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Evidence for the Existence of the Dianion of Cyclobutadiene

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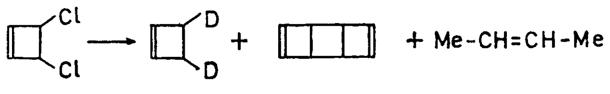
Summary Evidence is presented for the generation of cyclobutadiene dianion, a Hückel aromatic, from *cis*-dichlorocyclobutene and sodium naphthalide; although highly reactive, the dianion can be deuteriated to afford 3,4-dideuteriocyclobutene.

As with cyclo-octatetraene, the dianion of which is known,[1] the presence of a vacant low-energy molecular orbital in cyclobutadiene opens the possibility that the dianion of cyclobutadiene, in which all the carbon atoms would have equivalent electron densities, might also be thermodynamically stable.

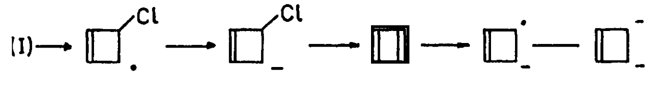
However, especially because of ring strain and electron repulsion forces it could be readily anticipated that the C_4 dianion, if stable at all, would be chemically much more reactive. We report data which are consistent with the predicted existence of the cyclobutadiene dianion and which are also indicative of its high chemical reactivity.[2]



(I) (II) (III) (IV)

cis-Dichlorocyclobutene (I) was added to a solution of excess of sodium naphthalide in tetrahydrofuran (THF) at −40 °C; the reaction mixture was allowed to stand for 4 min and was then poured into excess of MeOD maintained at −40 °C. Trap-to-trap vacuum distillation of the reaction mixture afforded 3,4-dideuteriocyclobutene (II) (*ca.* 4%), *syn*- and *anti*-tricyclo-octadiene (III) (*ca.* 20%) and *cis*- and *trans*-but-2-enes (IV) (*ca.* 6%).[3] The cyclobutene product obtained in this manner contained no perhydrocyclobutene or monodeuteriocyclobutene; however, previous experiments in which the reaction of dichloride with sodium naphthalide was conducted for varying times at −20 °C and MeOD then added to this mixture led to the same type of products which comprised varying amounts of perhydro- and 3,4-dideuterio-cyclobutenes. When dichlorocyclobutene was added to sodium naphthalide at −40 °C in THF and the reaction mixture warmed to 20 °C and distilled without adding any external proton source, then cyclobutene, together with the dimers of cyclobutadiene (III) and the but-2-enes, was obtained.

We consider these results to constitute strong evidence for the existence of the cyclobutadiene dianion and, in light of recent work on the mechanism of sodium naphthalide reactions, we propose the sequence of steps shown in the Scheme as being involved in its formation.[4] It is relevant to note that the ready dehalogenation of dihalogenocyclobutenes to cyclobutadiene with sodium has previously been reported.[5]



SCHEME.

Within this scheme the appearance of *syn*- and *anti*-tricyclo-octadiene could be rationalized through the dimerization of the intermediate cyclobutadiene while the formation of the but-2-enes could result from the ring opening of the chlorocyclobutenyl anion and subsequent reduction.[6] Of course, other routes leading to these products cannot be excluded by our data.[7]

The formation of dideuteriocyclobutene is good evidence that the cyclobutadiene dianion is formed under the conditions cited above; the fact that perhydrocyclobutene is generated in the absence of an external proton source suggests that the dianion can readily abstract protons from THF,[8] reflecting, as expected, a much greater reactivity than that exhibited by the cyclo-octatetraene dianion.

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[1] T. J. Katz, *J. Amer. Chem. Soc.*, 1960, **82**, 3784.

[2] An unsuccessful attempt to prepare the dianion of tetramethylcyclobutadiene has been reported (W. Adam, *Tetrahedron Letters*, 1963, 1387). Our results suggest that this dianion might have, in fact, been prepared but owing to its high reactivity escaped detection.

[3] (a) The deuterium content of the cyclobutene was measured by n.m.r. and by both high resolution and low voltage mass spectroscopy; (b) All other compounds were identified by comparison of their spectra and/or retention times with those of authentic samples.

[4] J. F. Garst, *Accounts Chem. Res.*, 1971, **4**, 400, and references therein.

[5] E. K. G. Schmidt, L. Brener, and R. Pettit, *J. Amer. Chem. Soc.*, 1970, **92**, 3240.

[6] (a) An analogous ring opening of a cyclobutenyl anion has been reported; H. H. Freedman, G. A. Doorakian, and V. R. Sandel, *J. Amer. Chem. Soc.*, 1965, **87**, 3019; (b) Reaction of *trans,trans*-1,4-dichlorobutadiene with sodium naphthalide under our reaction conditions does afford a mixture of *cis*- and *trans*-but-2-enes.

[7] For example, part of the tricyclo-octadienes could result from dimerization of the chlorocyclobutenyl radical followed by Wurtz type coupling.

[8] There is ample evidence that carbanions can abstract protons from ethereal solvents.[4]