

CYCLOAROMATIZATION AND CYCLODIMERIZATION OF BRIDGED DIALLENES¹

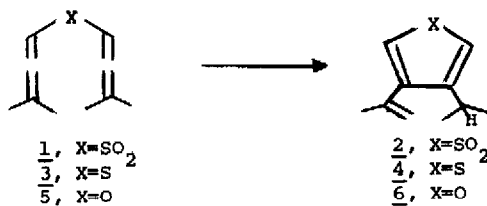
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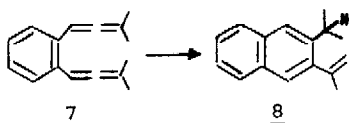
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Recently, we have shown that bis- γ,γ -dimethylallenyl sulfone (1) undergoes a novel and facile cyclization on heating at 75° to 3-isopropenyl-4-isopropylthiophene 1,1-dioxide (2)². The reaction mechanism may either involve a 2,2'-bisallyl-type biradical intermediate or may be described as a concerted intramolecular ene reaction². As a natural extension of this work, we decided to investigate the cyclization of various diallenic systems, especially those capable to undergo simultaneous aromatization. And as one of the most suitable candidates for such an extension, we have chosen the sulfide analog of 1, compound 3, which on cyclization should lead to thiophene 4. However, while the diallenic sulfone 1, can be obtained very conveniently by a double [2,3]-sigmatropic rearrangement of bis- α,α -dimethylpropargyl sulfoxylate, it is difficult to synthesize the diallenic sulfide 3, as well as the other diallenes reported below by simple methods. Apparently, this may be the reason for the lack of considerable activity on diallenic systems in the past.

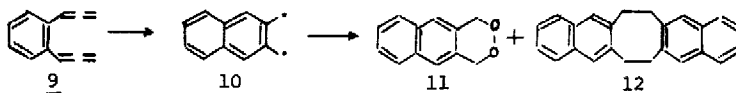


An attempt to prepare sulfide 3 by LAH reduction³ of sulfone 1, resulted in a quantitative yield of bis- γ,γ -dimethylallyl sulfone⁴, instead. Similarly, we have been unable to use the general and well known allene synthesis developed by Moore and by Skattebøl⁵, because of the surprising failure of dibromocarbene to add to bis- β,β -dimethylvinyl sulfide. However, on reaction of γ,γ -dimethylallenyllithium⁶ with sulfur dichloride in THF at dry ice-acetone temperature, a low yield of compound 4 was formed⁷. This result proves the occurrence of spontaneous cyclization of the postulated diallenyl sulfide 3, as expected⁸. In contrast to its sulfur analog, bis- β,β -dimethylvinyl ether¹⁰ undergoes dibromocarbene addition under normal conditions¹¹ to give the corresponding bis-gem-dibromocyclopropyl ether, which on reaction with MeLi in ether at appx. -35° was converted directly to the furan derivative 6⁷. However, this compound, which is formed by spontaneous cycloaromatization of the diallenyl ether 5, is itself unstable and decomposes within a few hours, even at room temperature.



The synthesis of *o*-bis-(γ,γ -dimethylallyl)benzene (7)⁷ was similar to that of 5, and involved addition of dibromocarbene to *o*-bis-(β,β -dimethylvinyl)benzene¹², followed by reaction of the product⁷ with methyllithium in ether at -35° . However, in sharp contrast to the diallenyl sulfide 3, and ether 5, which could not be isolated or even detected spectroscopically, the diallenylbenzene 7, is isolated in quantitative yield, and can be stored in the cold for several days. Furthermore, its transformation to the naphthalene derivative 8 (100% yield)⁷, proceeds at a measurable rate at room temperature in pentane¹³. This result is analogous to the cyclization of the diallenyl sulfone 1 to the thiophene dioxide 2, which also proceeds in quantitative yield but at higher temperatures². Obviously, the extra driving force provided by the simultaneous aromatization lowers the temperature of cyclization of 7 to 8, as expected.

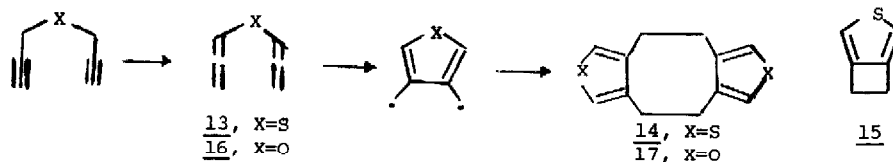
For comparison, it is interesting to point out that it has recently been reported by Sondheimer and coworkers¹⁴ that the unstable *o*-diallenylbenzene (9) undergoes oxidation by atmospheric triplet oxygen to the cyclic peroxide 11, as well as dimerization in low yield to the dinaphthocyclooctadiene 12, and an isomeric mixture of naphthalenic "complex dimers". The formation of these products was suggested to involve the biradical 10 as an intermediate.



Although, in principle, the formation of a 2,2'-bisallyl-type biradical¹⁵ would also appear quite reasonable for the first and rate-determining step of the rearrangement of 7 to 8, followed by a fast intramolecular hydrogen abstraction and formation of the new double bond, we have been unable to obtain supporting evidence for such a species, as yet. For example the conversion of 7 to 8 was not affected, by either bubbling through of oxygen¹⁴, sulfur dioxide¹⁶, or addition of tetracyanoethylene. Consequently, the second possible mechanism, which is based on the assumption that the reaction is essentially an intramolecular ene reaction¹⁷, cannot be excluded. This mechanism may alternatively be regarded as a variant of the symmetry-allowed 1,5-hydrogen shift¹⁸. Obviously, further work is required before a final conclusion can be reached with regard to the exact mechanism.

In spite of the contrast between the behaviour of diallenylbenzene (9)¹⁴ and that of its tetramethyl derivative 7, described above, it is of interest to note that the behaviour of the former compound, is however characteristic of other unsubstituted bridged diallenes, which are also unable to undergo 1,5-hydrogen migrations. For example, we have found^{1b} that isomerization of dipropargyl sulfide¹⁹ to diallenyl sulfide (13)^{7,20} occurs readily on treatment with freshly prepared *t*-BuOK in *t*-BuOH at 0° . Compound 13 is unstable and gradually undergoes dimerization to the bisthenocyclooctadiene 14^{7,21}. The same product was also obtained (20-30% yield) on treatment of dipropargyl sulfide with basic activated alumina²², sodium

ethoxide in ethanol at 50°, as well as under other base-catalyzed conditions. Nevertheless our efforts to improve the yields of 14 considerably were not successful²³, mainly due to competing isomerization of 13 to diprop-1-yne sulfide. The possibility that the thienocyclobutene 15, a molecule of theoretical interest²⁴, and originally the expected product²⁵, is a precursor of 14 may be ruled out, since it has been claimed²⁴ to be thermally stable up to 235°.



Treatment of dipropargyl ether²⁶ under similar conditions to those used with the corresponding sulfide, led to the formation of bisfurocyclooctadiene 17,^{7,23} through the intermediacy of diallenyl ether (16),⁷ as expected. Finally, it may be added that dipropargyl sulfoxide undergoes immediate decomposition, even in the presence of pyridine in chloroform, apparently due to the known unstability of the aromatic thiophene 1-oxide system²⁷, while dipropargyl sulfone very easily undergoes isomerization to diallenyl sulfone⁷, which however remains unchanged even after 18 hours of heating in chloroform at the reflux temperature. This should not be surprising in view of the/of possible aromatization or 1,5-hydrogen transfer upon cyclization.
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