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.

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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]

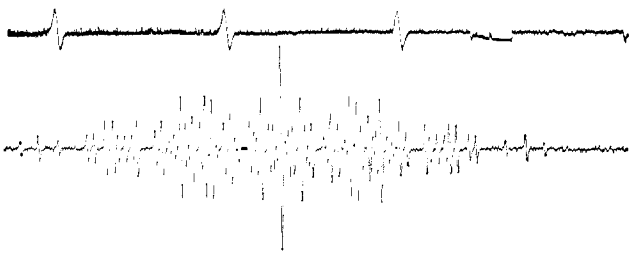
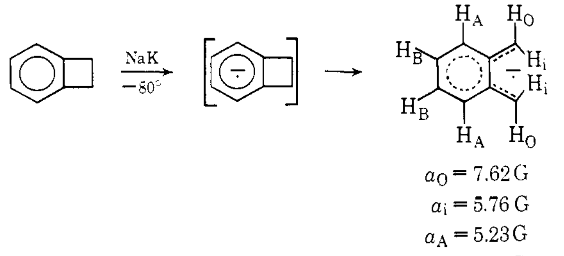


Figure 1. Esr spectrum of the *o*-xylylene anion radical in THF at −60° using NaK alloy. The computer simulation is virtually perfect. The upper trace is a simultaneously recorded spectrum of Fremy's salt.

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



$a_O = 7.62$ G
$a_i = 5.76$ G
$a_A = 5.23$ G
$a_B = 1.45$ G

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 analogy[2] 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.

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

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

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Perchloropolysilanes: Novel Reducing Agents for Phosphine Oxides and Other Organic Oxides[1]

Sir:

Perchloropolysilanes (Si_nCl_{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 tetradecachloride (Si_6Cl_{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 oxides[3] ($R_1R_2R_3PO$) are handily reduced by Si_2Cl_6 or Si_3Cl_8 with complete or nearly complete inversion of configuration.[4]

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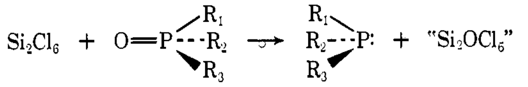
[1] This work was supported by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-1188-B.

[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).

In the case of hexachlorodisilane, the silicon-containing product, "Si_2OCl_6," appears to be a mixture of silicon tetrachloride, hexachlorodisiloxane ($Cl_3SiOSiCl_3$), and higher molecular weight perchloropolysiloxanes.



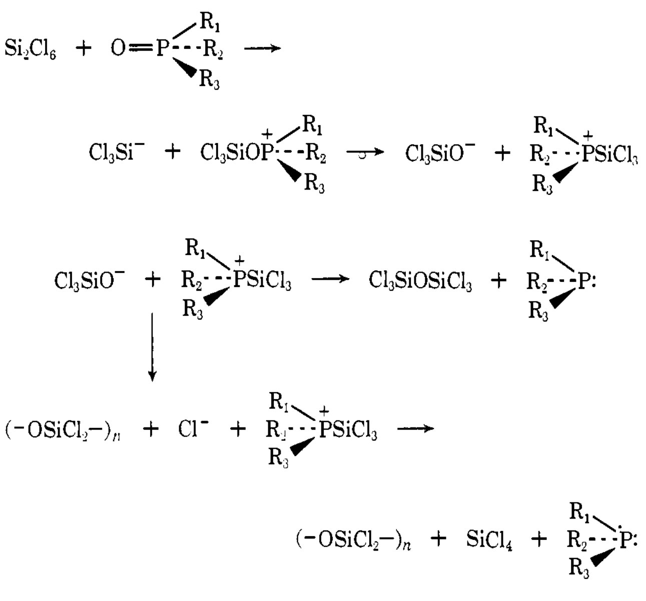
$$Si_2Cl_6 + O{=}PR_1R_2R_3 \longrightarrow R_1R_2R_3P{:} + \text{"}Si_2OCl_6\text{"}$$

A typical procedure for such a reduction is the following. A solution of optically pure (+)-(*R*)-benzylmethylphenylphosphine oxide[3] (336 mg, 1.46 mmol), $[\alpha]_D$ +51.4° (methanol), in benzene (9 ml) was refluxed under N_2 with hexachlorodisilane (0.32 ml, *ca.* 1.9 mmol) for 15 min.[5] The reaction mixture was cooled to 0° and hydrolyzed by cautious addition of 30% aqueous sodium hydroxide (3 ml). Benzene (16 ml) was added and the organic layer was washed with water and dried (magnesium sulfate). Removal of solvent under reduced pressure gave the reduction product, benzylmethylphenylphosphine, as a clear, colorless oil, which could be isolated by rapid distillation (kugelrohr) at reduced pressure, bp 90–95° (0.01 mm). Reoxidation with excess hydrogen peroxide yielded (−)-(*S*)-benzylmethylphenylphosphine oxide, $[\alpha]_D$ −46.9° (methanol), optical purity 91%. Quaternization with excess *n*-propyl bromide in acetonitrile (*ca.* 60°, 10 hr) afforded (+)-(*S*)-benzylmethylphenyl-*n*-propylphosphonium bromide,[6] $[\alpha]_D$ +32.8° (methanol), optical purity 89%. The hydrogen peroxide oxidation and *n*-propylation of benzylmethylphenylphosphine proceed with retention of configuration at phosphorus.[7]

The ready availability of hexachlorodisilane, the simplicity and mildness of the reaction conditions (thus the reduction may be carried out in chloroform at room temperature), the high product yield (70–90%), and the high stereospecificity of the reduction (*ca.* 90%) make this a most convenient method for the preparation of optically active phosphines.

A tentative mechanism which we suggest to account for the observed stereochemistry and stoichiometry of the hexachlorodisilane reduction of optically active acyclic phosphine oxides is represented by Scheme I. The intervention of trichlorosilyl anion as a reaction intermediate has also been suggested in the base-catalyzed decomposition of hexachlorodisilane with tri-*n*-butylamine[8] and triphenylphosphine.[9]

Scheme I



Hexachlorodisilane was also found to reduce amine oxides and sulfoxides. Typically, the reduction of 4-methylpyridine N-oxide to 4-methylpyridine could be readily effected in 60–70% yield by simply stirring a mixture of the N-oxide and hexachlorodisilane (molar ratio 1:1) in chloroform at room temperature for 1 hr. Likewise, the smooth reduction of diphenyl sulfoxide by hexachlorodisilane in benzene at room temperature for 1 hr yielded diphenyl sulfide (91%). The work-up procedure for these reactions was essentially the same as that described above.

Finally, we have found that reduction of cyclic phosphine oxides as well as of optically active acyclic phosphine sulfides with hexachlorodisilane proceeds with *retention* of configuration.[10] These results, as well as the mechanistic relevance of perchloropolysilanes in reductions of phosphine oxides with trichlorosilane in the presence of strongly basic tertiary amines,[4] will be discussed in detail in forthcoming papers.

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(4) Hydrides have been employed in the stereospecific reduction of phosphine oxides to phosphines, a particularly valuable reagent being trichlorosilane, whose utilization for this purpose was pioneered by L. Horner and W. D. Balzer, *Tetrahedron Lett.*, 1157 (1965).

(5) Reduction is generally complete in 15 min or less. An increase in contact time causes chemical racemization of the produced phosphines.

(6) A. F. Peerdeman, J. P. C. Holst, L. Horner, and H. Winkler, *Tetrahedron Lett.*, 811 (1965).

(7) L. Horner, *Pure Appl. Chem.*, **9**, 225 (1964).

(8) G. D. Cooper and A. R. Gilbert, *J. Amer. Chem. Soc.*, **82**, 5042 (1960).

(9) H. J. Emeléus and M. Tufail, *J. Inorg. Nucl. Chem.*, **29**, 2081 (1967).

(10) To our knowledge, the reduction of optically active phosphine sulfides to optically active phosphines by hexachlorodisilane represents the first reported stereospecific reduction of such compounds.

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A General Method for Determining the Optical Purity of Phosphines[1]

Sir:

Contemporary techniques for obtaining optically active phosphines and their derivatives[2] are not complemented by any single widely applicable method for the determination of optical purities in this class of compounds. Enantiomeric ratios, and consequently optical purities, may be reliably estimated by nmr analysis of the diastereomers which are obtained when enantiomers are suitably derivatized with optically active reagents.[3] We wish to communicate at this time our experience with one such reagent, 2-phenyl-2-methoxyethyl bromide (**1**), which possesses all of the requisite attributes: it is easily obtained in optically pure form, it reacts quantitatively with phosphines (**2**) to give 2-phenyl-2-methoxyethylphosphonium bro-

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

(2) For a recent review, see N. J. Gallagher and I. D. Jenkins in "Topics in Stereochemistry," Vol. 3, N. L. Allinger and E. L. Eliel, Ed., John Wiley & Sons, Inc., New York, N. Y., 1968, Chapter 1.

(3) M. Raban and K. Mislow in "Topics in Stereochemistry," Vol. 2, N. L. Allinger and E. L. Eliel, Ed., John Wiley & Sons, Inc., New York, N. Y., 1967, Chapter 4.