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SYNTHESIS OF A DIQUINOCYCLOBUTENE

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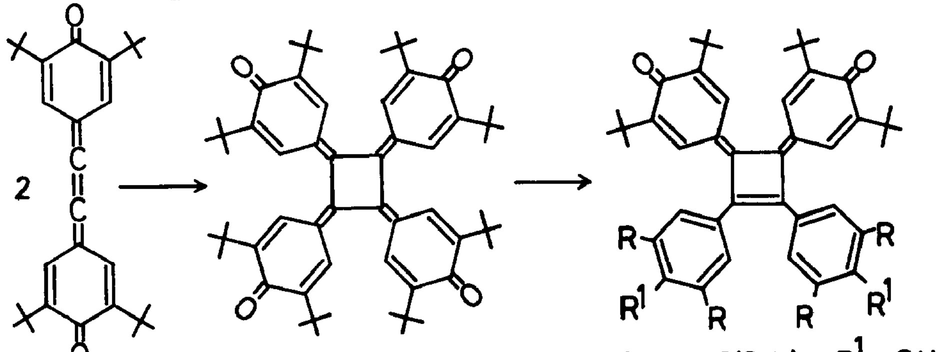
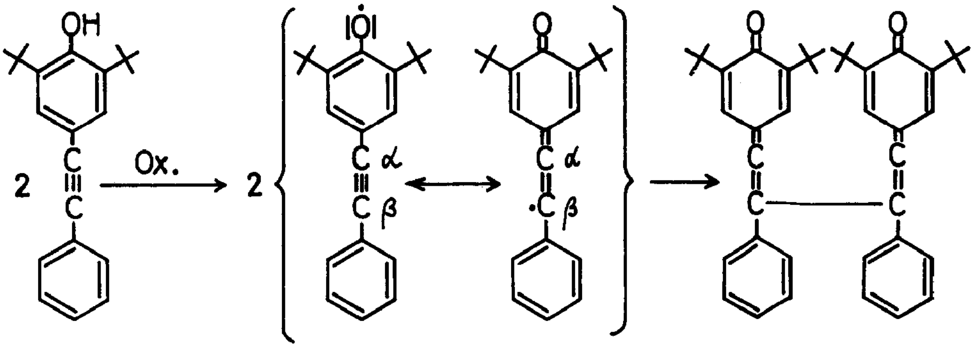
In a short communication R.West ⟨1⟩ reports on the synthesis of tetraquinocyclobutane 1 by thermal dimerization of diquinoethylene 2 and announces further work on the reduction of 1 to form the diquinocyclobutene 3a. This prompts us to publish some of our preliminary results on quinocyclobutanes and quinocyclobutenes ⟨2⟩. We also obtained 2, the synthesis and pyrolysis of which will be published elsewhere. In this paper we describe the synthesis of the first diquinocyclobutene (3b) via the following sequence of reaction steps:

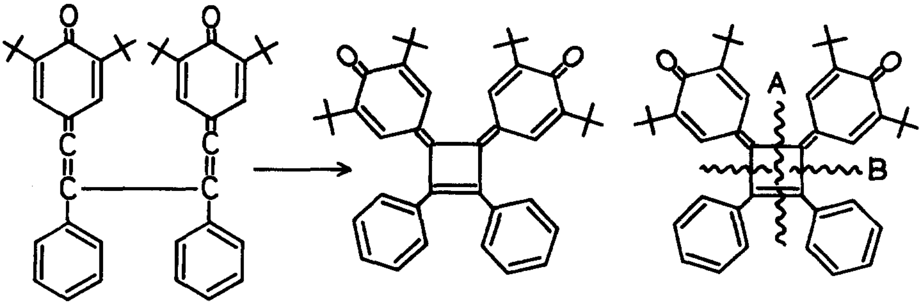


2 1

3a : $R = C(CH_3)_3$, $R^1 = OH$
3b : $R = H$, $R^1 = H$



4 5 6



6 3b

The acetylenic phenol 4⟨3⟩ on oxidation with PbO_2 or $K_3Fe(CN)_6$ in benzene affords a free radical, presumably 5, the ESR spectrum of which is complex in contrast to the spectra of other phenoxy radicals of this type ⟨3⟩. On evaporation of the solvent a bright orange-red product of mp. 240-241° C is obtained in 40 % yield. According to elementary analysis and mass spectrometry (M^+=610) the new substance is a dimer of 5. Since 4-alkinyl-2.6-di-tert.-butyl-phenoxy radicals reveal spin density on the β-carbon atom of the acetylenic bridge ⟨3⟩ it is obvious that 5 is also able to dimerize at the β-position to form the bis-quinobutadiene 6 as the primary reaction product. As in the case of simpler allenes, 6 undergoes cycloaddition to give the final product, which consequently should have structure 3b.

This conclusion is further supported by spectroscopic measurements. The expected high symmetry of the molecule is reflected by the ^{1}H-NMR spectrum [τ, CS_2: 2.6, broad singlet (phenyl protons); 2.65/2.73 (AB-pattern of the quinonoidal meta-ring protons); 8.72/8.94 (tert.-butyl protons)]. The IR spectrum shows no OH-absorption, but instead the C=O-absorption (1650 cm^{-1}) and a strong absorption band at 1540 cm^{-1}, which might be attributed to the C=C-valence vibration of the cyclobutene ring. The ^{13}C-Fourier-Transform-NMR spectrum exhibits no absorption for allenic carbon atoms, which would have been expected for 6. In the mass spectrum we observe peaks resulting from a fragmentation mode A [m/e = 305] and B [m/e = 178; 432] as expected.

By alcohols 3b is transformed to asymmetric adducts in which alcohol molecules seem to have reacted at one of the double bonds of the molecule.

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References

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