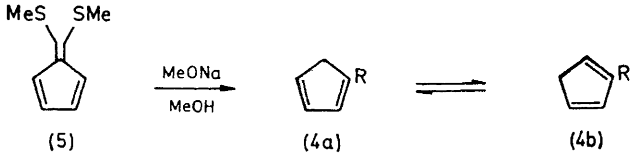
The Diels–Alder reactions of cyclopentadiene with dienophiles provide efficient routes for the synthesis of various bicyclo[2·2·1]heptene derivatives,[1] but the analogous reactions of substituted cyclopentadienes are often bedevilled by the ready tautomerization of the latter.[2] Although it has been found possible to develop efficient syntheses of 7-substituted bicyclo[2·2·1]heptenes by the rapid, catalysed[3] addition of dienophiles to 5-substituted cyclopentadienes (formed by alkylation of the cyclopentadienide ion) prior to tautomerization of the latter into the 1- and 2-substituted cyclopentadienes,[4] the synthesis of adducts derived from 1- or 2-substituted cyclopentadienes is frequently impractical because of the concurrent formation of adducts derived from the corresponding 2- or 1-substituted cyclopentadienes. Thus, reaction of the methyl cyclopentadienecarboxylates (**1**)[5] with dimethyl acetylenedicarboxylate (**2**) gave a 1 : 0·9 mixture of the bicyclo[2·2·1]heptene derivatives (**3a**) and (**3b**) (Scheme 1).[6]



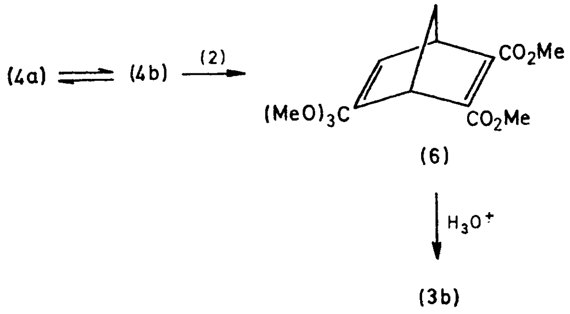
Scheme 1. R = CO_2Me

We have found that with certain dienophiles it is possible to obtain adducts from (trimethoxymethyl)cyclopentadienes (**4**) that are largely derived from the 2-substituted tautomer

(**4b**), in spite of the fact that under the conditions of the reaction compounds (**4**) exist as a 1·2 : 1 mixture of the 2- and 1-substituted tautomers (**4b**) and (**4a**), as shown by ^{1}H n.m.r. spectroscopy. The tautomeric mixture (**4**) was prepared from 6,6-bis(methylthio)fulvene (**5**),[7] as in Scheme 2. Unlike compounds (**1**) and many other mono-substituted cyclopentadienes, compounds (**4**) do not undergo dimerization, a circumstance that is advantageous in Diels–Alder reactions. Reaction of compounds (**4**) with the acetylene (**2**) in boiling benzene for 2 h gave the adduct (**6**)† derived from the tautomer (**4b**). This, on mild acidic hydrolysis, gave the triester (**3b**) (Scheme 3). Vapour-phase gas-chromatographic analysis showed that the ratio of the 2- and 1-substituted adducts was >20 : 1.

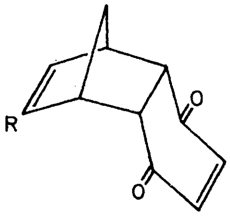


Scheme 2. R = C(OMe)$_3$

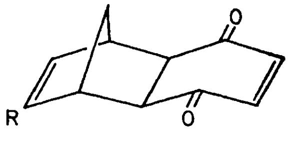


Scheme 3

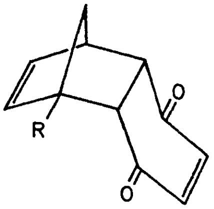
Similarly, reaction of compounds (**4**) with *p*-benzoquinone gave a 3 : 2 mixture of the *endo*- and *exo*-adducts (**7**), m.p. 92—93 °C, and (**8**), m.p. 137—138 °C, derived from the tautomer (**4b**), which were converted into the esters (**9**), m.p. 104—106 °C, and (**10**), m.p. 93—94 °C, respectively. However, reaction of compounds (**1**) with *p*-benzoquinone gave a 1 : 3 mixture of the esters (**9**) [or (**10**)] and (**11**), derived from both the carboxylates (**1b**) and (**1a**), respectively.[8] With methyl propiolate, compounds (**4**) gave a 2 : 1 mixture of the regioisomers (**12**) and (**13**), derived from the 2-substituted tautomer (**4b**); these were not separated, but the mixture was converted into a mixture of the diesters (**14**) and (**15**), which were separated and individually characterized. Vapour-phase chromatographic analysis showed that the ratio of 2- to 1-substituted adducts was >12 : 1, whereas in the reaction of methyl propiolate with the ester (**1**) it was 1·1 : 1.



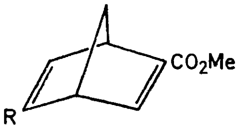
(7) R = C(OMe)$_3$
(9) R = CO$_2$Me



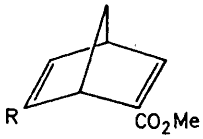
(8) R = C(OMe)$_3$
(10) R = CO$_2$Me



(11) R = CO$_2$Me

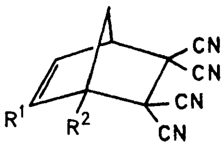


(12) R = C(OMe)$_3$
(14) R = CO$_2$Me

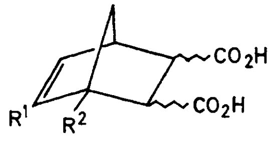


(13) R = C(OMe)$_3$
(15) R = CO$_2$Me

In contrast with these results, compounds (**4**) gave, with tetracyanoethylene, a 2 : 1 mixture of the cyanides (**16**) and (**17**) [derived from the tautomers (**4b**) and (**4a**), respectively] and gave with maleic anhydride, a 2 : 1 mixture of the adducts [again derived from the tautomers (**4b**) and (**4a**)]. In the latter case the individual products were not separated, but the product mixture was hydrolysed to give a mixture of the esters (**18**) and (**19**) which was analysed by ^{1}H n.m.r. spectroscopy.



(**16**) R^1 = C(OMe)$_3$, R^2 = H
(**17**) R^1 = H, R^2 = C(OMe)$_3$



(**18**) R^1 = CO$_2$Me, R^2 = H
(**19**) R^1 = H, R^2 = CO$_2$Me

It is known that tetracyanoethylene and maleic anhydride are more reactive dienophiles than dimethyl acetylenedicarboxylate, *p*-benzoquinone, and methyl propiolate.[9] Thus, the present results can be interpreted in terms of rapid reaction of the former two dienophiles with both the components of the tautomeric mixture (**4**) to give mixtures of adducts derived from both the tautomers (**4a**) and (**4b**) while reactions of dienophiles of the latter type occur more

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† Satisfactory elemental analytical data were obtained for all the isolated new compounds. The spectroscopic data for all compounds were in accord with the structural assignments.

slowly, and thus more selectively, to give adducts derived largely from the tautomer (**4b**) alone, since compound (**4a**) reacts more slowly because of steric hindrance.[10] It is possible that greater selectivity could be attained in the case of the more reactive dienophiles under milder conditions.‡ It may finally be noted that, although it has been possible to obtain a good yield of the adduct of tetracyanoethylene with methyl cyclopentadiene-2-carboxylate by reaction of the former with compounds (**1**) under conditions of thermodyanamic control,[10] this approach to the preparation of 2-substituted adducts is not generally applicable because we have found that the adducts of compounds (**1**) with the acetylene (**2**) and with methyl propiolate do not equilibrate in boiling benzene and undergo decomposition in boiling diglyme.

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‡ This would require that the rate of interconversion of the tautomers (**4a**) and (**4b**) remained rapid under these conditions.

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