Oxidation of Electron Rich Olefins with Sulphur Dioxide

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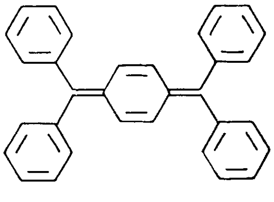
Summary In the reaction of sulphur dioxide with electron-rich olefins, the olefin cation radicals were observed; in some cases oxidized products in which oxygen from sulphur dioxide had been incorporated were obtained.

Liquid sulphur dioxide is known to act as a mild oxidant, in which the cation radicals formed are fairly stable.[1] However, electrophilic attack of SO_2 on enol ether groups to afford cyclic compounds or radical polymerization products has been reported only in the case of the reaction of an isolated double bond with SO_2.[2,3] In the light of these results, we investigated the possible oxidation of electron-rich olefins[4] with SO_2. Since SO_2 has a similar electronic structure to ozone, investigation of these reactions may also serve to clarify the mechanism of ozonolysis.[5]

The reaction of 3,6-bisdiphenylmethylenecyclohexadiene (**1**) with SO_2 in the dark in the absence of O_2 showed a u.v. spectrum (λ_{max} 572 and 415 nm) which is considered to be that of the cation radical of (**1**).[6] The e.s.r. spectrum of (**1**) in liquid SO_2 also supports the formation of the cation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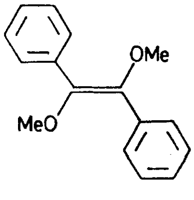

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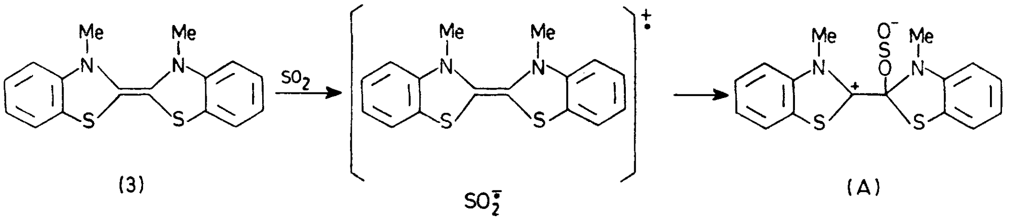
radical.[6] From the reaction mixture a 14% yield of benzophenone, together with starting material, was isolated. In the reaction of αβ-dimethoxystilbene (**2**) the intermediate cation radical was not detected, and the presence of only methyl benzoate (40% yield) and (**2**) was confirmed by the n.m.r. spectrum of the reaction mixture before treatment with water.

A strong e.s.r. signal (g 2·008, singlet, total width 5·6 mT) attributable to the cation radical of *NN'*-dimethylbis(benzothiazolin-2-ylidene) (**3**) was observed on mixing (**3**) with SO_2; the signal disappeared gradually during the reaction.



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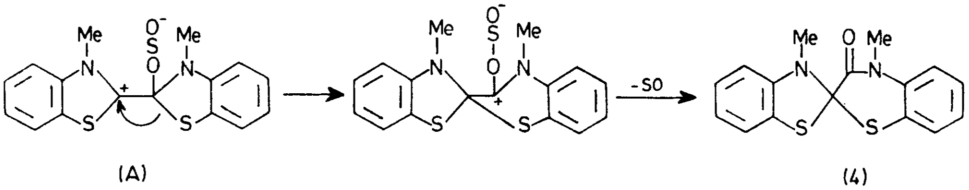

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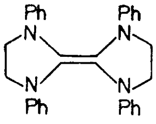
The n.m.r. spectrum of the reaction mixture before treatment with water suggested the formation of the spiro compound (**4**) in quantitative yield, and this result clearly suggests that SO_2 acts as an oxygen donor during the oxidation of (**3**). It is noteworthy that (**4**) was obtained in low yield by air oxidation. We have not undertaken a detailed study of the mechanism, but the selective formation of (**4**) may be explained by equations (1) and (2). An intermediate with a structure similar to (A) was postulated in the ozonization of sterically hindered olefins.[8]

The biimidazolidinylidene (**5**), which is known to be a highly electron-rich olefin, was oxidized in liquid SO_2 to the corresponding dication[9] *via* the cation radical of (**5**).[10] After hydrolysis of the reaction mixture 1,3-diphenylimidazolid-1-one and *N*-formyl-*NN'*-diphenylethylenediamine were obtained quantitatively in a molar ratio of 1 : 1.[9] The reaction of 4,4'-bisdiphenylmethylenebicyclohexadienylidene (**6**) with SO_2 afforded also the corresponding dication (λ_{max} 517 and 430 nm).



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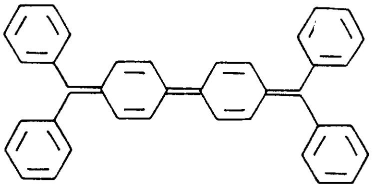

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