

t-butyl alcohol-*O-d* (the latter being the solvent mixture reported to yield 100% dideuterated dimer). Therefore, the fully conjugated anion is not formed, at least under our conditions.

Work aimed at the preparation of the cation, anion, and radical of the fully conjugated bicyclo[3.2.0]heptatrienyl system is in progress.

Nathan L. Bauld, Charles E. Dahl, Yong S. Rim
Department of Chemistry, The University of Texas
Austin, Texas 78712

Received February 15, 1969

The *o*-Xylylene Anion Radical

Sir:

We are pleased to report a synthesis of the previously unknown anion radical of the elusive molecule, *o*-xylylene. The synthesis is exceedingly simple, but involves an unusual reaction type which could have applications to the synthesis of other anion radicals.

Benzocyclobutene, a valence isomer of *o*-xylylene, appears to undergo thermal valence isomerization to the latter at 200°. The ephemeral existence of *o*-xylylene can be inferred from Diels-Alder trapping experiments.¹

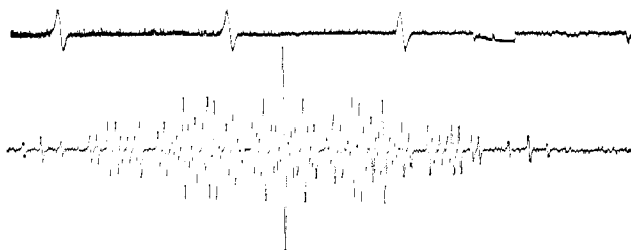
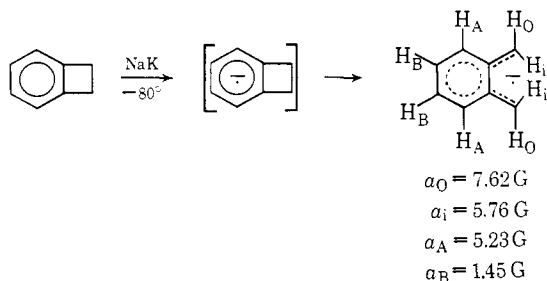


Figure 1. ESR spectrum of the *o*-xylylene anion radical in THF at -60° using NaK alloy. The computer simulation is virtually perfect. The upper trace is a simultaneously recorded spectrum of Fremy's salt.

Our thesis was that the anion radical of benzocyclobutene would undergo a similar, but much more rapid, isomerization, since *o*-xylylene should have a much higher electron affinity (the lowest vacant HMO has $E = \alpha - 0.29\beta$) than a benzene-like anion radical (LVMO, $E = \alpha - 1.00\beta$). Thus, if the isomerization could be brought about under sufficiently mild conditions, the *o*-xylylene anion radical might be detectable. In fact, when benzocyclobutene is contacted with K or NaK in THF or DME at -80° , the only radical which is observed, and this is formed virtually im-



(1) F. R. Jensen, W. E. Coleman, and A. J. Berlin, *Tetrahedron Letters*, 15 (1962).

mediately, is the anion radical of *o*-xylylene, as the data and arguments below indicate.

The ESR spectrum of the radical is reproduced in Figure 1. The hfs constants are listed below the structure. Splittings are observed from four nonequivalent pairs of protons, thereby immediately eliminating from consideration the benzocyclobutene anion radical, which can have at most three magnetically nonequivalent proton types. Moreover, the spectrum is unusually long for an anion radical (ca. 40 G), suggesting that some positions of fairly high spin density have more than one α proton attached, as would be the case with the benzylic positions of the *o*-xylylene anion radical. Thus, the splitting patterns and the spectrum length both constitute potent arguments for the assigned structure of the radical and against the benzocyclobutene anion radical.

The positional assignments given above are based upon HMO calculations and, in the case of $a_o > a_i$, upon the allyl radical analogy² and are thus tentative. If correct, the relatively large difference in splitting constants between H_i and H_o would be of considerable interest, and efforts are under way to substantiate the assignments as well as to determine the rotatory sense of the electrocyclic reaction presumably involved in the formation of the *o*-xylylene anion radical.

Acknowledgment. We wish to acknowledge support from the Welch Foundation and from the National Science Foundation, the latter for the purchase of an ESR spectrometer.

(2) P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, **90**, 7155 (1968).

Nathan L. Bauld, Frank Farr
Department of Chemistry, The University of Texas
Austin, Texas 78712
Received March 14, 1969

Perchloropolysilanes: Novel Reducing Agents for Phosphine Oxides and Other Organic Oxides¹

Sir:

Perchloropolysilanes ($\text{Si}_n\text{Cl}_{2n+2}$) constitute a class of compounds which have not been heretofore reported as reducing agents in organic synthesis, even though the possibility of such an application was foreshadowed by the earlier observation of Urry,² who noted the rapid reduction of antimony trichloride by hexasilicon tetrachloride ($\text{Si}_6\text{Cl}_{14}$) in ether solution and recognized the potential of this compound "as a reducing agent for use in nonaqueous systems for reactions where hydride or metallic reducing agents are incompatible." We wish to communicate at this time what we believe to be the first reported deoxygenations of organic compounds with hexachlorodisilane (Si_2Cl_6) and octachlorotrisilane (Si_3Cl_8), the first two members of the perchloropolysilane series, and the particular usefulness of these reagents in the synthesis of optically active phosphines.

Optically active acyclic phosphine oxides³ ($\text{R}_1\text{R}_2\text{R}_3\text{PO}$) are handily reduced by Si_2Cl_6 or Si_3Cl_8 with complete or nearly complete inversion of configuration.⁴

(1) This work was supported by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-1188-B.

(2) G. Urry, *J. Inorg. Nucl. Chem.*, **26**, 409 (1964).

(3) O. Korpiun, R. A. Lewis, J. Chickos, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4842 (1968).